Assessing the Role of Domestic Phosphorus Emissions in the Human Phosphorus Footprint

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ABSTRACT

Societal phosphorus (P) use is unsustainable; P is vital for food security and its increase in the ecosphere is the single greatest cause of water quality degradation on the planet. The following thesis focuses on the role domestic P emissions play in the human P cycle with an aim to support management in reducing the individual P footprint. Measurement of the P composition of private sewage system (PSS) effluent was used to assess domestic P emissions from properties located within the Loch Leven catchment, in East Scotland, UK. This thesis shows PSS treatment type (i.e. level of additional treatment further to a single settling tank) does not reduce effluent P concentration, challenging the efficacy of policies aiming to reduce P pollution from PSS by technological solutions. Using a questionnaire, assessment of domestic and PSS maintenance behaviours of 156 PSS users indicated reductions in P emissions may be achieved through behavioural change. To understand the impact of behaviour on the human P footprint, a novel method using ^{31}P nuclear magnetic resonance (NMR) spectroscopy was successfully developed to identify P compounds related to human behaviour (e.g. washing machine use) in PSS effluent. An assessment of the impact of behaviours on the human P footprint of ten individual households was conducted. Thesis findings conclude PSS desludging reduces concentrations of orthophosphate in PSS effluent; 85% of the variation in total soluble P in PSS effluent can be explained by ‘desludging frequency’ and ‘washing machine use’. Furthermore, PSS users feel responsible for correctly maintaining their PSS, but are potentially not maintaining them effectively or have poorly installed or inadequate systems, and do not know how to reduce domestic P emissions. A need for better public education on PSS maintenance and how to reduce domestic P emissions is required. This work highlights a critical need to integrate social sciences with natural sciences to tackle unsustainable P use.

DEDICATION *(if any)*

Many people helped me throughout the process of this project; some without whom this thesis may not have been written, and to those I am greatly indebted. I would like to take this opportunity to thank just a few.

My supervisors, Sue Roaf and Bryan Spears both deserve a paragraph each.

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Most of all, Laura, my incredible partner. You have made the knocks bearable, have given the celebrations reason, and without your care, intelligence, and wisdom I couldn’t have done it.

ACADEMIC REGISTRY

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Chapter 1 Introduction

1.1 Overview of the Thesis Topic

Freshwater resources are essential for life, and society is highly dependent on the unique and diverse ecosystems they support. Despite the *provisioning services* (i.e. food and water), *regulating services* (i.e. regulation of floods, drought, disease and land degradation), *supporting services* (nutrient cycling and soil formation) and *cultural services* (i.e. recreation) (MEA 2005) that freshwaters provide, there is a shared global concern that insufficient protection for increasingly precious freshwater resources currently exists, thereby threatening their future health (Heathwaite 2010; Moss et al. 2011).

Eutrophication of water bodies is the single greatest cause of water quality deterioration in freshwater and coastal marine ecosystems in the world (Smith and Schindler 2009). Eutrophication is caused by the redistribution of phosphorus (P) within the P cycle. Anthropogenic sources of P have already disrupted the global P balance (Filippelli 2008); P mining has increased the global biogeochemical cycle of P by an estimated 400% (Falkowski 2000). Successful management of eutrophication has to date involved the reduction of anthropogenic inputs of P from a range of point and diffuse sources (Schindler 2006; Smith and Schindler 2009). Population increase (Vorosmarty 2000) and economic development (Alcamo et al. 2003) both increase water demand whilst simultaneously increasing P pollution of waters. Global trends suggest that the intensity of these stressors will continue to increase into the future (Heathwaite 2010).

Households are the greatest source of P to UK rivers, making an estimated contribution of 68.7% of the estimated 41.6 kt of total P (TP) that is delivered to British UK rivers each year (White and Hammond, 2006). Properties in areas where connections to municipal sewage systems are not available must rely on private sewage systems (PSS) to treat their wastewater (Withers et al. 2012). Recent studies estimated that 80% of the 1.5 million PSS in the UK are potentially working inefficiently with respect to P losses (Selyf-Consultancy 2002; Kirk et al. 2003). In the US, one in four homes is served by a PSS and these 26.1 million properties contribute the largest volume of waste water (3.6 10^2 GL year^{-1}) to the subsurface (USEPA, 2002a).

The problem of reducing anthropogenic flows of P from buildings to the environment is a multidimensional one; the solution lies in whole system thinking and requires a multidisciplinary approach. As such, this project has demanded the combination of water chemistry, policy assessment and human behavioural psychology to answer its important question, ‘how do we reduce the human P footprint?’

Chapter 1 begins with an outline of the sustainable use of natural resources and the human global P cycle (Section 1.2), followed by an overview of eutrophication (Section 1.3), the role of P in eutrophication (Section 1.4), the effect of both climate change (Section 1.5) and population growth (Section 1.6) on eutrophication and freshwater availability, and the potential for reducing P delivery to freshwaters (Section 1.7). A background on P pollution from PSS and the policies that manage PSS (Section 1.9), national and international water policy (Section 1.10), the current health of British freshwaters (Section 1.9), life cycle analysis and P footprints (Section 1.11) and the importance of understanding human behaviour in the reduction of ecological deterioration is then provided (Section 1.12). Finally, the key aims of the thesis and its structure are outlined (Section 1.13).

1.2 The Issue of Phosphorus Flows in Sustainable Societies

Sustainable development is commonly defined as, “development that meets the needs of the present without compromising the ability of future generations to meet their own needs” a definition given by the Brundtland Commission in 1987 (WCED 1987). Although the term ‘sustainability’ was originally used in ecology to describe the ability of an ecosystem to remain unaltered over time (Jabareen 2006), its combination with the term ‘development’ has shifted its focus from the environment, toward a viewpoint of human and societal needs (Reboratti 1999; Moldan et al. 2012). Sustainable development can be viewed as paradoxical (Jabareen 2006; Geisinger 1999); whilst sustainability is characteristic of a system that can be maintained for an indefinite period, development is characteristic of change, often through environmental modification and exhaustive use of natural resources (Jabareen 2006).

