CRANFIELD UNIVERSITY

María del Mar Batista Seguí

Modelling phosphorus removal capacity and longevity in land treatment systems

School of Water, Energy and Environment

Doctor of Philosophy (PhD)
Academic Year: 2014 - 2017

Supervisors: Prof. Sean Tyrrel and Prof. Tim Hess
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This thesis is submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy

ABSTRACT

The wastewater industry is facing an increase in regulatory pressure to reduce excessive phosphorus (P) release to rivers. To address this issue there is a need for sustainable treatments, especially in small sewage treatment works (STW) (< 2000 inhabitants) which constitute 75 % of the systems in the UK. Land treatment systems (LTS) have long been used to treat wastewater, principally as a tertiary treatment at small rural sites. LTS are able to remove phosphorus but there are some uncertainties regarding their treatment capability. This research aims to address these uncertainties by developing improved estimations of P removal potential and longevity in LTS in the context of a sustainable water industry. First, the existing knowledge and tools available in long-term P removal behaviour are reviewed. Second, the soil P removal efficiency and accumulation in an LTS case study are estimated. Finally, the case study is used to develop a conceptual and mathematical model of P dynamics in LTS integrating water and solute transport in soils. The model is used to explain system behaviour in order to estimate system longevity under different soil conditions and management scenarios.

This research demonstrates that LTS can contribute to P removal for a number of years as a tertiary treatment for small STW and that through a combination of hydrological and solute transport modelling it is possible to get a prediction of P removal and longevity of LTS. Results indicate the need for an alternative methodology to assess P removal capacity that does not only rely on inputs and outputs while able to detect if the system is saturated and the need of improved methodological assessment of sorption processes over time. Further development of the current model to reduce limitations, mainly related to vegetation management and P transformation in the different soil pools, will support LTS contribution to the sustainable management of wastewater treatments and the enhancement of the ecosystem services that they provide.

Keywords: Modelling, longevity, retention, soil, wastewater tertiary treatment

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LIST OF ABBREVIATIONS

Al	Aluminium
BOD	Biological Oxygen Demand
c	Solute concentration of the liquid phase [ML^{-3}],
Ca	Calcium
CDE	Convection-dispersion equation
$C_i(x)$	Initial concentrations of P in soil [M^3L^{-3}]
CW	Constructed Wetland
D	Solute dispersion coefficient [L^2T^{-1}]
D_L	Longitudinal dispersivity [L]
DPS	Degree of Phosphorus Saturation
EA	Environment Agency
ET	Evapotranspiration
Fe	Iron
h	Soil water pressure head
k_d	Equilibrium constant-adsorption isotherm coefficient [L^3M^{-1}]
K_{sat}	Saturated hydraulic conductivity [LT^{-1}]
l	Pore connectivity parameter (-)
LTS	Land Treatment System
n	Empirical parameter (-)
NSI	National Soil Inventory
OF	Overland Flow
OM	Organic Matter
P	Phosphorus
PE	Person Equivalent
PO_4^{-3}	Phosphate
PSC	Phosphorus Sorption Capacity
q	Darcy–Buckingham volumetric water flux [LT^{-1}]
R	Retardation factor (-)
RI	Rapid Infiltration
RLE	Remaining Life Expectancy
S	Sink or source for water [L^3 L^{-3} T^{-1}]
S_{max}	Maximum Sorption Capacity
SR	Slow Rate

SS	Suspended Solids
STP	Soil Test Phosphorus
STW	Sewage Treatment Works
SUWM	Sustainable Urban Water Management
t	Time [T]
TN	Total Nitrogen
TP	Total Phosphorus
WFD	Water Framework Directive
z	Depth [L]
α	Empirical parameter [L]
η	Adsorption isotherm coefficient [L^3M^{-1}]
θ_r	Residual water content [L^3L^{-3}]
θ_s	Saturated water content [L^3L^{-3}]
ρ_b	Bulk density [ML^{-3}]
ϕ	Sink or source for solutes [$ML^{-3}T^{-1}$]

1 INTRODUCTION

1.1 Project background

1.1.1 Introduction

The discharge of large volumes of wastewater with high levels of phosphorus (P) during recent decades has contributed to the eutrophication of freshwater bodies. Despite recent progress in reduction of almost 50% of P loads since 1995, 50% of the river length suffers from excessive P concentrations in England and Wales (Comber, Crossman, Daldorph, *et al.*, 2012), with sewage effluent being the largest contributor of P to rivers (60-80% in England) (Environment Agency, 2012). Therefore, efforts have recently focused on reducing the effects of eutrophication through further controls on discharges. To fulfil the EU Water Framework Directive (WFD) (2000/60/EC) objectives, all river catchments are assigned to a corresponding River Basin Management Plan, where specific actions to achieve environmental objectives for each water body are set out. These actions may include reviewing permits for discharging to surface waters, thus, it is likely that the maximum allowed concentration of pollutants would be reduced. As a result, to meet this tighter consents requirements water companies will have the obligation to upgrade their sewage treatment works (STW).

These requirements would especially affect small STW (<2 000 p.e.), which constitute 75% of all the works in the UK (DEFRA, 2012). Before the adoption of the WFD in 2003, small STW in England and Wales were only required to meet consents for suspended solids and organic matter. The Environment Agency, after the adoption of the WFD, might review the existing permits tightening the current consents and adding ammonia and P removal requirements (Tyrrell, 2016). Additionally, as intense pressure is placed on the planet's limited water supplies, there is a need for sustainable water treatments that can offer pollutant removal methods that put less stress on resources and reduce their impact on natural systems offering low energy solutions and reuse applications such as stream flow augmentation or groundwater recharge. This raises the need for innovative and sustainable approaches to reducing P loading to rivers from small STW.

Natural wastewater treatment systems have the potential to reduce the concentration of pollutants from wastewater and they can offer an alternative sustainable tertiary treatment for small STW where low technology and low maintenance solutions are required (Crites, Middlebrooks & Sherwood, 2006). Land treatment was defined by Crites et al., (2000, p. 7) as the “controlled application of water onto the land surface to achieve a specified level of treatment through natural, physical, chemical, and biological processes within the plant-soil-water matrix”. Land Treatment Systems (LTS) have been used to treat wastewater since the nineteenth century and continue to be used today, principally at small rural STW, where adjacent pieces of land are used as a polishing step after the secondary treatment to remove solids, nutrients and pathogens (Tzanakakis, Paranychianakis & Angelakis, 2007). They are also recognised as low carbon and low-cost treatment alternatives (Tyrrell, 2016).However, these systems normally present a limitation regarding land footprint and P removal exhaustion.

Traditionally, the interaction between soil and P has been studied in relation with agronomic purpose and the effects caused by diffuse pollution onto surface waters, usually in the form of eutrophication. Eutrophication is the enrichment of a water body with nutrient excess, inducing a growth of plants and algae that may result in oxygen depletion of the water body. In this study, this previous knowledge of phosphorus transport pathways and mechanism in soils is used to determine the removal capacity of P in soils and, by adding a time variable, its longevity. For this reason, to begin with, it is necessary to present the major aspects of P chemistry, P transport pathways and modelling parameters in the soil-water environment.

The following sections 1.1.2 and 1.1.3 introduce the basic concepts of phosphorus cycle and P chemistry in soils, which are necessary for understanding the P transport processes and pathways in soils. Those sections are a summary based on the comprehensive textbooks and papers by Kadlec, Reddy & Wetzel, 2005, Nahra, 2006; Brady & Weil, 2008; Kadlec & Wallace, 2009; Kruse, Abraham, Amelung, et al., 2015, which can be consulted for further detail.

1.1.2 Soil phosphorus cycle

P is an essential element that sustains life (plants, animals and bacteria). P is indispensable for crop growing and hence for crop production. This has lead into a global environmental concern of fresh and marine waters been polluted by P excess and, at the same time, concerns about P global supplies availability (Ashley, Cordell & Mavinic, 2011).

The P cycle in the soil column describes the inputs, outputs, interactions and reactions that control the different P form and their availability (Figure 1-1). The main inputs in soils are organic phosphorus in the form of plant residues, animal manure and weathering of P minerals. P outputs from soil are plant uptake and crop removal, surface runoff and soil erosion, and leaching into the vadose zone and groundwater.

Phosphorus inputs in soils can be in organic and inorganic forms depending on soil, vegetation and land use. These can be also divided into dissolved and particulate. Dissolved inorganic P is bioavailable whilst organic and particulate need transformations to be considered available. The reactions that govern the pool size and reactions in the soil matrix are abiotic -sedimentation, adsorption, precipitation and exchange processes- and biotic -assimilation by vegetation and microorganisms.

1.1.2.1 Abiotic processes

Precipitation-Dissolution: precipitation reactions refer to reactions of phosphate ions with metallic cations such Fe, Al, Ca or Mg forming amorphous precipitate solids. Dissolution refers to the solubilisation of the precipitate and it occurs when the concentration decreases below the solubility product of the compound.

Sorption-Desorption: biotic and abiotic processes take place to regulate how the soil retains the inorganic P added to the soil. Adsorption takes places when soluble inorganic P from the soil solution accumulates in soil mineral surfaces. Desorption refers to the release of the adsorbed inorganic P in the mineral surfaces into the soil pore water. These reactions are balanced to reach the equilibrium between the solid phase and P in the pore water.

The sorption process is an abiotic process with is controlled by the capacity of the system to replenish the P in soil solution and its capacity to maintain equilibrium and it depends on the capacity of the soil to adsorb additional P. Additionally, the sorbed

P can diffuse into the soil phase forming additional discrete phosphates minerals, this process is called absorption and occurs slowly compared to adsorption. The term sorption used in literature normally refers to sorption and absorption processes.

The transformation rates and concentrations of each form in the soil depend on soil properties, climate conditions, and land use and management practices. These transformations and interactions are complex and dynamic and occur continuously in order to maintain equilibrium conditions.

Retention of P in soils through abiotic processes is regulated by:

- pH: which in acid soils is regulated by Fe and Al oxides, while in alkaline soils Ca-based minerals;
- Redox potential: Fe-based soils are stable under aerobic and drained conditions. Redox conditions in soils increases P solubility.
- Clay content: soils with high clay have the strongest P retention capacity.
- Organic matter content (OM): high OM content provides surfaces for P sorption.
- P content in soil: alkaline soils with $CaCO_3$ provide both surfaces for P sorption and Ca^{+2} ions for co-precipitation.

1.1.2.2 Biotic processes

Mineralization-Immobilization: mineralization takes place when microbial biomass converts organic P into PO_4 ions availed in soil solution for plan uptake. Immobilization is the process where microbial mass transform PO_4 ions into organic P

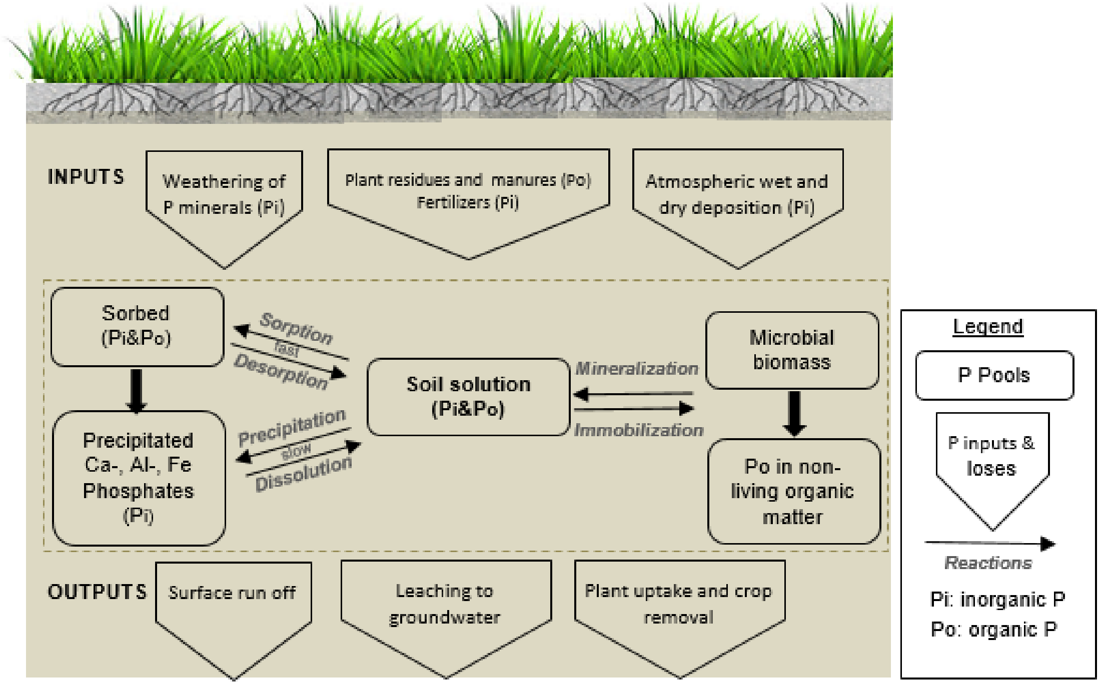

Figure 1-1 Schematic representation of the soil phosphorus cycle (based on Kruse et al. 2015)

1.1.3 Transport processes and pathways of P in soils

To define and identify P transport processes in soils are vital to model P transport in the soil matrix. P transport processes and pathways are defined by both the water cycle and the P cycle. The processes and conditions of the water and solute transport occurring in a system will define how much P is retained in the soil. P transported by water suffers a change in its characteristics as it flows through the soil profile. These changes in the water and solute transport in soils are mathematically translated by the ADE's and Richard's equation. Both equations need of a series of parameters that will describe the system (Figure 1-2). As the hydrological pathways can be classified in a large range of time and spatial scales they can become complex to describe.

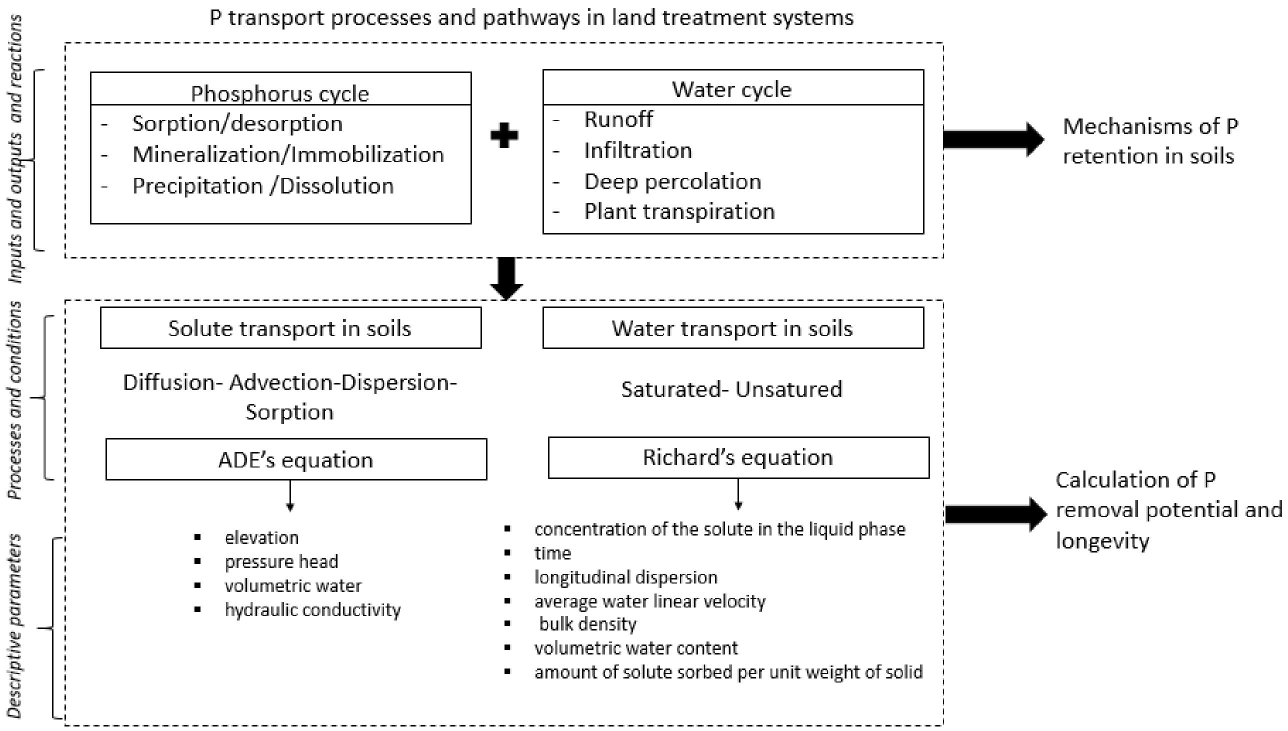

Figure 1-2 Diagram of interactions of phosphorus processes and pathways in soil treatment systems, soil conditions and descriptive parameters of solute and water transport in soils

1.1.3.1 Water transport

Water travels through the soil depending on different environmental factors, created by topography and vegetation patterns and soil moisture that will develop vertical and horizontal velocity patterns. The main pathways of water transport in soils are:

- Surface runoff: horizontal flow through the soil surface.
- Infiltration: the soil is a porous media; infiltration is the process by which water enters the soil pore spaces and becomes soil water. With agronomic purposes, this pore water can be divided into drainage (water that can be drained by gravity), plant-available (between permanent wilting point and the water that can be retained by capillarity forces) or non-plant –available (below wilting point). Water flow depends on the percentage of soil moisture and can be divided in flow through saturated or unsaturated conditions.
- Deep percolation: once the water has been infiltrated, it moves downward through the soil.
- Plant transpiration: combined loss resulting from evaporation loss occurred directly from the soil surface and the loss from the lead surfaces after plant uptake.

There are three types of water flow in soils: saturated-when all the pores are filled up with water, unsaturated- when the larger pores are filled with air, and vapour movement- when vapour pressure differences develop, normally in dry soils. All these three types respond to differences in energy gradients. In this thesis only saturated and unsaturated conditions are included due to the environmental conditions of the case study.

The soil water flow equation, Richard's equation (4-1), represents the movement of water under unsaturated soils, it was derived from Darcy's equation, which describes the flow of a fluid through an unsaturated porous media. The parameters that describe this equation are elevation (z), pressure head (h), and volumetric water content (θ) and the hydraulic conductivity (k), which defines the ease with which the soil transmits water.

1.1.3.2 Solute transport

Hydrodynamic processes affect solute transport by changing the form and concentration of the solute. These main processes are:

- Diffusion: when the water moves from an area of greater concentration toward an area where is less concentrated.

- Advection: dissolves solids are carried along with the flow of water. The amount of solute flowing is a function of the solute concentration in the water and the quantity of water flowing.

- Mechanical dispersion: water moves through the soil at different velocities. When the mixing occurs along the direction of the flow path is called longitudinal dispersion. There are three main causes: Pore size: Some pores are bigger than others; therefore, in bigger ones the fluid will move faster.

  - Path length: some fluid particles will travel through longer paths than others that will follow a more linear distance.
  - Friction Pore: as fluid moves, it moves faster in the centre of the pore than along the edges

- Sorption: as a result of sorption processes, some solutes will move at a different velocity than the average water transporting them, this effect is called retardation.

Sorption processes include the following reactions, and in this thesis, we will not attempt to separate these phenomena but will use the term sorption to indicate the overall result of the various processes.

- Adsorption: processes by which a solute clings to a soil surface.
- Chemisorption: when a solute is incorporated on a sediment, soil or rock surface by chemical reaction.
- Absorption: when the aquifer particles are porous so that the solute can diffuse into the particle and be sorted onto interior surfaces.
- Ion exchange: cations may be attracted to the region close to a negative charged clay-mineral surface and held by electrostatic forces.

The equation that describes these processes in one dimension is the convection-dispersion equation modified to include sorption (Described in Chapter 4 Eq. (4-2). Each term of the equation represents each of these processes. The parameters that control the equation are the concentration of the solute in the liquid phase, time, longitudinal dispersion, average water linear velocity, bulk density, volumetric water content and the amount of solute sorbed per unit weight of solid.

In LTS, whilst biological processes are sustainable, the chemical retention (sorption), is finite. Therefore, the sustainability of the P treatment has been called into question (Dzakpasu et al. 2015). Each type of soil is characterized by a P fixation capacity, which is dependent on the number of sites that can react with P. When all the P-fixation sites are filled, the maximum phosphorus-fixing capacity of the soil is reached, thus the soil is saturated with P and the excess P can be released to the environment, along with P from other sources such as runoff. Despite LTS being used worldwide, there is limited information regarding P lifespan estimations, P removal performance and adequate governance and guidelines (Eveborn et al. 2012; Sapkota et al. 2014; Dzakpasu et al. 2015; Bisone et al. 2016).

1.2 Treatment performance and longevity estimation in LTS

Treatment performance and longevity estimations of LTS are key parameters to achieve cost-effective treatments. They provide the treatment evidence needed by operators and regulators to have greater confidence in the sustainable operation of these systems in order to include them as a legitimate option in their investments programs (Sweaney, 2011). Although LTS consent regulations worldwide are very diverse and sometimes not clear, they normally require a percent of pollutant removal or a target outlet concentration as a treatment goal. Regulations have had a strong impact on wastewater engineering over the history of wastewater treatments. The Clean Water Act (The 92nd United States Congress, 1972) first set minimum standards discharges that were amended in 1985 to a percent removal requirements to provide flexibility to treatment facilities (Inc. Metcalf & Eddy, Tchobanoglous, Burton, *et al.*, 2003). This percentage of removal requirement was also set by the EU Council Directive Concerning Urban Waste Water Treatment (European Commission, 1991). Consequently, this approach based on inlet-outlet percentage removal of conventional wastewater treatments has been adopted by many EU countries to assess on-site systems' performance, in which group are included LTS.

For example, the Swedish Environmental Protection Agency set pollutant reductions for on-site treatments based on the level of protection of the discharge location (Swedish Environmental Protection Agency 2008): a normal level of protection requires a reduction of BOD_7 to 90%, TP to 70% and no recommendation for TN; high level of protection locations require a reduction of BOD_7 to 90%, TP to 90% and 50% TN. In Norway, decentralized wastewater treatment has similar general discharge limitations (Abbas, 2017). In sensitive and normal areas depending on the eutrophication risk a reduction of BOD_5 to 70-90%, TP to 60-90% is required and no recommendation for TN and in less sensitive areas: 20% suspended solids (SS) or 180 mg SS/l.

In the USA, regulatory requirements for LTS vary within states, and process monitoring is usually used as regulatory monitoring since sometimes they are similar in scope (USEPA, 2006). Treatments systems that collect effluent water in subsurface drains for surface discharge or groundwater recharge are usually required to have a discharge permit as well as overland flow systems. The systems where the water remains in the soils do not necessarily require a permit but they might be required to follow applications recommendations or some sort of monitoring even if they are not directly discharging to surface water. The criteria depend on the state and they range from very general guidelines to very specific law regulations (Crites, Reed & Bastian, 2000).

LTS in the UK are usually related to a tertiary treatment for a small STW, they normally have discharge consents set by the EA associated with SS, BOD and ammonia, however, sometimes compliance points refer to the associated STW and not directly to the LTS. From the 12 grass plots systems identified by Sweaney (2011) in the UK, 12 grass plots had numerical consents for BOD between 10-40 mg/l, 9 had numerical consents for ammonia between 3-25 mg/l and, 12 had consent standards for SS between 15 and 40 mg/l. A summary of performance in the study reports also refers to removal efficiencies between 12-78% for BOD, 25-62% for SS and from 54 to 88% for ammonia.

A finer understanding of how these systems work is crucially important to better establish where and under which conditions they could be successfully implemented without compromising the ecological status of fresh water because of P pollution. Previous studies identified partial gaps in determining valid estimates of P removal capacity of materials and systems (Hu, Zhang, Kendrick, *et al.*, 2006; Drizo, Comeau, Forget, *et al.*, 2002; Cucarella & Renman, 2009). They describe the limitations of laboratory standards operations procedures when trying to reproduce processes in the long-term and in full-scale systems and recognize that although the standard laboratory methodology proposed by Nair et al. (1984) based on soil:solution ratio of 1:25 (w:v), six initial P concentrations, and a 24 h equilibration period would produce consistent results over a wide range of soils, it is not reliable for management guidance and longevity estimations since they do not reflect field conditions. Previous studies also point out that P dynamics in LTS are complex and involve slow and fast reactions within the water, soil and plant matrix, with a number of related processes that must be taken into account: e.g. application rate, plant uptake, water movement through soil, climatic conditions, crop growth and soil erosion. The use of modelling tools to assess P-transport processes could help to understand the system behaviour and the effects of different governing influences of parameters that affect the functioning of LTS. Intensive research has been done to develop models able to simulate the interaction in between the soil matrix, the water transport and P, predominantly related to agricultural purposes (EPIC, ANIMO, GLEAMS, MACRO, DAYCENT, HYDRUS) (McGechan & Lewis, 2002; Vadas, Bolster & Good, 2013), however, none of them has been used to tackle the longevity and long-term P removal in LTS and to explain system behaviour.

This research aims to fill this gap by developing improved estimations of P removal and longevity in LTS.

1.3 Research aims and objectives

Aim: The aim of this thesis is to improve the quantification and prediction of P removal capability and longevity in LTS, and to support best LTS management strategies to maximize P removal by investigating the combination of hydrological and P solute transport processes in soil over time.

Objectives:

1. To review the existing knowledge and tools available for making predictions of LTS performance and identify the existing gap in the understanding of long-term P removal behaviour.
2. To assess P accumulation over time in a LTS to evaluate for how long this system can make a useful contribution to a sustainable wastewater treatment.
3. To develop a conceptual model of P dynamics in LTS and apply a combination of hydrological and solute transport model in soils to identify relevant P removal processes in soils and test the sensitivity of the model to changes in relevant parameters.
4. To investigate the role of alternative management practices and soil conditions in controlling system behaviour and P retention in response to changes in management variables and system conditions.

1.4 Methodology

The study is structured in four main phases.

- First, a problem identification phase where the existing knowledge and tools available for making reliable predictions was reviewed in relation to how long an LTS can be effective and what are the current knowledge gaps in long-term P removal behaviour.
- The second phase consisted of a problem interpretation phase through a case study of a long-term LTS where the main P and hydrological inputs and outputs were identified, and a mass balance approach was used to quantify the contributions of the different P pathways in the system and the accumulation of P in the soil.

- The third phase consisted of model development that proposed a conceptual model of P dynamics in LTS that was translated into a mathematical model. The model couples a hydrological and solute transport model with the objective to estimate the P concentration distribution of the soil solution over time at a given depth, and estimate when the system's capacity for P removal is finished.
- Finally, different scenarios were simulated in order to characterize system behaviour under different conditions and accordingly, propose management tools that will enhance longevity and maximize P removal in LTS.

This thesis purpose is to contribute significantly to the body of knowledge on LTS and associated P dynamics by providing improved P-removal lifespan predictions that will contribute to greater confidence in this technology and to support long-term wastewater treatment planning in the light of the current and future role of LTS in the sustainable wastewater industry

1.5 Thesis outline

The thesis has been structured in 4 paper format chapters which together constitute the thesis. The thesis structure and connections between the chapters are presented in Figure 1-3 . Chapter 2 refers to objective 1 by providing a critical literature review of knowledge gaps in long-term P removal in LTS. Chapter 3 assesses a selected LTS case study in the UK and addresses objective 2. Chapter 4 introduces the conceptual and mathematical model along with the parameterization based on the case study and model sensitivity analysis to meet objective 3. Chapter 5 compares the removal and longevity results with the case study and describes possible management scenarios to meet objective 4. Chapter 6 is the overall discussion of the thesis where results from previous chapters are discussed as a whole in relation to LTS's P removal capacity and their practical implications for the sustainable water industry.

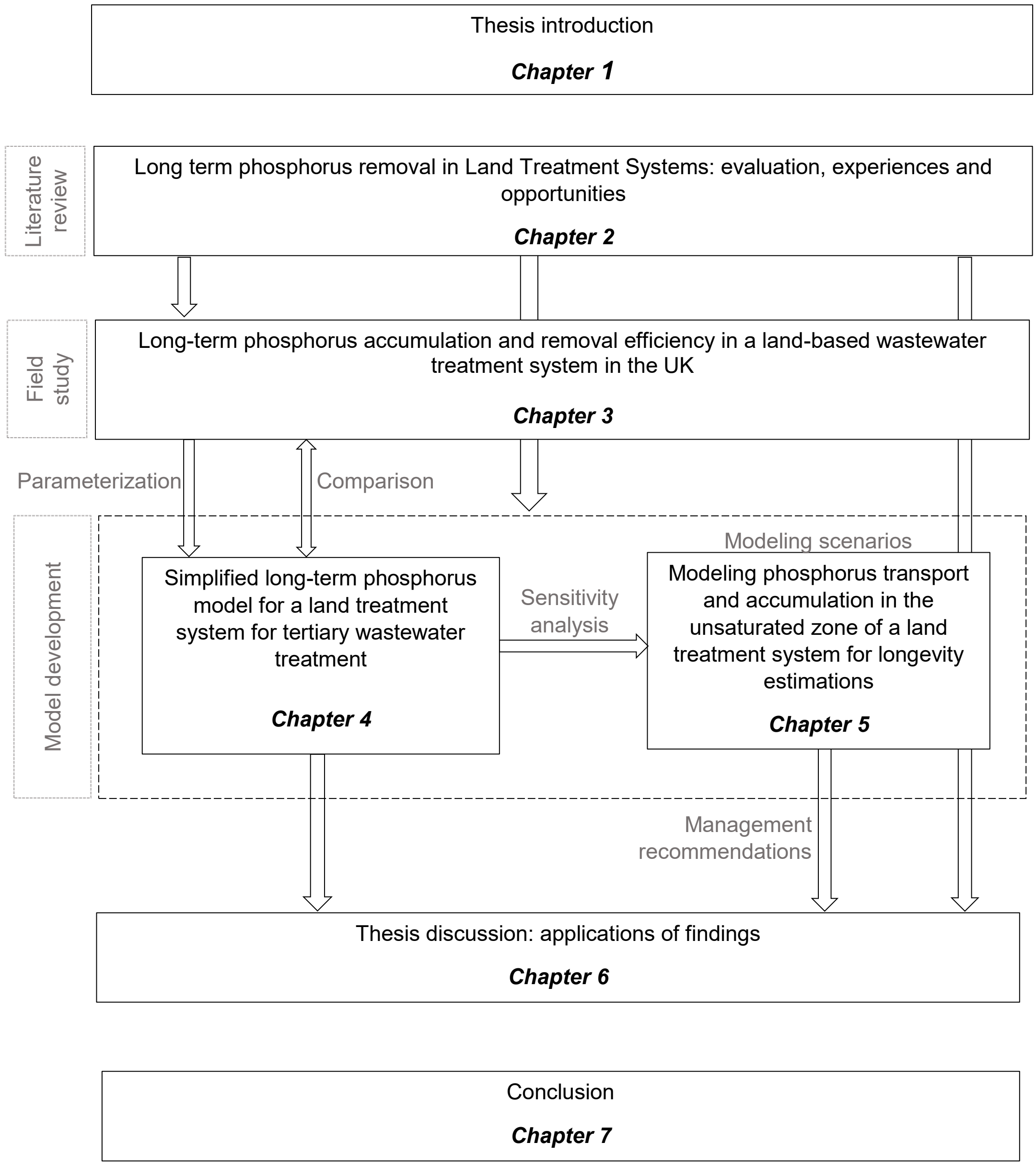

Figure 1-3 Thesis structure

1.6 Submitted and published papers

The following chapters of the thesis have been submitted and/or published in peer review journals. The contribution of Prof. Sean Tyrrel and Prof. Tim Hess to all papers was what would normally be expected from a supervisor and included guidance on structure and methods and commenting on drafts, Dr Ruben Sakrabani has contributed to supervising the experimental design and data interpretation related to nutrient dynamics in soils and David Knaggs has contributed with provision of access to the field site, the provision of data and background information on the study site and a stakeholder view of the potential future use of LTS. All original work was carried out by the PhD candidate.

- **Chapter 2**: Batista, M. del M., Hess, T., Sakrabani, R. and Tyrrel, S.F., 2017. Long-term phosphorus removal in Land Treatment Systems: evaluation, experiences and opportunities. Critical Reviews in Environmental Science and Technology, 47(5), pp.314–334.
- **Chapter 3** Batista Seguí, M. del M., Tyrrel, S.F., Hess, T., Sakrabani, R. and Knaggs, D., 2017. Long-term accumulation and phosphorus removal efficiency in a land-based wastewater treatment system in the UK. Submitted to Journal of Water and Environment.

2 LONG TERM PHOSPHORUS REMOVAL IN LAND TREATMENT SYSTEMS: EVALUATION, EXPERIENCES AND OPPORTUNITIES [1]

2.1 Introduction

The release of excessive soluble phosphorus (P) to water bodies is a significant global environmental concern and the resultant eutrophication is one of the most common water quality problems (Smith, Joye & Howarth, 2006; Carpenter & Bennett, 2011). The consequence of eutrophication is the degradation of water resources by toxic algal blooms, excessive aquatic plant growth, oxygen depletion, the death of aquatic life, and consequent loss of biodiversity. Together these water quality impacts can cause considerable loss of value of freshwater ecosystems in terms of diminished recreational value and profit reductions of the tourist sector (Carpenter & Caraco, 1998) and increased water treatment costs. Pretty et al. (2003) quantified the eutrophication damage in England and Wales to be around £155 million per year.

The sources of P in surface waters vary depending on each context, and they can be classified as diffuse and point sources. The main diffuse pollution sources in the UK are natural landscapes, agricultural fields, rural and urban surfaces, waste from non-sewered populations, farm animals and, atmospheric deposition. The principal point sources are municipal and industrial effluent. The total P load to surface waters in Great Britain is estimated to be 41.6 kt/a: municipal effluent is the largest fraction with 60.7% of the P contribution, while the agricultural and industrial contributions are 28.3% and 4.6% respectively (and others 6.4%) (White and Hammond, 2002). The total phosphorus (TP) concentration in typical municipal wastewater depends on the local water consumption and it ranges from 4-25 mg/l (Henze & Comeau, 2008). The principal sources of P in municipal wastewater in the UK are black water (66%) and grey water (34%) (White & Hammond, 2002).

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[1] Batista, M. del M., Hess, T., Sakrabani, R. and Tyrrel, S., 2017. Long-term phosphorus removal in Land Treatment Systems: evaluation, experiences and opportunities. *Critical Reviews in Environmental Science and Technology*, 47(5), pp.314–334.

Since domestic wastewater is a main source of P, the EU (EU Parliament Regulation 2004) and countries such as USA, Canada or Japan, have focused their efforts during the last decades on reducing the P content in detergents (European Commission, 2012). In 2010, the Detergents Regulations in the UK (UK Parlament, 2010) banned the commercialization of domestic laundry detergent that contained more than 0.4% of inorganic phosphates (Richards, Paterson, Withers, *et al.*, 2015). Hence, to complement the measures to control P at the source, many governments are setting strict pollutant discharge limits in their environmental policies. The European Waste Water Directive 91/271/ECC (European Commission, 1991) sets discharge limits concentrations in wastewater effluents to sensitive areas at 1-2 mg/l for TP (depending on the population). However, in order to meet the standards of the receiving waters, required by the Water Framework Directive 2000/60/EC (European Commission, 2000) it is expected that discharge P limits will have to be further reduced and in some cases it may be as low as 0.1 mg/l (Parliamentary Office of Science and Technology, 2014).

Due to of need for efficient treatment, new technologies have been developed to enhance P removal from sewage but with the increased effectiveness their cost has risen. Thus, to meet these legal requirements, the wastewater industry faces the problem of providing efficient but low cost, low energy and low carbon wastewater treatments. Land treatment - defined by Crites et al., (2000, p. 7) as the "controlled application of water onto the land surface to achieve a specified level of treatment through natural, physical, chemical, and biological processes within the plant-soil-water matrix"- can help to overcome these challenges, however such systems have a finite capacity for P removal because of the limited adsorption capacity of the soil.

The aim of this paper is to critically review the existing knowledge and tools available for making reliable predictions about how long a Land Treatment System (LTS) can effectively perform as a tertiary treatment for wastewater without compromising the quality of the nearby environment and to identify the current knowledge gaps in long-term P removal behaviour of these systems. In order to analyse the previous studies about long-term performance of LTS, the state-of-the-art is examined using the following approach: description of LTS and problems associated with P forms in this type of natural wastewater treatment; analysis of current knowledge regarding P removal and longevity in laboratory-scale and full-scale systems; and finally, evaluation of the gaps for further research needs.

2.2 Land Treatment Systems

Since humans established permanently in communities, LTS has been used as a way to manage wastewater (Inc. Metcalf & Eddy, Tchobanoglous, Burton, *et al.*, 2003). Historical reports illustrate the use of LTS in early Greek and Chinese civilizations as an irrigation and sanitation method (Tzanakakis, Paranychianakis & Angelakis, 2007), but it was not until the second half of the 19th century when “sewage farming” (a historical term used for LTS) was used to protect public health after the cholera epidemics in England. This expansion drove the development of the basic principles of planning, operation and management of the systems. By that time, the first LTS appeared in the USA, France and Germany contributing to the development of the technology. However, their use declined as a result of the development of more intensive treatments to cope with population growth and lack of land availability (Jewell & Seabrook, 1979). In the USA, the Clean Water Act (The 92nd United States Congress, 1972) renewed interest in land treatments when planners realized that these systems were able to meet new discharge requirements of the National Pollutant Discharge Elimination System. Recently, interest in these systems has been renewed due to the possibilities that they offer as on-site treatments for remote areas and small communities, overcoming the high energy cost of conventional systems. In addition, they have been used as a tertiary treatment for polishing effluent from Wastewater Treatment Plants (WWTP), in some cases utilising the supply of nutrient-rich water for biomass production for economic benefit (Paranychianakis, Angelakis, Leverenz, *et al.*, 2006; Nissim, Jerbi, Lafleur, *et al.*, 2015).

During the period 1920-1970, LTS were used as a tertiary treatment in the UK to provide confidence with respect to meeting the so-called Royal Commission 20:30 biological oxygen demand: suspended solids discharge consent standard which was widely applied at British wastewater treatment works (Gray, 1989). Many of these LTS were subsequently inherited by the regional water authorities following the Water Act (1973) and remain today. Sweaney (2011) gathered data in relation to organic matter, suspended solids and ammonia removal from 20 LTS used for tertiary treatment by UK water companies and found that the systems did not have any formal design and used different applications rates and sizes (probably due to the lack of official guidance), this made it difficult to draw conclusions about any performance trend. The study, however, did not show results for P (Sweaney, 2011).

Compared to mechanical or chemical wastewater treatments, LTS are cheaper to operate and maintain, whilst also being less energy demanding (Sapkota, Arora, Malano, *et al.*, 2014; Tzanakakis, Paranychianakis & Angelakis, 2007). Their main constraint is that they require larger amounts of land than conventional centralised wastewater treatments, so they have largely been used in rural areas, for a single household or small-scale applications, where land availability is not a problem. They have been successfully implemented for small communities (< 10 000 p.e.) in Scandinavia, the UK, Australia and USA.

Depending on the loading rate and flow path, LTS can be classified, into slow rate (SR), overland flow (OF) and rapid infiltration (RI) systems (USEPA, 2006). Each achieves different performance outcomes and can/not be implemented, depending on the site characteristics and the desired level of treatment (Table 2-1). In LTS, the main treatment mechanisms are chemical retention and transformation, mechanical retention and biological transformation. While mechanical retention (e.g. grass filters strips) and biological transformation can treat pollutants such as solids, organic matter (OM), nitrogen and pathogenic microorganisms; adsorption and precipitation are the main processes responsible for P removal in soils (Vohla, Kõiv, Bavor, *et al.*, 2011). These mechanisms differ from soil to soil and depend significantly on soil surface chemistry and pH.

Table 2-1 Comparison of land treatment process design features.

Source: (USEPA, 2006)

Feature	Slow rate (SR)	Overland flow (OF)	Rapid Infiltration (RI)
Minimum pre-treatment	Primary sedimentation	Screening	Primary sedimentation
Annual loading rate (m/yr)	0.5-6	3-20	6-125
Typical annual loading rate (m/yr)	1.5	10	30
Field area required (ha)	23-280	3.6-44	3-23
Typical weekly loading rate (cm/week)	1.9-6.5	6-40	10-240
Disposition of applied wastewater	Evaporation and percolation	Evapotranspiration surface runoff, limited percolation	Mainly percolation
Application techniques	Sprinkler, surface or drip	Sprinkler or surface	Usually surface
Need of vegetation	Required	Required	Optional
Climate needs	Winter storage in cold climates	Not critical	Not critical

Each type of soil is characterized by a P fixation capacity and is dependent on the number of reactive sites that can react with the phosphate. It depends on the amount and type of clay present, the soil pH and the OM content. When all the P-fixation sites are filled, the maximum phosphorus-fixing capacity of the soil is reached, thus the soil is supersaturated with P (Brady & Weil, 2008). Consequently, P removal in LTS is a finite process (Drizo, Comeau, Forget, *et al.*, 2002). In these situations, the required level of P removal is not achieved and excess P can be released to the environment either in leachate or runoff as dissolved P.

Although longevity of the LTS is one of the key parameters to achieve cost-effective treatments, little research has been carried out regarding effects of long-term wastewater application in LTS and the longevity of the system in terms of P removal (Hu et al., 2006). Three key questions regarding long-term P removal in LTS remain (Hu, Zhang, Huang, *et al.*, 2005; Hu, Zhang, Kendrick, *et al.*, 2006; Robertson, 2012;

Weiss, Eveborn, Kärrman, *et al.*, 2008; Moura, Silveira, O'Connor, *et al.*, 2011; Eveborn, Kong & Gustafsson, 2012; Eveborn, Gustafsson, Elmefors, *et al.*, 2014): i) is the required knowledge available about how long one of these systems can immobilize P?, ii) what are the mechanisms involved and what is their relative importance? and iii) what should be the approach to estimate of the P removal capacity by LTS in the long term?

2.3 Phosphorus removal processes in land treatment systems

The main phosphorus removal mechanisms in natural treatments are vegetation uptake, microbial processes, precipitation and adsorption (Reddy, Kadlec, Flaig, *et al.*, 1999). In overland flow systems, the vegetation uptake removal pathway can be significant (~20-30%) if vegetation is harvested regularly (Crites, Middlebrooks & Sherwood, 2006). Precipitation is the process in which phosphates can be removed from the soil solution when it reacts with Fe, Al, Mn (acidic soils) or Ca (basic soils) to form phosphate minerals. This process is considered to be irreversible but depends on pH, redox conditions and the concentration of the mineral ions in solutions required to precipitate (McCray, Lowe, Geza, *et al.*, 2009). Adsorption is the process of fixation (chemisorption) of PO_4 ions to soil particles. P interacts with soil particles in its exchangeable orthophosphate form, the pH drives the availability of each orthophosphoric form in the soil solution H_3PO_4, $H_2PO_4^{-1}$, HPO_4^{-2} and PO_4^{-3}, at soil pH, PO_4^{-3} has the strongest binding capacity (MacBride, 1994). Positively charged soils with Fe, Al, Ca content attract phosphate (PO_4) anions but they can also be adsorbed to the soil surface through non-electrostatic forces (Evangelou, 1998). Adsorption is a fast process but desorption is usually slower. It is driven by an equilibrium constant and if the concentration of PO_4 ions rises in the soil solution, the ion will adsorb to soil charged surfaces to restore the equilibrium. Adsorption is limited by the number of available sorption sites (McCray, Lowe, Geza, *et al.*, 2009)

Despite the numerous studies and significant knowledge regarding all these processes, it is complicated to predict P removal performance in LTS as different environments (soil pH, soil type, temperature, etc.) will promote different processes that operate at different rates (McCray, Lowe, Geza, *et al.*, 2009). Current understanding of soil P availability to plants gives us a conceptual model to help us to understand P dynamics in LTS. Syers, Johnston & Curtin, (2008) proposed that phosphorus in soil can be considered to be in one of four different pools on the basis of its availability to the plant: immediately available P in soil solution, readily available P that is adsorbed weakly at the soil surface, more strongly bound P that is less available, and finally very strongly bound P that is either of very low availability or inaccessible. High concentrations of P in soil solution due to wastewater irrigation (~10 mg P/l) will encourage an initial rapid phase of P sorption on high-affinity sites on the soil surface (Paranychianakis et al. 2006). The positive charges associated with soils with a high anion exchange capacity allow rapid, readily-reversible and non-specific electrostatic adsorption of anions such as phosphate. These sorption processes are pH dependent and are likely to be associated with the surfaces of Fe and Al minerals in strongly acid to neutral systems and on Ca minerals in neutral to alkaline systems (Lindsay, 1979). A slower phase of P removal is attributed to phosphorus diffusion in poorly accessible sites and/or to chemical precipitation which apportions P to the strongly-bound pool (Paranychianakis, Angelakis, Leverenz, *et al.*, 2006; Syers, Johnston & Curtin, 2008). Inorganic P compounds in soils are commonly associated with iron, aluminium, and calcium. These compounds have a high degree of variability in their solubility and stability, which are influenced by pH. Those compounds with very low solubility, such as apatite ($Ca_{10}(PO_4)_6(OH,F,Cl)_2$), would be associated with the very low availability pool.

One of the key issues related to the study of the lifespan of LTS is the time dependency component in the P immobilization reaction (Paranychianakis, Angelakis, Leverenz, *et al.*, 2006; Cucarella & Renman, 2009). It consists of a two-step reaction: an initial and fast sorption phase and a slower phase related to P diffusion or/and chemical precipitation. However, the secondary slow or irreversible sorption that has been widely documented in these laboratory studies was not evident in long-term P monitoring in septic tanks plumes in Canada by Robertson (2008). Consequently, Robertson concluded that, secondary P attenuation processes, such as P diffusion into soil particle microsites, slow recrystallization of sorbed P to insoluble metal phosphate minerals, or slow direct precipitation could be inactive in groundwater zones or too slow to be observed in the 16-year period of the study, suggesting that P can remain mobile for decades with the consequent risk of impact to nearby rivers and lakes.

If soil characteristics change over time, P sorption capacity (PSC) may not remain constant, which has implications for LTS lifetime estimations. Changes in physical and chemical soil properties due to continuous application of wastewater have been characterized in the following studies. Hu et al. (2006) described an increase in pH from 5.6 to 7.0 in the top 15 cm layer of the soil after more than 30 years of high pH (~8.5) wastewater application coming from a paper mill (25%), other industries (~25%) and (~25%) from domestic wastewater in the Muskegon Wastewater Treatment facility (USA) with major soil types categorized as sands. These results are consistent with those of Richardson et al. (1988) who reported statistically significant increases (P>0.95) in North Carolina in three acidic mineral soils at a coastal plain swamp after municipal wastewater additions for 30 years. On the contrary, Eveborn et al. (2014) in their study of P accumulation and mobility in soil treatment systems after 8 to 11 years of domestic wastewater application in sand filter beds, revealed that the pH of the top layer was between 1-2 units lower than in reference samples. Their interpretation, in this case, was that the pH change was due to the chemical dissolution and consumption of reactive calcium oxide and other alkaline minerals or acidifying organic degradation processes. However, the study points out that the results in the surface layer might be also have been affected by surface regeneration works carried out during the study. Moreover, due to long-term high salt content effluent application in the Muskegon studies, exchangeable Ca concentrations increased ten fold (Zhang, Dahab, Nunes, *et al.*, 2007; Hu, Zhang, Huang, *et al.*, 2005; Hu, Zhang, Kendrick, *et al.*, 2006). Hu et al. (2006) suggest that the increase in the pH might have as a consequence the increase in the exchangeable Ca in the topsoil and links this with the possibility of an extension of the lifespan of the LTS. The experiments of Eveborn et al. (2014) also suggest that the increase in oxalate extractable Al and Fe could be due to weathering mechanisms provoked by acidification of the soil after the wastewater additions, which will also affect the sorption capacity of the soil. These changes may also affect the P sorption capacity of the soil which is often assumed to remain constant for a certain site during the lifespan of the LTS (Hu, Zhang, Huang, *et al.*, 2005)

It is clear that efficiency of P removal declines with time, with slower sorption processes approaching the equilibrium, and that a number of factors affect it (soil mineral type, amount of clay, pH, OM, anion presence or temperature). However, Drizo et al. 2002 and Hu et al. 2005 pointed out the possibility of long-term P accumulation and removal capacity regeneration. The proposed mechanism depends upon the formation of new P-retentive surface clusters through phosphate compound adsorption that acts as new reactive sites for adsorption and precipitation. Eveborn et al. 2014 also suggest that P bound to the surface in stable pools may in the long term increase the P sorption capacity of soils due to changes in pH and in oxalate-extractable metals during the wastewater application. Furthermore, Drizo et al. 2002 demonstrated that a wetland constructed using electric arc furnace slag as a filter medium got back 74% of its P retention capacity after four weeks rest and claim that other studies observed that soils had restored their P adsorption capacity after repeated wetting and drying cycles. The mechanisms involved are not well understood, but it is suggested that it is related with elevated pH after draining the material that will bring Ca, Fe and other mineral ions in supersaturation with the solution to create new sites for P adsorption/precipitation in the filter pores. Bisone et al. (2016) studied the behaviour of a clay soil with wastewater additions and the influence of hydraulic loading. The study focused on the evaluation of wetting and drying cycles in clay soil used for wastewater treatment and results indicated the potential to adsorb P and that saturation and desaturation cycles did not influence phosphate retention but enhanced nitrification. However, the soil saturation can lead into P desorption caused by Fe reduction and therefore intermittent loading can favour infiltration and help to avoid desorption. Therefore, LTS design and management approaches which permit resting periods could allow the use of clay soils as a longer term polishing treatment for P removal.

Organisms within the land treatment system require P for growth and incoporate it into their tissues. The biota in a land treatment system follows a cycle of growth, death and partial decomposition. Therefore, P can also be taken up and stored by biota. Microbiota (bacteria, microinvertebrates) undergo the most rapid uptake due to the high mutiplication and growth rates, the biomass of microbiota is small compared with vegetation. On the contrary, vegetation use phosphorus at a slower rate, where plant roots constitute a significant fraction of the active phosphorus storage, as roots extract P from the soil solution as it becomes available. The decomposition of this plant litter is a very slow process (Kadlec & Knight, 1996).

2.4 Methods to assess phosphorus removal capacity in soils

The standard tests to assess P transport in soils (such as water extractable phosphate, exchangeable phosphate, sorption and desorption isotherms) are usually based on agronomic aspects of P availability for the plant and not to determine environmental risk of P loss in soils (Moura, Silveira, O'Connor, *et al.*, 2011). Although they can be used to quantify the nature and quantity of P concentrations in the soil, a better understanding is needed to determine which of those indices are more suitable to better assess long-term P fate in LTS.

Hooda et al. (2000) studied the potential of different soil tests to predict P release to water of different soils in the UK that had received long-term fertilization or sewage sludge: Soil Test P (STP), sorption-desorption indices, the degree of saturation of P (DPS) and the amount of water dissolvable-P. The study discussed that the DSP of the soils is more important than other indices because soil extractable-P does not integrate the P soil characteristics, but the DSP index associates P management and soil type factors helping to identify soils that are likely to become diffuse sources. Moura et al. (2011) studied the effects of long-term reclaimed water application on P leaching potential in rapid infiltration basins, the study concluded that extractable P and P-saturation ratio are good indicators of soluble concentrations in the leachates. Furthermore, Hu et al. (2005) reported that labile P distribution is not a good indicator of P leaching in soil wastewater treatments since it is not correlated with TP, Fe-bound P, or Ca/Mg-bound P, but, identified the need for a new index that integrates DSP and Ca adsorption.

Traditionally, the P removal capacity of the soils has been related to the absorption-adsorption P capacity. This can be determined by batch-scale experiments where the soil interacts with solutions at different P concentrations until the equilibrium is reached, and translated to Langmuir or Freundlich equations to represent their kinetic relationship (Kovar & Pierzynski, 2009). However, many researchers agree that there is a lack of studies advising how to interpret and use such batch experimental results to assess long-term effects and life expectancy of soil infiltration systems (Zhang, Dahab, Nunes, *et al.*, 2007; Cucarella & Renman, 2009; Hu, Zhang, Kendrick, *et al.*, 2006; Eveborn, Kong & Gustafsson, 2012; Drizo, Comeau, Forget, *et al.*, 2002).

Nair et al. (1984) identified a wide range of methodologies that had been used to determine P adsorption. Although diverse methodologies made the comparison among studies difficult, they proposed a standard method to predict the partioning of the dissolved inorganic P. In addition, Graetz & Nair (2000) pointed out that the laboratory procedures to determine the P adsorption had advantages; such as the possibility to separate the soil and solution or the possibility to obtain the necessary volume sample for carrying out the tests. However, they also described experimental disadvantages such as particle breakdown while shaking. The study of Hooda et al. (2000) asserts that phosphorus adsorption-sorption isotherms are useful to compare soil characteristics but their empirical nature makes them unsuitable to explain mechanisms of sorption-desorption of P in soils, as they do not reflect field conditions like runoff or rainfall.

The Onsite Wastewater Treatment Systems Manual from the Office of Research and Development of the U.S. Environmental Protection Agency (2002) states that the estimation of soil capacity removal can be based on sorption isotherms but it totally underestimates the capacity of P removal since they do not reflect the slow reactions that take place (the standard procedure extraction time is 24h) and declare that studies revealed that, in the long term, the capacity could be extended from standard isotherms predictions by 1.5-3 times. Similarly, Hu et al. (2006) evaluated the effects of long-term wastewater application on sorption capacity of the soil by comparing the 1-day maximum sorption capacity (S_{max}) before and after long-term wastewater application. The study revealed that the 1-day S_{max} increased by ~3 times since the start of wastewater application indicating that it is possible for the soil to continuously adsorb P and therefore, difficult to get a reliable estimate of S_{max}. Ádám et al. (2005) attempted to estimate the long-term P sorption capacity of filter materials. The study criticizes the use of 24-h sorption batch tests claiming that results differ from full-scale systems. To get more reliable long-term P sorption estimations they proposed a long-term experiment of a full scale horizontal constructed wetland (CW) and also concluded that batch experiments are not appropriate to measure sorption capacity materials because the experimental parameters (e.g. soil solution P concentration and water: soil ratio) are usually higher than in full-scale systems. However, with full-scale constructed wetlands, the extrapolation of the results are more difficult because of the complexity of the systems due to biofilm developments or the presence of plants that can enhance the P removal but can also generate cracks or pores in the material leading to preferential flow (Ádám & Krogstad, 2006).

Cucarella and Renman (2009) exhaustively and critically reviewed batch experiments used to estimate the PSC of filter materials used in on-site wastewater treatments. The study confirmed the findings of Nair et al. (1984) by certifying that different studies are not comparable because they are arbitrarily run under different experimental conditions and with different experimental parameters such as solution-ratio during shaking, P concentrations of the soil water, contact time, agitation characteristics and temperature. As those parameters have the potential to significantly influence P processes they should be properly established in the experimental set up to reduce their influence in the PSC determination. Additionally, experiments should, as much as possible, represent real field conditions. Drizo et al. (2002) recommended to couple batch experiments with long-term column experiments for P removal efficiency studies in order to integrate the effect of soil chemical and hydrological properties.

Column experiments are frequently used to determine hydrological properties, evaluate transport models and monitor fate and mobility of pollutants in soil (Lewis & Sjöstrom, 2010). However, Zhang et al. (2007) criticised previous column tests used to predict the fate of P in slow rate wastewater treatment soils. The tests used high hydraulic loading rates (up to 250 times those typically used in slow rate systems) and were fed continuously, which does not correspond with typical LTS management parameters. In addition, according to Hu et al. (2006), these column tests were not run for long enough to allow slow P precipitation. Eveborn et al. (2014) set up experimental columns to study the P removal and leaching potential of soil materials using deionized water. Results indicated that P removal in unsaturated soil depends on P loading, and that wash-out processes can take place in these systems, for example, during rain events and that dissolution of aluminium phosphates and the shift in ionic strength could be a possible P release mechanism. Drizo et al. (2002) aimed to determine the long-term P saturation of filter materials through column experiments. The study revealed the advantages of P saturation obtained from column experiments compared to batch experiments, for example, particles do not break down as a result of the shaking and the saturation is progressive. The study finally recommended P feeding concentration in column tests between 40-400 mg/l to reach the saturation point of filter materials in a practical timescale and experiments lasting 3-5 months to allow time for slower P retention processes to occur.

Direct mass balance calculations ($P_{accumulated} = P_{inlet} - P_{outlet}$) of long-term performance systems have also been used to assess the P removal capacity of soils although few attempts of evaluating the P removal performance of full-scale long-term sewage effluent irrigated soils have been reported. Kardos & Hook (1976) quantified the P added, removed by crops or leached over 10 years of irrigation with treated municipal wastewater. They concluded that soluble P concentrations at 120 cm depth in a clay loam soil remained close to 0.05 mg/l and <2% of the P added was leached in 10 years without vegetation removal. The same experience in sandy loam reported 3% leaching. Hu et al. (2006) performed a 27 years mass balance of the Muskegon wastewater treatment plant (USA), reporting 99% retention of the P applied. Eveborn et al. (2012) studied the performance of four Swedish uncovered soil treatment community-scale systems aged from 14 to 22 years old. Using a mass balance approach, the treatments presented much poorer P removal (8-16%) than previous soil treatment reports. Robertson (2012) quantified the P retained in a lakeshore non-calcareous sand filter with water table fluctuations, and compared it with the estimated lifetime after 20 years of operation. Contrary to Eveborn's findings, the results showed that the filter bed had retained almost all of the P loaded with the wastewater over the two decades of operation. More recently, Dzakpasu et al. (2015) studied the long-term capacity and efficiency of a soil substrate full-scale integrated constructed wetland in Ireland, by studying the wastewater inflow, outflow and storage of P in plants and sediments. Results revealed a 91% a total P removal, where 58% of P storage is accounted for P removal in the soil. One of the largest experiences with soil infiltration systems is situated in Bardu (Norway), where municipal wastewater from 5 000 inhabitants has been pumped into glaciofluvial sand and gravel deposit infiltration basins at a mean temperature of +0.7ºC. After 25 years of operation the treatment performance was 99% P removal and still, it was estimated to last 12 years more (Jenssen, Krogstad & Halvorsen, 2014). Reddy et al. (1999) identified the main difficulties when trying to assess P retention in wetlands as: failure to identify and measure inputs and outputs of P and water, use of only one form of P, comparison of synchronous flows and grabbing samples from strong variable flow or concentration. Therefore, few attempts at quantifying the P removal efficiency of long-term full-scale experiences in natural treatments have been reported, mainly in grasslands and temperate climates, with variable results. The results comparison among studies indicates high removal variability probably due to differences in soil chemical properties, age of the system or sampling and calculation methodologies.

2.5 Towards estimates of longevity

There is not a clear definition regarding life expectancy or longevity of LTS (Yu, 2012). In fact, there is a common misunderstanding between exhaustion of P, retention capacity of the material and longevity of the system. From the point of view of on-site treatments, longevity must be interpreted as the time when the system reaches the effluent P discharge limit (Heistad et al., 2006), which differs among countries and legislations in terms of both concentration and exceedance statistics. A number of studies have calculated longevity from a simple approach, the S_{max} sorption capacity of the soil (g of P/kg), the volume of land being used for treatment (m^3), P content of applied wastewater (g of P/PE) and the discharge rate (g P/day) (Table 2-2). However, the limitations discussed in previous sections highlighted how experimental conditions in S_{max} assessment can contribute to errors in such a lifetime forecast. Cucarella & Renman (2009), Vohla et al. (2011) and Chang et al. (2014) noted those limitations and suggested that life expectancy calculations could not be entirely addressed through filter materials characteristics and that, to forecast precisely the lifespan of the system, other factors (including hydrological conditions, temperature and microbiological transformations) must be taken into consideration.

Table 2-2 Previous longevity estimations in different substrates and systems*

Source[1]	Substrate/type systems	Longevity (years)	Land use	Wastewater type	Soil Texture
Drizo et al. (2002)	Electric Arc Furnace (EAF) Steel slag shale	13-37	Batch experiment	Municipal wastewater	-
Dong et al. (2005)	Oyster shell	8-23	Batch experiment	-	-
Xu et al. (2006)	Furnace slag	22	Batch experiment	-	-
Hu et al. (2006)	Soil	29-49-151**	Unproductive	~50% mill industry ~25%from other industries and ~25% from domestic waste-water.	Four major types of sandy soil on the site: Rubicon, Roscommon, Augers, and Granby
Heistad et al. (2006)	Filtralite®	5	Sub-surface flow CW	Domestic wastewater	-
Weiss et al. (2008)	Filtralite® Filtra P Soil	5 10 25	-	Domestic wastewater	-
Jenssen et al. (2014)	Infiltration basin	36	-	Domestic wastewater	Glaciofluvial sand and gravel deposit

*Different volumes, loading and wastewater characteristics assumptions for calculations.,– not stated.
**depending on the type of soil

Simulation models can help to better understand the importance of bio-physico-chemical and hydraulic processes relevant to pollutant removal, while helping to further understand how design parameters affect the performance of the system and predict longevity and exhaustion of the material (Beach & McCray, 2003). Recently, researchers have gone beyond the black-box, empirical models, to develop mechanistic models that consider the hydrodynamic and biodegradation process in natural treatments (García, Rousseau, Morató, *et al.*, 2010). They cover a wide range of biokinetic, process-dedicated, and design support models (Meyer, Chazarenc, Claveau-mallet, *et al.*, 2015). Process dedicated models represent degradation and transfer of compounds; hence they can help with understanding the fate of P and removal in LTS. These models describe P transport and sorption by soil or filter materials under different hydrological conditions and some of them predict breakthrough curves (Langergraber & Šimůnek, 2012; Claveau-Mallet, Courcelles & Comeau, 2014; Sinclair, Jamieson, Gordon, *et al.*, 2014; Sinclair, Jamieson, Madani, *et al.*, 2014; Liolios, Moutsopoulos & Tsihrintzis, 2015).

Intensive research has been produced since the late-1970's to develop models able to simulate the interaction in between the soil matrix, the water transport and P. The main aims of these models was to evaluate non-point source pollution of subsurface waters by agricultural P (Vadas, Bolster & Good, 2013). Many of these models have been updated through time and continuously developed. Different models have been used to accomplish the aims depending on spatial scale and resolution (watershed, field-scale), time scale (long-term, short-term), and the hydrological system (saturated flow, variable saturated flow, horizontal flow and, vertical flow). These models can be divided into ones that use a water balance model and the ones that use numerical solution of Richard's equation. The models based on Richard's equation are more input-intensive and computationally demanding than the water balance models but they provide more accurate solutions for field scale modelling. Regarding the overview of soil phosphorus dynamics of those models, McGechan & Lewis (2002b) provided an exhaustive review of a number of field scale P dynamics models and the equations used (e.g. ANIMO (Groenendijk & Kroes, 1999), GLEAMS (Leonard, Knisel & Still, 1986), MACRO (Jarvis & Larsbo, 2012) and DAYCENT (Parton, Hartman, Ojima, *et al.*, 1998)), pointing out MACRO as the most complete model for soil transport processes but with more simple representations of P transformation.

Some of the most recent experiences of numerical modelling of on-site wastewater treatments and phosphorus fate predictions are related to the use of HYDRUS (J. Šimůnek, M. Šejna, H. Saito, M. Sakai, 2013). HYDRUS-1D and 2D are able to simulate one and two-dimensional movement of water, heat and multiple solutes in variably-saturated media and can be coupled with different specific modules like wetland module (CW2D) to be able to run P degradation along with other processes (Langergraber & Šimůnek, 2012). Recently, Langergraber (2016) reviewed process-based models applicable to subsurface flow wetlands treatment, and identified the

HYDRUS Wetland Module as one of the most advanced ones because of its multi-component biokinetics-models and stated that it is a powerful tool for understanding wetland processes. PHREEQC (Parkhurst & Appelo, 1999) can also be coupled with HYDRUS and be used to solve complex geochemical calculations (Claveau-Mallet, Courcelles & Comeau, 2014) such as interactions with minerals, gases, exchangers and sorption surfaces based on thermodynamic equilibrium, kinetic, or mixed equilibrium-kinetic reactions. In addition, MODFLOW (Twarakavi, Simunek & Seo, 2008) is a 3D finite-difference groundwater model that can be also coupled and adapted with HYDRUS.

The HYDRUS-1D and 2D numerical code since version 4.0, released in 2007, is capable of simulating a large quantity of non-equilibrium flow and transport processes. They can be divided into physical non-equilibrium and chemical non-equilibrium processes. The study by Šimůnek & van Genuchten (2008) gave an overview of the conceptual models, and the specifications of each model with the water flow equations, the solute transport equations and the number of parameters needed in each. This new feature provides a wide range of possibilities to simulate phosphorus transport in soils, such as dual-permeability models to simulate water flow in two different domains, with different flow velocities and non-equilibrium chemical models. These models range from the simple one kinetic site model described as a first-order rate equation to two sites models with different sorption kinetics for different fractions, where one fraction is assumed to be instantaneous and the other one is kinetic. Vogel et al. (2015) successfully simulated flow and transport in a two-dimensional dual–permeability system with spatially variable hydraulic properties permitting to compare different spatial distributions of hydraulic properties with model responses comparison.

Regarding P studies with HYDRUS, Naseri et al (2011) compared physical modelling of silty clay-loam texture columns against the numerical modelling of HYDRUS-3D, the results concluded that it simulated the water flow in the columns successfully, but overestimated the final sorbed PO_4 concentrations in the soil. Elmi et al. (2012) found similar over-estimation results when using HYDRUS-1D to study the vertical distribution and transport processes of PO_4 in soil columns. The simulation indicated that 98% of the P applied was accumulated in the first 0.2 m of the column and decreased with depth. Sinclair et al. (2014a) also used HYDRUS-2D to simulate different lateral flow sand filters in on-site wastewater treatments after septic tanks showing poor removal rates and effluent exceeding 1 mg P/l concentration at the end of the study. Morrissey et al. (2015) studied with HYDRUS-2D the impact of un-sewered cluster housing simulating the attenuation of contaminants through the unsaturated zone and revealed limited impact to groundwater quality. Afterwards, the calibrated model was used to simulate the impact of increasing the housing density with new developments. All those studies were focused on studying transport and contamination effects but none of them introduced the time variable in the study in order to predict remaining lifetime.

Although a number of studies point out the potential for exhaustion of the P sorption capacity in treatment systems, there have only been a few attempts to forecast P longevity in soil infiltration systems. The first one is related to the Muskegon (USA) (Zhang & Dahab, 2006) wastewater treatment plant which was part of the large-scale demonstration project for nutrient removal. The project aimed to evaluate long-term P performance, as it is known to be one of the most important lifespan limiting factors. The first phase of the study calculated new 1-day S_{max} after 30 years of operation and the new remaining life expectancy (RLE). The new estimations had an extension in the RLE because of the changes in soil properties after long-term wastewater application in the soil (Hu, Zhang, Kendrick, *et al.*, 2006). The second phase of the same study consisted of column breakthrough modelling, where they re-calculated the RLE (Zhang, Dahab, Nunes, *et al.*, 2007). As a result, the study proposed a remaining life expectancy prediction formula:

$$RLE = t_b * F/180 \quad \textbf{(2-1)}$$

$t_{b=}$ the breakthrough day

180=the irrigation days per year at the Muskegon plant

F= the correction factor for the inlet P concentration and the concentration used in the study.

RLE=remaining life expectancy (days)

The same project proposed a model based on the mass balance principle. The empirical model is able to predict the life expectancy on a yearly basis through the effects of the main operational parameters of the system (rotating crop type, hydraulic loading rate, annual precipitation, soil type, etc.). However, the interaction between the soil and the hydraulic systems are not reflected upon. Parkhurst et al. (2003) described a reactive-transport model developed to simulate P in the sewage plume from treated sewage effluent to ground-infiltration disposal beds at the Massachusetts Military Reservation on western Cape Cod (USA). The simulations covered the discharged period (1936-1995) and the 60 following years after cessation of disposal. The three-dimensional reactive-transport model used to develop the base-case was PHAST (Parkhurst & Kipp, 2002), with model limitations associated with loading, flow systems and sorption characteristics of the aquifer uncertainties. Despite the fact that the aim was not to study the longevity of the system because the activity of the filter beds had stopped, it is a useful exercise in long-term plume migration modelling. Yu (2012) attempted a one-dimensional model that aimed to provide the longevity of any point of the infiltration system considering a homogeneous and isotropic soil, and constant and unsaturated flow. It was aimed to estimate the longevity, the exhaustion time and sorbed P. The model proposed was a contaminant solute transport model where advection, diffusion, dispersion and sorption reactions were represented. The simulation indicated that the most sensitive factors for P concentration in a soil column to reach critical concentration were the average pore flow velocity and the P sorption capacity of the soil. The longevity estimations from the model compared to the service time of the infiltration study sites were shorter. Herrmann et al. (2013) modelled the transport and removal of PO_4 in a reactive filter using the hydro-geochemical transport code PHREEQC (Parkhurst & Appelo, 2011). The study claims that in order to be used to forecast performance and longevity it needs to be further tested and developed due to that it does not take into consideration adsorption processes or the effect of biofilms growth in the filter material. Claveau-Mallet et al. (2014) proposed a prediction tool for slag filter longevity based on dissolution and precipitation kinetics. The proposed methodology was based on three steps: (1) experimental batch tests methodology, (2) numerical calibration of the batch test; and (3) numerical simulations of the filter. However, the study assumed several limitations and highlighting the principal one as being the assumption that the contact between the water and the filter particles is limited, and not being affected by clogging from precipitates or particulate OM. The model needs to be calibrated before being used as a design tool and proposes to couple a hydrodynamic and geochemical code such as HYDRUS-PHREEQC to overcome those drawbacks.

2.6 Synthesis and conclusions

LTS have been in use since wastewater treatments were applied to protect public health and they still have a role to play at the current wastewater industry as a low energy and low maintenance polishing step for small wastewater treatments. They are normally used before the wastewater treatment plant effluent is released into the environment to avoid environmental problems, mainly eutrophication, related to excessive P concentrations.

P removal mechanisms in LTS are physical retention, sorption processes and microbial and plant uptake. Sorption is a finite process and depends on the interaction with the environment and the chemical properties of the soil (ion presence, pH, OM, clay content, etc). Thus, if these conditions change over time, mainly due to long-term wastewater irrigation, the P removal potential will also change.

It is well accepted that estimation of the P sorption capacity of soils by batch experiments has several limitations when it is used to calculate the S_{max} in the long term or when used to forecast the longevity of the system. The standard methodology is a short-term sorption analysis (24h) that underestimates the long-term removal capacity because it does not take into account the slow precipitation processes and because the experimental set up does not represent the real systems and interactions with the ecosystem. Thus, studies advise that these methods are not used for lifespan prediction but to compare materials and soils characteristics. Column experiments should also be correctly designed when addressing long-term P removal characterization and filter material saturation, mainly regarding the length of the experiment and hydraulic loading in order to correctly translate results to full-scale experiences.

Regarding lifetime predictions in LTS, usually, direct mass balance approach using the S_{max} has been used, however, the drawbacks previously pointed out also affect this methodology. Using modelling tools to assess the water flow, contaminant transformation and contaminant-transport processes can help to assist in the integration of all the parameters that affect the functioning of the system. However, few attempts to estimate the P longevity of LTS through models have been found and none of them has been completed and published due to several limitations and further development and research needed (uncertainties in data acquisition, empirical models, models not validated or neglecting important variables of the removal processes).

LTS's modelling challenge lies in getting useful results from batch and column experiment regarding soil P adsorption behaviour in the long term, and how to transfer those experimental results into the solute transport equation. The longevity of the LTS is one of the key parameters to achieve cost-effective treatments and if new studies are able to successfully model treatment scenarios then we will become a useful LTS management tool and provide greater confidence in the sustainable operation of these systems required by both operators and regulators.