Currently, societal use of the natural resource P is unsustainable (Cordell and White 2011; Smil 2000; Childers et al. 2011). Over the last 75 years, increase in P mining, largely to support requirements for P fertiliser, has caused an estimated 400% increase in the biogeochemical cycle of P (Falkowski 2000). A simplified framework for the cycle of an element (such as phosphorus (P)) between the lithosphere, the technosphere and the ecosphere is provided in Figure 1.1.

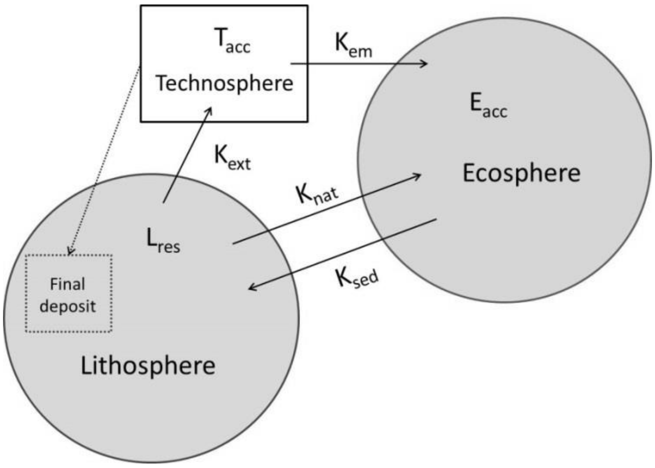


Figure 1.1 The cycle of an element extracted from the lithosphere to be used in the technosphere and its subsequent release into the ecosphere (modified from Azar et al. (1996)). L_{res} represents the elements reserves in the lithosphere; K_{ext} the extraction rate of the element from the lithosphere; T_{acc} is accumulation of that element in the technosphere; K_{em} is the rate at which it is emitted to the ecosphere; K_{nat} the rate of flow of the element into the ecosphere by natural processes (such as weathering); E_{acc} the accumulation of the element in the ecosphere, whilst K_{sed} represents the rate the element is returned to the lithosphere by sedimentation processes. Anthropogenic methods to remove the element from the technosphere into final deposits in the lithosphere are represented by the dashed arrow.

The framework shows an element (such as phosphorus (P)) stored in the lithosphere in reserves (L_{res}). The rate it is extracted (K_{ext}), is determined by how much is required in the technosphere (in regards to P, uses in the technosphere include fertilisers, detergents, food additives, industrial reagents). The more an element is used, the higher its accumulation (T_{acc}), and subsequently the greater emission rate to the ecosphere (K_{em}). The accumulation of the element in the ecosphere (E_{acc}), is also determined by the release rate of that element from the lithosphere by natural processes such as weathering and volcanic deposition (K_{nat}). The return of the element to the lithosphere is determined by the rate of its sedimentation processes (K_{sed}) (in regards to P, mineralisation of P can take thousands to millions of years (Childers et al. 2011); combined with any anthropogenic methods used to permanently redeposit elements into the lithosphere. If the combined flow of an element from the lithosphere to the ecosphere, as determined by K_{ext} and K_{em} and K_{nat}, exceeds its return rate to the lithsphere (K_{sed}), its concentration will continue to increase in the ecosphere.

Very few indicators of sustainability focus on the relationship between society and ecosystems (Azar et al. 1996). Most non-monetary measures used to indicate the level to which the use of a natural resource is sustainable (or a societal activity or environmental state or function is sustainable), are based on environmental quality indicators (Moldan et al. 2012; Bergstrom 1993; Haines-Young et al. 2006). Such indicators define thresholds and limits, such as the water quality indicators used in the Water Framework Directive (WFD) (EU 2000) (Section 1.10) that, if exceeded, will produce undesirable environmental conditions.

Societal impacts on the environment can be viewed as a chain of causal effects that begin with the causes in society and end with the impacts caused to the environment. Azar et al. (1996) argues that socio-ecological indicators (Holmberg and Karlsson 1992) may provide much earlier warning signs of unsustainable activities than environmental quality indicators (Azar et al. 1996), suggesting four socio-ecological principles that must be met to ensure a sustainable society (outlined below). These principles focus on the relationship between society and ecosystems, internal societal resource use and societal factors that impact the environment.

- *"Principle 1: substances extracted from the lithosphere must not systematically accumulate in the ecosphere"*
- *"Principle 2: society produced (man-made) substances must not systematically accumulate in the ecosphere"*
- *"Principle 3: the physical conditions for production and diversity within the ecosphere must not become systematically deteriorated"*
- *"Principle 4: the use of resources must be efficient and just, with respect to meeting human needs"* (Azar et al. 1996).

Based on these principles, Azar et al. (1996) states that in a sustainable society elements must not be extracted from the lithosphere at a rate that causes disruption to the natural cycles of that element. Accumulation of an element in the technosphere will result in the inevitable release of that element into the ecosphere, until removal into the lithosphere, either by natural or anthropogenic processes. Compounds produced in the technosphere must not be emitted faster than they can degrade, highlighting a need for restrictions on the production of persistent (non-degradable) compounds that do not occur naturally. Sustainability of society relies on the long term production capacity and biotic diversity of ecosystems. Therefore a sustainable society must not take more resources than can be regenerated within the ecosphere, or alter physical conditions that support natural systems that may result in ecosystem degradation. In order to support principles 1, 2 and 3, and support a growing global population, resources taken from nature must be used efficiently, and recycled where possible.

The global human P cycle is presented in Figure 1.2. It is of note that there are large uncertainties and variability in many P flow estimates.

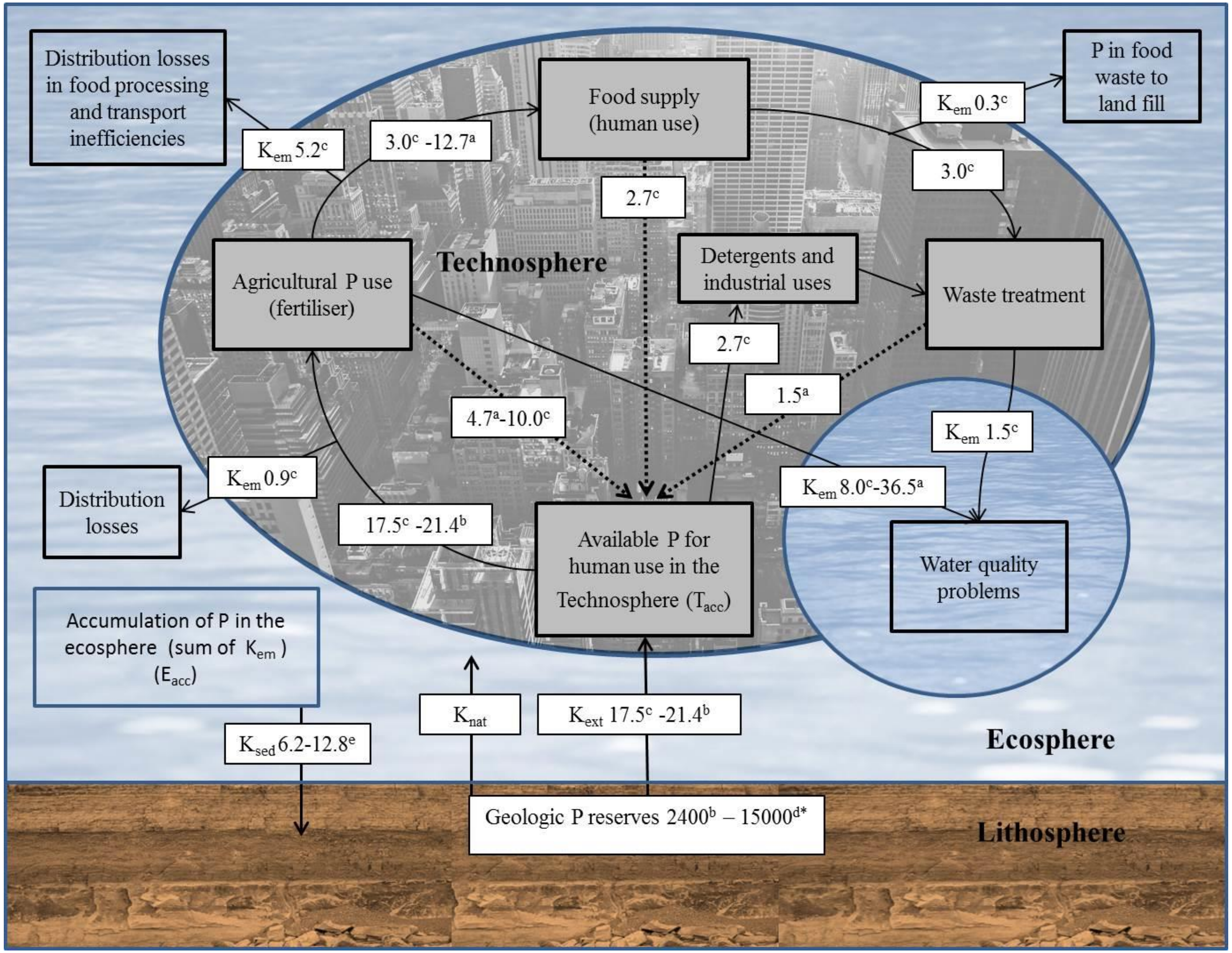


Figure 1.2 The global human P cycle. Solid arrows represent flows of phosphorus (P), dashed lines represent recycling of P within the technosphere (grey area). Figures in boxes represent estimates of P flows in million tons (MT) year^{-1} (*estimated P reserves in MT). Superscripts correspond to the data source for each P flow estimate: a) Liu et al. 2008, b) Villalba et al. 2008, c) Cordell et al. 2009, d) Gilbert 2009 e) Pierrou 1976. K_{ext} is the rate of P extraction due to mining; K_{nat} is the rate of P release from the lithosphere (brown area) due to natural processes (such as weathering); K_{em} is the P emission rate from the technosphere to the ecosphere (blue areas); K_{sed} is the rate of sedimentation of P from the ecosphere to the lithosphere. T_{acc} is the accumulation of P in the technosphere; E_{acc} is the accumulation of P in the ecosphere.

Despite the variation and clear uncertainties in estimated P flows, accumulation of P in the ecosphere from unsustainable P use is evident. The combined estimated P K_{em} ranges from 15.9-44.4 MT yr^{-1}, whilst the K_{sed} is estimated to be 6.2-12.8 MT yr^{-1}, resulting in a global accumulation of P in the ecosphere of between 3.1-38.2 MT yr^{-1}, not including P inputs to the ecosphere from weathering of rock (K_{nat}). The increase in P in the ecosphere is the single greatest cause of water quality degradation on the planet (Smith and Schindler 2009).

The following thesis focuses on the element P and its relationship between society and ecosystems; specifically in terms of internal societal resource use and societal factors that impact the aquatic environment. Measurement of P emissions from housing is conducted by assessment of the composition of P in the effluent of private sewage systems.

1.3 Eutrophication

Eutrophication is caused largely by the redistribution of P within the P cycle. Enrichment of waters with P (and in some cases nitrogen (N)), is the single greatest cause of water quality deterioration in freshwater and coastal marine ecosystems in the world (Smith & Schindler 2009).