3 LONG-TERM PHOSPHORUS ACCUMULATION AND REMOVAL EFFICIENCY IN A LAND-BASED WASTEWATER TREATMENT SYSTEM IN THE UK[2]

3.1 Introduction

Land Treatment Systems (LTS) are terrestrial systems where pre-treated wastewater is applied onto the land surface to achieve a specified level of treatment through natural physical, chemical, and biological processes within the plant-soil-water matrix (Crites, Middlebrooks & Sherwood, 2006). Soil P retention mechanisms are physical, chemical, biological processes and/or plant uptake (Crites, Reed & Bastian, 2000). Physical retention can retain P by deposition and infiltration, where vegetation and dense root systems help to decrease water velocity and increase contact time of P with the soil surface, this mechanism has greater influence in particulate P than dissolved P (Roberts, Stutter & Haygarth, 2012). They have been used to treat wastewater since the nineteenth century and continue to be used today, principally at small rural works as a polishing step, after secondary treatment to remove solids, nutrients and pathogens (Tzanakakis, Paranychianakis & Angelakis, 2007). They can offer a sustainable alternative tertiary treatment to small treatment works with available land, where low tech, low carbon, and low maintenance solutions are required (Tyrrell, 2016). They can also be an option for small-scale applications such as sustainable urban drainage systems where vegetated units are used to favour infiltration, detention and moderate stormwater while improving water quality (Charlesworth, Bennett & Waite, 2016) or advance treatments for industrial wastewaters in places where there is a lack of specialized operators and land is relatively affordable (Taebi & Droste, 2008). However, these systems normally present limitations that can influence the treatment performance, such as higher land requirements than other treatments, or constraints based on the site conditions (e.g. soil texture or soil chemistry). The main phosphorus (P) removal mechanisms in natural treatments are vegetation and microbial uptake, and soil chemical precipitation and adsorption (Reddy, Kadlec, Flaig, *et al.*, 1999). While vegetation and microbial uptake are biological processes that can be restored through appropriate design and maintenance; chemical processes such

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as precipitation and adsorption, depend on soil properties that are reduced over time and eventually exhausted when the equilibrium in the pore water is reached or the functional groups on the soil surface are saturated. This can potentially lead to the release of soluble phosphorus to water bodies causing eutrophication, and consequent impacts on the quality of the aquatic ecosystem by oxygen depletion (Smith, 2003).

Although these systems have been in use since the mid-nineteenth century and in a wide range of soils and climate conditions, most monitoring studies have been conducted on young treatment systems and for short periods of time. Therefore, there is limited information regarding removal performance in the long-term and lifespan estimations. Batista et al. (2017) reviewed field and laboratory experiences, and methodologies to estimate P removal in the long-term in LTS. They found that laboratory experiments can be used to compare materials but not for lifespan predictions because the standard methodology (short contact time or liquid-solid solutions ratio) does not represent the systems and interactions with the ecosystem. In addition, results from P removal field experiments presented highly variable removal rates (8-99%) in different aged unsaturated soil infiltration systems (14-27 years), and different soil types and climates, making difficult the comparison between studies difficult.

In the UK, during the period 1920-1970, LTS were used as a tertiary treatment to provide confidence with respect to meeting the so-called Royal Commission 20:30 biological oxygen demand: suspended solids discharge consent standard which was widely applied at British wastewater treatment works (Gray, 1989). Those LTS were subsequently transferred to the corresponding water companies following the Water Act (1973) and remain today (Tyrrell, 2016). Sweaney (2011) aimed to identify sustainable wastewater technologies used by the water industry and provided evidence of the wastewater quality achieved by British water companies using LTS technologies. The study identified 20 LTS in the form of grass plots mostly and obtained performance data from 13 systems belonging to two water companies in relation to organic matter, suspended solids and ammonia removal, but there is a lack of knowledge about long-term P removal behaviour or age of the systems.

The aim of this study is to assess long-term phosphorus removal in an LTS in order to evaluate for how long this type of system can make a useful contribution to wastewater treatment. Additional objectives are to estimate the soil P removal efficiency and the P accumulated over time and to evaluate the impact of the degree of saturation of soil phosphorus on the quality of the water entering surface and groundwater bodies. The chosen case study is an LTS in the south of England (UK), where different parts of the field have been irrigated with secondary wastewater effluent for different periods of time (up to 85 years).

3.2 Materials and Methods

3.2.1 Study site description

The site is a riparian meadow of approximately 20 000 m^2 surface, bordering the River Meon in Knowle, Hampshire, England, (50º53'00"N 1º12'31"W). It is situated on a Plateau Gravel and alluvium parent material with clay loam soil texture (Tyrrell, 2016). The field has been irrigated with secondary wastewater effluent from Knowle Sewage Treatment Works (STW) for approximately 85 years. The vegetation is presently grassland with perennial herbaceous plants such as stinging nettles (*Urtica dioica*) in the irrigated parts. The vegetation is not harvested or removed from the site.

Knowle STW (Figure 3-1) is thought to have been installed in the early 1930's to serve the Knowle psychiatric hospital which, between 1852 and 1996 had an average population of 2 000 (patients and staff) and large laundries and workshops (Burt, 2003). From 2000 onwards the hospital site was redeveloped into a residential area with 700 domestic properties, a high-security hospital and commercial businesses. The STW utilises primary and secondary treatment processes prior to discharge to the riparian meadow (the "discharge field") for tertiary treatment.

The secondary wastewater effluent is discharged via a chamber distributing flows through a sluice system onto the discharge field (irrigation). Prior to the 1990's, the effluent delivery system consisted of a channel and floodgate system that irrigated a larger area of the discharge field. Historical maps (Landmark Information Group 1932) show that the original discharge channel that covered half of the field was elongated to irrigate the whole field around 1950. This system was replaced in the 1990's with a pipeline along approximately half of the discharge field with outlets of 150 mm diameter and 15 m spacing between outlets. The wastewater discharge is controlled by the plant operator, who opens the outlets, based on observation and experience. All secondary wastewater effluent discharged on to the site infiltrates into the soil and no surface runoff has been observed from the discharge field to the river. The system has no flow meters; hence the amount of water discharged to the field is uncertain.

For this study, the discharge field was divided into three sections (Figure 3-1). Section A has been irrigated with secondary wastewater effluent from the STW since the early 1930’s and is still in operation; section B was irrigated until the end of the 1990’s, when the sluice system was replaced by the pipe; and Section C, which, based on historical maps, was irrigated from approximately 1950 until 1990 (Landmark Information Group, 1932).

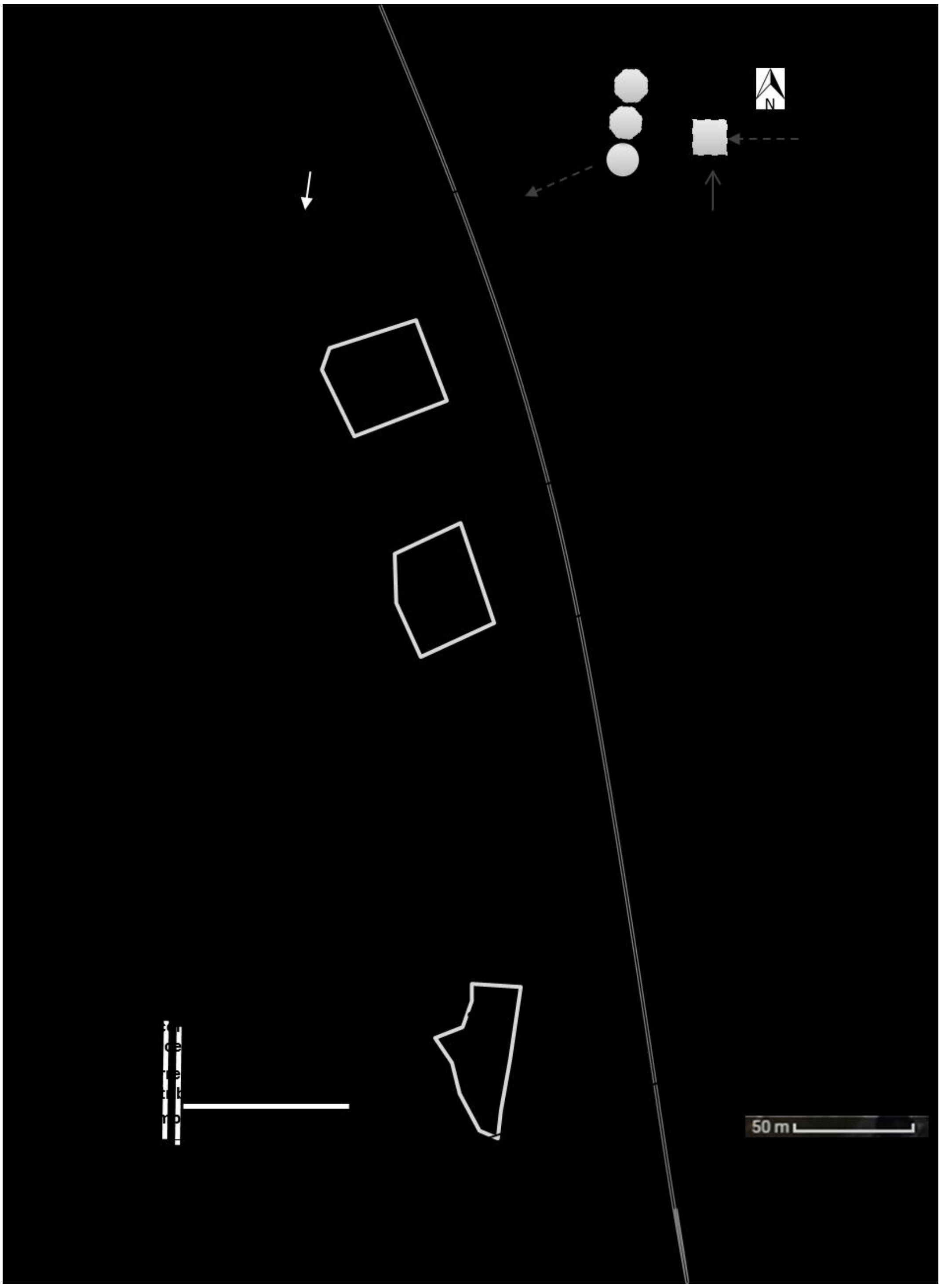

Figure 3-1 Diagram of the land treatment system in Knowle (UK) showing the sewage treatment works location, the historical discharge systems, the division of the sampling sections and sample locations.

3.2.2 Soil analysis

Stratified random sampling was used to sample the soil in each of the three sections. Due to the unclear boundaries between the sections, and to avoid sampling in, or close to, the boundaries, equal-sized plots of 2 000 m^2 were defined in each section. In each plot, 10 points were randomly selected with 10 m minimum distance between them. It was judged that the sampling density (equivalent to 50 samples/ha) would provide sufficient information about the total phosphorus (TP) variability, since sampling protocols for P in crop production recommend 4-8 samples/ha as a trade-off between practicality and accuracy (Force, Mallarino, Beegle, *et al.*, 2006). At each point, a composite sample of the 0-40 cm layer was taken with a Dutch auger, based on the method of Falkiner (1999). The samples were pre-treated (BSI Standards Limited., 2006) and TP was determined with aqua regia digestion (BSI Standards Limited., 1998), and phosphorus measured colorimetrically. The mean TP concentration (C_p) from triplicates laboratory samples of n=10 samples in each section (kg P/kg) by acid digestion was used for mass balance calculations since it should have included the majority of the phosphorus sorbed from the wastewater application. Bulk density was estimated to be 940 kg/m^3 from topsoil properties (Centre for Ecology & Hydrology, 2007) for topsoil bulk density representative of 0 – 15 cm soil depth. Two different sources were used as a reference samples of unirrigated soil: the topsoil background levels for TP of 560 samples in a 50 km radius of clay loam soils type and grassland land use from the National Soil Inventory (NSI) (National Soil Resources Institute, 2014), referred to in the text as ‘regional average’; and Tyrrell's (2016) results from an adjacent clay loam, grass field situated in Knowle STW, referred to as ‘adjacent site’. A one-sample t-test showed that the TP of the adjacent site was not significantly different from the regional average ($t=0.298$; $p=0.766$).

3.2.3 Water balance of the site over the study period

The water inputs to the systems considered are precipitation and irrigation. Long-term average monthly rainfall was estimated from the CEH – Gridded Estimates of Areal Rainfall (CEH – GEAR) which contains 1 km gridded estimates of monthly rainfall for UK from 1890 to 2015 (Keller, Tanguy, Prosdocimi, *et al.*, 2015). It is assumed that the volume of water consumed in the hospital and the village equals the secondary wastewater effluent. Therefore, irrigation was calculated from the estimated water consumption in Knowle hospital and village over the study period. Average domestic water consumptions were estimated to be 126 l/capita in 1930 and currently 150 l/capita (Anglian Water Ltd. 2008). The water consumptions between these dates were interpolated linearly.

The water outputs of the system are evapotranspiration and percolation, runoff was assumed to be zero since it has not been observed in the study field. The reference evapotranspiration was calculated using the Penman-Monteith equation (Land and Water Division of FAO, 2012). Air humidity, wind speed and radiation were estimated with the ETo calculator by the missing data estimation procedures described in Allen et al. (1998). Monthly maximum and minimum temperature were obtained for 1903 to 1999 period from Southampton (Mettoffice, 2016) (50° 53' 59" N 01° 23' 44" W) to calculate long-term average monthly evapotranspiration (ETc), in this case, ETc is equal to reference evapotranspiration since the crop at the site is well-watered grass.

3.2.4 Phosphorus inputs to the site over the study period

The total mass of P discharged to the discharge field (P_d) was estimated using Eq. (3-1) from the site history accounting for population and different P content in domestic wastewater for every year through the entire study period (1932-2016). Although P levels in the faeces changes with diet over time and space, in this study, they are assumed to be constant since the impact of changes in diet on P content effluent of on-site wastewater treatment is unknown (O'Keeffe, Akunna, Olszewska, *et al.*, 2015). A 25% P removal was applied to account for effect of primary sedimentation, the P biologically removed in the biofilters and consequently, the P exported from the works in the sludge. This P removal rate in primary and secondary treatments was calculated from wastewater inflow and outflow data from Knowle sewage treatment plant from December 2014 to March 2016.

Therefore, total P added to the discharge field was calculated from:

$$P_d = \sum_{i=y_0}^{y_f} 365 \cdot \mathrm{C}_i \cdot \mathrm{P}_i \cdot 0.75 \qquad \textbf{(3-1)}$$

where

P_d is the P added to the discharge field with the secondary wastewater effluent (kg)

P_i is the population in year i (capita)

C_i is the daily amount of P discharged to the field in the year i (kg/capita/day)

y_0=1932

y_f=2016

The population each year was estimated from admission registers of the hospital from Burt (2003). In between, the population data was interpolated linearly until the hospital closed in 1996. From 2000 to 2016, when the area was redeveloped for residential use, the population was calculated considering 2.4 persons/household occupancy (Office of National Statistics, 2013) for 700 houses. C_i was estimated from (Gilmour, Blackwood, Comber, *et al.*, 2008) study of human waste contributions to P loads to domestic wastewater in the UK and allowing for the UK P detergent consumption from 1950 to 1998 (Foundation for Water Research, 2006).

The estimated load (P_l) (kg/m^2) discharged to each section was calculated in relation to the pipe length that irrigates each of the sections.

3.2.5 Phosphorus removal

The average long-term P removal (P_r) (%) was determined by Eq. (3-2) :

$$P_r = \frac{(Cp - R)}{P_l} 100 \tag{3-2}$$

where

Cp is the mean TP concentration from triplicates of n=10 samples in each section (kg /m^2)

R is site reference for TP soil concentration (kg/m^2).

P_l is the estimated P load discharged to each section (kg/m^2).

3.2.6 Statistical analysis

Measurements of TP in soil samples were tested for normality by using the Shapiro-Wilk U test. Significant differences were determined at α=0.05. Comparisons of means were by one –sample and paired samples t-tests and one-way analysis of variance (ANOVA). Tukey's HSD (Honestly Significant Difference) tests were applied for Post-ANOVA pair- wise comparisons to identify significant differences among means. All statistical analyses were performed using IBM SPSS Statistics 23 (IBM Corporation, Armonk, NY, USA).

3.3 Results

3.3.1 Water balance

The hydrological (natural and engineered) cycle drives the balance of P inputs and outputs of the system while the soil system controls the P removal processes. The inputs and outputs of Knowle's land treatment system for a long-term average year (Figure 3-2) show that the secondary wastewater effluent discharged to the field (irrigation) has dominated in comparison with precipitation in both main irrigation periods. The average irrigation for the study period is 272 m^3/day. For the last period of operation (2000-2016) the estimated domestic water consumption for Knowle village is 250 m^3/day (Table 3-1), which corresponds to recent Albion Water STW influent monitoring.

Table 3-1 Water consumption in Knowle during the study period.

From	to	Population	Water consumption	
(year)		(persons)	(l person day)	(m^3/day)
1932	1950	2 000	131.0	262
1951	1955	2 000	132.2	264
1956	1960	2 000	133.3	267
1961	1970	2 000	135.8	272
1971	1977	2 000	137.5	275
1978	1981	2 000	138.3	277
1982	1987	2 000	139.7	279
1988	1990	2 000	140.3	281
1991	1994	2 000	141.1	282
1995	1996	2 000	141.4	283
2000	2016	1 680	150.0	252
			Average	272

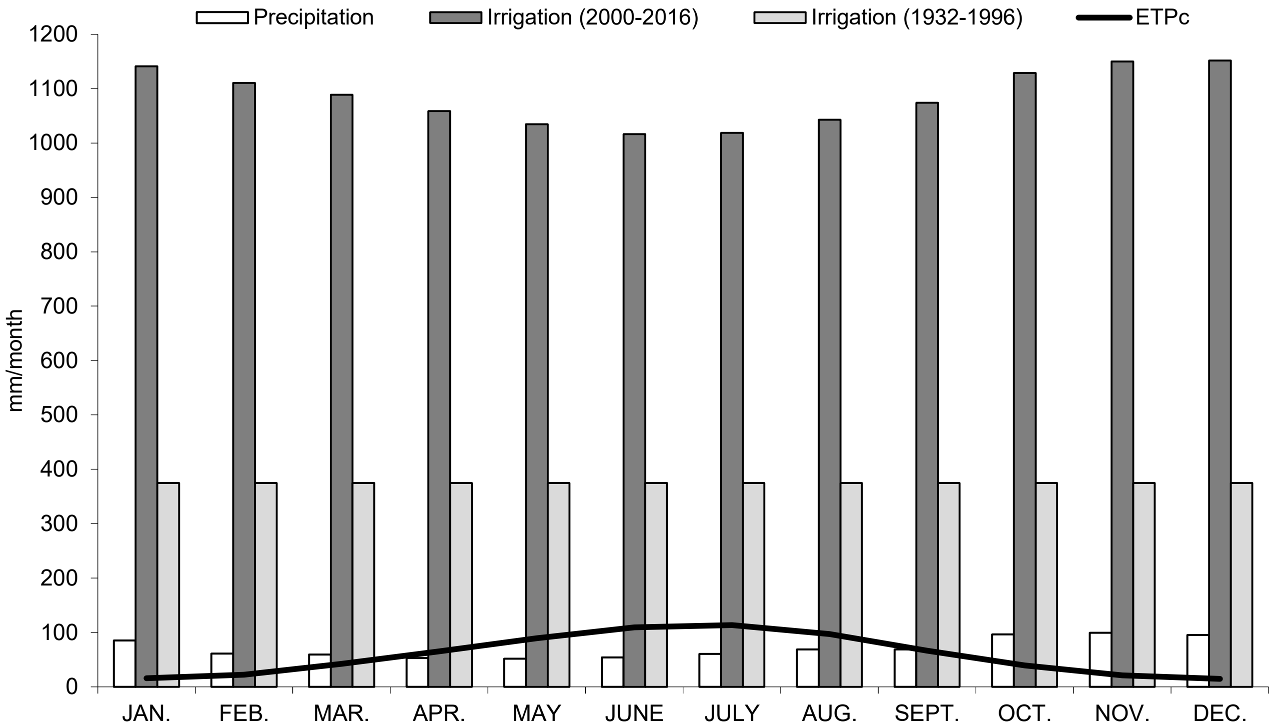

Figure 3-2 Monthly average (1890 to 2015) rainfall, ET_c and irrigation during the two main irrigation periods, 1932-1996 and 2000-2016 at Knowle (UK) land treatment system.

3.3.2 Phosphorus inputs over the study period

The total amount of P discharged through irrigation (P_d) during the entire period (1932-2016) of operation was ≈90 000 kg (equivalent to 4.5 t/ha) (Table 3-2 and Table 3-3). Estimated P loading rates in the early period, when the entire field was irrigated, was 0.04 kg/m^2/a. For the later period when only Section A was irrigated, P load was calculated to be 0.06 kg/m^2/a. Assuming uniform application, P loading rates are in the range of other wastewater irrigation experiences such as Eveborn et al. (2014) with loading rates ranging from 0.03-0.54 kg/m^2/a, or Dzakpasu et al. (2015) constructed wetland loading rate of 0.016 kg/m^2/a.

Table 3-2 Estimated total phosphorus P added to the discharge field with the secondary wastewater effluent during the study period.

From	to	Population	TP load to sewer by domestic wastewater in the UK[a]	TP influent by domestic wastewater in Knowle STW	Years	TP after primary and secondary treatment
(year)		(persons)	(g person day)	(kg/year)		(kg)
1932	1950	2 000	1.40	767	19	14 564
1951	1955	2 000	1.42	777	5	3 887
1956	1960	2 000	1.72	942	5	4 709
1961	1970	2 000	2.04	1 117	10	11 169
1971	1977	2 000	2.43	1 330	7	9 313
1978	1981	2 000	3.10	1 697	4	6 789
1982	1987	2 000	3.25	1 779	6	10 676
1988	1990	2 000	3.22	1 763	3	5 289
1991	1994	2 000	2.87	1 571	4	6 285
1995	1996	2 000	2.26	1 237	2	2 475
2000	2016	1 680	1.90	874	17	14 855
				Total	82	90 010

[a](Gilmour, Blackwood, Comber, *et al.*, 2008)Foundation for Water Research, 2006).

Table 3-3 Total estimated phosphorus discharged (Pd) distributed during the different irrigation periods and to the sections, total phosphorus load (Pl) to each section, total phosphorus concentration (Cp), site reference concentration (R) and P removal (Pr) for

each section of the discharged field. (-) no irrigation during this period. Smax from Tyrell (2016).

		Section A	Section B	Section C	Total
	1932-1950	12 537	6 757	-	17 145
Period	1950-2000	15 537	8 087	30 003	53 577
	2000-2016	17 145	-	-	19 288
P_d (kg)	Total	42 219	14 788	30 003	90 010
P_l (kg/m^2)		6.75	7.39	2.80	
C_p (kg/m^2)		0.57	0.67	0.41	
R(kg/m^2)		0.35	0.35	0.35	
P_r (%)		3	4	3	
Smax (mg P/kg)			1240		

3.3.3 P removal

The percentage of P removal, which includes the difference with the reference sample, varies between 3 and 4% in the different sections (Table 3-3). If the P removal is calculated without considering natural P in the soil (for which we have no measured starting value), the removal percentages would vary between 8% and 9% for sections A and B and 17% for section C.

3.4 Discussion

3.4.1 Water balance

Since no runoff has been observed in the discharge field, the significant amounts of irrigation and precipitation compared with the evapotranspiration suggest that the soil water retention capacity would have been exceeded and the excess of water will be percolated to deeper layers. Currently, Knowle's irrigation rate is 13 600 mm/a; which situates it in the high rate range (Crites, Middlebrooks, & Sherwood (2006). This percolation to deeper layers may be also be enhanced by preferential flow produced in soil macro-pores.

3.4.2 Phosphorus inputs over the study period

The P inputs estimations of the discharge field are feasible when compared to other published values, however, they have to be carefully approached due to several limitations in the calculations of the P added to the field. The main constraint in the analysis is the lack of a complete dataset of inlet-outlet P concentrations of the STW over the study period. To calculate the P load into the field, the preliminary hypothesis of the irrigation periods from the water company operating the plant of a section of the field never been irrigated was discarded, and instead, the irrigation periods were stabilised in relation to the evidence of the presence of the irrigation pipe on historical maps (from 1881) (Landmark Information Group, 1932). However, the maps referred to broad periods of time with the consequent inaccuracy.

Although other studies, such as White and Hammond (2009), quantified very similar values of P contributions from human excreta, household waste, and detergents (2.05 g/capita/day) in England and Wales, its evolution over time in the hospital was assumed to resemble the domestic national trend, which was driven by the introduction of washing machines. It is assumed that domestic wastewater composition is comparable to that of hospitals because it was not a surgical hospital and patients were living there. The influence of changes in diet over time could also be relevant to the P content in the wastewater, but this was not accounted for in this study since it has not been quantified yet. In addition, there is uncertainty regarding the hospital population between known data from hospital registrations.

Despite the differences in the P loads, no significant differences were found in the mean TP concentration (Cp) of the three sections. Cp values were higher than the regional average (943 mgP/kg) and adjacent site references (938 mgP/kg) and close to the soil P sorption maximum (Smax) of 1240 mg P/kg reported by Tyrrell (2016) for the adjacent site, suggesting, that the soil is saturated with P irrespective of the duration of the irrigation (Figure 3-3). However, it is unknown when this Smax removal capacity was reached. All but one TP concentrations of the 30 samples were between the maximum (3 996 mg P/kg) and minimum (296 mg P/kg) values for TP background levels from topsoil analyses of 50 km radius for loam clay texture soils and permanent grassland land use (National Soil Resources Institute, 2014). The sampling point that is out of the upper range is situated very close to a former discharge point, which means that it is more likely that has received more P through irrigation than other points of the field.

3.4.3 Phosphorus removal

The removal was low compared with other similar mass balance calculation studies of P removal in soils. Those studies reported P removal between 58% and 99%, for treatments aged between 10 and 27 years old (Dzakpasu, Scholz, McCarthy, *et al.*, 2015a; Jenssen, Krogstad & Halvorsen, 2014; Zhang & Dahab, 2006). Only Eveborn et al. (2012) identified low removal (~12%) such as the ones obtained for Knowle's system. The main difference between Eveborn's experiments and the other studies is that removal was calculated through P concentrations in the soil, as in this study, rather than inlet/outlet water quality samples of the system. The main drawback of using P concentrations for P removal calculations is the strong influence in the results of the P concentration in the reference sample. However, it simplifies the process of selecting the outlet sampling points, which are usually harder to identify, or to access than in large and engineered soil treatment systems studies. Traditional inlet/outlet field measurements entail methodological limitations such as the difficulty of finding representative inlet/outlet flow and sampling locations, insufficient monitoring time, or lack of representation of groundwater interactions (Eveborn, Kong & Gustafsson, 2012). Reddy et al. (1999) pointed out the difficulty to identify outputs and inputs of P and water as one of the main challenges in P assimilation studies in natural wastewater treatments, along with the lack of monitoring and laboratory methodologies. Such discrepancies make it difficult to compare studies and removal performances of different treatments. P removal at the sections indicates that not all the phosphorus discharged has been accumulated, and that if the soil could accumulate all the P discharged, the binding capacities would have been higher than engineered filter materials such as Filtralite© or steel slag, which have P sorption capacities between 1350 and 4300 mg P/kg (Cucarella & Renman, 2009; Herrmann, Jourak, Lundström, *et al.*, 2012)

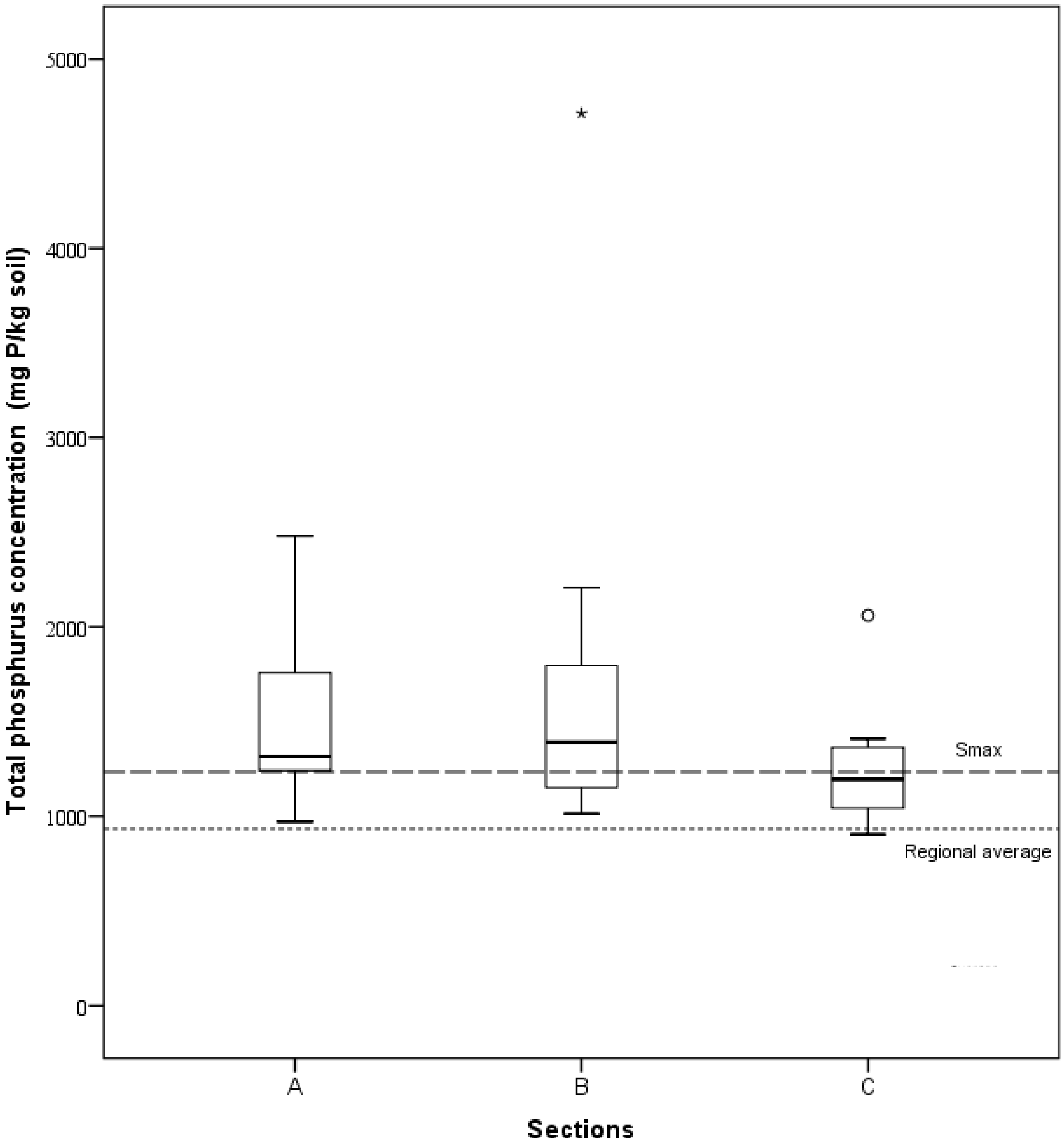

Figure 3-3 Measured total phosphorus in soil in each section. Box plot show median values (solid horizontal line), boundaries of the box indicate the interquartile (IQ) and whiskers show sample minimum and maximum. Outliers (o) are cases with values between 1.5 and 3 times the IQ range and extremes (*) are cases with values more than 3 times the IQ range. Regional average value shows the National Soil Inventory mean value of 560 samples for total phosphorus analysis within a 50 km radius from the sampling site for clay loam type soil and permanent grassland land use (mean= 943.0, min= 269.0, max= 3996.0 st.dev= 403.02). Smax, P maximum sorption capacity from Tyrrell (2016) clay loam soil texture and grassland land use from Knowle STW site.

3.4.4 Phosphorus pathways (where is the P?)

The difference between the TP soil concentration and the estimated P load raises questions concerning the fate of the discharged P Analysis of wastewater at Knowle (Albion Water, personal communication 2015) reported that 90% of TP is dissolved phosphate, which means that this physical retention mechanism will be less influential than others. Plant and microbial uptake can also remove P from the soil. Crites et al. (2006) proposed typical annual phosphorus nutrient uptake rates for forage crops in LTS to be in the range of 20-84 kg/ha/a. Since the history of the site land management is uncertain, no plant uptake has been considered in this study, however, if P was assimilated at this rate and vegetation had been harvested and removed then plant uptake would account for ≈5% of the P applied to the soil (P_d). Phosphorus can be also stored as soil microbial biomass. Brookes et al. (1984) quantified the microbial P mean annual flux of 8 grasslands to be 23 kg P/ha/a, what will account for ≈4% of the P applied to the soil (P_d).

It is also plausible that part of the discharged P is retained in the soil but the sampling method was not representative due to the high variability of P in the field because of the irrigation methodology. This could be linked to the high variability of TP concentration found in sections A and B, represented by the higher interquartile in sections A and B compared to C, and by the outlier point with high TP content situated close the discharge pipe (Figure 3-3). The high variability could be caused by non-uniform distribution of the wastewater over the field generated by the natural topography of the field, enhanced by the channelling caused by running water flow for long periods and the arbitrary opening of the discharge gates for irrigation. Moura et al. (2011) also observed high spatial variability in water extractable phosphorus concentrations after 25 years of reclaimed water application in rapid infiltration basins. The minimum values in each section are close to the reference concentrations, which could also suggest a poor uniformity of distribution in the field.

However, if P has flowed downwards to deeper soil layers, it could be either adsorbed at deeper levels (if the soil solution in deeper layers is less concentrated) or leached to the groundwater. The subsurface water connections between the field, the River Meon and the groundwater are unknown. However, Tyrrell (2016) measured the PO_4^{-3} concentration in the River Meon, upstream and downstream of the discharge field monthly from June 2012 to July 2014. This revealed no statistical significance ($t=1.459$; $p=0.156$) in paired samples t-test between both sampling sites. Therefore, the discharge field has no detectable effect on the PO_4^{-3} concentration in the river. It is plausible that P from the discharge field reaches surface and groundwater but in insufficient loads to affect concentrations appreciably. However, this hypothesis was not possible to test in this study by obtaining data from a groundwater assessment. This unfeasibility is due to limitations in the accessibility by the landowner. If access for groundwater studies can be granted in the future, a further study would be necessary to be able to provide additional data of groundwater quality to support this hypothesis and to assess whether the P has been storage or release.

3.4.5 Practical implications of the study

There is a lack of field case studies of P removal capability in existing LTS, in longevity methodology predictions and discussion of future applications. This case study has demonstrated that, although the sorption capacity of the system seems to be saturated, it has retained significant amounts of P, and that the P that has not been retained has appeared to have had no significant impact on the receiving water bodies. The P retention capacity is finite and this has to be taken into consideration for the future role of these systems. Therefore, there is a need to build knowledge regarding: management practices for P removal optimization, such as, which P loads and P loading modes would contribute towards a higher removal rate or which type of plant and how to vegetation manage could improve longevity. This results can help designers and operators to evaluate LTS performance and their potential implementation. However, such evaluations need to consider P removal in the context of the other functions and services provided by LTS.

3.5 Conclusions

The duration of wastewater irrigation activity at Knowle (~85 years) offered the possibility to study a unique LTS by comparing the P concentration in the soil of areas that have been irrigated with wastewater for different periods. The different sections of the discharge field did not show a significant difference in the soil TP concentration despite being irrigated for different periods with secondary treated wastewater and the P concentration levels indicated that the soil has reached P saturation capacity. The TP retention (4%) was low compared with similar previous studies, which was mainly attributed to the exhaustion of the sorption capacity – possibly many years or even decades ago. However, no evidence of nutrient pollution has been detected in the nearby water bodies (River Meon and East Hants Chalk aquifer), suggesting that the LTS is not affecting phosphate levels in the river or producing relevant nutrient contamination.

Assessment of P removal performance in small long-term LTS can be challenging due to the lack of historical datasets and outlet monitoring, thus methodologies based on P accumulation in the soil could help to overcome this drawback, however, representative reference samples are needed since the results are strongly influenced by them.