The term eutrophication, is commonly used to describe enrichment of waters by nutrients, most commonly P inputs of anthropogenic origin, which have deleterious impacts on receiving freshwater ecosystems (Jeppesen et al. 2000; Carpenter 2005; Smith & Schindler 2009). Due to its relative scarcity P is commonly the limiting factor of algal growth in freshwaters (Karl 2000). In shallow lakes, once a threshold concentration of P has been reached an often rapid dynamic regime shift can transform clear waters and healthy ecosystems into waters favouring algal dominance, anoxia, toxic cyanobacterial blooms and low socioeconomic value (Scheffer & Nes 2007; Smith & Schindler 2009). Internal lake mechanisms, such as sediment re-suspension, temperature or pH change, can make in lake reserves of P bioavailable, playing an important role in prolonging recovery from eutrophication following catchment management (Spears et al. 2007).

It has been shown that the restoration of deep (thermally stratified) lakes can respond quickly to reduction in nutrient loading (Carpenter et al. 1999; Wetzel 2001) whilst restoration of shallow (thermally unstratified) lakes can take significantly longer (years to decades) involving long term management (Søndergaard et al. 2003; Hilton et al. 2006). The ‘alternative stable states theory’ (Scheffer and Carpenter 2003; Scheffer and Nes 2007) and the ‘dynamic regime concept’ (Mayer and Rietkerk 2004; Scheffer and Nes 2007) suggests that both clear and turbid states in a shallow lake are stabilised by a number of mechanisms. As a result, once a shallow lake becomes turbid it can resist restoration. In such eutrophic lakes, restoration may not follow a linear pathway but rather a hysteric response to P input reductions (Mayer & Rietkerk 2004). In some cases P concentrations must be reduced to lower than the threshold level, currently set at 100 µg P l^{-1} (Neal and Heathwaite 2005), before a return to a stable and healthy ecosystem is observed (Scheffer & S. Carpenter 2003; Mayer & Rietkerk 2004).

1.3.1 Effects of Eutrophication on Freshwater Ecosystems

Eutrophication is commonly associated with intensified algal growth (Sayer et al. 2010) (Figure 1.3a). This results in increased metabolism and respiration of decomposing bacteria, due to the higher concentration of food source (sinking dead algae) (Moss 1998; Wetzel 2001; Hilton et al. 2006), and can create anoxic conditions (Wetzel 2001; Foley et al. 2012). In deep stratified lakes anoxic conditions in the epilimnion (Scheffer and Nes 2007) can cause a barrier for migrating salmonids (Hendry et al. 2003), and can result in fish kills (Chen et al. 2009) (Figure 1.3b). Increased turbidity during algal blooms reduces the photic zone (Hautier et al. 2009) and inhibits photosynthetic oxygen production by aquatic macrophytes, further promoting anoxia (Scheffer and Nes 2007; Penning et al. 2008). In extreme cases macrophytes can die off completely (Sayer et al. 2010), removing valuable habitat and food for invertebrates, fish and wild bird species (Ronka et al. 2005), disrupting the food web (Hendy 2002, Scheffer 2007) and reducing species diversity (Jeppesen et al. 2000).

Figure 1.3 a) Algal bloom associated with eutrophication, and b) fish kills, a deleterious effect of eutrophication (images courtesy of www.cranfield.ac.uk).

Eutrophication has been associated with conditions that favour the dominance of cyanobacterial growth (O'Neil et al. 2012). Some cyanobacteria, such as *Microcystis aeruginosa* and *Anabaena spiroides,* release neurotoxins, although why they are produced and what biological role they serve is unknown (Moss 1990). It has been suggested that they may aid in reduction of predation by zooplankton and competition with other algae (Yoo et al. 1995). These chemicals are toxic to mammals and have been responsible for deaths of livestock (Briand et al. 2003).

Algal blooms can also significantly increase filtration costs in potable water reservoirs, and in some cases make water unsuitable for drinking (Agrawal and Gopal 2013; Qin et al. 2010). Recreational activities such as fishing, sailing and swimming have been reduced as a result of the unpleasant aesthetic and potentially harmful nature of algal blooms (**Error! Not a valid bookmark self-reference.**). This can impact the local economy, significantly lowering the economic value of the water body (Pretty et al. 2003; Dodds et al. 2009).

Figure 1.4 Eutrophic algal bloom affecting the coastline around Qingdao, China, during the 2008 Chinese Olympics (Photo taken from EyePress, www.nysun.com).

The main effects of eutrophication are summarised in Table 1.1.

Table 1.1 Summary of the common effects of eutrophication.

Effects of Eutrophication	Reference
Increased biomass of phytoplankton and macrophyte vegetation	(Sayer et al. 2010)
Increased biomass of consumer species	(Smith and Schindler 2009)
Shifts to bloom-forming algal species that may be toxic or inedible	(O'Neil et al. 2012)
Changes in species composition of macrophyte vegetation	(Sayer et al. 2010; Dudley et al. 2012)
Increased incidence of fish kills	(Chen et al. 2009)
Reductions in species diversity	(Jeppesen et al. 2000)
Speciation reversal and subsequent reduction in genetic diversity	(Vonlanthen et al. 2012)
Reductions in harvestable fish and shellfish biomass	(Anderson et al. 2002)
Decrease in water transparency	(Hautier et al. 2009)
Taste, odour and drinking water treatment problems	(Qin et al. 2010)
Oxygen depletion	(Foley et al. 2012)
Decrease in perceived aesthetic value of the water body	(Dodds et al. 2009)
Considerable economic cost	(Pretty et al. 2003; Dodds 2006)

The combined costs for the treatment and restoration of water bodies affected by eutrophication and the losses of local economies due to eutrophication have been estimated to be between £75 to £114.3 million per year for England and Wales (Pretty et al. 2003), and $2.2 billion per year for the United States of America (US) (Dodds et al. 2009). The wealth of knowledge, literature and number of research programme surrounding nutrient enrichment reflect the global economic and ecological importance of eutrophication (Bailey-Watts et al. 1987; Pretty et al. 2003).