These findings suggest that LTS can play a role in low energy phosphorus removal at small works, in addition to the other contributions they make to tertiary treatment and habitat provision. Gaps remain, however, in our knowledge of how to optimise their performance through design and operational measures, and in how to forecast their longevity and how to manage the finite adsorption potential of the soil.

4 SIMPLIFIED LONG-TERM PHOSPHORUS MODEL FOR A LAND TREATMENT SYSTEM FOR TERTIARY WASTEWATER TREATMENT

4.1 Introduction

Since P removal capacity is finite in LTS, lifetime estimation of P removal is an important management tool. However, the study of LTS behaviour in the long-term is complicated, especially regarding the associated temporal and spatial variability, which makes the studies expensive and time-consuming (DeJong & Bootsma, 1996). Research is usually based on experimental data where observations of experiments can provide accurate datasets in order to develop and test theories. However, there are cases where getting experimental data is a daunting task due to spatial and/or temporal scales (Wainwright & Mulligan, 2004). Environmental models can offer to researchers rapid simulations of long periods and vast extension of space, helping them to understand how variable contexts determine the nature and functioning of the system under study. This is of critical importance in long-term studies, where models are used as predictive tools to understand the impacts of current process over time. These environmental research models offer a valuable aid in contexts where time is a limited resource and a major constraint. Additionally, models offer a controllable environment where mathematical descriptions of the system and processes can be forced in a controlled way in order to isolate the impact of individual factors on the behaviour of the study system (Graves, Hess, Matthews, *et al.*, 2002). Moreover, mathematical calculations and simulations can improve the understanding of diverse aspects since experimental data in this type of systems are usually expensive to obtain (Beach & McCray, 2003).

The use of numerical models for soil water dynamics relies on measurement of physical, soil hydraulic and solute sorption characteristics. However, due to the large number of parameters needed and the difficulty to measure some them at plot scale, it is crucial to undertake a sensitivity analysis to examine the effect on the model results of changing a particular parameter and to identify which parameters are most important in describing the system behaviour (Carey, Erskine, Heathcote, *et al.*, 2001). The aim of the chapter is to apply a acombination of hydrological and solute transport model to identify relevant P removal proceses in LTS.

The objectves of this chapter is to:

- To describe the conceptual model that simulates water flow and P transport in a soil profile in a LTS.
- To parameterize a numerical model that simulates water flow and P transport in a soil profile in a LTS.
- To test the model sensitivity to changes in these parameters.

4.2 Conceptual model: model domain, boundary conditions and initial conditions.

The one-dimensional conceptual model represents the field as an isolated bucket with upper and bottom boundaries to quantify the water and P inputs and outputs. The water inputs are precipitation and secondary wastewater effluent discharge from the WWTP, the water then is returned to the atmosphere through evaporation from the land surface or, after plant uptake and use, by vaporization from the stomata on the surfaces of leaves (transpiration), because of the difficulty to assess these two pathways separately, the water balance is presented instead with the evapotranspiration as a simple term that quantifies together the two evaporative parameters. The water, when it reaches the soil can either penetrate by infiltration or be lost by surface runoff. The infiltrated water can either continue to downward percolation or be retained in the soil as stored water. The P input comes from the irrigation with the secondary wastewater effluent, and the P outputs are represented by plant uptake, runoff, plant residue and leaching (Figure 4-1).

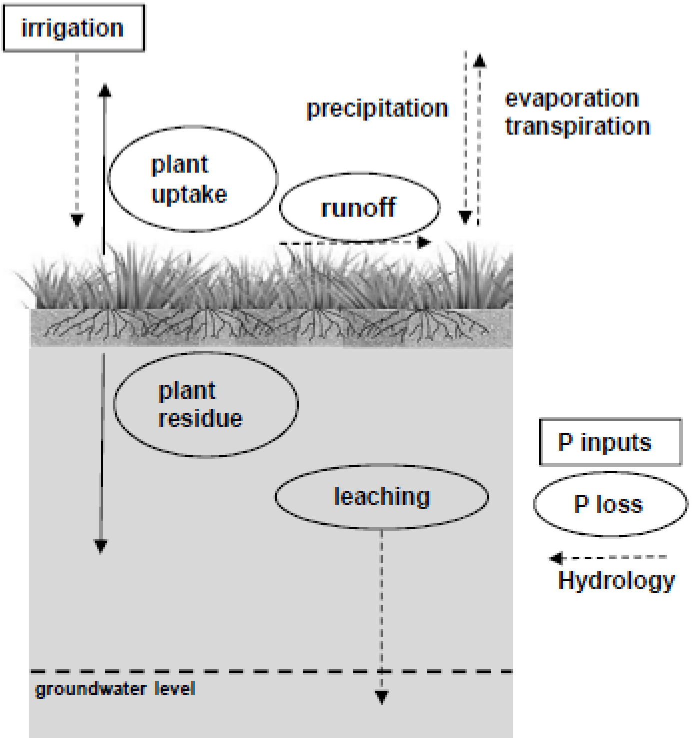

Figure 4-1 Conceptual model

A simplified model was built to simulate vadose-zone phosphorus transport. The modelling tool selected was HYDRUS-1D (v4.16.0110). HYDRUS-1D is a software package for simulating water, heat and solute movement in one-dimensional variably-saturated media (Šimůnek, Šejna, Saito, *et al.*, 2013). This numerical model is used to(Falkiner & Polglase, 1999) simulate long-term (steady-state) vertical migration of secondary wastewater effluent from the infiltrative surface to the bottom of a 40 cm soil profile.

This study used one isotropic profile, 0.4 m below ground surface based on Falkiner and Polglase (1999) results on municipal effluent irrigation for 5 years where only the first 50 cm of the soil profile participated in all the changes and distribution of P through the soil profile. Discretization into 100 finite elements. The soil hydraulic model is the single porosity van Genuchten-Mualem model with air entry value of -2 cm with no hysteresis. The stability criterion (ratio of Peclet to Courant's number) was set to 2 in all simulations. Boundary conditions for water flow and solute transport are specified at the top and bottom of the soil profile. The top boundary conditions included time-variable (atmospheric) boundary conditions, which included precipitation, irrigation and potential evapotranspiration rates for a grass cover. The solute transport top boundary condition was set as constant concentration flux boundary. These boundary conditions were chosen to represent the long-term secondary effluent loading rates. The lower boundary conditions consisted of a free drainage boundary for water flow and a zero concentration gradient for the solute transport. These lower boundary conditions are appropriate since the groundwater level is unknown. The solute transport model was an equilibrium model. The initial soil water conditions were set to field capacity and zero initial concentration of the solute through the entire soil profile. The water root uptake model selected was the Feddes with no solute stress and only passive root solute uptake. Initial time step 0.05 days and maximum time step 0.5 days. The maximum number of iterations was set to 10, and the rest of criteria were set to the default values. Results have been checked for a water balance and solute error <1%.

4.3 Model description

HYDRUS-1D model (v.4.16) (Šimůnek, van Genuchten & Šejna, 2008) is a Windows-based software for simulating water, heat and solute movement in one-dimensional variably-saturated media using numerical analysis schemes. It requires, as input, three sets of parameters: the soil hydraulic, solute transport, and solute reaction parameters.

Water flow is modelled using Richards's Equation (4-1), and the solute transport is modelled using the convection-dispersion equation (4-2)

$$\frac{\partial \theta(h)}{\partial t} = \frac{\partial}{\partial x}\left[K_x(h)\left(\frac{\partial h}{\partial x} + 1\right)\right] \pm S \qquad \textbf{(4-1)}$$

$$\frac{\partial (\theta R c)}{\partial t} = \frac{\partial}{\partial x}\left(\theta D \frac{\partial c}{\partial x} - qc\right) - \phi \qquad \textbf{(4-2)}$$

Where:

θ is the volumetric water content (−),

h is the soil water pressure head (L),

t is time (T),

z is depth (L),

K is the hydraulic conductivity (LT^{-1}),

R is a retardation factor accounting for sorption or exchange (−)

c is the solute concentration of the liquid phase (ML^{-3}),

D is the solute dispersion coefficient (L^2T^{-1}),

q is the Darcy–Buckingham volumetric water flux (LT^{-1})

S (T^{-1}) is the sink or source of water,

and ϕ ($ML^{-3}T^{-1}$) is the sink or source for solutes.

The HYDRUS-1D is a software tool that enables the translation of the transport processes and pathways of P in soils of the model described in section 1.1.3 into mathematical equations. It operates first the water module (Figure 4-2) that is driven by the Richard's equation (A-1)which, under the initial conditions and the boundary conditions, determines the moisture content (*θ)* and pressure head (*h*) at each spatial *(dx)* and each temporal increment (*dt)* in the soil profile. These results are transferred it into Richard's equation, where Richard's velocity is determined (*q*) together with the seepage velocity (*v*) at each *dx* and *dt* and time step, which is incorporated into the ADE equation (A-8)to estimate solute transport by advection and dispersion. The portion of PO_4 adsorbed to the soil to PO_4 soluble in solution (∂s/ ∂c) is determined by the HYDRUS assumption of equilibrium interaction between solution (*c*) and sorbed (*s*) concentrations and it is related by a non-linear adsorption isotherm, and expressed as the retardation factor (R) at the ADE equation. Finally, the ADE will be numerically solved and will provide the PO4 concentration in soil solution at each spatial and temporal increment. The complete development of the equations is described in 7Appendix

B

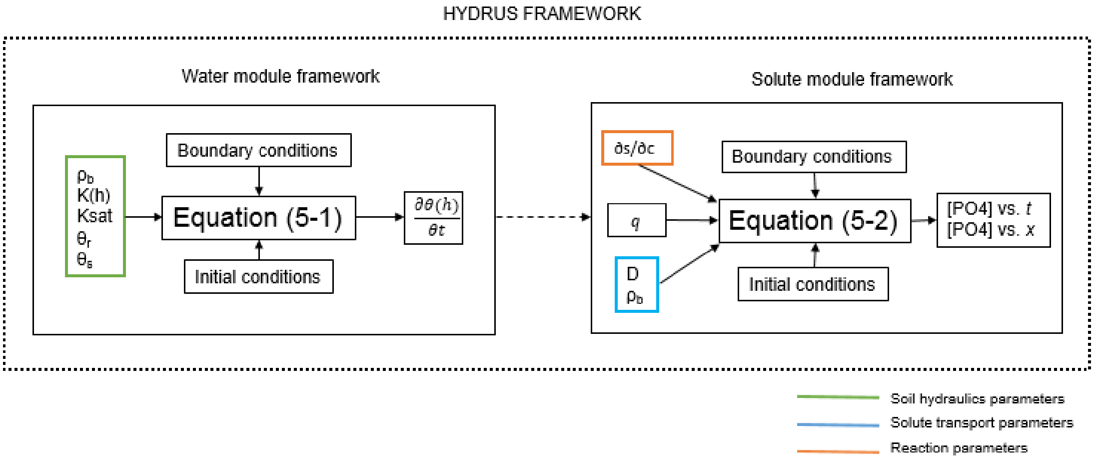

Figure 4-2 Framework of the water and solute model

The baseline parameters and scenario proposed are based on Knowle's (UK) LTS which location and operational characteristics are described in Chapter 3.

4.4 Parameterization

The model has been parameterized for the discharge field in Knowle (UK), which is described in section 3.2.1.

4.4.1 Assumptions and assertions of the model

Once the model has been described, along with the processes and the objectives that the model will cover, it is necessary to set up a series of assumptions and conditions under which the equations of the model will be solved (based on (Nahra, 2006)).

- The model simulates P form as PO_4^{-3} (PO_4).
- The model takes into consideration matrix flow only; macro-pore flow is not considered in the model.
- The nature of P adsorption is considered to be non-linear.
- Both steady-state and transient boundary conditions are considered.
- The model simulates water flow under variably saturated conditions.
- Only one-phase flow is considered. Air and water vapour flow are not modelled.

- Constant temperatures are considered throughout the soil profile.
- The model operates on homogeneous and isotropic soil column.
- Root water uptake and solute uptake are simulated in the model.
- The model simulates solute transport and water flow in one-dimension, vertically down the soil profile because the flow in the soil profile is predominantly in the vertical direction and to simplify long-term simulations.
- The model considers three main processes to simulate PO_4 transport in the soil- water environment: advection, hydrodynamic dispersion, and adsorption.
- The sorption processes include adsorption, chemisorption, absorption, and ion exchange reactions, together with precipitation processes (Jourak, Frishfelds, Staffan, *et al.*, 2011)

4.4.2 Meteorological parameters

Meteorological data were obtained from Southampton (50° 53' 59" N 01° 23' 44" W) (Mettofice, 2016) (Table 4-1). Average monthly max and min temperature for the period 1855 to 2000 was used to calculate long-term average monthly evapotranspiration (ETc) with the Penman-Monteith equation. Air humidity, wind speed and radiation were obtained from Southampton (Southampton Weather, 2016) for 2011. Daily precipitation of the year 2011 was selected as an average year (annual precipitation for 2009-2015 period is 828.2 mm/a and 663 mm/a for 2011) based in its similarity with an average year for the study period.

Table 4-1 Meteorological data (Southampton Weather, 2016)

	TMax (°C)	Tmin (°C)	ETc (mm/month)	Average precipitation 2011 (mm/day)
January	8.2	2.0	0.5	3.3
February	8.6	1.9	0.8	2.4
March	11.0	2.9	1.6	0.5
April	13.9	4.6	2.7	0.1

	TMax (°C)	Tmin (°C)	ETc (mm/month)	Average precipitation 2011 (mm/day)
May	17.2	7.8	3.4	1.4
June	20.0	10.6	4.1	2.6
July	21.7	12.5	4.2	1.0
August	21.7	12.4	3.6	3.0
September	19.5	10.2	2.6	1.9
October	15.6	7.9	1.4	1.3
November	11.3	4.3	0.7	1.6
December	8.7	2.3	0.5	2.8

4.4.3 Irrigation

Irrigation, as the secondary wastewater effluent discharged from the STW to the discharge field, was obtained from the average water consumption in Knowle hospital and village over the study period. Average domestic water consumptions were estimated to be 126 l/capita in 1930 and currently 150 l/capita (Anglian Water Ltd. 2008), resulting in an estimated discharged average of 250 m^3/day over the field surface (20000 m^2). Weekly water quality analysis of the discharged wastewater were carried out by an independent laboratory for Albion Water from December 2014 to March 2016 with an average of 8.17±1.14 mg/L for TP and 7.08 ±0.51 mg/L PO_4^{-3}.

4.4.4 Crop data

The crop data necessary to calculate potential evapotranspiration are crop height, albedo, LAI (Leaf Area Index), and root depth. Crop height was specified based on observational data over the different seasons (60 cm for April, May and June, 120 cm for July, August, and September and 30 cm for the rest of the year), albedo was set 0.23 , typically set equal to 0.23 for most green field crops with a full cover (Jensen, Burman & Allen, 1990) and root depth to 20 cm, with a spatial root distribution of the root occupation in the soil from 100% on the top to 0% at 20 cm (Ramos, Šimůnek, Gonçalves, *et al.*, 2011). The LAI was calculated from surface cover fraction with a constant for the radiation extinction by the canopy of 0.463 and Fedde's parameters for the plant water stress response functions were taken from the default HYDRUS-1D software.

4.4.5 Soil physical and hydraulic parameters

Soil hydraulic parameters (θ_s, θ_r, α and n) Table 4-2) were obtained using the Rosetta Lite v1.1 (Schaap, Leij & Van Gencuhten, 2002) program. Rosetta Lite is integrated into the HYDRUS software package and estimates water retention and saturated and unsaturated hydraulic conductivity using soil texture, bulk density and one or two water retention points and it is based on neural network analyses and pedotransfer functions. Soil texture, bulk density and water retention points at 33 and 1500 kPa and the longitudinal dispersivity (D_L) were obtained from Tyrrell (2016). D_L represents the effects of the porous media (pore size, path length and friction) in the average water flow direction (Fetter, 1999). A 1D model assumes dispersion along the vertical direction of transport and neglecting lateral dispersion. This is a conservative approach from an environmental-protection perspective because lateral dispersion would reduce the concentrations obtained with the 1D model (Heatwole & McCray, 2007). Pore connectivity parameter was assumed equal to an average value of 0.5 for many soils (Li, Šimůnek, Jing, *et al.*, 2014).

4.4.6 Adsorption parameters

Equilibrium isotherm experiments were performed with air-dried and sieved soil samples from a composite sample of Section C, which is the section that has been irrigated for the shorter period. The sampling site and methodology for the soil sampling undergone in this experiment have been presented in section 3.2.2. 2 g of each composite sample was placed in 100 ml flask with 50 ml solution (1:20) prepared with KH_2PO_4 at known P concentrations (pH 7.0) of 0, 0.5, 2, 5, 8, 10 and 15 mg P/l with water as solvent. The concentrations were chosen to mimic typical domestic wastewater concentrations, and to replicate sorption processes at low concentrations. The mixture was continuously shaken at 175 rpm for 5 days at a room temperature (21°C). 175 rpm is suggested to be appropriate to avoid abrasion and altering the properties of the soil (Cucarella & Renman, 2009; Drizo, Comeau, Forget, *et al.*, 2002). The contact time was longer than the normal 24h to enable the solution to reach equilibrium and to allow more realistic measurements of P maximum sorption (Hu, Zhang, Kendrick, *et al.*, 2006; Eveborn, Kong & Gustafsson, 2012; Eveborn, Gustafsson, Elmefors, *et al.*, 2014). The soil suspension was allowed to settle and the supernatant was filtered through a 0.45 μm membrane. The absorption capacity was calculated using the difference between the initial P concentrations added to the solution and the P concentration in the filtered solution. Sorption maximum was estimated using Langmuir sorption model Eq. (4-3)

$$S = \frac{S_{max} \cdot K \cdot C}{1 + K \cdot C} \tag{4-3}$$

where

C is the concentration of P in the solution at equilibrium (mgP/l)

S_{max} is the maximum P adsorption capacity (mg P/kg soil)

K the constant related to the binding strength of P onto the material (l/mgP)

S is the amount of P adsorbed per unit mass of the material (mg P/kg soil)

Input parameters required for HYDRUS-1D input were determined using the best available data (Table 4-2). The baseline parameters and scenario proposed are based on Knowle's (UK) LTS, the location and operational characteristics of which are described in Chapter 3.

Table 4-2 Parameters required in the HYDRUS-1D model

Module	Parameter	Description	Method of estimation	Value	Units
Hydraulic model	θ_s	Saturated water content [L^3L^{-3}]	Rosetta-Lite model	0.505	cm^3/cm^3

Module	Parameter	Description	Method of estimation	Value	Units
	θ_r	Residual water content [L^3L^{-3}]	Rosetta-Lite model	0.0794	cm^3/cm^3
	α	Empirical parameter [L^{-1}] (inverse of the pore entry value)	Rosetta-Lite model	0.0286	cm
	n	Empirical parameter [-] (pore size distribution index)	Rosetta-Lite model	1.2982	-
	l	Pore connectivity parameter [-]	Li et al. 2014	0.5	-
	K_{sat}	Saturated hydraulic conductivity [LT^{-1}]	Rosetta-Lite model	60.06	cm/day
Solute reaction	k_d	Equilibrium constant- adsorption isotherm coefficient [$M^{-1}L^3$]	Fitted from experimental results from adsorption experiment.	0.0434	cm^3/ mg
	η	Shape fitting parameter – adsorption isotherm coefficient [$M^{-1}L^3$]		35	cm3/mg
Solute transport	ρ_b	Bulk density [M^3L^{-3}]	Tyrrell (2016)	1.12	kg/cm^3
	D_L	Longitudinal dispersivity [L]	Tyrrell (2016)	10	cm
	$C_i(x)$	Initial concentrations	Tyrrell (2016)	0.960	mg/cm^3

Module	Parameter	Description	Method of estimation	Value	Units
		of P in soil [M^3L^{-3}]			

4.5 Sensitivity analysis

A sensitivity analysis was undertaken to examine the effect on the model results of changing a particular parameter and to identify which parameters are most important in describing the system behaviour (Carey, Erskine, Heathcote, *et al.*, 2001). This is of critical importance in the study model since limited field observations are available to test the model. The results from the sensitivity analysis were later used to define the scenarios that needed to be tested for management purposes.

The results of the sensitivity analysis will:

- Show which parameters have a greater influence on the model results
- If results stay in an observed range after value change.

The test was performed according to the following equation (4-4) at 'one-parameter at-a-time' procedure. Although this procedure does not show interactions between parameters, it is simple to understand and implement, which simplifies the interpretation of the results. This advantage is the main reason why this method was selected due to the complexity of factor interactions in environmental modelling:

$$\Delta R = \left(\frac{R_t - R_b}{R_b}\right)100 \tag{4-4}$$

where

ΔR is the percent change in the result value of the output

R_t is the result value for using the test parameter

Rb is the result value for using the baseline parameter value

Two output parameters were selected:

- The cumulative bottom flux in order to observe the influence of the hydraulic parameters
- The cumulative solute bottom flux to study the influence of the solute transport parameters.

The values for the parameters tested were obtained from the literature (Table 4-3). The values were chosen from a range of physically possible values of the parameters. The three values selected correspond to upper, middle and lower value ranges for typical parameter values. Simulations were run for 5, 10, 50, 85 and 100 years.

HYDRUS-1D reports the amount of solute in the entire flow domain (mg/cm^2) at differently selected print-times. Therefore, the quantity of solute (PO_4) accumulated in the field surface can be calculated multiplying it by the surface of the discharge field (20 000 m^2). The soil accumulation under a different range of values for the selected parameters will help to identify the trend in the long-term.

Table 4-3 Values selected for the input parameters used in the sensitivity analysis

Output	Parameter	Source	θ_s	θ_r	K_{sat}	k_d	C_i	D_L	ρb
			$[L^3L^{-3}]$	$[L^3L^{-3}]$	$[LT^{-1}]$	$[M^1L^{-3}]$	$[M^3L^{-3}]$	[L]	$[ML^{-3}]$
			cm^3/cm^3	$cm^3/cm3$	cm/day	cm^3 /mg	mg/cm^3	cm	mg/cm^3
	Baseline		0.505	0.0794	60.06	0.0434	0	10	1200
Cumulative value of the bottom boundary flux (cm^3/cm^2)	θ_s	Rawls et al. (1982)	0.32						
			0.41						
			0.55						
	θ_r	Rawls et al. (1982)		0.174					
				0.001					
				0.794					
	K_{sat}	(U.S. Department of Agriculture, 2005)			12.18				
					36.54				
					120				
Cumulative solute flux across the bottom of the soil profile (mg/cm^2)	k_d	Hanson et al. (2006)				0.019			
						0.0593			
						0.185			
	C_i	National Soil Resources Institute, (2014)					0.0089		
							0.1		
							0.96		
	D_L	Bourazanis et al., (2017)						5	
								12	
								15	
	ρb	Nahra (2006)							500
									1500
									2000

4.6 Results and discussion

The sensitivity analysis showed (Table 4-4) that the most influential parameters in the HYDRUS-1D of water and solute transport model under a variable saturated soil conditions are: the equilibrium constant-adsorption isotherm coefficient *(K_d)*, saturated hydraulic conductivity *(K_s)*, bulk density (ρ_b) and the initial solute concentration of the soil (C_i):

Table 4-4 Results of the sensitivity analysis for a 100 years simulation time

Parameter	Parameter change (%)	ΔR Cumulative flux (%)	ΔR Cumulative solute flux (%)
	-37%	0%	0%
$\boldsymbol{\theta_s}$	-19%	0%	0%
	+9%	0%	0%
	+335%	0%	0%
$\boldsymbol{\theta_r}$	-98%	0%	0%
	+99%	0%	0%
	-80%	-0.10%	0.81%
$\boldsymbol{K_{sat}}$	-39%	-0.07%	0.00%
	+99%	-0.14%%	-0.01%
	-56%	0%	2%
$\boldsymbol{k_d}$	+37%	0%	-1%
	+326%	0%	-11%
	-	0%	0%
$\boldsymbol{C_i^*}$	-	0%	1%
	-	0%	11%
	-50%	0%	0%
$\boldsymbol{D_L}$	+20	0%	0%
	+50%	0%	0%
	-55%	0%	14.99%
$\boldsymbol{\rho b}$	+34%	0%	0%
	+79%	0%	-7.49%

* The data cannot be presented in relation to the change in the parameter since the baseline value is zero mg/cm^3 concentration.

K_d is the most influential parameter for the P accumulation and leaching related output tested. This is reasonable because it is the parameter that defines the sorption capacity of the soil and it is a key parameter in the CE equation. Figure 4-3 shows a negative linear relationship (R^2= 1) and very similar slope in the long-term simulations of 50, 85 and 100 years, which indicate that one unit change in K_d causes a decrease in the cumulative solute flux by 0.003. For years 5 and 10 the relationship is still close to a linear relationship (R^2= 0.79 and 0.97) but the negative values of the slope are higher (0.28 and 0.41), meaning that in the long term the changes in the K_d affect the mass of solute that flows through the bottom boundary less than in the first years of operation.

The bulk density (*ρb*) (Figure 4-4) is also an influential parameter of the cumulative bottom solute flux. There is a linear relationship for all values (R^2 from 0.89 to 1) and negative slopes from 0.47 in year 10 to 0.16 in year 100, indicating as well, that it is more influential during the first years of operation. This is logical because higher ρ_b entails more solids per unit volume of soil and therefore more retention capacity, where higher ρ_b can affect infiltration volumes. Moreover, these results should be carefully approached since a change in the ρ_b must also be associated with a change in the θ_s (saturated soil water content) because it is associated with the water retention capacity of the soil. However, since the sensitivity analysis has revealed that changes in the saturated soil water content (θ_s) and residual soil water content (θ_r) has no influence in the output tested, it is assumed that for the sensitivity study purposes the results can be endorsed. In this case, the one-at-a-time procedure was considered as an initial step of examination of HYDRUS-1D sensitivity to different parameters over different simulation time-steps, the reason is that it would allow a clear identification of single parameter effects, regardless that in some changes in parameters are not isolated and may affect others.

The initial concentration of the solute in the soil (C_i) also has an influence on the cumulative solute bottom flux (Table 4-4). The data cannot be presented in relation to the change in the parameter since the baseline value is zero mg/cm^3 concentration. A change in the concentration from 0 mg/cm^3 to 0.93 mg/cm^3, which is close to saturation, produces a change in the cumulative value of the solute bottom flux of 11% at year 100, however a change in the initial concentration from 0 mg/cm^3 to the minimum regional value has no influence on the results. Therefore, small changes in the initial concentration will not have a strong impact on the cumulative solute flux at the bottom boundary.

Regarding the sensitivity analysis of the hydraulic parameters, the saturated hydraulic conductivity *(K_s)* is the only parameter that has a small influence on the change in the cumulative bottom flux. It was expected that K_{sat} would have an influence since it is a key parameter in the Richards' equation (J. Šimůnek, M. Šejna, H. Saito, M. Sakai, 2013). The change in the parameter follows a less clear linear relationship (R^2=0.6 and 0.8) than the solute transport related parameters and the change in the output tested is less than in the case of solute transport parameters, being < 1% in all cases. With respect to the other parameters θ_s and θ_r, their influence on the results can be neglected which changes in the output tested of 0%.

These results are consistent with results from other sensitivity analyses of HYDRUS-1D such as Cheviron & Coquet, (2009) study of dual-porosity, transient mobile–immobile case study related with the fate of pesticides fate in soils. In this study, the parameters related to the retardation effects such as the sorption coefficient were identified as very sensitive. Nahra's (2006) sensitivity analysis simulating water flow and PO_4 transport with HYDRUS-1D also found that the K_{sat} and C_i were the most influential parameters on the solute transport bottom flux, which also influenced following a linear relationship. However, the researchers did not find K_d or ρ_b to be sensitive to the changes even if the study points out that it would expect to be sensitive to K_d due to the fact that it has a direct relationship with the concentration of solute in solution. This study also did not show D_L as a sensitive parameter, which is surprising because it is a key parameter in the advection-dispersion equation. In addition, Tyrrell's (2016) sensitivity analysis with HYDRUS-1D, which was only performed for hydraulic parameters, showed the K_s as the most sensitive parameter for water content output. Complete results of the sensitivity analysis for all parameters and simulation time can be founded in 7Appendix B Sensitivity analysis results

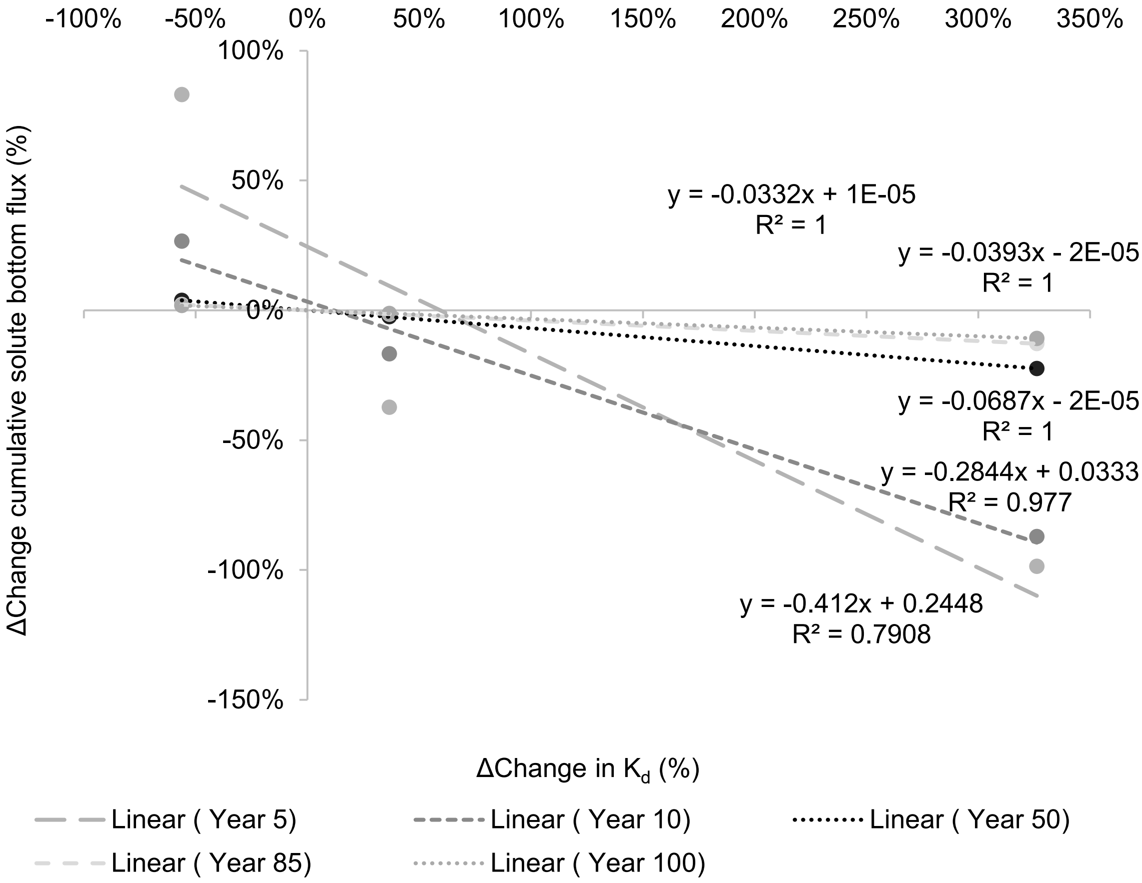

Figure 4-3: Sensitivity analysis results for fitting parameter for the Langmuir adsorption isotherm coefficient (K_d) parameter

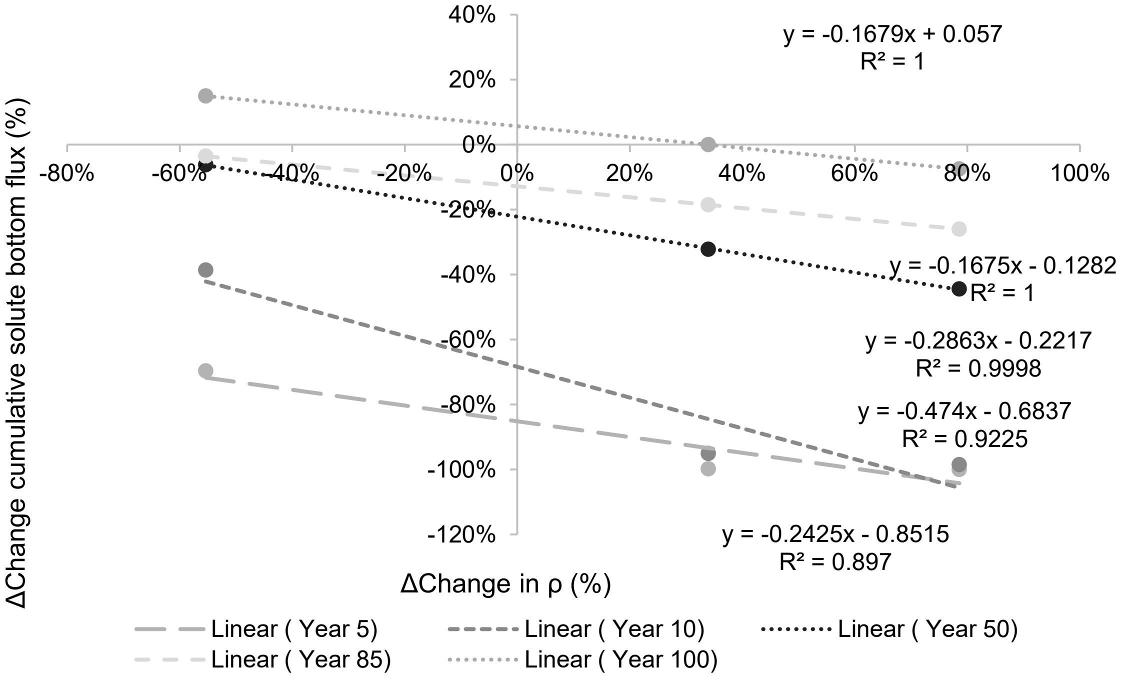

Figure 4-4 Sensitivity analysis results for bulk density (ρ_b) parameter

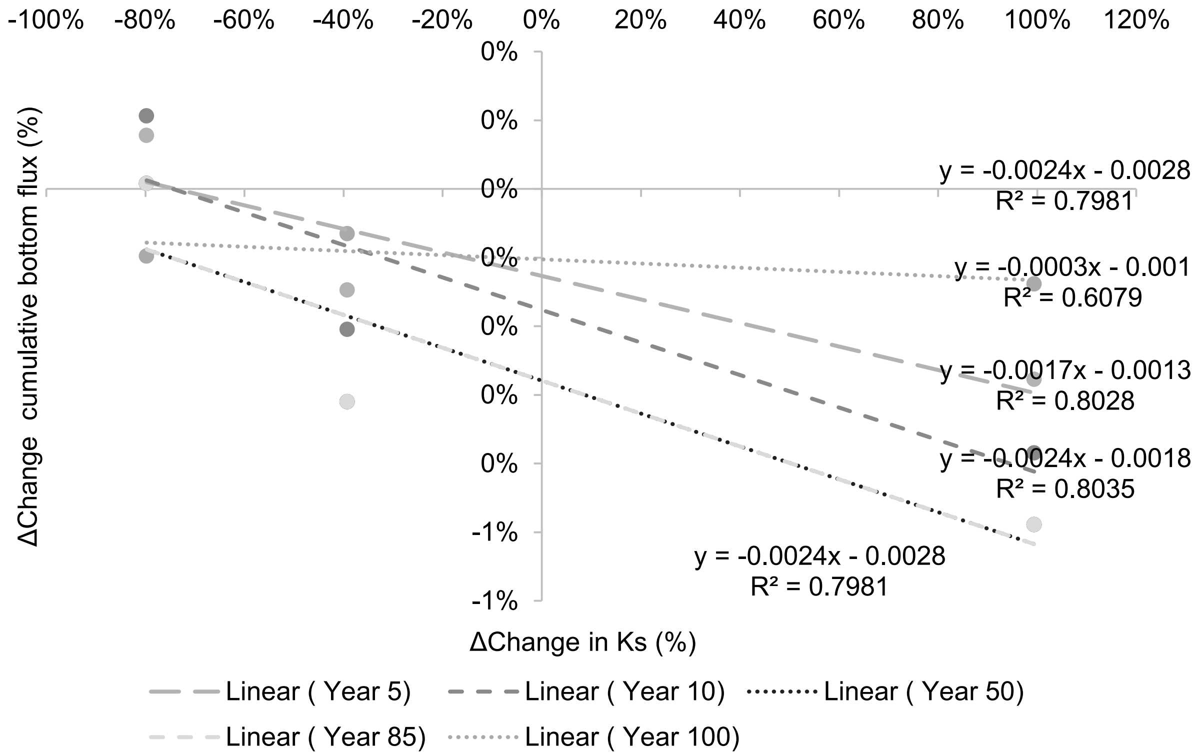

Figure 4-5 Sensitivity analysis results for hydraulic conductivity (Ks) parameter

Regarding the mean P accumulated in the first 40 cm of the soil Table 4-4, results show that the P retained reaches a steady state in between 10 and 50 years of irrigation simulation.