1.4 Phosphorus in the Environment and its Role in Eutrophication

Phosphorus is of key importance in biological metabolism, despite being present in the world in relatively small quantities (0.09 wt %), since between 2 to 4% of the dry weight of cells are made of P. P is not stable in gas form, therefore transport of P within the P cycle depends on passage through aquatic ecosystems. P concentrations in the aquatic environment are relatively low, with typical soluble P concentrations in pristine rivers often < 30 µg l^{-1} (Mainstone et al. 2000).

In general the onset of eutrophication is mostly associated with anthropogenic sources of P, although the geology, morphology and certain fluvial processes within a catchment can cause natural variation in total phosphorus (TP) levels found in waters. Certain minerals, such as apatite, vivianite, mitridatite and anapaite as well as rocks such as rock phosphate, can provide a large source of phosphate to waters, increased by the physical and acidic erosive action of water on such deposits (Stamatakis and Koukouzas 2001; Stamatakis 2004).

In the context of eutrophication P is often viewed as a pollutant, but P is an incredibly important resource in its own right. P fertilisers are essential for modern agriculture, with Cordell (2008) suggesting that without access to P we cannot produce sufficient food to feed the population. Parallels between peak oil and peak P have been made, but unlike oil which can be replaced with other forms of energy, there are no other elements that can replace P as a plant fertiliser (Cordell 2008; Beardsley 2011). Peak P is estimated to be between 61 to 400 years away and a decrease in the quality and accessibility of remaining P reserves is expected (Cordell and White 2011). Concerns about the effect this will have on future P prices was confirmed by the 2008 food and phosphate fertiliser price spike (Cordell and White 2011). Further concern that scarcity could potentially lead to international conflicts has been voiced (Dawson and Hilton 2011). Reduction in the amount of P we use individually is required not only to protect the quality of our waters, but also to ensure future food security.

1.4.1 Forms of Phosphorus and Transformation Processes in Aquatic Systems

Total Phosphorus (TP) found in the water column can be separated by filtration into particulate P (PP) and total soluble P (TSP) (Wetzel and Likens 2000) (summarised in equation 1).

$$TP = PP + TSP$$

Equation 1

PP is composed of organic and inorganic material and is defined as the fraction of P that does not pass through a 0.45 µm filter (Mckelvie et al. 1995). PP is not generally considered immediately bioavailable, but may become bioavailable over time through solubilisation processes (Sonzogni et al. 1984). The organic pool comprises of P compounds found within organisms, such as deoxyribonucleic acid (DNA), adenosine triphosphate (ATP), adenosine diphosphate (ADP). The inorganic particulate P includes P adsorbed to minerals including clays, carbonates and ferric hydroxide complexes (Wetzel 2001).

TSP is mainly composed of orthophosphates (PO_4^{3-}), polyphosphates commonly used in synthetic detergents, colloid phosphates such as organic colloids or P bound with adsorptive colloids and low molecular weight phosphate esters (Wetzel 2001). TSP can be subdivided into two further categories for detailed analysis (summarised in equation 2). These are soluble reactive P (SRP), which describes the bioavailable portion of dissolved P, predominantly orthophosphate and soluble unreactive P (SURP), the acid-soluble suspended (sestonic) P which is regarded as predominantly organic P.

$$TSP = SRP + SURP$$

Equation 2

P is highly reactive and exists in the hydrosphere almost entirely in an oxidised state. Inorganic P can be taken up by macrophytes, commonly aided by a symbiotic relationship with fungi forming mycorrhiza, although orthophosphate is also assimilated by algae and non-rooted aquatic macrophytes directly from the water column. Orthophosphate is highly bioavailable and is the P form most associated with nuisance algal growth in rivers and lakes (Jarvie et al. 2006). These primary producers convert inorganic phosphate into organic forms that act as a substrate for heterotrophic microbial food webs. As organisms die, bacterial communities in the benthos convert organic P into inorganic forms and the cycle is continued (Figure 1.5).