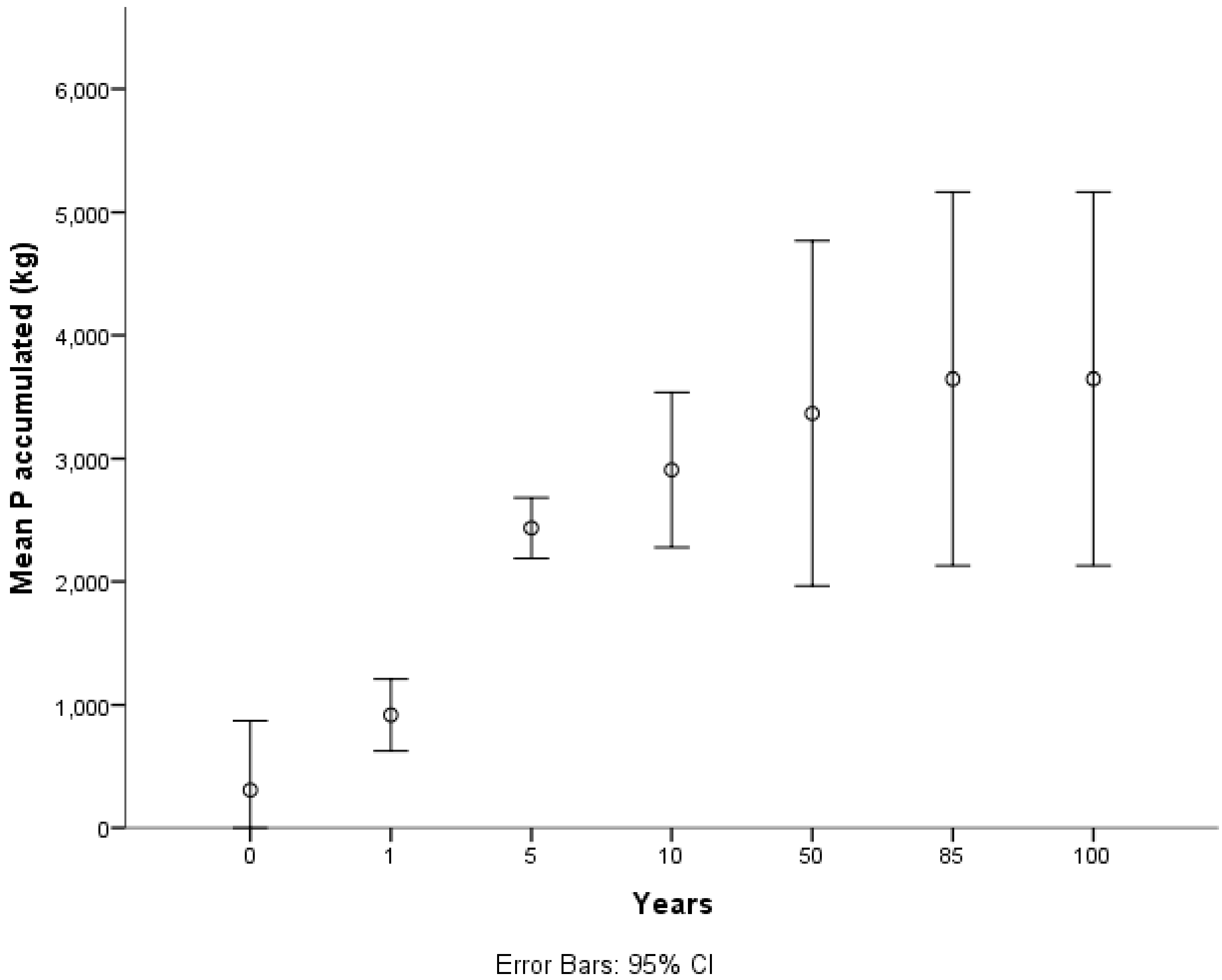

Figure 4-6 Mass (kg) of phosphorus accumulated in the first 40 cm of the discharge field for different simulation periods and the sensitivity analysis values used for each parameter tested.

4.7 Conclusions

The sensitivity analysis showed that the cumulative bottom flux and solute flux are most sensitive to the equilibrium constant-adsorption isotherm coefficient (K_d) and bulk density (ρ_b). In addition, the saturated hydraulic conductivity (K_s) is influential but to a lesser extent. Small changes in the soil initial concentration (C_i) will not have a strong impact on the amount of P leached. The rest of the parameters studied residual (θ_r), saturated water content (θ_s), and longitudinal dispersivity (D_L), had no influence on the results of the output tested. Regarding the mean P accumulated in the first 40 cm of the soil, results revealed that the P retained reaches a steady state between 10 to 50 years of irrigation simulation. Therefore, the model will be used to study the system behaviour in order to estimate system longevity for soils with different equilibrium constant-adsorption isotherm coefficient (K_d).

5 MODELLING PHOSPHORUS TRANSPORT AND ACCUMULATION IN THE UNSATURATED ZONE OF A LAND TREATMENT SYSTEM FOR LONGEVITY ESTIMATIONS.

5.1 Introduction

In the field of environmental research, especially with forecasting purposes, there are a number of management and process interactions that are relevant enough to justify its study, but a limited number of them can be physically monitored due to time and resource constraints. The use of computer models allows the simulation and prediction of the outcomes of those management and process interactions in a timely and cost-efficient manner (Vadas, Bolster & Good, 2013).

The model presented in Chapter 4 can be used as a tool to study land treatment system (LTS) behaviour under long-term secondary wastewater effluent irrigation. Alternatively, it can also aid in the assessment of the remaining longevity of actual systems by foreseen P leaching or can also be used as a planning tool to study the potential longevity of new systems before initiating the planning process or upgrading existing ones. Additionally, it is necessary to test the model to check its ability to predict system behaviour by comparing it with time and space domain for which data are available (Wainwright & Mulligan, 2004). Afterwards, the model can be run under different scenarios that are defined as changes in relevant variables under plausible values designed as management scenarios, to evaluate how changes in management inputs affect P accumulation and longevity.

The aim of this chapter is to explain system behaviour in order to estimate system longevity under different soil conditions and management practices.

The objectives are:

- To compare the model performance with respect to the field measurements to explain system behaviour.
- To assess the impacts of soil conditions and management practices on system longevity.

- To propose management practices that can improve the longevity of the systems.

5.2 Materials and methods

5.2.1 Longevity in Knowle LTS system

Firstly, the acceptability of the model needs to be tested, which depends on its purpose, which in this case is to explain system behaviour in order to estimate system longevity. The complexity and long-term basis of the present study are bounded by a lack of data sets to calibrate and validate the model. Due to this limitation, a simple comparison based on the results of soil analysis of TP concentration in the soil at Knowle system (see Chapter 3), and the model results of the amount of solute in the entire flow domain (mg/cm^2) at the end of a simulation run of 85 years with Knowle baseline parameters and boundary conditions was proposed. Despite that the results from the field study are expressed in TP concentrations, and the results from the sorption experiment in PO_4 (filterable reactive phosphorus), they still can be compared since analysis of wastewater at Knowle (Albion water, personal communication 2015) reported that 87% of the TP of the secondary effluent (irrigation) accounts for PO_4.

5.2.2 Management scenarios and soil conditions

To understand the impacts of model variable changes in system dynamics over time, different management scenarios were simulated. The scenarios selected are based on changes in input variables and relevant parameters that influence the model behaviour that can be adjusted under management practices and based on system location. The variables selected were: soil cover, loading rate, loading mode, P concentration of the secondary wastewater and soil type (Table 5-1). All the scenarios were run with the baseline parameters, model domain, boundary conditions and initial conditions described in Chapter 4 parameterized for Knowle LTS. Based on the sensitivity results from Chapter 4, the simulation period was set to 15 years to allow the system to reach a steady state (when the pore water at the bottom of the model soil profile reaches the same concentration as the irrigation wastewater), this is the moment when it is reached the maximum longevity of the system.

5.2.2.1 Soil cover

Vegetation plays different roles in LTS. They are used for nutrient removal, economic return, support of the biological activity and erosion protection (Crites, Reed & Bastian, 2000). In connection with the aim of the study, only the influence of nutrient uptake is considered, which depends on the type of vegetation. Herbaceous vegetation obtains most of the P that it needs from the soil pore water and translocates it to aboveground vegetation to support active vegetative growth. As it is referred in Chapter 1, biotic P is assimilated by vegetation, After senescence, the residual detrital material is deposited on the soil surface and released back into the water column as a result of decomposition (Reddy, Kadlec, Flaig, *et al.*, 1999). Hence, the nutrient removal of herbaceous vegetation is defined by the nutrient content of the plant at the moment of harvest, which has been quantified to make up generally around 0.2% of the plant's dry weight (Schachtman, Reid & Ayling, 1998), being 0.22 % of the dry percent of P harvested material for alfalfa and 0.18% for ryegrass (USEPA, 2006).

HYDRUS-1D assumes that P uptake can be described by the interaction of the soil and plant modules by balancing the supply of the soil and the plant needs. The sink terms in Eq (4-1) and Eq (4-2), S and ϕ, are related to root water and solute uptake. The sink term S, is defined as the volume of water removed from unit volume soil per unit time due to plant water uptake and it is dependent on the plant potential transpiration and the capacity of the plant to uptake water based on the water content of the soil, which is defined by the water stress response function defined by the Feddes (Feddes, Kowalik & Zaradny, 1978) for each crop (J. Šimůnek, M. Šejna, H. Saito, M. Sakai, 2013). The sink term ϕ represents nutrient uptake through the product of root water uptake, S, and available phosphorus concentration in the soil solution. However, HYDRUS-1D through this unlimited sink term does not consider the return of the P to soil after death and decomposition, simulating that all the P that the vegetation assimilates is removed by the system, continuously exporting P from the system.

The nutrient uptake intensity is determined by the root distribution, for this model it is set up so that the roots grow in between the first 20 cm of the soil profile because it is when they are supposed to be denser. The passive root water uptake is simulated by multiplying root water uptake with the dissolved nutrient concentration for soil solution concentration values below a threshold concentration. In this case, the threshold concentration is defined to be equal to the P concentration of the irrigation water, therefore all the solute uptake is driven by passive nutrient uptake. This is because the crop is assumed to uptake as much PO_4 as available by passive means since the concentrations of P in plant available form is usually very low in natural systems.

The soil cover scenarios that have been proposed are vegetation cover scenarios based on low maintenance and low manpower inputs. This condition is related to how LTSs are currently managed in the UK water industry and how the trends of future implementation of these systems are planned, with minimum maintenance requirements for minimum costs. Therefore, the proposed vegetation covers are grass and forage crops that have no rotation, are easy to establish under the site weather conditions and with minimum management requirements. The scenarios were selected among the available by default HYDRUS-1D software root water uptake parameters.

Two scenarios have been proposed:

- V1: Alfalfa.
- V2: Grass.

5.2.2.2 Loading rate

The optimal hydraulic loading rate is a function of the site-specific hydraulic characteristics, including infiltration, percolation, lateral flow, and depth to groundwater, as well as the quality of the applied wastewater and the treatment requirements (USEPA, 2006). Small sewage treatment works (STW) usually lack hydraulic structures design to retain, regulate and control the flow of water. Therefore, changes in the loading rates with no supplementary regulation infrastructure have to be addressed through changes in the areas of irrigation.

The proposed loading rate scenarios are based on current and lower loading rates for Knowle STW effluent flow (250 m^3/d) in different discharge areas (See Chapter 3). Higher loading rates scenarios are not considered because they would rapidly saturate the soil profile and increase runoff and therefore it would cause direct discharge of the secondary effluent to the nearby water bodies. Three scenarios have been proposed:

- LR1: 35.7 mm/d: irrigation only over the section A (current situation).

- LR2: 12.5 mm/d: irrigation over the whole area of the discharge field (Sections A, B, and C).

- LR3: 6.3 mm/d: irrigation over a field an area double than at Knowle LTS, in order to test the impact of lower irrigation rates than the current ones.

5.2.2.3 Loading mode

Design and operation manuals of LTS advise that drying periods are necessary to restore the infiltration capacity and to renew the biological and chemical treatment capability of soil system (USEPA, 2006). The ratio of wetting to drying in LTS varies but normally is less than 1.Two loading mode scenarios have been tested: intermittent loading (LM1) and continuous loading (LM2). In this study, to provide an intermittent loading to small LTS without storage capacity during no irrigation periods, the discharge field has been divided into two equally sized sections that will be irrigated continuously with a loading rate of 25 mm/d for 1 week, while the other half of the field remains drying (LM1) (

Figure 5-1). The wetting/drying ratio it is set to 1 also to allow a simple management practice to the plant operator.

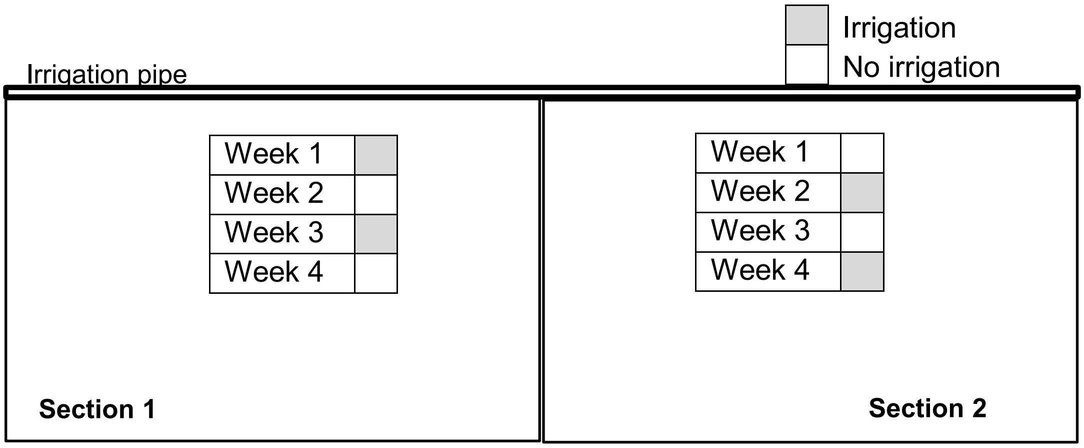

Figure 5-1 Monthly schedule for intermittent loading rate for the discharge field

5.2.2.4 Irrigation phosphorus concentration

Two main scenarios were considered for the PO_4 concentration of the secondary treated effluent. The current situation in Knowle STW discharging an average PO_3^{-4} concentration of 7.96 mg/l (C1) and 1 mg/l (C2). This concentration was selected because recent consideration about the environmental risk associated with the discharge of P from wastewater treatment plants to freshwater, has led to the introduction of permissible direct discharge to medium and small SWT to a waterbody limit to 0.5-2 mg/l (Parliamentary Office of Science and Technology, 2014). HYDRUS-1D includes precipitation and irrigation in the same input variable, therefore, both are assumed to have the same concentration. This assumption will not lead to a major impact on results as the secondary wastewater effluent discharged to the field (irrigation) dominates in comparison with precipitation (see Chapter 3).

5.2.2.5 Soil type

Treatment performance depends on wastewater characteristics, loading rates, and soil type. Thus, it is required to analyze a modelling scenario based on soil type. Moreover, soil type affects water flow parameters of the soil and reaction parameters that describe the sorption capacity (K_d), which was found to be the most influential parameter during the sensitivity analysis of the model (Section 4.4). Two main study scenarios were proposed: the first one is based on a sandy soil. Sandy soils generally have higher saturated conductivities than finer textured soils because they have more macropore space, which is the is the factor that accounts for most of the water moment in saturated soils (Brady & Weil, 2008). Additionally, sandy soils are expected to have low P sorption capacity since they have lower clay, Al and Fe content than a clay loam soil (Ho & Notodarmojo, 1995).

The soil hydraulic parameters that define the sandy soil were derived from HYDRUS-1D default parameters (Šimůnek & van Genuchten, 2008) and the reaction parameters are based on Kadlec and Wallace (2009) summary of Freundlich isotherm parameters for various substrates in treatment wetlands (sand) (ST1). The second scenario is a clay loam soil type scenario (ST2) based on soil characterization of the soil at Knowle´s LTS.

5.2.2.6 Scenarios evaluation

The scenarios evaluation will be based on the following outputs from HYDRUS-1D: P accumulated at the discharge field (kg), which is derived from the concentration in the soil profile and the area of irrigation; P leached (kg) obtained from the cumulated solute across the bottom of the soil profile, long-term P removal (%), and time to achieve steady state.

The long-term removal was calculated with Eq. (5-1):

$$P_r = \frac{P_c}{P_l} 100 \qquad \textbf{(5-1)}$$

Where

P_c is the mass of P in the first 40 cm of the soil profile (kg), that can be calculated as the sum of the solute leached and the solute accumulated.

P_l is the estimated mass of P discharged to the field (kg).

5.3 Results and discussion

5.3.1 Longevity in Knowle LTS system

The comparison of soil analysis of TP concentration in the soil and model results points towards an underestimation of P concentration in the soil profile by model simulations. The average soil P concentration of the three sections from soil analysis was 0.57 kg/m^2 for section A, 0.67 kg/m^2 for section B and 0.41 kg/m^2 for section C and 0.35 kg/m^2 for reference samples (See Chapter 3), whilst, model results presented an average concentration for the entire discharge field of 0.12 kg/m^2 which corresponds to around 5 times less P concentration in the soil. Our results are consistent with the recommendations from the USEPA (2006) process design manual for LTS of municipal wastewater effluents, which advises that actual phosphorus retention in long-term soil treatments can be from 2 to 5 times greater than values obtained with 5-day phosphorus adsorption, however this is recommendation is exclusively from sorption models and no from integrated water and solute transport models.

There are no other studies that compare long-term full-scale irrigation with HYDRUS-1D results for P transport. The ones that compare HYDRUS-1D results with column studies found that whilst water flow was accurately modelled, the final P sorbed was overestimated, probably due to preferential flow and incorrect adsorption isotherm (Nahra 2006; Naseri et al. 2011; Elmi et al. 2012;). However, there are several drawbacks inherent in column studies that affected the model results that hinder the comparison with full-scale systems studies. For instance, the preferential flow that might occur between the walls of the columns and the soil, or the time-scale of the studies being hours rather than years. Other factors that might affect the comparison of the results from both studies is that, in the sorption experiment in the column study was run over a shorter period of time (18h rather than 5 days), that regardless of the effect of the vegetation has been demonstrated to be very limited, the column study did not take into account the effect of vegetation on water flow and P uptake, or that the column study calculates the final sorbed concentrations by using the isotherm model. That means that the final mean concentrations in soil solution are plugged in the isotherm model to calculate concentrations sorbed to the soil. However, in our study it was decided to compare concentrations that the model provides as an output directly, to avoid to use the model isotherm again for calculations due to its limitations. Additionally, the column experiment obtains reaction parameters from non-irrigated samples whilst, the in this study, model's P reaction parameters were derived from sorption experiments in irrigated soil samples, consequently, the lower soil P concentration might be a result of the effects of previous saturation of the soil samples.

Based on modelling results, the estimation is that Knowle system retains P during approximately 12 years. The outlet concentration follows an S-shaped curve with a slow beginning where the concentration remains low, a more steep phase where the rate of retention decreases as the concentration of the outlet increases until a plateau phase when the equilibrium is achieved at soil saturation (Figure 5-2). After that period, the P concentration of the irrigation equals the concentration of the leaching through the lower model boundary (0.40 cm) and therefore the soil does not retain additional P. Although the depth of the unsaturated layer in Knowle LTS system is unclear, it is expected to be around 2 m (Tyrrell, 2016), therefore the remaining thickness of soil might also contribute to increasing the LTS longevity. That might be the reason why the longevity estimation is lower than other treatments such as the 36 years calculated by Jenssen et al. (2014) for Bardu (Norway) wastewater infiltrations basins, which considers, for longevity calculations, the sorption capacity of the soil (gravel deposit) and a depth of 6 m. In fact, additional simulation modelling results obtained in this study considering an isotropic soil layer of 2 m at Knowle, achieved steady state in 28 years, doubling longevity with respect previous calculations with a 40cm soil profile layer. However, it has to be considered that previous studies suggested that the accumulation of P in the soil was higher in the uppermost soil layer (0.5 m) (Falkiner and Polglase 1999; Nahra 2006; Eveborn et al. 2012)

5.3.2 Impacts of management scenarios and soil conditions on system longevity

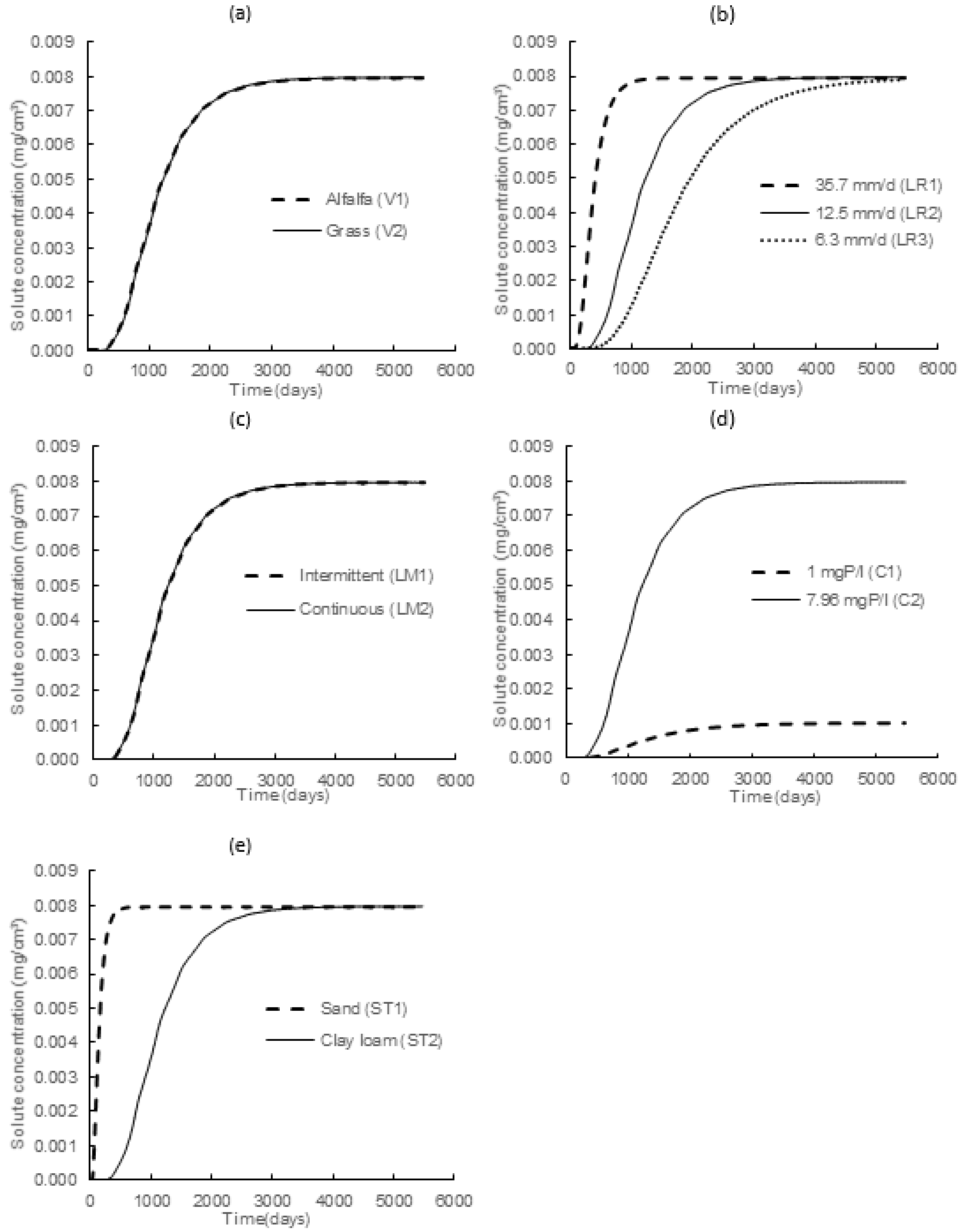

Figure 5-2 Modelling scenario results for 15 years simulation of P concentration at 40 cm deep of the soil profile a) soil cover b) loading rate c) loading mode d) irrigation concentration e) soil type. Solid line show baseline results for Knowle system.

Table 5-1 Results of the amount of P retained at the discharge field, amount of P leached and P retained for the simulated management scenarios after 15 years of irrigation.

Variable	Scenario	ID	P retained at the discharge field (kg)	P leached (kg)	P retained (%)	Time to achieve steady state (years)
Vegetation	Alfalfa	V1	2451	8224	23%	11.8
	Grass	V2	2451	8224	23%	11.8
Loading rate	6.3 mm/d	LR1	2444	4641	34%	>15
	12.5 mm/d	LR2	2451	8224	23%	11.8
	35.7 mm/d	LR3	2451	30260	14%	4.6
Loading mode	Intermittent loading	LM1	2451	10625	23%	11.8
	Continuous loading	LM2	2451	10675	23%	11.8
P concentration	1 mg P/l	C1	374	364	51%	>15
	7.96 mg P/l	C2	2451	8224	23%	11.8
Soil type	Sand	ST1	350	12130	3%	1.8
	Clay loam	ST2	2451	8224	23%	11.8

5.3.2.1 Soil cover

Different vegetation cover (grass and alfalfa) had no influence in the P leached through the bottom boundary of the model (Table 5-1). This can be explained because the potential transpiration and root water uptake parameters (Fedde's parameters) for the selected vegetation are almost equal. The parameters specify the water stress response functions and they only differ for grass and alfalfa in the limiting values below which roots can no longer extract water at the maximum possible rate. Consequently, type of vegetation cover will have a small influence in well-irrigated systems such as LTS for wastewater treatment where the evapotranspiration is very small compared with irrigation (see Chapter 3) because of the high water availability. Higher uptake rates could be achieved with vegetation with higher water consumption such as corn or sugar cane, however, those type of vegetation are annual crops that would require more intense maintenance task and therefore would be not suitable for low maintenance LTS, additionally the incorporation of non-native grass would prevent the LTS from providing alternative ecosystem services such as biodiversity and wildlife (Charlesworth, Bennett & Waite, 2016).

Model results present a long-term P uptake of 6.1 kg/ha/a. In LTS designed for high infiltration rates, perennial grasses are the most recommended vegetation cover as they generally achieve the highest uptake of phosphorus. Crites et al. (2000) presented P uptake rates for a selection of forage crops and field crops and estimated alfalfa P uptake to be 22-33 kg/ha/a. The difference in the uptake rates might be associated with the HYDRUS-1D calculation of P assimilated by the plants, which is not based on phosphorus crop harvest content (kg/unit yield) but on water needs and P availability in the soil solution.

Forage and turf crops used in LTS need to be well adapted to conditions of the place (climate, soil type or soil moisture), to be low sensitive to wastewater components (salinity or trace metals) and tolerate waterlogged conditions. Field crops are not strongly recommended for LTS due to this low capacity of wastewater renovation until the crop is fully established and that harvesting require expensive machinery and labour that would increase maintenance cost (Kadlec & Wallace, 2009). Additionally, if vegetation is used as food crops it should be taken into account that they need a suitable pre-application treatment to be harmful to human health, although no risk has been identified any risk when they are used for grazing purposes. Therefore, modelling results suggest that alternative vegetation with the requirements of being low maintenance crops has little influence in the net P removal in the long-term, but literature has extensively demonstrated other benefits that vegetation, especially perennial grasses, can provide in the short-term to LTS such as erosion control, effects on hydraulic loading rate, biomass production, microbial community structure, and activity, or toxic organic degradation and habitat provision (Paranychianakis, Angelakis, Leverenz, *et al.*, 2006). However, as Roberts et al. (2012) points out in his study related to phosphorus retention in vegetated buffer strips it would be beneficial to identify and evaluate plant traits that enhance physical and biological retention of dissolved phosphorus, and to extend Charlesworth et al. (2016) study of heavy metals and TSS of uptake effectiveness and retention of grass species to phosphorus.

5.3.2.2 Loading rate

The three loading rates tested have different effects on the P concentration of the bottom of the soil profile over time. The steady state is reached first by the highest loading rate 35 mm/d in 4.6 years, while it takes 11.8 years with 12.5 mm/d and >15 years (23.9 years) with a loading rate of 6.3 mm/d. If the loading rate is doubled the time to achieve steady state is doubled and if the loading rate is increased 2.8 times the time the longevity increases by 2.5. Therefore, there is a proportional relationship in the years needed to achieve steady state and the loading rate. The relationship is not exact maybe due to the numerical methods that HYDRUS uses to solve the equations, which will deliver approximate solutions. It is clear that when more P is added to the soil profile through higher loading rates the sooner the saturation is reached. However, even if the time to achieve steady state is proportional, in lower loading rates the contribution to phosphorus removal after 15 years is lower because the portion of PO_4 adsorbed to the soil to PO_4 soluble in solution ($\partial s / \partial c$) reduces over time, and regardless the soil might not be strictly saturated, the further contributions to nutrient removal will be insignificant.

If the system is not correctly designed it can result in the release of untreated wastewater because it was been exceed the infiltration capacity (O'Keeffe, Akunna, Olszewska, *et al.*, 2015). Published process design manuals for LTS (USEPA, 2006; Crites, Reed & Bastian, 2000) propose annual loading rates for systems irrigated with secondary wastewater based on measured infiltration rates and recommend that it should be not greater than 2-4% of the measured infiltration (using cylinder infiltrometers). This is because cylinder infiltrometers overestimate infiltration rates in the long-term, which may vary over time due to solids clogging and macropore development. Tyrrell (2016) obtained an infiltration rate of 13.7±10.7 cm/h with a double ring infiltrometer for trial plots at Knowle STW. This infiltration rate would allow, for tertiary treatments following the mentioned recommendations, loading rates between 65-131 mm/day, which is in the high range of the one tested. Management practices based on this high loading rate would allow the system to work properly hydraulically but will saturate the system in less than 5 years.

Loading rate in LTS is closely related to land availability, and it is one of the main constraints in the planning process of this type of systems. They are normally design based on the nearby STW effluent volumes and the land area available, that is the reason why is very unlikely that water companies decide to install LTS in locations where land it is difficult and expensive to obtain. Consequently, these systems are usually recommended for small and rural STW, where it is more feasible to obtain the necessary land to achieve treatment requirements. Therefore it is recommended that even if infiltration tests would allow the system to perform well hydraulically under high loading rates, it has to be taken into account that the soil profile will saturate faster not being able to further contribute to nutrient removal.

5.3.2.3 Loading mode

Intermittent irrigation application in LTS allows ammonia removal, restoration of aerobic conditions, renew infiltration rates, and allow oxidation of organic matter (USEPA, 2006). The scheduled loading mode based on one week of drying period and one week of irrigation was tested based on recommendations from irrigation design manuals (Crites & Pound, 1976; USEPA, 2006). Regardless of the wetting and dry periods, no differences were found in the modelled solute concentration at the bottom of the profile or in the amount of P retained in the soil profile after 15 years of simulation and consequently in longevity estimations (Figure 5-2). This is because in both scenarios the same amount of water and solute was applied, due to the increase in the loading rate to allow the discharge of all the effluent from the STW. The main reason is associated with the fact that drying periods are too short to have any influence due to almost permanent water saturation of the soil. In the light of the results, it was considered to be interesting to test the possibility of applying rapid infiltration systems management strategies to overland flow systems, that means that, instead of short non-irrigation periods of one week, to consider 6 months every year of no irrigation; during this time, the only water input will be the rainfall (with no P concentration). The loading rate considered for the irrigation period was 25 mm/d to allow all the STW effluent to be discharged and 12.5 mm/d in case there is land availability to extend the surface area, the irrigation months was considered to be during the summer season (April to September). The results obtained (Figure 5-3) suggested that long resting periods might be beneficial to reduce P leached, achieving lower solute concentrations in the steady state (0.0068 mg/cm^3), probably due to non-continuous irrigation and the non-solute concentration in the rainfall contributing with some dilution of the solute plume, the extension of the longevity up to 20 years, and that the benefits will be further enhanced by a reduction of the loading rate.

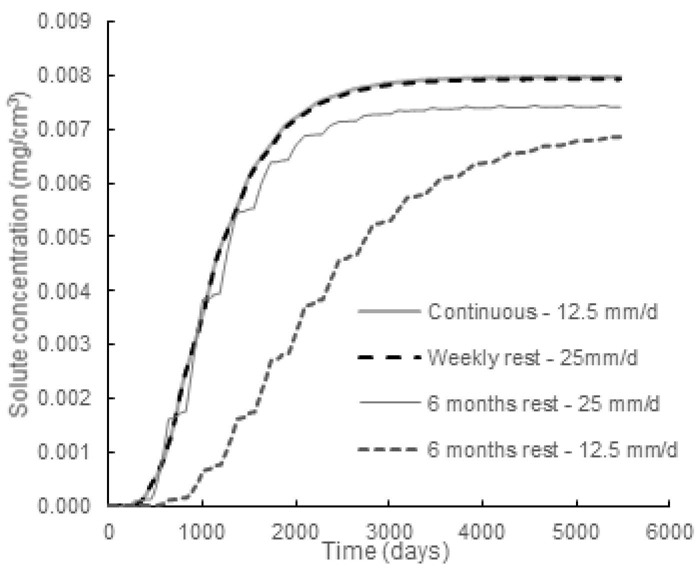

Figure 5-3 Loading mode and loading rate combination scenarios

Usually drying and wetting cycles have been studied in relation to restore aerobic conditions and renew infiltrates rates, but they have not been extensively studied related to their influence in P removal, for instance, not studies other than Bisone et al. (2016) studied the influence of loading rate and modes on infiltration of treated wastewater in soil-based constructed wetland columns. The study reported no differences between continuous and intermittent loadings regarding P retention. However, the same study confirmed the benefits of intermittent feeding (3 days and ½ followed by a rest period of 7 days) in a clay soil enhanced infiltration, nutrient removal, and nitrification.

5.3.2.4 Irrigation phosphorus concentration

The P concentration of the secondary treated wastewater has a strong influence on the total amount of P retained and longevity. When the influent concentration is 1 mg P/l the P retained in 15 years simulation is 50% of the P applied with irrigation, whilst it will be retained 23% with an influent P concentration of 7.96 mg/l. The leaching with a 1 mg/l P concentration is 22 fold less than with a concentration of 7.96 mg/l. Regarding the behaviour of the solute concentration at the bottom of the soil profile, the concentration does not reach steady state after 15 years while it takes 11.8 years with 7.96 mg/l of P irrigation concentration. Lower concentrations of P achieve a concentration plateau in less time than it might be expected, however, this can be as a result of the irrigation rate, not allowing enough contact time with the soil particles. Additionally, it has to be taken into account that in all simulations, the model assumption of equal P concentration of precipitation and irrigation, which will lead to an underestimation of longevity predictions.

5.3.2.5 Soil type

The two soil types proposed have a clear influence on P retention in soils. Steady state is reached in the sandy soil in less than two years while it takes 11.8 years in clay loam soils. The amount of P retained after 15 years of simulation is 3% in a sandy soil and 23% in a clay loam soil, indicating the limited capacity of the sandy soil for phosphorus sorption. This can be caused because of the poor hydraulic retention time of sandy soils under high irrigation loads, and because of low sorption for phosphate that sandy soils are expected to have since they have lower clay, Al and Fe content than a clay loam soil (Ho & Notodarmojo, 1995) and higher reactive surface area of clay soils.

Sand P sorption capacity is considerably lower than other substrates and soils types. Xu et al. (2006) screened different subtracts and soils used in constructed wetlands for P removal and demonstrated that sandy soils had the lowest sorption capacity (0.13-0.29 g P/kg) and that it was because of physicochemical characteristics and OM content. A summary of Freundlich isotherm parameters for various subtracts in wetland treatments also showed the lowest values for sand (Kadlec & Wallace, 2009). Alternative studies of P sorption materials and soil sorption capacity (Cucarella & Renman, 2009; Vohla, Kõiv, Bavor, *et al.*, 2011) also report low values of P sorption for sand. Additionally, high infiltration rates in sandy soils can allow effluent to move rapidly towards deeper layers not allowing enough time for treatment. The sensitivity analysis also revealed P sorption characteristics as the most influential parameter affecting the model P retention capacity. Therefore, the longevity of LTS is strongly influenced by the type of soil.

Whereas in other engineered natural treatments systems, such as wetlands or soil infiltration systems, the filter material can be chosen within a large range of P-sorbing substrates (slag material, LECA, Filtralite, etc), in LTS soil type is associated with the location and therefore their sorption characteristics are predetermined. However, studies point out that P retention capacity in soils capacity can be enhanced by the addition of amendments substances. Dong et al. (2005) studied the addition of oyster shell to different filter media used in constructed wetlands and concluded that the P adsorption could be increased. However, Ann et al. (1999) indicated that it was required a high amount of them to effectively minimize P release due to complexation of P binding cations with organic matter of the use of chemical amendments. Nevertheless, it would be interesting to study how long-term modelling results vary under different combinations of soil and amendments, in order to estimate optimal combinations for longevity optimization in natural soils.

5.3.3 Model limitations and improvements

The model limitations and improvements can be associated with the inherent drawbacks of environmental modelling and model conceptualization, model inputs assumptions or how HYDRUS-1D calculates and simulates water flow and solute transport.

First, environmental modelling has a number of limitations that must be taken into account when assessing the performance of the model such as it is a simplification of processes or the limitations associated with parameterization; especially sorption parameterization, since it is based on empirical models such as sorption isotherms, where parameters are valid for the conditions under which the experiment has been conducted, or the vast number of parameters interactions and unpredictability of natural processes. Secondly, the assumption of regular inputs, such an average climatic year over the simulation period or the assumptions of constant flow and concentration of the irrigation water. Those limitations could be overcome with reliable input data from the STW or weather stations and the model being simulated in batches of known inputs. However, the lack of long-term monitoring in this type of system makes this model improvement nonviable. Finally, there are several limitations from HYDRUS-1D that might be responsible for the underestimation of the model results of P concentration in the soil profile when they are compared with the field scale results. This limitation will be further addressed in the final discussion of the thesis (Chapter 6).

It would be desirable that the root water uptake was determined by a crop model simulation, such as STICS model (Zimmer, Sierra, Bertuzzi, *et al.*, 2003) or EPIC (Jones, Cole, Sharpley, *et al.*, 1981), where the growth and plant development are simulated as a function of the soil-plant-atmosphere dynamics and plant density, and where the decay and plant harvesting it can be also incorporated. It would also be advisable to incorporate the description of clogging processes due mainly to bacterial growth or particulate organic matter. However, the main limitation of HYDRUS-1D comes as it fails to simulate the multiple solute pools and their chemical connections based on soil pH and OM, and simulates P sorption by batch experiments and sorption isotherms which have been demonstrated to have several limitations when they are used solely to forecast the longevity of LTS. Additionally, and even if in this particular case losses by runoff are not relevant, it would be beneficial to have the possibility to model losses of particulate and dissolved P as well as desorption processes to study the P flushed out of the system after rainfall events.

5.4 Conclusions

Model results of Knowle LTS underestimate P concentration in the soil profile in comparison with field analysis. According to the simulations results, the system has successfully accumulated P in the soil surface (40 cm) during the first 15 years of operation. The extrapolation of the model to different scenarios explained how, vegetation, loading rate, loading mode, soil type characteristics and P concentration of the irrigation affected the longevity. Loading rate and soil type are both related to specific site characteristics and land availability, rather than management variables that can be adjusted by operational procedures, whilst irrigation's P concentration depends on the treatment capacity of the STW. Long term simulations suggest that different types of low maintenance vegetation have no influence in the time the systems takes to achieve steady state, therefore they do not affect the longevity of LTS. An increment in the loading rates decreases proportionally the time to achieve steady state, however, the P retention rate after 15 years is very limited. Loading modes based on weekly wet/drying cycles have no effect on longevity, but longer resting periods (6 months) can enhance the longevity of the system several years. Soil type and P concentration is the most influential scenario affecting longevity, with clay-loam soils being able to, under the same management conditions, increase longevity by five times compared to sandy soils, and P concentrations changes from ~8 mg /L to 1 mg/l reduces the amount of P leached 22 times while increases longevity.

Regardless that the model seems to underestimate the P longevity of the soil treatment due to modelling limitations, it can be used as a tool to predict a range minimum of longevities under different scenarios, for example, different loading rates and loading concentrations for a specific site. However, to withdraw conclusions the modeller has to be aware that the fate of P in soils in the long-term have a large uncertainty associated with the sorption characterization of soil samples and its transferability to the model reaction parameters, the inherent simplifications of reality, the vast number of parameters needed and the natural unpredictability of natural processes.

6 DISCUSSION

Due to the finite nature of P removal processes in LTS, improved P-removal and lifespan predictions are beneficial to operators and regulators as they provide greater confidence in this technology and support long-term wastewater treatment planning. In this section, how the findings from the previous chapters can contribute to improving P-retention and longevity in LTS are discussed, and support, as an indicator of the treatment's sustainability, the current and future role of LTS in the sustainable wastewater industry.

6.1 Knowle: a long-term land treatment system in the UK.

The duration of wastewater irrigation activity at Knowle (~85 years) offered the possibility to study a unique LTS and identify management practices and processes that help to better understand the P dynamics in long-term full-scale systems.

The secondary effluent discharged to the field (irrigation) dominates the hydrological balance in comparison with precipitation during the operation period which suggests that the soil water retention capacity might be exceeded and the excess of water is percolated to deeper layers. The study field has been irrigated with secondary wastewater effluent for different periods and, despite the differences in the P loads, no significant differences were found in the mean TP concentration of the field sections. Additionally, the P concentration values in soil samples were higher than the regional average and adjacent site references and close to the soil P sorption maximum reported in the literature for that adjacent site suggesting, that the soil is saturated with P irrespective of the duration of the irrigation. The long-term P removal was low compared with other similar mass balance calculation studies of P removal in soils. These results were confirmed by the modelling simulations, explaining that this saturation took place after approximately 12 years of irrigation. Therefore, due to the P saturation and the high hydraulic loads, it is plausible that P from the discharge field reaches surface and groundwater but no evidence of nutrient pollution has been detected in the nearby water bodies (River Meon and East Hants Chalk aquifer).

However, as shown by the results from the modelling section, the system would have prolonged its longevity from 12 to more than 24 years and would have achieved lower solute concentrations in the steady state if the irrigation area had been constant and made maximum use of the entire field over the entire operation period, and by introducing alternate periods of irrigation and long resting periods. However, the current management of Knowle LTS is tied by the land ownership. The water company that operates the system is not the owner of the discharge land, and consequently, there are many impediments associated that prevent an optimal management of the system such as the need for permissions to operate and investigate. In fact, the irrigation area in Knowle system, as was described in Chapter 3, is currently restricted by these impediments to a small section of the irrigation field which leads to high loading rates. This situation brings the soil to be close to saturation for many months of the year, which may result in additional removal processes, such as nitrification, being slowed down or eliminated.

The soil measurement results also presented a high variability that is attributed to the lack of design and management procedures of the site, with the minimum values in each section being close to the reference concentrations, which suggests poor irrigation uniformity of distribution in the field. As a result, it produces high variability of the soil and the associated difficulty of finding representative samples to characterize the site and, to link management practices and their impacts on the system treatment. This is one of the main drawbacks when it comes to assessing the performance of this type of system along with insufficient monitoring. Moreover, the lack of site long-term monitoring at Knowle hindered the characterization of the secondary treated wastewater quantity and quality over time that had to be calculated based on literature assumptions of water use and P content in wastewater for the operation period, with the consequent impact on the confidence in the results. The lack of a clarity in the irrigation history of the site meant the lack of a clear reference or control sample for the study. The preliminary hypothesis of the irrigation periods from the water company operating the plant of a section of the field never been irrigated was discarded, and instead, the irrigation periods were stabilised in relation to the evidence of the presence of the irrigation pipe on historical maps (from 1881).

However, the maps referred to broad periods of time with the consequent inaccuracy.

Even if the system is no longer contributing significantly to P removal, when it comes to evaluating the contribution of the LTS to the sustainability of the sewerage services of Knowle village, the water company in charge recognizes the site contribution beyond its nutrient removal potential and acknowledges the creation of a richer biodiversity habitat in the area. The operator highlights how the field creates a high soil invertebrates biomass that provide a source of food for a thriving population of reptiles, amphibians, bats and birds, and contributes as support for threatened species of bees and wasps and hibernation sites for bats and reptiles (Knaggs, 2014; Albion Water, 2017).

However, future work should be done to confirm the sustainability results obtained from Knowle by increasing the knowledge of the current situation of these long-term LTS systems that are still functioning in the UK. Therefore it is urgent to complete the results obtained by Sweaney (2011) for 13 grass plots in operation in the UK to complete the data collection of P performance in LTS, and determine if they have also achieved their longevity, when, and if there is any risk of P pollution to the nearby water bodies.

6.2 Phosphorus retention processes in land treatment systems

As described in Chapter 1, soil P retention processes are physical, chemical and biological processes. Through a combination of measurements and literature, the main phosphorus pathways were identified for Knowle LTS (Chapter 3) and results have improved our understanding of the long-term P retention processes in LTS as follows:

First, physical retention mechanism will be less influential in LTS treating wastewater because the nature of the P coming from the STW is dissolved (Albion Water, personal communication 2015). Physical retention mechanisms have greater influence in removing particulate P than dissolved P because it uses the above-ground vegetation and a dense root system to decrease the overland flow velocity and energy to transport particulates that will be deposited in the soil.

Second, regarding the plant uptake, the P and hydrological inputs are driven by the secondary wastewater irrigation, which is on average 5.5 times larger than the precipitation. The evapotranspiration, which accounts for the evaporation from the soil and the plant transpiration, was on average 13% of the water inputs (rainfall and irrigation), with a minimum contribution in the winter months of only 3%. Since P uptake is related to the plant transpiration potential; this pathway is not critical in well-irrigated systems where the evapotranspiration is very small compared with irrigation. Additionally, the vegetation management does not remove vegetation from the site with the consequent re-incorporation to the system of the P that has been previously assimilated by the plant.

Third, the P microbial biomass storage was calculated through literature to be 4% of the total P discharge for the 85 years operation period, but literature quantification was related to agricultural fields and therefore for more accurate quantification of this removal pathway the microbial biomass storage for an LTS should be better quantified.

Finally, since no runoff was observed, the main P removal process contributing to P removal are chemical processes, which include a range of processes (solution–precipitation, ion exchange, complexation, redox reactions and sorption-desorption processes), which are difficult to differentiate and characterized in the long–term. These results agree with previous studies that identified sorption processes, which mainly refer to adsorption capacity, to be the most important process in natural wastewater treatments (Drizo, Frost, Grace, *et al.*, 1999; Reddy, Kadlec, Flaig, *et al.*, 1999; Kadlec & Wallace, 2009; Vohla, Kõiv, Bavor, *et al.*, 2011; Dzakpasu, Scholz, McCarthy, *et al.*, 2015b), therefore adsorption capacity characterization is crucial to determining the P-removal capacity and longevity.

6.3 Methods of estimating phosphorus removal in land treatment systems

Estimations of removal efficiency in full-scale LTS are needed as an indicator of treatment performance, however, there are no simple alternative methods to predict phosphorus removal rates at the site level in an LTS (Office of Research and Development U.S. Environmental Protection Agency, 2002). The field case study presented in Chapter 3, aimed to calculate the P removal efficiency of an LTS based on P concentrations in the soil. This method is based on the capacity of the soil to adsorb P and calculates P accumulation as a percentage based on the concentration of P in the soil before and after the discharge of wastewater. This methodology overcomes the challenge of obtaining inlet-outlet monitoring datasets, because of the difficulty to identify inputs and outputs of P and water when there are no clear outlets or after-treatment collection points. This method also eliminates the difficulties associated with the use of lysimeters or suction cups to collect soil moisture samples when there are no free water samples available because of their implementation cost and skills needed to install it and operate (USEPA, 2006). However, as discussed in Chapter 3, this method has two main limitations. Firstly, it is strongly influenced by the pre-treatment reference soil sample and therefore, reference sample locations have to be carefully chosen in order to accurately represent P accumulation due to wastewater irrigation and no other possible P sources, such as diffuse pollution from agriculture. Second, it only considers the removal processes associated with the sorption capacity of the soil that are the main removal processes in LTS but not the only one. Additionally, this method is very dependent on finding representative samples due to the previously mentioned soil variability in this type of systems and in the assumption that the removal capacity is only taken place in the first 40cm of the soil layer. Modelling could also be used to assess the P-removal in an LTS, however, the inherent incapacity of a model to accurately represent full-scale systems and the vast amount of parameters needed prevent the use of modelling exclusively for this purpose.

Therefore, due to the previously mentioned limitations, this method is not very strong to determine P removal in the long term. However, it could be valid to assess the changes in the removal capacity regularly in order to detect when the saturation of the P retention capacity of the soil is reached, and hence, notice when the soil will no longer contribute to further treatment. However, it would be necessary to compare the results of both methods, even if this is difficult to do with confidence, in the same system treatment to obtain further conclusions about the accuracy and suitability of this method for assessing treatment performance in LTS.

6.4 Modelling phosphorus dynamics in land treatment systems

As discussed in Chapter 2, it is well accepted that estimation of the P sorption capacity of soils by batch or column experiments has several limitations when it is used solely to forecast the longevity of the system and that lifespan predictions of LTS based exclusively on sorption experiments would share that series of limitations. These limitations include the incapacity to represent long-term soils modifications and sorption's evolution after long-term wastewater irrigation, and the inability to simulate field conditions that can provide results that could be translated to full-scale experiences. Modelling tools have been proposed in this thesis to link the discrepancies discussed between laboratory experiments and full-scale systems and to overcome the temporal limitations of long-term studies. As was identified in Chapter 2, few attempts to estimate the P longevity of LTS through models have been found and none of them has been completed and published due to several limitations and further development and research needs (uncertainties in data acquisition, empirical models, models not validated or neglecting important variables of the removal processes).

The modelling tool selected aimed to improve the previous attempts by calculating the P changes in the concentration in the soil solution over time. The longevity is achieved when the system reaches the steady state (when the pore water at the bottom of the model soil profile reaches the same concentration as the irrigation wastewater). The modelling tool selected in this study, HYDRUS-1D, is a mathematical model based on Richard's equation that adapts Darcy's law to water flow under variably saturated conditions. The Richards equation's solution requires specification of initial boundary conditions for the domain study area as well as flow initial condition but presents some limitations such as the definition of boundaries conditions in continuous models, the requirement of demanding computational numerical solutions and the need of intense number of inputs to describe the soil system (Nelson & Parsons, 2007). Regardless of these limitations, it was preferred from field capacity-water balance models or tipping bucket algorithms because the latter assumes that the water exceeding field capacity flows to the soil layer below if the following layer is not saturated (Nolan, Bayless, Green, *et al.*, 2005). This assumption does not consider the possibility of water flow under other different water contents and might lead to large percolation events forecast rather than continuous drainage (Nelson & Parsons, 2007). HYDRUS-1D was also selected for its capacity of simulating in the long-term because it has a windows interface, it is easily available and, it also provides stable numerical solutions through the finite element techniques for governing equations in space and the finite difference in time. Additionally, it has an active user support and discussion forum available, and it has been reasonably well tested against column and field conditions in several previous studies, including P transport (Naseri, Hoseini, Moazed, *et al.*, 2011b; Elmi, Nohra, Madramootoo, *et al.*, 2012; Ben-Gal & Dudley, 2003; Morrissey, Johnston & Gill, 2015; Sinclair, Jamieson, Gordon, *et al.*, 2014; Beach & McCray, 2003; Radcliffe & Bradshaw, 2014; Claveau-Mallet, Courcelles & Comeau, 2014).

HYDRUS-1D is not specifically designed to model P but, through sorption equations and soil hydraulics parameters, can simulate P transport within the soil profile (Radcliffe, Reid, Blombäck, *et al.*, 2015). The conceptual model representing the hydrological and P inputs and outputs required to simulate long-term (steady-state) vertical migration of secondary wastewater effluent was presented in Chapter 4, where leaching and soil P concentration were used as parameters indicators for removal estimation and longevity.

The convection-dispersion equation used in HYDRUS-1D to model PO_4 retention and leaching in the soil profile incorporates the theory of the Langmuir isotherm, which is referred to sorption processes of gases to uniform surfaces. These sorption processes were clarified by Fetter (1999) to be referred to surface reactions (adsorption, chemisorption, absorption and ion exchange). However, other studies such as Jourak et al. (2011) allow the Langmuir isotherm also to account for classical chemical reactions such as precipitation, as it is considered in this study because of the long shaking time (5 days) executed at the adsorption experiment (Chapter 4) would allow also precipitation reactions to take place.

This longer shaking time and concentrations close to average discharge from secondary wastewater treatments were also chosen to overcome the limitations of traditional methods discussed in Chapter 2. These long-term batch experiments were selected based on Hu et al. (2006) and Eveborn et al. (2014) long-term sorption experiment experiences. They were preferred to long-term exhaustion columns studies as the one performed by Drizo et al. (2002) during 278 days because of time constraints of the project. One-year column experiment is unreasonable time-consuming to characterize small rural sites. However, long-term column experiments can be appropriate to characterize man-made filter materials which characteristics are homogeneous and constant, compared with natural soils. However, further work is needed to increase our understanding of P retention in soils in the long-term and to identify measures at laboratory scale that will lead to more reliable methods to test long-term sorption processes in soils.

Chapter 5 revealed a model underestimation of P concentrations in the soil profile after long-term wastewater irrigation. This is the first study that compares long-term full-scale irrigation with HYDRUS-1D results for P transport. The ones that compare HYDRUS-1D results with column studies found that whilst water flow was accurately modelled, the final P sorbed was overestimated, probably due to preferential flow caused in the between the column walls and the soil and incorrect adsorption isotherm (Nahra 2006; Naseri et al. 2011; Elmi et al. 2012;). The previously discussed incapacity of the sorption experiment and the sorption isotherm to represent long-term sorption processes in the long-term could be one of the reasons for this discrepancy. In fact, as discussed in section 6.2 sorption processes are the most relevant in LTS and model sensitivity analysis (Chapter 4) revealed that the sorption parameter is the most influential model parameter. However, even if the sorption isotherms have been extensively criticized to calculate binding capacity for soils or filter materials, especially in the long-term, it is how HYDRUS-1D models the solute reactions. Thus, until HYDRUS-1D code offers an alternative model for sorption solute representation or an improved methodology for sorption experiments is proposed, it would be advisable in order to use HYDRUS-1D to compare longevity estimations from different sites to set up the same sorption experiment methodology to determine the sorption parameters. To overcome this limitation, Nahra (2006) coupled the non-ideal competitive adsorption (NICA) model, introduced by Koopal et al. (1994) with the HYDRUS-1D code by replacing the sorption isotherms with the NICA model equations. The study obtained better results than the predictions with HYDRUS-1D using Freundlich isotherms for agricultural soils in southern Quebec (Canada. The incorporation of the NICA model to the HYDRUS-1D code would broaden the offer of solute reaction parameters of the modelling tool by incorporating a chemical aqueous model coupled by a hydrological-transport model that considers pH and ionic strength that theoretically could get more accurate results. However, the model has not been tested against other soils and regions and was only tested in re-packed column experiments, and the code has not been incorporated into HYDRUS-1D commercial version.

If the model wants to be used to model alkaline's filters materials longevity, such as Filtra P, Filtralite® P and Polonite®, sandy soils or aquifers, it would require a more accurate description of precipitation processes, in these cases, it is advisable to use the HP1 model which is a model that results from HYDRUS-1D been coupled with the biogeochemical program PHREEQC. However, as it is discussed by Herrmann (2014), it neglects several potential variables and processes that might occur in filter materials for wastewater treatment such as adsorption, removal of particle–bounded P from wastewater or effects of bacterial growth. For a complete representation of precipitation and sorption processes, it would be needed to add a first-order decay term to the ADE equation. However, this multi-component approach where different forms of P and pH are required is uncommon in P studies due to the difficulty to differentiate adsorption and precipitation in data, and the additional complexity in model parameterization and computational requirements (McCray, Lowe, Geza, *et al.*, 2009).

Nevertheless, not only could the sorption representation be responsible for the discrepancies found in the modelling results. They could be also associated with the fact that HYDRUS-1D is not representing other P removal mechanisms such as microbial uptake or filtration of particulate P, and also does not take into account the soil organic matter content in the soil, which improves P retention in soils by providing additional retention sites (Paranychianakis, Angelakis, Leverenz, *et al.*, 2006). The model could be improved if HYDRUS-1D could offer the biokinetic model for describing biochemical transformation and degradation processes that are available in the HYDRUS wetland module (Langergraber & Šimůnek, 2005). Additionally, HYDRUS-1D does not represent soil P transformation in the different P soil pools such as mineralization/immobilization, the movement of particulate material, or desorption process, which are relevant to study the P flush-out processes in saturated systems caused by rainfall or flooding events. HYDRUS-1D describes dispersion and sorption processes of P transport in soils through water movement, while other dynamics models represent P in the soil in the field scale where P flows between pools are quantified. These dynamics models are mainly used to calculate the P available for the plant for agronomics purposes, but they could be also used in the context of this research to calculate how much P it is retained in the soil. However, these models are based on preliminary results using empirical equations for specifics countries and soil types for fertilization applications (McGechan & Lewis, 2002) preventing them from being generally implemented and applied in this context.

P uptake by vegetation might be also a limitation to a more accurate model result. Plant nutrient uptake in HYDRUS is simulated by evapotranspiration and capabilities of roots to extract water from different water content conditions in soils. The model considers the P uptake by plants to be removed from the system but does not consider additions for plant death and decomposition with the consequent possible leaching and resolubilization of P into the system. Therefore related to the P dynamics representation of plant uptake, growth and decay, HYDRUS-1D is a very limited tool that would need further improvements. Another reason for the inaccuracy of the model results might be also due to the assumptions of irrigation and soil uniformity assumed by the model. The model fails to simulate as a simplification of the reality, the soil heterogeneities, as a one-dimensional model the lateral transport and, possible preferential flows or macropores that are happening at the field scale and could affect P transport were not considered due to the lack of parameters need to accurately represent it. However, HYDRUS-1D offers the possibility to simulate a number of non-equilibrium flow and transport processes such as macropores it if the corresponding parameters are acquired.

It would be desirable to validate the model or test it in alternative long-term treatment systems by either the same method as in the study, through P concentration in soils, or if possible through direct comparison of HYDRUS-1D outputs such as solute flux concentrations. In this study, this comparison was not possible due to the limited permit to operate in the field described in section 6.1.The model will achieve better results if: is used to simulate LTS where vegetation is cut and removed from the site, if reactions parameters for the solute transport are obtained from long-term laboratory experiment, and if the P concentrations used to obtain the reactions parameters in the laboratory are similar to the ones that will be used on site.

Regardless of all these model limitations, the model proposed is a practical tool that is sufficient to provide site operators with indications of P accumulation and leaching behaviour over long periods of time in full-scale LTS by integrating the water and solute transport reactions of the system. Therefore, the model can be still valid and easily used with two main purposes, firstly, to evaluate the current situation and effects of LTS or secondly, during the planning process of a construction of a new LTS. To fulfil those purposes, the model can be easily adjusted using meteorological data from any location and the corresponding loading rate as an input parameter for variable boundary conditions, and by changing the soil hydraulic parameters to the ones from the new location. If the model needs to be used to evaluate the current situation of a recently installed LTS, it is recommended that the meteorological data used is the one for the study period instead of an average year as was done in this study.

The results of the different management scenarios showed that despite of no differences in low maintenance vegetation with respect to P removal in LTS where low maintenance is a management priority, the model can be used to forecast P removal dynamics and trends in systems where vegetation is used with different purposes such as biomass production. Additionally, it can be used to test system behaviour for a specific treatment capacity in terms of volume of sewage disposal and effluent quality (loading rate and P concentration of the effluent). Depending on the water storage capacity of the sewage treatment work, it can be managed under different loading modes to enhance P removal, as demonstrated with the modelling in Knowle LTS, where longer resting periods (6 months) can enhance the longevity of the system over several years. Soil type, again as shown in the modelling results, is one of the most influential scenarios affecting longevity, through influencing flow and reactions parameters of the system. Although soil type cannot be considered a management practice, differences in soil absorption parameters and hydraulic conductivity can be found in different locations of the same site and therefore, the modelling could be used to test the best location for the LTS.

6.5 Land treatment system and sustainability

This research has contributed to improving our understanding of the long-term sustainability of the LTS. Although some of the processes are sustainable in time such as microbial and plant uptake, the main sorption processes reduce over time, and consequently, LST can successfully contribute to P removal for a number of years depending on site conditions and management practices. Modelling simulations showed that in a clay loam soil irrigated with a secondary effluent from a small STW, with native vegetation and minimum management the system longevity can range from 4.6 to 24 years. The minimum longevity is obtained with high loading rates and with soils types with less P and water retention capacity (sandy soil). The maximum longevity is reached with low loading rates and introducing long resting periods and low loading rates. Modelling simulations also confirmed that if the STW associated with the LTS increases its P-removal capacity and therefore the P concentration in the irrigation is lower, the longevity can be also enhanced. The vegetation in LTS should be easy to establish under the site weather conditions and with minimum management requirements, modelling simulations demonstrated that longevity and P removal was not affected in the long-term by variations on this type of vegetation, but the incorporation of native grass would benefit the LTS to provide alternative ecosystem services previously mentioned such as biodiversity and wildlife habitat (Charlesworth, Bennett & Waite, 2016). It would be beneficial to further study the identification and evaluation of P uptake in LTS of different combination of native grass. This knowledge would be also valuable in other areas such as the design and operation of sustainable drainage systems (SuDS).

However, as it was discussed in Chapter 3 although the system is no longer contributing to significant P removal, it does not necessary means it harms the nearby water bodies. Indeed, it is important to remark that longevity of LTS usually is related to the time when the material sorption capacity is exhausted. However, if the purpose is to assess the sustainably of the system it is more appropriate to consider the time during the effluent it is under a target effluent concentration (Heistad, Paruch, Vråle, *et al.*, 2006). This target concentration is usually related to the national legislation of nutrient discharge. Thus, to test a specific system's sustainability the results of the scenarios need to be tested against a standard, for example, a target leaching concentration. Therefore, should be preferable to favour, in this type of sustainable treatments, more flexible and smart legislation regarding environmental permitting based on risk assessment and monitoring effects rather than percentages of removal or target concentrations, which will also contribute to alleviating the drawbacks of current legislation of assessment performance discussed in section 6.3.

This research has provided a tool to gain confidence in this prediction and to demonstrate that although they have a limited lifespan of P removal, they can still contribute for a number of years depending on the site design and management. Therefore, they can be considered as a tertiary treatment option upgrade to meet tighter P removal requirements in small and rural STW by providing the appropriate tertiary treatment in a flow sheet of a low carbon, low cost and low maintenance STW. Additionally, they can also provide a security barrier on peak flow events or treatment failures. LTS treatment capacity and longevity, as it has been demonstrated, could be enhanced the better the primary and secondary P removal treatments perform and the lower the designed loading rates.

In the light of the study results about the P treatment capacity and its sustainability, LTS systems can be also implemented in the context of the sustainable urban water management (SUWM) which aims to approach the urban water cycle to produce ecologically sustainable water services (Sapkota, Arora, Malano, *et al.*, 2014). They can contribute as a final polishing step in urban hybrid systems that aim to provide fit-for-purpose water quality to each demand (Marlow, Moglia, Cook, *et al.*, 2013) and that not necessary can cause a risk after reaching their maximum P removal capacity. Although LTS are recommended to be considered as a part of the flow sheet of a STW, this system could be also used to treat the P contained in the urban run-off which main sources are atmospheric deposition, residential fertilizers, pet excrements or soil weathering (Hobbie, Finlay, Benjamin, *et al.*, 2017) and where P concentration is lower than secondary wastewater (TP<2 mg/l) (Miguntanna, Goonetilleke, Egodowatta, *et al.*, 2010). These urban LTS treatments could be implemented to help to develop green urban areas such as parks, green roofs or vegetated roadsides that would benefit for few years of pollutants treatment (including P) while contributing to alleviating the effects urban water demands by using storm and reclaimed water for irrigation of urban landscapes (Toor, Occhipinti, Yang, *et al.*, 2017). This thesis has contributed to gain knowledge about P removal capacity and longevity of LTS, and the more we know about LTS, the more they could be implemented to assist in the current challenges of the sustainable water industry.

7 CONCLUSIONS

This research aimed to develop improved estimations of P removal and longevity in LTS in the context of sustainability. By combining the review of existing knowledge, the assessment of a unique long-term field case study and the development of a water and solute transport model, this research has contributed to advance the empirical knowledge of P removal and dynamics in LTS and improve the methodology of P longevity assessment in LTS as follows:

First, this research demonstrates that, although the P removal processes are finite, they can contribute as a sustainable option for tertiary treatment in small STW, supporting STW with further treatment for a number of years. However, the process design and management practices, such as low hydraulic load and long resting periods, should be adjusted to maximize their treatment potential.

Second, when assessing the system treatment removal performance, the difficulty in identification and quantification of system inputs and outputs demonstrated the need for an alternative methodology that does not rely on inlet and outlet samples but able to detect if the system still can contribute to P removal. The methodology tested was based on the comparison of soil P concentration before and after the irrigation and confirmed that it can detect the soil' P saturation. However, its main drawback is that it is dependent on accurate reference samples.

Third, a compilation of previous research and new empirical data has confirmed soil sorption process as the main removal processes in LTS. Therefore, to accurately predict P removal and longevity it is needed an adequate model able to describe long-term sorption properties over time. However, this is a hard task that researchers have not solved. Therefore, to add accuracy to long-term sorption estimations studies, it is recommended to use variations from the standard sorption methodology such as longer testing times or P loads close to the real loading.

Finally, the use of hydrological and solute transport model can enhance P removal and longevity estimations by incorporating not only sorption soil properties but hydrological and solute transport characterization and management practices. The findings provide empirical evidence that highlight the need for further research mainly to accurately represent P soil sorption processes over-time, P plant uptake and management, and soil P transformation in the different P soil pools.

In conclusion, through a profound revision of the previous knowledge of practice, new empirical evidence and new methodological approach, this research demonstrate that LTS is a sustainable option as a tertiary treatment for small STW for a number of years and that modelling can be used to get a prediction of P removal performance and longevity in LTS through a combination of hydrological and solute transport modelling. However, the need of improved methodological assessment of sorption processes over time, and their links with the changes in the system are key aspects that need further improvement to get accurate P removal and longevity estimations of P in LTS and to identify management practices that will enhance the longevity of the systems. Further development of the current model limitations will support LTS contribution in the sustainable management of wastewater treatments and the enhancement of the ecosystem services that they provide.

REFERENCES

Abbas, M. (2017) *Survey of Onsite Wastewater Treatment Systems in Kristiansand Municipality Norway : Pollutants Removal Performance and Solutions : Performance Analysis Based on Web- GIS Model.* MSc Thesis. Norwegian University of Life Science.

Ádám, K. & Krogstad, T. (2006) Sorption of phosphorous to Filtralite-P--the effect of different scales. *Water Research*. [Online] 40 (6), 1143–1154. Available from: doi:10.1016/j.watres.2006.01.009.

Ádám, K., Krogstad, T., Suliman, F.R.D. & Jenssen, P.D. (2005) Phosphorous sorption by Filtralite P—Small scale box experiment. *Journal of Environmental Science and Health, Part A*. [Online] 40 (6–7), 1239–1250. Available from: doi:10.1081/ESE-200055673.

Albion Water (2017) *Albion Water: Knowle 6 years on*. [Online]. 2017. Available from: https://www.albionwater.co.uk/who-we-are/environment/knowle-6-years [Accessed: 22 September 2017].

Allen, R.G., Pereira, L.S., Raes, D. & Smith, M. (1998) *Crop evapotranspiration - Guidelines for computing crop water requirements - FAO Irrigation and drainage paper 56*.

Anglian Water Ltd. (2008) *Fact file 5 'Using water at home'*. [Online]. 2008. Available from: https://www.anglianwater.co.uk/_assets/media/Fact_File_5_-_Using_water_at_home.pdf [Accessed: 3 December 2015].

Ann, Y., Reddy, K.R. & Delfino, J.J. (1999) Influence of chemical amendments on phosphorus immobilization in soils from a constructed wetland. *Ecological Engineering*. [Online] 14 (1–2), 157–167. Available from: doi:10.1016/S0925-8574(99)00026-9.

Ashley, K., Cordell, D. & Mavinic, D. (2011) A brief history of phosphorus: From the philosopher's stone to nutrient recovery and reuse. *Chemosphere*. [Online] 84 (6), 737–746. Available from: doi:10.1016/j.chemosphere.2011.03.001.

Batista, M. del M., Hess, T., Sakrabani, R. & Tyrrel, S.F. (2017) Long-term phosphorus removal in Land Treatment Systems: evaluation, experiences and opportunities. *Critical Reviews in Environmental Science and Technology*. 47 (5), 314–334.

Beach, D.N.H. & McCray, J.E. (2003) Numerical modeling of unsaturated flow in wastewater soil absorption systems. *Groundwater Monitoring & Remediation*. [Online] 23 (2), 64–72. Available from: doi:10.1111/j.1745-6592.2003.tb00672.x.

Ben-Gal, A. & Dudley, L.M. (2003) Phosphorus availability under continuous point source irrigation. *Soil Science Society of America Journal*. [Online] 67 (5), 1449–1456. Available from: doi:10.2136/sssaj2003.1449.

Bisone, S., Gautier, M., Masson, M. & Forquet, N. (2016) Influence of loading rate and modes on infiltration of treated wastewater in soil-based constructed wetland. *Environmental Technology*. [Online] 3330 (June), 1–12. Available from: doi:10.1080/09593330.2016.1185165.

Bourazanis, G., Psychogiou, M. & Nikolaou, N. (2017) Chloride Transport Parameters Prediction for a Clay-Loam Soil Column. *Bulletin of Environmental Contamination and Toxicology*. [Online] 98 (3), 378–384. Available from: doi:10.1007/s00128-016-1867-7.

Brady, N.C. & Weil, R.R. (2008) *The nature and properties of soils.* 14th edition. New Jersey, Pearson Prentice Hall.

Brookes, P.C., Powlscin, D.S. & Jenkinsdn, D.S. (1984) Rothamsted IN THE SOIL MICROBIAL BIOMASS NaHCO ,. In this work we investigated the re-. *Soil Biology and Biochemistry*. 16 (2), 169–175.

BSI Standards Limited. (1998) *BS 7755-3.13:1998, ISO 11047:1998 Soil quality. Chemical methods. Determination of cadmium, chromium, cobalt, copper, lead, manganese, nickel and zinc in aqua regia extracts of soil. Flame and electrothermal atomic absorption spectrometric methods*.

BSI Standards Limited. (2006) *BS ISO 11464:2006 Soil quality. Pretreatment of samples for physio-chemical analysis*.

Burt, S.M. (2003) *'Fit Objects for an Asylum' The Hampshire County Lunatic Asylum and its Patients, 1852-1899.* P.h.D Thesis. [Online]. University of Southampton. Available from: http://eprints.soton.ac.uk/158357/ [Accessed: 5 November 2015].