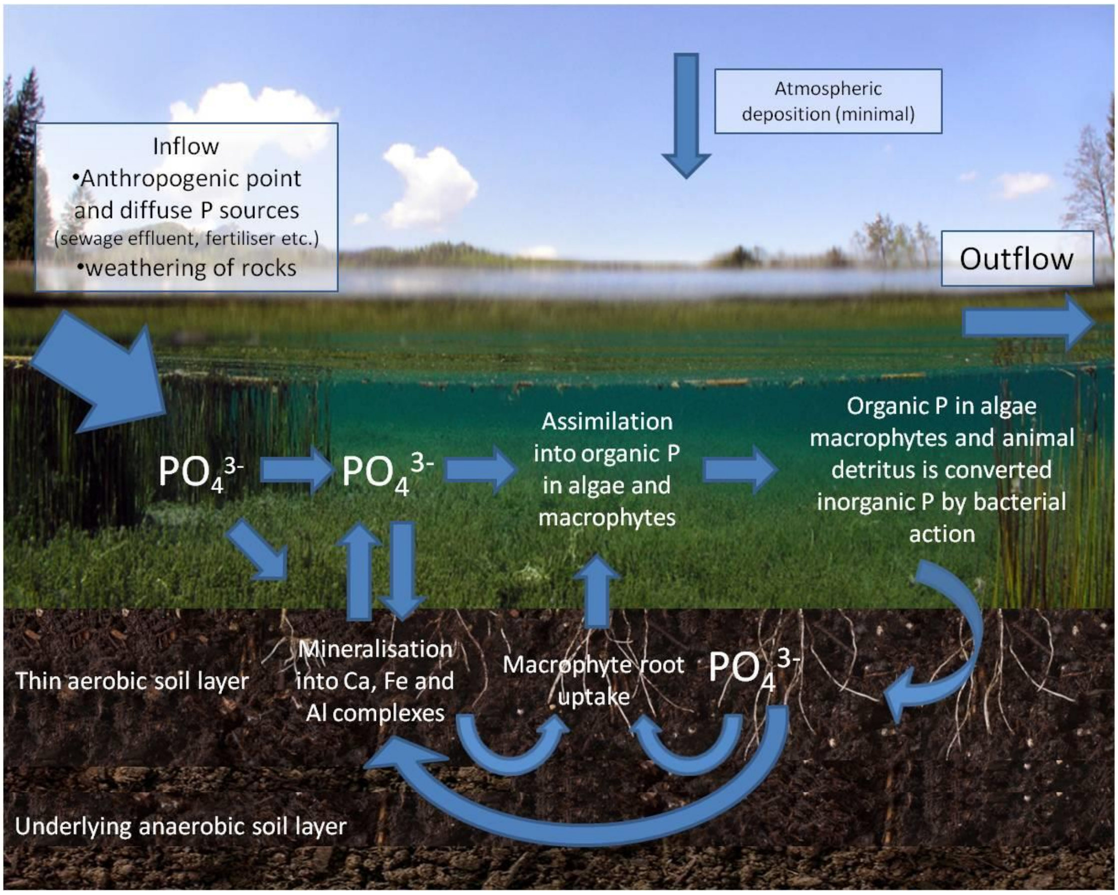


Figure 1.5 Diagram outlining the main features that coordinate the cycling of phosphorus within the aquatic environment.

Colloidal and particulate P can be mobilised in runoff and groundwater, thus TSP in river water can increase significantly following heavy rainfall events. Mains sewage treatment works (STW) and agricultural runoff can increase TSP concentration in rivers by up to 1000 µg P l^{-1}, and 50 µg P l^{-1}, respectively (Meybeck 1982), and are commonly associated with increased SRP concentrations in waters. Downstream of point sources SRP concentrations decrease, outlined in the Nutrient Spiralling Concept (Newbold et al. 1983). This is in part due to physical adsorption onto benthic substrata aided by the 'sticky' nature of SRP, and subsequent assimilation into fauna and flora driven by adsorptive equilibrium conditions (Spears et al. 2007; Spears et al. 2011). Disruption of sediment, by sources such as wind mixing or bioturbation, can cause the release of sediment bound P into the water column (Spears et al. 2011; Spears and Jones 2010).

Orthophosphate can be converted to phosphine, phosphite and hydrophosphite by anaerobic bacterial reduction (Glindemann et al. 2005). Release of phosphine gas, PH_{3}, into the atmosphere is typically from organic rich wetlands and shallows and can cause atmospheric transportation of P. Although this is extremely rare and phosphine soil concentrations are measured in the range of ng kg^{-1} (Glindemann et al. 2005).

1.4.2 Sources of Phosphorus to Aquatic Systems

Reduction of P concentration in waters lies at the core of control and management of eutrophication. To achieve this, it is often first necessary to identify anthropogenic sources of the P within the catchment and understand how they are transported and transformed within the water system (Neal and Heathwaite 2005; Hilton et al. 2006; Anderson et al. 2002; Sharpley et al. 2013). The main P sources within a catchment are summarised in Figure 1.6

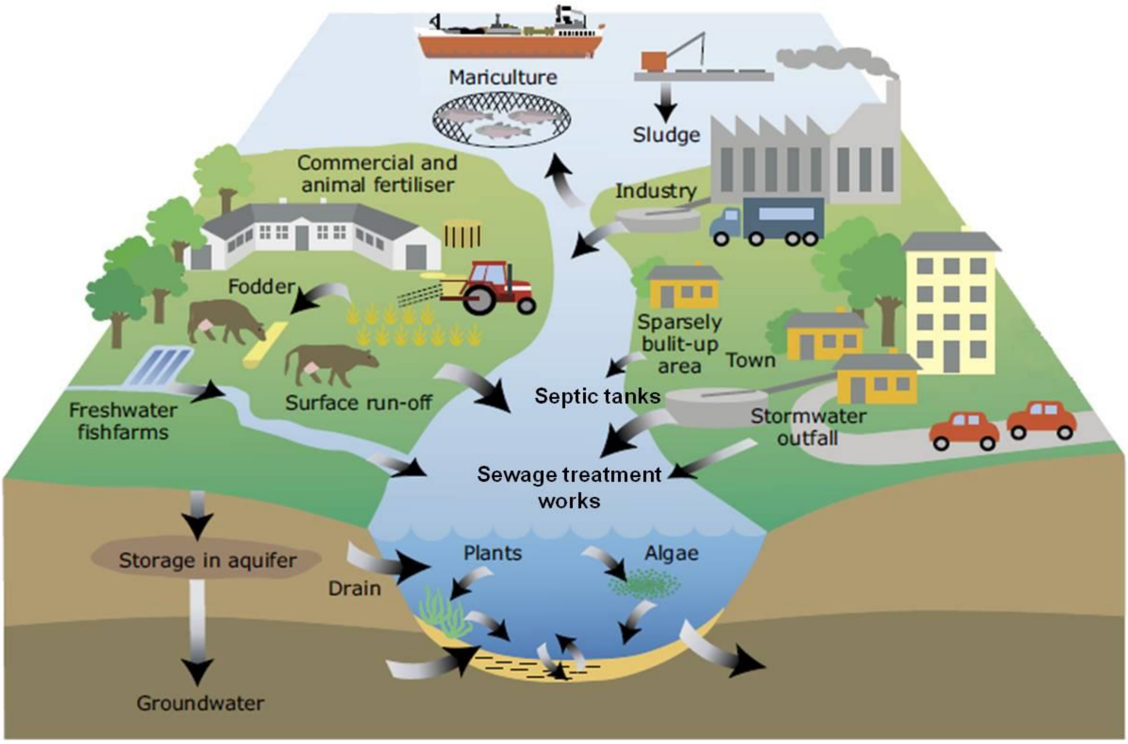


Figure 1.6 Anthropogenic sources of P to the aquatic environment. The main anthropogenic nutrient sources are discharges from agricultural runoff, sewage wastewater treatment plants and industry (Diagram modified from (Ærtebjerg et al. 2003).