Carey, M., Erskine, A., Heathcote, J. & McMahon, A. (2001) *Guide to Good Practice for the Development of Conceptual Models and the Selection and Application of Mathematical Models of Contaminant Transport Processes in the Subsurface*.

Carpenter, S.R. & Bennett, E.M. (2011) Reconsideration of the planetary boundary for phosphorus. *Environ. Res. Lett*. [Online] 614009–14012. Available from: doi:10.1088/1748-9326/6/1/014009.

Carpenter, S.R. & Caraco, N.F. (1998) Nonpoint pollution of surface waters with phosphorus and nitrogen. *Ecological Applications*. [Online] 8 (3), 559–568. Available from: doi:10.1890/1051-0761(1998)008[0559:NPOSWW]2.0.CO;2.

Centre for Ecology & Hydrology (2007) *Model estimates of topsoil properties [Countryside Survey] data owned by NERC — Centre for Ecology &*

Hydrology. [Online]. Available from: http://mapapps2.bgs.ac.uk/ukso/home.html?layer=CEHTSBulkDensity [Accessed: 9 September 2016].

CH2M Hill (2003) *PSTA Research and Demonstration Project Phase 1, 2 and 3 Summary Report*. (March 2003).

Chang, J., Wu, S., Zhang, S., Zhang, S., et al. (2014) Comparative evaluation of total phosphorus removal performances for treatment of domestic and secondary wastewater using integrated vertical-flow constructed wetlands: two years' experience. *Desalination and Water Treatment*. [Online] 56 (5), 1379–1388. Available from: doi:10.1080/19443994.2014.950343.

Charlesworth, S.M., Bennett, J. & Waite, A. (2016) An evaluation of the use of individual grass species in retaining polluted soil and dust particulates in vegetated sustainable drainage devices. *Environmental Geochemistry and Health*. [Online] 38 (4), 973–985. Available from: doi:10.1007/s10653-016-9791-7.

Cheviron, B. & Coquet, Y. (2009) Sensitivity Analysis of Transient-MIM HYDRUS-1D: Case Study Related to Pesticide Fate in Soils. *Vadose Zone Journal*. [Online] 8 (4), 1064–1079. Available from: doi:10.2136/vzj2009.0023.

Claveau-Mallet, D., Courcelles, B. & Comeau, Y. (2014) Phosphorus removal by steel slag filters: modeling dissolution and precipitation kinetics to predict longevity. *Environmental Science & Technology*. [Online] 48 (13), 7486–7493. Available from: doi:10.1021/es500689t.

Comber, S., Crossman, J., Daldorph, P., Johnes, P., et al. (2012) Phosphorus contributions from wastewater discharged to watercourses and their long term impact relative to other sources. *UK Water Industry Research Limited*.

Crites, R.W., Middlebrooks, J.E. & Sherwood, C.R. (2006) *Natural wastewater treatment systems*. Boca Raton, CRC Press.

Crites, R.W. & Pound, C.E. (1976) Land treatment of municipal waste water. *Environmental Science & Technology*. [Online] 10 (6), 548–551. Available from: doi:10.1021/es60117a008 [Accessed: 20 January 2015].

Crites, R.W., Reed, S.C. & Bastian, R.K. (2000) *Land treatment systems for municipal and industrial wastes*. New York, McGraw-Hill.

Cucarella, V. & Renman, G. (2009) Phosphorus sorption capacity of filter materials used for on-site wastewater treatment determined in batch experiments - a comparative study. *Journal of Environmental Quality*. [Online] 38 (2), 381–392. Available from: doi:10.2134/jeq2008.0192 [Accessed: 21 November 2014].

DEFRA (2012) *Waste water treatment in the United Kingdom-2012 Implementation of the European Union Urban Waste Water Treatment*

Directive 91/271/EEC. [Online]. Available from: www.defra.gov.uk/environment/quality/water/sewage/sewage-treatment [Accessed: 1 February 2016].

DeJong, R. & Bootsma, A. (1996) Review of recent developments in soil water simulation models. *Canadian Journal of Soil Science*. 76 (95), 263–273.

Dong, C.S., Ju, S.C., Hong, J.L. & Jong, S.H. (2005) Phosphorus retention capacity of filter media for estimating the longevity of constructed wetland. *Water Research*. [Online] 39 (11), 2445–2457. Available from: doi:10.1016/j.watres.2005.04.032.

Drizo, A., Comeau, Y., Forget, C. & Chapuis, R.P. (2002) Phosphorus saturation potential: A parameter for estimating the longevity of constructed wetland systems. *Environmental Science & Technology*. [Online] 36 (21), 4642–4648. Available from: doi:10.1021/es011502v.

Drizo, A., Frost, C.A., Grace, J. & Smith, K.A. (1999) Physico-chemical screening of phosphate-removing substrates for use in constructed wetland systems. *Water Research*. [Online] 33 (17), 3595–3602. Available from: doi:10.1016/S0043-1354(99)00082-2.

Dzakpasu, M., Scholz, M., McCarthy, V. & Jordan, S. (2015a) Assessment of long-term phosphorus retention in an integrated constructed wetland treating domestic wastewater. *Environmental Science and Pollution Research*. [Online] 22 (1), 305–313. Available from: doi:10.1007/s11356-014-3350-5.

Dzakpasu, M., Scholz, M., McCarthy, V. & Jordan, S. (2015b) Phosphorus retention and mass balance in an integrated constructed wetland treating domestic wastewater. *Water and Environment Journal*. [Online] 29 (2), 298–306. Available from: doi:10.1111/wej.12107.

Elmi, A., Nohra, J.S.A., Madramootoo, C.A. & Hendershot, W. (2012) Estimating phosphorus leachability in reconstructed soil columns using HYDRUS-1D model. *Environmental Earth Sciences*. [Online] 65 (6), 1751–1758. Available from: doi:10.1007/s12665-011-1154-1.

Environment Agency (2012) *Freshwater eutrophication. A nationally significant water management issue.* [Online]. Available from: http://www.rivermease.co.uk/wp-content/uploads/2015/07/Freshwater_Eutrophication_Briefing_Note_December_20121.pdf [Accessed: 8 November 2016].

EU Parlament Regulation (2004) EU Parlament Regulation (EC). No 648/2004 on detergents. *Official Journal of the European Communities*. [Online]. pp.1–15. Available from: doi:2004R0726 - v.7 of 05.06.2013.

European Commission (1991) Council Directive 91/271/ECC of 21 May 1991 concerning urban waste water treatment. *[1991] OJ L135/40*. [Online].

pp.40–52. Available from: http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:31991L0271 [Accessed: 18 August 2015].

European Commission (2000) Directive 2000/60/EC of the European Parlament. *Directive 2000/60/EC of the European Parlament and of the Council of 23 October 2000 establising a framework for Community action in the field of water policy*. [Online]. L327 (October 2000) pp.1–82. Available from: doi:10.1039/ap9842100196.

European Commission (2012) Regulation (EU) 259/2012 of 14 March 2012 amending Regulation (EC) No 648/2004 as regards the use of phosphates and other phosphorus compounds in consumer laundry detergents and consumer automatic dishwasher detergents. *[2012] OJ L94/17*. [Online]. Available from: http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2012:094:0016:0021:en:PDF [Accessed: 8 April 2015].

Evangelou, V.P. (1998) *Environmental soil and water chemistry. Principles and applications.* Nre York, John Wiley & Sons.

Eveborn, D., Gustafsson, J.P., Elmefors, E., Yu, L., et al. (2014) Phosphorus in soil treatment systems: accumulation and mobility. *Water research*. [Online] 6442–52. Available from: doi:10.1016/j.watres.2014.06.034 [Accessed: 26 November 2014].

Eveborn, D., Kong, D. & Gustafsson, J.P. (2012) Wastewater treatment by soil infiltration: Long-term phosphorus removal. *Journal of Contaminant Hydrology*. [Online] 140–14124–33. Available from: doi:10.1016/j.jconhyd.2012.08.003 [Accessed: 3 November 2014].

Falkiner, R.A. & Polglase, P.J. (1999) Fate of applied phosphorus in an effluent-irrigated Pinus radiata plantation. *Australian Journal of Soil Research*. 37 (6), 1095–1106.

FAO (1990) *Food And Agriculture Organization of the United Nations. Expert Consultation on Revision of FAO Methodologies for CropWater Requirements, ANNEX V. FAO Penman–Monteith Formula*.

Feddes, R.A., Kowalik, P.J. & Zaradny, H.X. (1978) *Simulation of Field Water Use and Crop Yield*. Wageningen, The Netherlands, Centre for Agricultural Publishing and Documentation.

Fetter, C.W. (1999) *Contaminant hydrogeology*. Upper Sanddle River, New Jersey, Prentice Hall.

Force, T., Mallarino, M. a P., Beegle, D.B. & Joern, B.C. (2006) Soil Sampling Methods for Phosphorus – Spatial Concerns A SERA-17 Position Paper. *Methods*. 11–16.

Foundation for Water Research (2006) *Eutrophication of freshwaters*. [Online].

Available from: www.fwr.org/eutrophi.pdf [Accessed: 30 September 2016].

García, J., Rousseau, D.P.L., Morató, J., Lesage, E., et al. (2010) Contaminant removal processes in subsurface-flow constructed wetlands: a review. *Critical Reviews in Environmental Science and Technology*. [Online] 40 (7), 561–661. Available from: doi:10.1080/10643380802471076.

Van Genuchten, M.T. (1980) A closed-form equation for predicting the hydraulic conductivity od unsaturated soils. *Soil Science Society of America Journal*. 44 (5).

Gilmour, D., Blackwood, D., Comber, S. & Thornell, A. (2008) Identifying human waste contribution of phosphorus loads to domestic wastewater. In: *Preceedings at the 11th International Conference on Urban Drainage, Held in Edinburgh, Scoltand, UK,*. 2008 pp. 1–10.

Graetz, D.. & Nair, V.D. (2000) Phosphorus sorption isotherm determination. In: G.M. Pierzynski (ed.). *Methods of Phosphorus Analysis for Soils, Sediments, Residuals and Waters.* Bulletion. Manhattan, Southern Cooperative Series. p. 110.

Graves, A.R., Hess, T., Matthews, R.B., Stephens, W., et al. (2002) Crop Simulation Models as Tools in Computer Laboratory and Classroom-Based Education. *Journal of Natural Resources and Life Science Education*. 3148–54.

Gray, N.F. (1989) *Biology of wastewater treatment*. New York, Oxford University Press.

Groenendijk, P. & Kroes, J.G. (1999) *Modelling the nitrogen and phosphorus leaching to groundwater and surface water; ANIMO 3.5. Report 144*.

Hanson, B.R., Šimůnek, J. & Hopmans, J.W. (2006) Evaluation of urea-ammonium-nitrate fertigation with drip irrigation using numerical modeling. *Agricultural Water Management*. [Online] 86 (1–2), 102–113. Available from: doi:10.1016/j.agwat.2006.06.013.

Heatwole, K.K. & McCray, J.E. (2007) Modeling potential vadose-zone transport of nitrogen from onsite wastewater systems at the development scale. *Journal of Contaminant Hydrology*. [Online] 91 (1–2), 184–201. Available from: doi:10.1016/j.jconhyd.2006.08.012.

Heistad, A., Paruch, A.M., Vråle, L., Ádám, K., et al. (2006) A high-performance compact filter system treating domestic wastewater. *Ecological Engineering*. [Online] 28 (4), 374–379. Available from: doi:10.1016/j.ecoleng.2006.06.011 [Accessed: 28 January 2015].

Henze, M. & Comeau, Y. (2008) *Wastewater characterization*. Mogens Henze, Mark C.M. van Loosdrecht, G.A. Ekama, & Damir Brdjanovic (eds.). London, IWA Publishing.

Herrmann, I. (2014) *Filter Beds for On-Site Wastewater Treatment*. Ph.D. Thesis. Luleå University of Technology.

Herrmann, I., Jourak, A., Gustafsson, J.P., Hedström, A., et al. (2013) Modeling phosphate transport and removal in a compact bed filled with a mineral-based sorbent for domestic wastewater treatment. *Journal of Contaminant Hydrology*. [Online] 15470–77. Available from: doi:10.1016/j.jconhyd.2013.08.007.

Herrmann, I., Jourak, A., Lundström, T.S., Hedström, A., et al. (2012) Phosphorus binding to Filtra P in batch tests. *Environmental technology*. [Online] 33 (7–9), 1013–1019. Available from: doi:10.1080/09593330.2011.604878.

HMSO (1973) Water Act, Chapter 37. London: HMSO, 120. *1973*.

Ho, G. & Notodarmojo, S. (1995) Phosphorus movement through soils and groundwater: Application of a time-dependent sorption model. *Water Science and Technology*. [Online] 31 (9), 83–90. Available from: doi:10.1016/0273-1223(95)00409-G [Accessed: 10 October 2014].

Hobbie, S.E., Finlay, J.C., Benjamin, D., Nidzgorski, D.A., et al. (2017) Contrasting nitrogen and phosphorus budgets in urban watersheds and implications for managing urban water pollution. *Proceedings of the National Academy of Sciences*. [Online] 114 (20), E4116–E4116. Available from: doi:10.1073/pnas.1706049114.

Hooda, P.S., Rendell, A.R., Edwards, A.C., Withers, P.J.A., et al. (2000) Relating soil phosphorus indices to potential phosphorus release to water. *Journal of Environmental Quality*. [Online] 29 (4), 1116–1171. Available from: doi:10.2134/jeq2000.00472425002900040018x.

Hu, C., Zhang, T.C., Huang, Y.H., Dahab, M.F., et al. (2005) Effects of long-term wastewater application on chemical properties and phosphorus adsorption capacity in soils of a wastewater land treatment system. *Environmental Science & Technology*. [Online] 39 (18), 7240–7245. Available from: doi:10.1021/es050526p.

Hu, C., Zhang, T.C., Kendrick, D., Huang, Y.H., et al. (2006) Muskegon wastewater land treatment system: fate and transport of phosphorus in soils and life expectancy of the system. *Engineering in Life Sciences*. [Online] 6 (1), 17–25. Available from: doi:10.1002/elsc.200620118 [Accessed: 21 January 2015].

Inc. Metcalf & Eddy, Tchobanoglous, G., Burton, F.L. & Stensel, H.D. (2003) *Wastewater engineering. treatment and reuse.* 4th edition. Boston, McGraw-Hill.

J. Šimůnek, M. Šejna, H. Saito, M. Sakai, and M.T. van G. (2013) *The HYDRUS-1D Software Package for Simulating the One-Dimensional Movement of*

Water, Heat, and Multiple Solutes in Variably-Saturated Media. Version 4.17. (June).

Jarvis, N. & Larsbo, M. (2012) MACRO (v5.2) Model use, calibration, and validation. *American Society of Agricultural and Biological Engineers*. 55 (4), 1413–1423.

Jensen, M.E., Burman, R.D. & Allen, R.G. (1990) *Evapotranspiration and Irrigation Water Requirements*.

Jenssen, P.D., Krogstad, T. & Halvorsen, K. (2014) Community wastewater infiltration at 69 o northern latitude – 25 years of experience. In: *Soil Science Society of America Onsite Wastewater Conference , Albuquerque NM, 7-8 April 2014*. 2014 p.

Jewell, W.J. & Seabrook, B.L. (1979) *MCD-40: A history of land application as a treatment alternative*.

Jones, C.A., Cole, C.V., Sharpley, A.N. & Williams, J.R. (1981) A simplified soil and pland phosphorus mdodel:1. Documentation. *Soil Science Society of America journal*. 48 (4), 800–805.

Jourak, A., Frishfelds, V., Staffan, T., Herrmann, I., et al. (2011) Modeling of Phosphate Removal by Filtra P in Fixed-bed Columns. *Proceedings of the 2nd International Conference on Environmental Science and Technology (ICEST 2011)*. 241–248.

Kadlec, R.H. & Knight, R.L. (1996) *Treatment wetlands*. Boca Raton, FL, CRC Lewis.

Kadlec, R.H., Reddy, K.R. & Wetzel, R.G. (2005) Biogeochemistry of Phosphorus in Wetlands. In: *Phosphorus: Agriculture and the Environment*. Monograpah. Madison, WI, American Society of Agricultural and Biological Engineers. pp. 263–315.

Kadlec, R.H. & Wallace, S.D. (2009) *Treatment Wetlands, Second Edition*. [Online]. Boca Raton, FL, CRC Lewis. Available from: doi:10.1201/9781420012514.

Kardos, L.T. & Hook, J.E. (1976) Phosphorus balance in sewage effluent treated soils. *Journal of Environmental Quality*. 187–90.

Keller, V.D.J., Tanguy, M., Prosdocimi, I., Terry, J.A., et al. (2015) CEH-GEAR: 1 Km resolution daily and monthly areal rainfall estimates for the UK for hydrological and other applications. *Earth System Science Data*. [Online] 7 (1), 143–155. Available from: doi:10.5194/essd-7-143-2015.

Knaggs, D. (2014) *Anecdotal information noted from conversations with David Knaggs of AlbionWater during a visit to Knowle Village wastewater treatment works. 5th November 2014*.

Koopal, L.K., van Riemsdijk, W.H., de Wit, J.C.M. & Benedetti, M.F. (1994) Analytical Isotherm Equations for Multicomponent Adsorption to Heterogeneous Surfaces. *Journal of Colloid and Interface Science*. [Online] 166 (1), 51–60. Available from: doi:10.1006/jcis.1994.1270 [Accessed: 31 August 2017].

Kovar, J.L. & Pierzynski, G.M. (2009) Methods of Phosphorus Analysis for Soils , Sediments , Residuals , and Waters. Second Edition. *Southern Extension/Research Activity - Information Exchange Group 17*. [Online]. Available from: doi:citeulike-article-id:7529961.

Kruse, J., Abraham, M., Amelung, W., Baum, C., et al. (2015) Innovative methods in soil phosphorus research: A review. *Journal of Plant Nutrition and Soil Science*. [Online] 178 (1), 43–88. Available from: doi:10.1002/jpln.201400327.

Land and Water Division of FAO (2012) *ETo Calculator. Version 3.1 Land and Water Digital Media Series No 36*.

Landmark Information Group (1932) *Ordnance Survey County Series 1:2500, 1:2500, 1st Revision 1893-1915 and 3rd Revision 1924-1949 [TIFF geospatial data], County/Tile: Hampshire and Isle of Wight, Published: 1932-1940. Using: EDINA Historic Digimap Service, <http://digimap.edina.ac.uk/>*.

Langergraber, G. (2016) Applying Process-Based Models for Subsurface Flow Treatment Wetlands: Recent Developments and Challenges. *Water*. [Online] 9 (1), 5. Available from: doi:10.3390/w9010005.

Langergraber, G. & Šimůnek, J. (2005) Modeling Variably Saturated Water Flow and Multicomponent Reactive Transport in Constructed Wetlands. *Vadose Zone Journal*. [Online] 4 (4), 924–938. Available from: doi:10.2136/vzj2004.0166.

Langergraber, G. & Šimůnek, J. (2012) Reactive transport modeling of subsurface flow constructed wetlands using the HYDRUS Wetland Module. *Vadose Zone Journal*. [Online] 11 (2). Available from: doi:10.2136/vzj2011.0104 [Accessed: 17 December 2014].

Leonard, R.A., Knisel, W.G. & Still, D.A. (1986) GLEAMS: Groundwater Loading Effects of Agricultural Management Systems. *Transaction of the ASAE*.

Lewis, J. & Sjöstrom, J. (2010) Optimizing the experimental design of soil columns in saturated and unsaturated transport experiments. *Journal of Contaminant Hydrology*. [Online] 115 (1–4), 1–13. Available from: doi:10.1016/j.jconhyd.2010.04.001.

Li, Y., Šimůnek, J., Jing, L., Zhang, Z., et al. (2014) Evaluation of water movement and water losses in a direct-seeded-rice field experiment using Hydrus-1D. *Agricultural Water Management*. [Online] 14238–46. Available from:

doi:10.1016/j.agwat.2014.04.021.

Lindsay, W.L. (1979) *Chemical Equilibria in Soils*. [Online]. Chichester, Wiley-Interscience Publication. Available from: doi:10.1346/CCMN.1980.0280411.

Liolios, K.A., Moutsopoulos, K.N. & Tsihrintzis, V.A. (2015) Numerical simulation of phosphorus removal in horizontal subsurface flow constructed wetlands. *Desalination and Water Treatment*. [Online] 56 (5), 1282–1290. Available from: doi:10.1080/19443994.2014.983550 [Accessed: 17 December 2014].

MacBride, M.B. (1994) *Environmental Chemistry of Soils*. New York, Oxford University Press.

Marlow, D.R., Moglia, M., Cook, S. & Beale, D.J. (2013) Towards sustainable urban water management: A critical reassessment. *Water Research*. [Online] 47 (20), 7150–7161. Available from: doi:10.1016/j.watres.2013.07.046.

McCray, J.E., Lowe, K., Geza, M., Drewes, J., et al. (2009) *State of the Science : Review of Quantitative Tools to Determine Wastewater Soil Treatment Unit Performance (WERF Report DEC1R06)*.

McGechan, M.B. & Lewis, D.R. (2002) A Review of Field Scale Phosphorus Dynamics Models. *Biosystems Engineering*. [Online] 81 (1), 3–34. Available from: doi:10.1006/bioe.2001.0013.

Mettofice (2016) *UK climate - Historic station data*. [Online]. 2016. Available from: https://www.metoffice.gov.uk/public/weather/climate-historic/#?tab=climateHistoric [Accessed: 24 February 2016].

Meyer, D., Chazarenc, F., Claveau-mallet, D., Dittmer, U., et al. (2015) Modelling constructed wetlands : Scopes and aims – a comparative review. *Ecological Engineering*. [Online] 80205–213. Available from: doi:10.1016/j.ecoleng.2014.10.031.

Miguntanna, N.P., Goonetilleke, A., Egodowatta, P. & Kokot, S. (2010) Understanding nutrient build-up on urban road surfaces. *Journal of Environmental Sciences*. [Online] 22 (6), 806–812. Available from: doi:10.1016/S1001-0742(09)60181-9.

Morrissey, P.J., Johnston, P.M. & Gill, L.W. (2015) The impact of on-site wastewater from high density cluster developments on groundwater quality. *Journal of contaminant hydrology*. [Online] 18236–50. Available from: doi:10.1016/j.jconhyd.2015.07.008 [Accessed: 27 October 2015].

Moura, D.R., Silveira, M.L., O'Connor, G.A. & Wise, W.R. (2011) Long-term reclaimed water application effects on phosphorus leaching potential in rapid infiltration basins. *Journal of Environmental Monitoring*. [Online] 13 (9), 2457–2462. Available from: doi:10.1039/c0em00785d [Accessed: 15 January 2015].

Mualem, Y. (1976) New Model for Predicting The Hydraulic Conductivity of Unsaturated Porous Media. *Water Research*. 12 (3).

Nahra, J.A. (2006) *Modeling phosphorus transport in soil and water*. PhD Thesis. McGill University. Montreal.

Nair, P.S., Logan, T.J., Sharpley, A.N., Sommers, L.E., et al. (1984a) Interlaboratory Comparison of a Standardized Phosphorus Adsorption Procedure. *J. Environ. Qual.* 13591–595.

Nair, P.S., Logan, T.J., Sharpley, a. N., Sommers, L.E., et al. (1984b) Interlaboratory comparison of a standardized phosphorus adsorption procedure. *Journal of Environmental Quality*. [Online] 13 (4), 591. Available from: doi:10.2134/jeq1984.00472425001300040016x.

Naseri, A.A., Hoseini, Y., Moazed, H., Abbasi, F., et al. (2011a) Phosphorus transport through a saturated soil column: comparison between physical modeling and HYDRUS-3D outputs. *Journal of Applied Sciences*. 11 (5), 815–823.

Naseri, A.A., Hoseini, Y., Moazed, H., F. Abbasi, H.M.V.S., et al. (2011b) Phosphorus Transport Through a Saturated Soil Column: Comparison Between Physical Modeling and HYDRUS-3D Outputs. *Journal of Applied Sciences*. 11 (5), 815–823.

National Soil Resources Institute (2014) *Full Soils Site Report for location 455716E, 108933N, 2km x 2km, National Soil Resources Institute, Cranfield University.* 2014.

Nelson, N.O. & Parsons, J.E. (2007) Basic Approaches to Modeling Phosphorus Leaching. In: David E. Radcliffe & Miguel L. Cabrera (eds.). *Modeling Phosphorus in the Environment*. Boca Raton, FL, CRC Press. pp. 81–103.

Nissim, W.G., Jerbi, A., Lafleur, B., Fluet, R., et al. (2015) Willows for the treatment of municipal wastewater: Performance under different irrigation rates. *Ecological Engineering*. [Online] 81395–404. Available from: doi:10.1016/j.ecoleng.2015.04.067.

Nolan, B.T., Bayless, E.R., Green, C.T., Garg, S., et al. (2005) Evaluation of unsaturated-zone solute-transport models for studies of agricultural chemicals. *U.S. Geological Survey Open-File Report*. (2005–1196), 16.

O'Keeffe, J., Akunna, J., Olszewska, J., Bruce, A., et al. (2015) Practical measures for reducing phosphorus and faecal microbial loads from onsite wastewater treatments systems discharged to the environement. A review. *Scotland´s Center of Expertise for Waters (CREW)*.

Office of National Statistics (2013) *Census: Population and household estimates for the United Kingdom, March 2011*. [Online]. (March 2011). Available from: https://www.ons.gov.uk/peoplepopulationandcommunity/populationandmigr ation/populationestimates/bulletins/populationandhouseholdestimatesforthe unitedkingdom/2011-03-21 [Accessed: 1 January 2017].

Office of Research and Development U.S. Environmental Protection Agency (2002) Onsite wastewater treatment systems manual. EPA/625/R-00/008. *Environmental Protection*. [Online]. Available from: http://water.epa.gov/aboutow/owm/upload/2004_07_07_septics_septic_2002_osdm_all.pdf [Accessed: 27 May 2015].

Paranychianakis, N. V., Angelakis, A.N., Leverenz, H. & Tchobanoglous, G. (2006) Treatment of wastewater with Slow Rate Systems: A review of treatment processes and plant functions. *Critical Reviews in Environmental Science and Technology*. [Online] 36 (3), 187–259. Available from: doi:10.1080/10643380500542756.

Parkhurst, B.D.L. & Appelo, C. a J. (1999) User's Guide To PHREEQC (version 2) — a Computer Program for Speciation, and Inverse Geochemical Calculations. *Exchange Organizational Behavior Teaching Journal*. [Online] D (Version 2), 326. Available from: doi:Rep. 99-4259.

Parkhurst, D.L. & Appelo, C.A.J. (2011) *PHREEQC forWindows.A hydrogeochemical transport model. Version 2.18.00. (Available at) http://pfw.antipodes.nl/download.html*.

Parkhurst, D.L. & Kipp, K.L. (2002) Parallel processing for PHAST: a three-dimensional reactive-transport simulator. *Developments in Water Science*. [Online] 47 (C), 711–718. Available from: doi:10.1016/S0167-5648(02)80128-9 [Accessed: 16 March 2017].

Parkhurst, D.L., Stollenwerk, K.G. & Colman, J. a (2003) Reactive-Transport Simulation of Phosphorus in the Sewage Plume at the Massachusetts Military Reservation, Cape Cod, Massachusetts. *Water-Resources Investigations Report 03-4017*.

Parliamentary Office of Science and Technology (2014) *Phosphate Resources*. [Online]. 2014. Available from: http://researchbriefings.parliament.uk/ResearchBriefing/Summary/POST-PN-477#fullreport [Accessed: 11 December 2015].

Parton, W.J., Hartman, M., Ojima, D. & Schimel, D. (1998) *DAYCENT Its land surface submodel Description and testing.PDF*. 35–48.

Pretty, J.N., Mason, C.F., Nedwell, D.B., Hine, R.E., et al. (2003) Environmental costs of freshwater eutrophication in England and Wales. *Environmental Science & Technology*. [Online] 37201–208. Available from: doi:10.1021/es020793k.

Radcliffe, D.E. & Bradshaw, J.K. (2014) Model Test of Proposed Loading Rates for Onsite Wastewater Treatment Systems. *Soil Science Society of America*

Journal. [Online] 78 (1), 97. Available from: doi:10.2136/sssaj2013.07.0257.

Radcliffe, D.E., Reid, D.K., Blombäck, K., Bolster, C.H., et al. (2015) Applicability of models to predict phosphorus losses in drained fields: a review. *Journal of Environmental Quality*. [Online] 44 (2), 614–628. Available from: doi:10.2134/jeq2014.05.0220.

Ramos, T.B., Šimůnek, J., Gonçalves, M.C., Martins, J.C., et al. (2011) Field evaluation of a multicomponent solute transport model in soils irrigated with saline waters. *Journal of Hydrology*. [Online] 407 (1–4), 129–144. Available from: doi:10.1016/j.jhydrol.2011.07.016.

Rawls, W.J., Brakensiek, D.L. & Saxton, K.E. (1982) Estimation of soil water properties. *American Society of Agricultural Engineers*. 25 (5), 1316–1320 & 1328.

Reddy, K.R., Kadlec, R.H., Flaig, E. & Gale, P.M. (1999) Phosphorus Retention in Streams and Wetlands: A Review. *Critical Reviews in Environmental Science and Technology*. [Online] 29 (1), 83–146. Available from: doi:10.1080/10643389991259182.

Richard, L.A. (1931) Capillary conduction of fluid through porous mediums. *Physics*. 1318–333.

Richards, S., Paterson, E., Withers, P.J. a. & Stutter, M. (2015) The contribution of household chemicals to environmental discharges via effluents: Combining chemical and behavioural data. *Journal of Environmental Management*. [Online] 150427–434. Available from: doi:10.1016/j.jenvman.2014.12.023.

Richardson, C.J., Walbridge, M.R. & Burns, A. (1988) *Soil chemistry and phosphorus retention capacity of North Carolina coastal plain swamps receiving sewage effluent. UNC-WRRI-88-241*. [Online]. 1988. Available from: http://repository.lib.ncsu.edu/dr/bitstream/1840.4/1860/1/NC-WRRI-241.pdf [Accessed: 13 November 2015].

Roberts, W.M., Stutter, M.I. & Haygarth, P.M. (2012) Phosphorus Retention and Remobilization in Vegetated Buffer Strips: A Review. *Journal of Environment Quality*. [Online] 41 (2), 389. Available from: doi:10.2134/jeq2010.0543.

Robertson, W.D. (2008) Irreversible phosphorus sorption in septic system plumes? *Ground Water*. [Online] 46 (1), 51–60. Available from: doi:10.1111/j.1745-6584.2007.00389.x.

Robertson, W.D. (2012) Phosphorus retention in a 20-year-old septic system filter bed. *Journal of Environmental Quality*. [Online] 41 (5), 1437–1444. Available from: doi:10.2134/jeq2011.0427 [Accessed: 3 November 2014].

Sapkota, M., Arora, M., Malano, H., Moglia, M., et al. (2014) An overview of hybrid water supply systems in the context of urban water management: challenges and opportunities. *Water*. [Online] 7 (1), 153–174. Available from: doi:10.3390/w7010153.

Schaap, M.G., Leij, F.J. & Van Gencuhten, M.T. (2002) A computer program for estimating soil hydraulic parameters with hierarchical pedotransfer functions. *Journal of Hydrology*. 251163–176.

Schachtman, D.P., Reid, R.J. & Ayling, S.M. (1998) Update on Phosphorus Uptake Phosphorus Uptake by Plants: From Soil to Cell. *Plant Physiology*. [Online] 116447–453. Available from: doi:10.1104/pp.116.2.447.

Shouse, P.J., Ayars, J.E. & ŠimŮnek, J. (2011) Simulating root water uptake from a shallow saline groundwater resource. *Agricultural Water Management*. [Online] 98 (5), 784–790. Available from: doi:10.1016/j.agwat.2010.08.016.

Šimůnek, J. & van Genuchten, M.T. (2008) Modeling Nonequilibrium Flow and Transport Processes Using HYDRUS. *Vadose Zone Journal*. [Online] 7782. Available from: doi:10.2136/vzj2007.0074.

Šimůnek, J., van Genuchten, M.T. & Šejna, M. (2008) Development and Applications of the HYDRUS and STANMOD Software Packages and Related Codes. *Vadose Zone Journal*. [Online] 7 (2), 587. Available from: doi:10.2136/vzj2007.0077.

Šimůnek, J. & Hopmans, J.W. (2009) Modeling compensated root water and nutrient uptake. *Ecological Modelling*. [Online] 220 (4), 505–521. Available from: doi:10.1016/j.ecolmodel.2008.11.004.

Šimůnek, J., Šejna, M., Saito, H., Sakai, M., et al. (2013) *The HYDRUS-1D software package for simulating the one-dimensional movement of water, heat, and multiple solutes in variably-saturated media. Version 4.0. HYDRUS Software Ser. 3. Dep. of Environmental Sciences, Univ. of Cali- fornia, Riverside*. (June).

Sinclair, A., Jamieson, R., Gordon, R.J., Madani, A., et al. (2014) Modeling phosphorus treatment capacities of on-site wastewater lateral flow sand filters. *Journal of Environmental Engineering*. [Online] 140 (2), 04013002–04013013. Available from: doi:10.1061/(ASCE)EE.1943-7870.0000796.

Sinclair, A., Jamieson, R., Madani, A., Gordon, R.J., et al. (2014) A watershed modeling framework for phosphorus loading from residential and agricultural sources. *Journal of Environmental Quality*. [Online] 43 (4), 1356–1369. Available from: doi:10.2134/jeq2013.09.0368 [Accessed: 26 October 2015].

Smith, V.H. (2003) Eutrophication of freshwater and coastal marine ecosystems: a global problem. *Environmental Science and Pollution Research*. [Online] 10 (2), 126–139. Available from: doi:10.1065/espr2002.12.142.

Smith, V.H., Joye, S.B. & Howarth, R.W. (2006) Eutrophication of freshwater and marine ecosystems. *Limnol. Oceanogr.* [Online] 51 (2), 351–355. Available from: doi:10.4319/lo.2006.51.1_part_2.0351.

Southampton Weather (2016) *Southampton Weather Station*. [Online]. 2016. Available from: http://www.southamptonweather.co.uk/wxabout.php [Accessed: 2 February 2016].

Sweaney, G. (2011) *The performance of sustainable wastewater treatment works solutions. Report Ref. NO. 11/WW/04/16*.

Swedish Enviromental Protection Agency (2008) Wastewater treatment in Sweden. *Sustainable Development*. [Online]. Available from: doi:isbn 978-91-620-8704 [Accessed: 17 August 2017].

Syers, J.K., Johnston, a. E. & Curtin, D. (2008) *Efficiency of soil and fertilizer phosphorus use*. [Online]. Rome, FAO Fertilizer and Plant Nutrition Bulletin 18. Food and Agriculture Organization of the United Nations. Available from: doi:10.1017/S0014479708007138.

Taebi, A. & Droste, R.L. (2008) Performance of an overland flow system for advanced treatment of wastewater plant effluent. *Journal of Environmental Management*. [Online] 88 (4), 688–696. Available from: doi:10.1016/j.jenvman.2007.03.038.

The 92nd United States Congress (1972) Federal Water Pollution Control Act of 1972. *33 U.S.C. 1251 et seq*. [Online]. Available from: http://www2.epa.gov/laws-regulations/summary-clean-water-act [Accessed: 18 August 2015].

Toor, G.S., Occhipinti, M.L., Yang, Y.Y., Majcherek, T., et al. (2017) Managing urban runoff in residential neighborhoods: Nitrogen and phosphorus in lawn irrigation driven runoff. *PLoS ONE*. [Online] 12 (6), 1–17. Available from: doi:10.1371/journal.pone.0179151.

Twarakavi, N.K.C., Simunek, J. & Seo, S. (2008) Evaluating Interactions between Groundwater and Vadose Zone Using the HYDRUS-Based Flow Package for MODFLOW. *Vadose Zone Journal*. [Online] 7 (2), 757–768. Available from: doi:10.2136/vzj2007.0082.

Tyrrell, S.R. (2016) *Microtopographic enhancement of land-based wastewater treatment.* PhD Thesis. Cranfield University.