Sources are often distinguished as 'point' or 'diffuse' in origin. The next section describes each in more detail.

1.4.3 Characteristics of Point Sources of Phosphorus

Nutrients from point sources enter the water at a specific site and are often persistent and continuous in delivery (Wetzel 2001). This can make them easier to identify and monitor than diffuse sources. Primary P point sources include:

- municipal wastewater effluent (e.g. STW, small holdings with private sewage systems (PSS))
- industrial wastewater effluent (e.g. power stations and factories)
- runoff and leachate from construction, waste disposal and industrial sites and confined livestock units in agriculture
- outfalls and overflows from storm sewers and combined storm and sanitary sewers

P point sources are typically high in SRP (bioavailable P) (Withers et al. 2009).

1.4.4 Characteristics of Diffuse Sources of Phosphorus

Diffuse sources of P originate from spatially widespread activities that do not have one discrete source and are often episodic in delivery (Edwards and Withers 2008), often as a result of a heavy rainfall (Stutter et al. 2007). Typical diffuse sources of P are in the form of runoff and percolation of groundwater through soils rich in P due to the addition of fertilisers, pesticides and manure (Ærtebjerg et al. 2003; Haygarth et al. 2012). Common diffuse sources of P are:

- agricultural land that has been treated with fertilisers and pesticide
- land with roaming livestock
- runoff from roads and construction sites
- runoff from recreational areas treated with fertilisers, such a golf courses

Stromqvist et al. (2008) suggest P delivery can be separated into the following groups:

- Particulate P: the potential P release via erosion, reliant on the P content of the soil.
- Soluble P: potential release heavily influenced by the sorption capacity of the soil, after the point of saturation is reached.
- Additional P loading which has not had time to equilibrate with the soil. This is dependent on anthropogenic input.

P retention is considered the sum capacity of a landscape to remove, transform or retard the transport of P to water bodies via geochemical, biological, hydrological and physical means (Heckrath et al. 2007; Heathwaite et al. 2005; Schippers et al. 2006; Shigaki et al. 2007). This includes uptake by assimilation in to biological molecules by plants and animals and sequestration into sediments. Soil type will control P retention via its P sorption capacity. The metal cations of compounds present in soils, such as iron, aluminium, and calcium hydroxides, can bind orthophosphate (Søndergaard et al. 2003). Soils with high P binding capacities will therefore capture dissolved P in runoff and retard delivery from source to water. Equilibrium between groundwater and soil bound P will establishes whether the soil acts as a source or sink; once saturated soils can effectively lose their capacity to bind further P (Bogestrand et al. 2005). Transport of ground water through the aquifer effectively captures impurities and pollutants, naturally cleaning our waters, although aquifers themselves can become contaminated in extreme pollution events (Behrendt 1999). Transport time of P to rivers is also controlled by the land slope gradient, vegetation cover, transpiration and physical distance to the water body.

Annual variation in the magnitude of diffuse P pollution is observed due to seasonal weather patterns (Bailey-Watts and Kirika 1999). In the UK, P mobility tends to be less in summer due to lower levels of precipitation and subsequent water flow, whereas in autumn and winter, when greater rainfall is typically experienced, greater P delivery to aquatic systems is observed (White and Hammond 2006). Conversely, dry spells can reduce soil moisture and cause cracks and fissures, increasing sediment delivery from sporadic rainfall (Domínguez et al. 2004; Sade et al. 2010; Shipitalo 2004). High earthworm burrow density will have the same effect, speeding flow of PP by providing direct transport routes for water movement (Shipitalo 2004; Domínguez et al. 2004).

1.5 Climate Change and its Effect on Eutrophication

Warming of the climate is unequivocal. The temperature of the oceans and the atmosphere are rising, atmospheric concentrations of greenhouse gases have increased, snow and ice have diminished, and sea levels have risen (IPCC 2013). There is little doubt anthropogenic activity is responsible for global warming (IPCC 2013).

In many cases climate change will promote conditions favouring eutrophication, such as increasing water temperatures, lake stratification and in many areas greater nutrient delivery from increased catchment runoff (Rabalais 2009). Spatial and seasonal distribution of fresh water will change under the pressures of a changing climate (Şen 2009, Oki and Kannae 2006). Understanding how these changes will affect availability, quality and distribution of our fresh water resources on a global and regional scale is complex due to the variation in the geographical, hydrological and climatic systems involved (Vorosmarty 2000; Oki and Kanae 2006; Woodward et al. 2010; Sen 2009; Rabalais 2009).

An increase in atmospheric temperature will cause an increase in precipitation intensity and alter rainfall patterns regionally (Alcamo et al. 2007; Sen 2009). An increase between 1.5 and 4.5°C in global temperature is predicted to increase global mean precipitation by 3 to 15% (Şen 2009). In temperate regions, such as Northern Europe, increased precipitation and greater flooding is predicted, especially in winter, whilst in arid and semiarid landscapes, characteristic of Southern Europe, a decrease in precipitation and an increase in the occurrence of droughts are expected (Alcamo et al. 2007; IPCC 2013). Increased solar flux will increase evapotranspiration and may cause reduction in surface runoff (Şen 2009). A decrease in surface water flow may reduce dilution of point source pollution in waters (Sen 2009; Rabalais 2009; Paerl and Huisman 2009), but may also reduce mobility of soil bound P, and thus reduce diffuse pollution to proximal waters. Increased rainfall will result in greater nutrient delivery to coastal zones, likely enhancing eutrophication and hypoxia (Lotze et al. 2006; Rabalais 2009). Climate change will increase frequency of extreme weather events (IPCC 2013). The recent storms during the winter of 2013/2014 are likely to have severe long term effects on the flooded agricultural pastures of southern England. Storm events, especially after prolonged dry conditions, have been shown to dominate annual diffuse pollution delivery of P to proximal water sources (Evans et al. 2004; Evans 2010). Increased wind induced wave mixing may alter littoral habitat in shallow lakes and increase mobilisation of P laden sediments; increasing eutrophication in shallow lakes (Spears et al. 2011).