Tzanakakis, V.E., Paranychianakis, N. V. & Angelakis, A.N. (2007) Soil as a wastewater treatment system: Historical development. *Water Science and Technology: Water Supply*. [Online] 7 (1), 67–75. Available from: doi:10.2166/ws.2007.008.

U.S. Department of Agriculture, N.R.C.S. (2005) *Natural Resources Conservation Service Soils*. [Online]. 2005. Saturated Hydraulic Conductivity in Relation to Soil Texture. Available from: https://www.nrcs.usda.gov/wps/portal/nrcs/detail/soils/survey/office/ssr10/tr/

?cid=nrcs144p2_074846 [Accessed: 7 July 2017].

UK Parlament (2010) *Detergents Regulations 2010 (SI 740/2010)*. [Online]. 2010. Available from: http://www.legislation.gov.uk/uksi/2010/740/pdfs/uksi_20100740_en.pdf [Accessed: 4 April 2015].

USEPA (2006) Process Design Manual - Land Treatment of Municipal Wastewater Effluents. EPA/625/R-06/016. *Development, U.S. Environmental Protection Age*. [Online]. Available from: http://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=2000ZYD5.txt [Accessed: 24 August 2015].

Vadas, P.A., Bolster, C.H. & Good, L.W. (2013) Critical evaluation of models used to study agricultural phosphorus and water quality. *Soil Use and Management*. [Online] 29 (SUPPL.1), 36–44. Available from: doi:10.1111/j.1475-2743.2012.00431.x.

Vogel, T., Gerkeb, H.H., Zhang, R. & Genuchtend, M.T. Van (2000) Modeling flow and transport in a two- dimensional dual-permeability system with spatially variable hydraulic properties. *Journal of Hydrology*. [Online] 23878–89. Available from: doi:10.1016/S0022-1694(00)00327-9.

Vohla, C., Kõiv, M., Bavor, H.J., Chazarenc, F., et al. (2011) Filter materials for phosphorus removal from wastewater in treatment wetlands—A review. *Ecological Engineering*. [Online] 37 (1), 70–89. Available from: doi:10.1016/j.ecoleng.2009.08.003 [Accessed: 27 November 2014].

Wainwright, J. & Mulligan, M. (2004) Modelling and Model Building. In: *Environmental Modelling- Finding simplicity in complexity*. West Sussex, John Wiley & Sons Ltd. p.

Weiss, P., Eveborn, D., Kärrman, E. & Gustafsson, J.P. (2008) Environmental systems analysis of four on-site wastewater treatment options. *Resources, Conservation and Recycling*. [Online] 52 (10), 1153–1161. Available from: doi:10.1016/j.resconrec.2008.06.004 [Accessed: 27 November 2014].

White, P.A. & Hammond, J.P. (2009) The sources of phosphorus in the waters of Great Britain. *Journal of environmental quality*. [Online] 3813–26. Available from: doi:10.2134/jeq2007.0658.

White, P.J. & Hammond, J.P. (2002) *Updating the estimate of the sources of phosphorus in UK waters. Defra project WT0701CSF*.

Xu, D., Xu, J., Wu, J. & Muhammad, A. (2006) Studies on the phosphorus sorption capacity of substrates used in constructed wetland systems. *Chemosphere*. [Online] 63 (2), 344–352. Available from: doi:10.1016/j.chemosphere.2005.08.036.

Yu, L. (2012) *A modeling method for longevity study of infiltration for phosphorous* *removal*. Master thesis. Royal Institute of Technology, Stockholm.

Zhang, T.C. & Dahab, M.F. (2006) *Phosphorous sorption capacity and distributions in soil after long-term wastewater land treatment in Muskegon, Michigan*. Kansas City, EPA.

Zhang, T.C., Dahab, M.F., Nunes, G., Hu, C., et al. (2007) Phosphorus fate and transport in soil columns loaded intermittently with influent of high phosphorous concentrations. *Water Environment Research*. 79 (11), 2343–2351.

Zimmer, D., Sierra, J., Bertuzzi, P., Burger, P., et al. (2003) An overview of the crop model STICS. *Europ. J. Agronomy*. [Online] 18309–332. Available from: doi:10.1016/S0223-5234(03)00100-4.

APPENDICES

Appendix A Representational model

A.1 Water module

The modelling approach used assumes one-dimensional vertical flow and transport in the vadose zone.

Limitations of this approach with respect to lateral dispersion are described in more detail in the section on input parameters (4.4.5-Soil physical and hydraulic parameters).

HYDRUS-1D solves the mixed water content–pressure head form of Richards equation (Richard, 1931) Eq. (A-1):

$$\frac{\partial\theta(h)}{\theta t} = \frac{\partial}{\partial x}\left[K_x(h)\left(\frac{\partial h}{\partial x} + 1\right)\right] \pm S \qquad \textbf{(A-1)}$$

where

θ(h) is the volumetric water content [L^3 L^{-3}]

h is the pressure head [L]

x is the vertical spatial coordinate [L]

t is the time coordinate [T]

S is the sink term accounting for root water uptake [L^3 L^{-3} T^{-1}],

K(h) is the unsaturated hydraulic conductivity [L T^{-1}]

Equation (A-1) simulates water flow in variably saturated conditions in one dimension assuming that water flow in the soil porous media follows laminar flow conditions. The expression needed to solve Richards' equation is obtained by combining the Van Genuchten (1980) function with the Mualem (1976) pore-size distribution model and is shown below in (A-2). The water content is calculated for each element and each time step in the simulation, and the unsaturated hydraulic conductivity K(h) [LT^{-1}], is calculated from water content using (A-3)(A-4)(A-5)(A-6).

$$\theta(h) = \begin{cases} \theta_r + \dfrac{\theta s - \theta r}{[1 + |\alpha h|^n]^m} & h < 0 \\ \theta_s \quad h \geq 0 \end{cases} \tag{A-2}$$

$$S_e = \frac{\theta - \theta_r}{\theta_s - \theta_s} \tag{A-3}$$

$$K(h) = K_{sat} . S_e^l . \left[1 - (1 - S_e^{\frac{1}{m}})^m\right]^2 \tag{A-4}$$

$$m + 1 - \frac{1}{n}, \quad n > 1 \tag{A-5}$$

$$q = -K\frac{dh}{dx} \tag{A-6}$$

where

θ_r is residual water content

θ_s is the saturated water content

α is an empirical constant that is inversely related to the air-entry pressure value $[L^{-1}]$

m and n are empirical parameters related to the pore-size distribution.

S_e is the effective saturation

From the above equations, five parameters are specified in HYDRUS-1D for each soil type: θ_r, θ_s, α, n, K_s.

A.2 Solute module

For solute transport, HYDRUS-1D solves the convection-dispersion equation (CDE) (A-7) for one-dimensional (vertical) unsaturated flow and transport. The model simulates advection, hydrodynamic dispersion and adsorption of PO_4 in the soil water environment. HYDRUS-1D represents the CDE partial differential equation represented as (A-8) (A-9). When the solid phase concentration is expressed by an adsorption isotherm, it is reduced to the following form (A-8) (A-9) (Šimůnek & Hopmans, 2009).

$$P_{soil-solution} = J_{advection} + J_{dispersion} + J_{sorption} \quad \textbf{(A-7)}$$

$$\theta \, . R \frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(\theta D_1^w \frac{\partial c}{\partial x}\right) - q\frac{\partial c}{\partial x} + cS \quad \textbf{(A-8)}$$

$$\mathrm{R} = 1 + \frac{\rho_b}{\theta}\frac{\partial s}{\partial c} \quad \textbf{(A-9)}$$

where

θ is the volumetric water content [L^3 L^{-3}],

ρ_b is the bulk density [M L^{-3}],

q is the volumetric flux density [L T^{-1}],

S is the sink term [L^3 L^{-3} T^{-1}],

c is the solute concentration in solution [M L^{-3}],

s is the solute concentration adsorbed to the soil [M M^{-1}],

D is the dispersion coefficient [L^2 T^{-1}] in the liquid,

R is the retardation factor, defining the partitioning of nutrient between the solid and liquid phase.

x is the vertical distance,

t is time.

The ratio ∂s/ ∂c is the portion of PO_4 adsorbed to the soil to PO_4 soluble in solution.

The dispersion coefficient [L^2 T^{-1}] is defined as:

$$D = \lambda v \quad \textbf{(A-10)}$$

Where

λ is dispersivity [L],(D_L for HYDRUS-1D) and

v is average pore water velocity [L T^{-1}].

A.3 Root water and solute uptake model

The root water uptake sink term (A-8), S, is defined by the volume of water removed from unit volume of soil per unit of time (Šimůnek, Šejna, Saito, *et al.*, 2013). The selected model is the one defined by Feddes et al. (1978) where S is defined in terms of pressure head (h) to account for water stress (Shouse, Ayars & ŠimŮnek, 2011). The root water uptake rate S is normally related to the potential transpiration rate, T_p ($L \cdot T^{-1}$), which is spread in the root zone according to the normalized root density distribution function, β (z, t) (L^{-1}). The potential transpiration is determined by the atmospheric demand, and controlled by meteorological variables such as net radiation, air temperature, wind speed, and relative humidity, but does not consider the plant soil and environment (Šimůnek & Hopmans, 2009). The potential transpiration rate can be calculated from the meteorological variables using the FAO-recommended Penman-Monteith combination equation (FAO, 1990). No solute stress is considered in the model. Passive root solute uptake is considered since the crop is assumed to uptake as much PO_4 as available by passive means since the concentrations of P in plant available form is usually very low on solution.

Appendix B Sensitivity analysis results

Table_Apx B-1 Sensitivity analysis results for saturated water content (θ_s)

Years	θ_s (cm^3/cm^3)	Cumulative solute flux across the bottom of the soil profile (mg/cm^2)	Amount of P in the discharge field (kg)	Amount of P in the entire flow domain (mg/cm^2)	Cumulative value of the bottom boundary flux (cm)	% change in the indicator accumulative solute bottom flux	% change in the P accumulation	% change in the indicator accumulative bottom flux	% change in θ_s
Year 0	0.32	0.00E+00	1.9	0.0096988	0.07601	-	-1.7%	98052%	-37%
(t=1 days)	0.41	0.00E+00	2.0	0.0098632	0.000870383	-	0.0%	1024%	-19%
	0.5057	0	2.0	0.0098643	7.74409E-05	-	0.0%	0%	0%
	0.55	0	2.0	0.0098646	3.34949E-05	-	0.0%	-57%	9%
Year 1	0.32	7.16E-03	783.3	3.9166	436.195	0%	0%	0%	-37%
(t=365 days)	0.41	0.0071478	783.4	3.9168	433.345	0%	0%	0%	-19%
	0.5057	0.0071389	783.5	3.9173	430.278	0%	0%	0%	0%
	0.55	0.0071296	783.5	3.9175	428.911	0%	0%	0%	9%
Year 5	0.32	6.821	2436.6	12.183	2191.97	0%	6%	6%	-37%
(t=1825 days)	0.41	6.8071	2306.0	11.53	2189.13	0%	0%	0%	-19%
	0.5057	6.7926	2309.4	11.547	2186.08	0%	0%	0%	0%
	0.55	6.785	2311.2	11.556	2184.7	0%	0%	0%	9%
Year 10	0.32	23.685	2441.4	12.207	4386.73	0%	0%	0%	-37%
(t=3650 days)	0.41	23.663	2441.0	12.205	4383.85	0%	0%	0%	-19%
	0.5057	23.641	2446.0	12.23	4380.83	0%	0%	0%	0%
	0.55	23.629	2448.6	12.243	4379.45	0%	0%	0%	9%
Year 50	0.32	163.69	2441.4	12.207	21944.9	0%	0%	0%	-37%
(t=18250 days)	0.41	163.66	2445.8	12.229	21942.2	0%	0%	0%	-19%
	0.5057	163.64	2451.0	12.255	21939	0%	0%	0%	0%

Years	θ_s (cm^3/cm^3)	Cumulative solute flux across the bottom of the soil profile (mg/cm^2)	Amount of P in the discharge field (kg)	Amount of P in the entire flow domain (mg/cm^2)	Cumulative value of the bottom boundary flux (cm)	% change in the indicator accumulative solute bottom flux	% change in the P accumulation	% change in the indicator accumulative bottom flux	% change in θ_s
	0.55	163.62	2453.6	12.268	21937.3	0%	0%	0%	9%
Year 85	0.32	286.21	2441.4	12.207	37307.1	0%	0%	0%	-37%
(t=31025 days)	0.41	286.17	2445.8	12.229	37305.1	0%	0%	0%	-19%
	0.5057	286.16	2451.0	12.255	37302.2	0%	0%	0%	0%
	0.55	286.14	2453.6	12.268	37300.8	0%	0%	0%	9%
Year 100	0.32	338.71	2441.4	12.207	43889	0%	0%	0%	-37%
(t=36500 days)	0.41	338.68	2445.8	12.229	43888.4	0%	0%	0%	-19%
	0.5057	338.67	2453.4	12.267	43885	0%	0%	0%	0%
	0.55	338.67	2453.6	12.268	43884.5	0%	0%	0%	9%

Table_Apx B-2 Sensitivity analysis results for residual water content (θ_r)

Years	Θ_r (cm^3/cm^3)	Cumulative solute flux across the bottom of the soil profile (mg/cm^2)	Amount of P in the discharge field (kg)	Amount of P in the entire flow domain (mg/cm^2)	Cumulative value of the bottom boundary flux (cm)	% change in the indicator accumulative solute bottom flux	% change in the P accumulation	% change in the indicator accumulative bottom flux	% change in θ_r
Year 0	0.174	0	2.0	0.0098646	0.00175706	-	0.0%	2169%	335%
(t=1 days)	0.001	0	2.0	0.0098646	0.00049108	-	0.0%	534%	-98%
	0.04		2.0	0.0098643	0.00007744	-	0.0%	0%	0%
	0.0794	0	2.0	0.0098643	0.00000000	-	0.0%	-100%	99%
Year 1	0.174	0.0071225	783.5	3.9175	431.0	0%	0%	0%	335%
(t=365 days)	0.001	0.0071299	783.5	3.9175	430.6	0%	0%	0%	-98%
	0.04	0.0071389	783.5	3.9173	430.3	0%	0%	0%	0%
	0.0794	0.0071539	783.5	3.9173	429.7	0%	0%	0%	99%
Year 5	0.174	6.7937	2311.2	11.556	2186.8	0%	0%	0%	335%
(t=1825 days)	0.001	6.7929	2306.0	11.53	2186.4	0%	0%	0%	-98%
	0.04	6.7926	2309.4	11.547	2186.1	0%	0%	0%	0%
	0.0794	6.7906	2303.0	11.515	2185.4	0%	0%	0%	99%
Year 10	0.174	23.643	2448.6	12.243	4381.5	0%	0%	0%	335%
(t=3650 days)	0.001	23.641	2441.0	12.205	4381.2	0%	0%	0%	-98%
	0.04	23.641	2446.0	12.23	4380.8	0%	0%	0%	0%
	0.0794	23.637	2436.6	12.183	4380.2	0%	0%	0%	99%
Year 50	0.174	163.64	2453.6	12.268	21939.7	0%	0%	0%	335%
(t=18250 days)	0.001	163.64	2445.8	12.229	21939.2	0%	0%	0%	-98%
	0.04	163.64	2453.4	12.267	21939.0	0%	0%	0%	0%

Years	Θ_r (cm^3/cm^3)	Cumulative solute flux across the bottom of the soil profile (mg/cm^2)	Amount of P in the discharge field (kg)	Amount of P in the entire flow domain (mg/cm^2)	Cumulative value of the bottom boundary flux (cm)	% change in the indicator accumulative solute bottom flux	% change in the P accumulation	% change in the indicator accumulative bottom flux	% change in θ_r
	0.0794	163.63	2441.4	12.207	21938.6	0%	0%	0%	99%
Year 85	0.174	286.16	2453.6	12.268	37303.1	0%	0%	0%	335%
(t=31025 days)	0.001	286.17	2445.8	12.229	37302.1	0%	0%	0%	-98%
	0.04	286.16	2453.4	12.267	37302.2	0%	0%	0%	0%
	0.0794	286.15	2441.4	12.207	37301.9	0%	0%	0%	99%
Year 100	0.174	338.68	2453.6	12.268	43887.4	0%	0%	0%	335%
(t=36500 days)	0.001	338.69	2445.8	12.229	43885.7	0%	0%	0%	-98%
	0.04	338.67	2453.4	12.267	43885.0	0%	0%	0%	0%
	0.0794	338.65	2441.4	12.207	43885.0	0%	0%	0%	99%

Table_Apx B-3 Sensitivity analysis results for bulk density (ρ_d)

Years	ρ_d (g/cm^3)	Cumulative solute flux across the bottom of the soil profile (mg/cm^2)	Amount of P in the discharge field (kg)	Amount of P in the entire flow domain (mg/cm^2]	Cumulative value of the bottom boundary flux (cm)	% change in the indicator accumulative solute bottom flux	% change in the P accumulation	% change in the indicator accumulative bottom flux	% change in ρ_d
Year 0	0.5	0	1.97302	0.0098651	-7.74409E-05	0.00%	8.11005E-05	0	-55%
(t=1 days)	1.12	0	1.97286	0.0098643	-7.74409E-05	0.00%	0	0	
	1.5	0	1.97286	0.0098643	-7.74409E-05	0.00%	0	0	34%
	2	0	1.97324	0.0098662	-7.74409E-05	0.00%	0.000192614	0	79%
Year 1	0.5	0.000048187	708.46	3.5423	430.278	-99.33%	-0.10	0.00	-55%
(t=365 days)	1.12	0.0071389	783.46	3.9173	430.278				
	1.5	7.0552E-13	821.08	4.1054	430.278	-100.00%	0.05	0.00	34%
	2	2.0828E-16	823.64	4.1182	430.278	-100.00%	0.05	0.00	79%
Year 5	0.5	2.0647	1107.8	5.539	2186.08	-69.60%	-0.52	0.00	-55%
(t=1825 days)	1.12	6.7926	2309.4	11.547	2186.08				
	1.5	0.018186	3945.4	19.727	2186.08	-99.73%	0.71	0.00	34%
	2	0.0022183	3988.6	19.943	2186.08	-99.97%	0.73	0.00	79%
Year 10	0.5	14.519	1108.98	5.5449	4380.83	-38.59%	-0.55	0.00	-55%
(t=3650 days)	1.12	23.641	2446	12.23	4380.83				
	1.5	1.1656	7444.4	37.222	4380.83	-95.07%	2.04	0.00	34%
	2	0.34784	7702	38.51	4380.83	-98.53%	2.15	0.00	79%
Year 50	0.5	153.48	1108.98	5.5449	21939	-6.21%	-0.55	0.00	-55%
(t=18250 days)	1.12	163.64	2451	12.255	21939				
	1.5	110.94	13805.2	69.026	21939	-32.20%	4.63	0.00	34%

Years	ρ_d (g/cm^3)	Cumulative solute flux across the bottom of the soil profile (mg/cm^2)	Amount of P in the discharge field (kg)	Amount of P in the entire flow domain (mg/cm^2]	Cumulative value of the bottom boundary flux (cm)	% change in the indicator accumulative solute bottom flux	% change in the P accumulation	% change in the indicator accumulative bottom flux	% change in ρ_d
	2	90.915	18129	90.645	21939	-44.44%	6.40	0.00	79%
Year 85	0.5	276.01	1108.98	5.5449	37302.2	-3.55%	-0.55	0.00	-55%
(t=31025 days)	1.12	286.16	2451	12.255	37302.2				
	1.5	233.18	13863	69.315	37302.2	-18.51%	4.66	0.00	34%
	2	211.84	18460.6	92.303	37302.2	-25.97%	6.53	0.00	79%
Year 100	0.5	328.52	1108.98	5.5449	43885.2	14.99%	-0.55	0.00	-55%
(t=36500 days)	1.12	285.69	2451	12.255	43885.2				
	1.5	285.69	13864	69.32	43885.2	0.00%	4.66	0.00	34%
	2	264.29	18472.2	92.361	43885.2	-7.49%	6.54	0.00	79%

Table_Apx B-4 Sensitivity analysis results for the equilibrium constant-adsorption isotherm coefficient (K_d)

Years	K_d (cm^3/mg)	Cumulative solute flux across the bottom of the soil profile (mg/cm^2)	Amount of P in the discharge field (kg)	Amount of P in the entire flow domain (mg/cm^2]	Cumulative value of the bottom boundary flux (cm)	% change in the indicator accumulative solute bottom flux	% change in the P accumulation	% change in the indicator accumulative bottom flux	% change in K_d
Year 0	0.019	0	0.0	0	-7.74409E-05	0%	0%	0%	-56%
(t=1 days)	0.04341	0	2.0	0.0098643	-7.74409E-05	0%	0%	0%	
	0.0593	0	0.0	0	-7.74409E-05	0%	0%	0%	37%
	0.185	0	0.0	0	-7.74409E-05	0%	0%	0%	326%
Year 1	0.019	0.25438	704.8	3.5239	430.278	3463%	-10%	0%	-56%
(t=365 days)	0.04341	0.0071389	783.5	3.9173	430.278				
	0.0593	0.00087346	794.3	3.9716	430.278	-88%	1%	0%	37%
	0.185	4.7716E-10	817.7	4.0886	430.278	-100%	4%	0%	326%
Year 5	0.019	12.435	1086.8	5.4339	2186.08	83%	-53%	0%	-56%
(t=1825 days)	0.04341	6.7926	2309.4	11.547	2186.08				
	0.0593	4.2531	2866.0	14.33	2186.08	-37%	24%	0%	37%
	0.185	0.098949	3884.4	19.422	2186.08	-99%	68%	0%	326%
Year 10	0.019	29.932	1087.8	5.4389	4380.83	27%	-56%	0%	-56%
(t=3650 days)	0.04341	23.641	2451.0	12.255	4380.83				
	0.0593	19.689	3299.4	16.497	4380.83	-17%	35%	0%	37%
	0.185	3.0517	6970.4	34.852	4380.83	-87%	184%	0%	326%
Year 50	0.019	169.96	1087.8	5.4389	21939	4%	-56%	0%	-56%
(t=18250 days)	0.04341	163.64	2451.0	12.255	21939				
	0.0593	159.52	3338.4	16.692	21939	-3%	36%	0%	37%

Years	K_d (cm^3/mg)	Cumulative solute flux across the bottom of the soil profile (mg/cm^2)	Amount of P in the discharge field (kg)	Amount of P in the entire flow domain (mg/cm^2]	Cumulative value of the bottom boundary flux (cm)	% change in the indicator accumulative solute bottom flux	% change in the P accumulation	% change in the indicator accumulative bottom flux	% change in K_d
	0.185	126.96	10352.2	51.761	21939	-22%	322%	0%	326%
Year 85	0.019	292.48	1087.8	5.4389	37302.2	2%	-56%	0%	-56%
(t=31025 days)	0.04341	286.16	2451.0	12.255	37302.2				
	0.0593	282.04	3338.4	16.692	37302.2	-1%	36%	0%	37%
	0.185	249.45	10358.6	51.793	37302.2	-13%	323%	0%	326%
Year 100	0.019	345	1087.8	5.4389	43885.2	2%	-56%	0%	-56%
(t=36500 days)	0.04341	338.67	2451.0	12.255	43885.2				
	0.0593	334.56	3338.4	16.692	43885.2	-1%	36%	0%	37%
	0.185	301.96	10358.6	51.793	43885.2	-11%	323%	0%	326%

Table_Apx B-5 Sensitivity analysis results for the equilibrium constant-adsorption isotherm coefficient (K_d)

Years	D_L(cm)	Cumulative solute flux across the bottom of the soil profile (mg/cm^2)	Amount of P in the discharge field (kg)	Amount of P in the entire flow domain (mg/cm^2)	Cumulative value of the bottom boundary flux (cm)	% change in the indicator accumulative solute bottom flux	% change in the P accumulation	% change in the indicator accumulative bottom flux	% change in D_L
Years	5	0.00	1.97	0.01	7.74409E-05	0%	0%	0%	-50%
Year 0	10	0.00	1.97	0.01	7.74409E-05	0%	0%	0%	
(t=1 days)	12	0.00	1.97	0.01	7.74409E-05	0%	0%	0%	20%
	15	0.00	1.97	0.01	7.74409E-05	0%	0%	0%	50%
	5	0.00	779.12	3.90	430.278	-96%	0%	0%	-50%
Year 1	10	0.01	779.12	3.90	430.278				
(t=365 days)	12	0.01	784.06	3.92	430.278	80%	1%	0%	20%
	15	0.02	784.14	3.92	430.278	231%	1%	0%	50%
	5	6.24	2381.40	11.91	2186.08	-8%	3%	0%	-50%
Year 5	10	6.79	2309.40	11.55	2186.08				
(t=1825 days)	12	6.96	2309.40	11.55	2186.08	2%	0%	0%	20%
	15	7.16	2264.60	11.32	2186.08	5%	-2%	0%	50%
	5	23.40	2450.40	12.25	4380.83	-1%	0%	0%	-50%
Year 10	10	23.64	2446.00	12.23	4380.83				
(t=3650 days)	12	23.73	2451.00	12.26	4380.83	0%	0%	0%	20%
	15	23.84	2441.00	12.21	4380.83	1%	0%	0%	50%
	5	163.42	2451.00	12.26	21939	0%	0%	0%	-50%
Year 50	10	163.64	2451.00	12.26	21939				
(t=18250 days)	12	163.71	2451.00	12.26	21939	0%	0%	0%	20%
	15	163.81	2451.00	12.26	21939	0%	0%	0%	50%

Years	D_L(cm)	Cumulative solute flux across the bottom of the soil profile (mg/cm^2)	Amount of P in the discharge field (kg)	Amount of P in the entire flow domain (mg/cm^2)	Cumulative value of the bottom boundary flux (cm)	% change in the indicator accumulative solute bottom flux	% change in the P accumulation	% change in the indicator accumulative bottom flux	% change in D_L
	5	285.94	2451.00	12.26	37302.2	0%	0%	0%	-50%
Year 85	10	286.16	2451.00	12.26	37302.2				
(t=31025 days)	12	286.24	2451.00	12.26	37302.2	0%	0%	0%	20%
	15	286.33	2451.00	12.26	37302.2	0%	0%	0%	50%
	5	338.46	2451.00	12.26	43885.2	0%	0%	0%	-50%
Year 100	10	338.67	2451.00	12.26	43885.2				
(t=36500 days)	12	338.75	2451.00	12.26	43885.2	0%	0%	0%	20%
	15	338.85	2451.00	12.26	43885.2	0%	0%	0%	50%

Table_Apx B-6 Sensitivity analysis results for the solute initial concentration of the soil profile (Ci)

Years	Ci (mg/cm3)	Cumulative solute flux across the bottom of the soil profile (mg/cm2)	Amount of P in the discharge field (kg)	Amount of P in the entire flow domain (mg/cm2]	Cumulative value of the bottom boundary flux (cm)	% change in the indicator accumulative solute bottom flux	% change in the P accumulation	% change in the indicator accumulative bottom flux	% change in Ci
Year 0	0	0	1.97286	0.0098643	7.74409E-05	-			-
(t=1 days)	0.0089	1.4208E-08	73.172	0.36586	7.74409E-05	-	3609%		-
	0.1	1.7082E-07	801.98	4.0099	7.74409E-05	-	40551%		-
	0.96	4.7508E-06	7682	38.41	7.74409E-05	-	389284%		-
Year 1	0	0.0071389	783.46	3.9173	430.28				-
(t=365 days)	0.0089	0.086443	836.54	4.1827	430.28	1111%	7%	0%	-
	0.1	0.96045	1366.74	6.8337	430.28	13354%	74%	0%	-
	0.96	18.56	4655	23.275	430.28	259884%	494%	0%	-
Year 5	0	6.7926	2309.4	11.547	2186.08				-
(t=1825 days)	0.0089	7.097	2314.8	11.574	2186.08	4%	0%	0%	-
	0.1	10.237	2365.4	11.827	2186.08	51%	2%	0%	-
	0.96	42.75	2603.2	13.016	2186.08	529%	13%	0%	-
Year 10	0	23.641	2446	12.23	4380.83				-
(t=3650 days)	0.0089	23.971	2446	12.231	4380.83	1%	0%	0%	-
	0.1	27.344	2451	12.255	4380.83	16%	0%	0%	-
	0.96	60.976	2457	12.287	4380.83	158%	0%	0%	-
Year 50	0	163.64	2451	12.255	21939				-
(t=18250 days)	0.0089	163.97	2451	12.255	21939	0%	0%	0%	-
	0.1	167.35	2451	12.255	21939	2%	0%	0%	-

Years	Ci (mg/cm3)	Cumulative solute flux across the bottom of the soil profile (mg/cm2)	Amount of P in the discharge field (kg)	Amount of P in the entire flow domain (mg/cm2]	Cumulative value of the bottom boundary flux (cm)	% change in the indicator accumulative solute bottom flux	% change in the P accumulation	% change in the indicator accumulative bottom flux	% change in Ci
	0.96	201.03	2451	12.255	21939	23%	0%	0%	-
Year 85	0	286.16	2451	12.255	43885.2				-
(t=31025 days)	0.0089	286.49	2451	12.255	43885.2	0%	0%	0%	-
	0.1	291.93	2451	12.255	43885.2	2%	0%	0%	-
	0.96	323.55	2451	12.255	43885.2	13%	0%	0%	-
Year 100	0	338.67	2451	12.255	43885.2				-
(t=36500 days)	0.0089	339	2451	12.255	43885.2	0%	0%	0%	-
	0.1	342.39	2451	12.255	43885.2	1%	0%	0%	-
	0.96	376.07	2451	12.255	43885.2	11%	0%	0%	-

Table_Apx B-7 Sensitivity analysis results for the saturated hydraulic conductivity (K_s)

Years	K_s (cm^3/cm^3)	Cumulative solute flux across the bottom of the soil profile (mg/cm^2)	Amount of P in the discharge field (kg)	Amount of P in the entire flow domain [mg/cm^2]	Cumulative value of the bottom boundary flux (cm)	% change in the indicator accumulative solute bottom flux	% change in the P accumulation	% change in the indicator accumulative bottom flux	% change in K_s
Year 0	12.18	0	1.97292	0.0098646	1.59E-05	-	0.00%	-79%	-80%
(t=1 days)	36.54	0	1.97264	0.0098632	4.78E-05	-	0.00%	-38%	-39%
	60.19	0	1.97286	0.0098643	7.74E-05	-			
	120	0	1.93976	0.0096988	0.0001571	-	-1.70%	103%	99%
Year 1	12.18	0.0074951	78.35	0.39175	431.885	4.99%	-90.00%	-90.00%	-80%
(t=365 days)	36.54	0.0071414	783.36	3.9168	429.689	0.04%	-0.01%	-0.01%	-39%
	60.19	0.0071389	783.46	3.9173	430.278				
	120	0.0071309	783.32	3.9166	431.129	-0.11%	-0.02%	-0.02%	99%
Year 5	12.18	6.8829	2311.2	11.556	2201.87	1.33%	0.08%	0.08%	-80%
(t=1825 days)	36.54	6.7905	2306	11.53	2185.51	-0.03%	-0.15%	-0.15%	-39%
	60.19	6.7926	2309.4	11.547	2186.08				
	120	6.7948	2303	11.515	2186.91	0.03%	-0.28%	-0.28%	99%
Year 10	12.18	23.875	2448.6	12.243	4414.35	0.99%	0.11%	0.11%	-80%
(t=3650 days)	36.54	23.638	2441	12.205	4380.28	-0.01%	-0.20%	-0.20%	-39%
	60.19	23.641	2446	12.23	4380.83				
	120	23.644	2436.6	12.183	37302	0.01%	-0.38%	-0.38%	99%
Year 50	12.18	164.99	2453.6	12.268	22113.7	0.82%	0.01%	0.01%	-80%

Years	Ks (cm^3/cm^3)	Cumulative solute flux across the bottom of the soil profile (mg/cm^2)	Amount of P in the discharge field (kg)	Amount of P in the entire flow domain (mg/cm^2]	Cumulative value of the bottom boundary flux (cm)	% change in the indicator accumulative solute bottom flux	% change in the P accumulation	% change in the indicator accumulative bottom flux	% change in Ks
(t=18250 days)	36.54	163.64	2445.8	12.229	21938	0.00%	-0.31%	-0.31%	-39%
	60.19	163.64	2453.4	12.267	21939	0.00%			
	120	163.64	2441.4	12.207	21939.8	0.00%	-0.49%	-0.49%	99%
Year 85	12.18	288.49	2453.6	12.268	37600.5	0.81%	0.01%	0.01%	-80%
(t=31025 days)	36.54	286.17	2445.8	12.229	37300.4	0.00%	-0.31%	-0.31%	-39%
	60.19	286.16	2453.4	12.267	37302.2				
	120	286.15	2441.4	12.207	37302	0.00%	-0.49%	-0.49%	99%
Year 100	12.18	341.42	2451	12.255	44237.9	0.81%	-0.10%	-0.10%	-80%
(t=36500 days)	36.54	338.67	2451.8	12.259	43883.4	0.00%	-0.07%	-0.07%	-39%
	60.19	338.67	2453.4	12.267	43885				
	120	338.65	2450	12.25	43884.3	-0.01%	-0.14%	-0.14%	99%

Table_Apx B-8 Mass (kg) of phosphorus accumulated in the first 40 cm of the discharge field for different simulation periods and the sensitivity analysis values used for each parameter tested

	Parameters						
Years	θs	θ_r	ρb	D_L	K_d	C_i	K_{sat}
	kg						
Year 0	1.9	2.0	2.0	2.0	0.0	2.0	2.0
(t=1 days)	2.0	2.0	2.0	2.0	2.0	73.2	2.0
	2.0	2.0	2.0	2.0	0.0	802.0	2.0
	2.0	2.0	2.0	2.0	0.0	7682.0	1.9
Year 1	783.3	783.5	708.5	779.1	704.8	783.5	78.4
(t=365 days)	783.4	783.5	783.5	779.1	783.5	836.5	783.4
	783.5	783.5	821.1	784.1	794.3	1366.7	783.5
	783.5	783.5	823.6	784.1	817.7	4655.0	783.3
Year 5	2436.6	2311.2	1107.8	2381.4	1086.8	2309.4	2311.2
(t=1825 days)	2306.0	2306.0	2309.4	2309.4	2309.4	2314.8	2306.0
	2309.4	2309.4	3945.4	2309.4	2866.0	2365.4	2309.4
	2311.2	2303.0	3988.6	2264.6	3884.4	2603.2	2303.0
Year 10	2441.4	2448.6	1109.0	2450.4	1087.8	2446.0	2448.6
(t=3650 days)	2441.0	2441.0	2446.0	2446.0	2451.0	2446.2	2441.0
	2446.0	2446.0	7444.4	2451.0	3299.4	2451.0	2446.0
	2448.6	2436.6	7702.0	2441.0	6970.4	2457.4	2436.6
Year 50	2441.4	2453.6	1109.0	2451.0	1087.8	2451.0	2453.6
(t=18250 days)	2445.8	2445.8	2451.0	2451.0	2451.0	2451.0	2445.8
	2451.0	2453.4	13805.2	2451.0	3338.4	2451.0	2453.4
	2453.6	2441.4	18129.0	2451.0	10352.2	2451.0	2441.4
Year 85	2441.4	2453.6	1109.0	2451.0	1087.8	2451.0	2453.6
(t=31025 days)	2445.8	2445.8	2451.0	2451.0	2451.0	2451.0	2445.8
	2451.0	2453.4	13863.0	2451.0	3338.4	2451.0	2453.4
	2453.6	2441.4	18460.6	2451.0	10358.6	2451.0	2441.4
Year 100	2441.4	2453.6	1109.0	2451.0	1087.8	2451.0	2451.0
(t=36500 days)	2445.8	2445.8	2451.0	2451.0	2451.0	2451.0	2451.8
	2453.4	2453.4	13864.0	2451.0	3338.4	2451.0	2453.4
	2453.6	2441.4	18472.2	2451.0	10358.6	2451.0	2450.0

*sensitivity analysis values for each parameter can be found in Table 4-3

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