The impact climate change will have on eutrophication of lakes will depend on lake size, structure and the net effect of multiple competing factors (Veraart et al. 2011; Moss et al. 2011; Carvalho and Kirika 2003), and often may not be easy to predict. It has been observed that the relationship between P concentration and algal biomass does not change consistently along a temperature gradient (Kosten et al. 2011). Gerten & Adrian (2001) showed under identical climatic conditions that water temperature increase varied substantially between lakes of different thermal structure and mixing regime. In modelled scenarios, Trolle et al (2011) showed by 2100 under predicted temperature rise (IPCC-A2 scenario), the change in annual mean surface water concentrations of TP in three oligotrophic lakes in New Zealand would be equivalent to increasing P loading by between 25 to 50% (Trolle et al. 2011). Management schemes to control eutrophication will need to site specific and be supported by annual appraisal based on regular water quality monitoring programmes.

Eutrophication may also further promote climate change through the release of nitrous oxide from increased denitrification (Bastviken et al. 2011), and methane from anoxic waters and sediments (Huttunen et al. 2003).

1.6 Population Growth and its Effect on Eutrophication

Population growth and economic development whilst increasing water demand (Oki and Kanae 2006; Alcamo et al. 2003) will simultaneously cause greater water pollution (Heathwaite 2010; Vorosmarty 2000), effectively reducing availability of clean waters. Together they are considered to represent a greater stress on global freshwater resources than climate change (Vorosmarty 2000; Kummu et al. 2010).

Whilst 71% of the world surface is covered by water, only 2.5% of global water is fresh water (Oki and Kanae 2006). Most of this is not freely available or renewable as it is stored in glaciers or reserves of paleo-water (groundwater sealed in aquifers, taking up to 1000 years to recharge) (Oki and Kanae 2006). Almost 40% of the earth's available freshwater resources are used for agriculture, industrial or domestic services, and will be polluted through these practices (Schwarzenbach et al. 2006; Oki and Kanae 2006). This leaves an estimated 60% to support freshwater ecosystems, and the remaining services (MEA 2005) they provide.

The global population is increasing, and in 2011 reached 7 billion (Ezeh et al. 2012). By 2050, the global populations is predicted to be between 8.1 to 10.6 billion (Ezeh et al. 2012). Growth by region is summarised in Table 1.2.

Table 1.2 Population projections (2010-50) in billion by region, UN medium variant, modified from (United Nations 2010).

	Population (billion)		% increase
	2010	**2050**	**2010-50**
Africa	1.02	2.19	114%
Sub-Saharan	0.86	1.96	129%
Asia	4.16	5.14	23%
China	1.34	1.3	-3%
Latin America and Caribbean	0.49	0.75	27%
Europe	0.74	0.72	-3%
USA and Canada	0.34	0.45	30%
Developing countries	5.66	7.99	41%
Developed countries	1.21	1.31	6%
Worldwide	6.9	9.31	35%

Four distinct patterns in population growth were observed between 2005 and 2010 (Ezeh et al. 2012):

- The population in the poorest countries, in particular Sub Saharan Africa, increased rapidly at around 2% year^{-1}.
- The populations of India, Indonesia, Western Latin America and North Africa increased at < 1% year^{-1}.
- The populations of the richer countries including USA, Canada, China and much of Europe, have near zero growth rates, and death rates decreased.
- Population in most of Eastern Europe, Japan and Russia declined due to reductions in fertility.

Although growth in many of the major developed countries is levelling off, a simple reduction in global birth rate of lower income countries will not make a significant difference to water consumption or water pollution. Resource consumption of citizens in all high income countries is far greater than in low income countries (Bapna 2011). It is the exponential growth of 'middle class' populations that is placing a much greater demand on global water resources, both in terms of water demand and P pollution. This is driven in part by water requirements to supply a meat-based diet (Bapna 2011).

Population growth and economic development over the next 25 years are expected to dictate the relationship between water supply and demand to a much greater degree than climate change (Vorosmarty 2000). Under modelled projections, an almost pandemic increase in relative water demand between 1985 to 2025 is expected (Vorosmarty 2000). Currently over one third of the world's population live in physical water scarcity (Kummu et al. 2010) with two billion people living in highly water stressed areas (Oki and Kanae 2006). Although arid climates will face the challenge of water shortage, in water rich areas the challenge will not be providing adequate quantities of water, but more providing supplies that are of sufficient quality for use (Vorosmarty 2000; Heathwaite 2010).

An increasing population increases the need for food production, demanding greater fertiliser use (Childers et al. 2011) causing increasing diffuse P pollution to waters (Van Vuuren et al. 2010). Pollution from urban and agricultural runoff will increase with population growth and urban development, posing challenges for future water management infrastructure at high economic costs (Heathwaite 2010). In developed countries a substantial reduction in water consumption and the magnitude of individual P use is required to protect future water quality.

1.7 Reducing Sources of Phosphorus Pollution to Aquatic Systems

Historically, a logical focus on the more economic and achievable control of P point sources has been followed (May et al. 2012; Moss et al. 2011). Increase in P stripping in wastewater treatment by chemical and enhanced biological P removal has resulted in significant reductions of P in effluent (Brandes 1977; Morse et al. 1998; Mullan et al. 2006; Berretta and Sansalone 2012). Tertiary P stripping treatment has now been introduced into all STW in North Western Europe serving greater than 10^4 population equivalents, with an aim to reduce SRP effluent concentration to less than 2.0 mg P l^{-1} (Neal et al. 2005). The increasing sophistication in the treatment of both sewage and industrial effluents has reduced the relative importance of point source P pollution across much of Europe (Kristensen and Hansen 1994).

In contrast to point sources, diffuse sources of P can be difficult to identify as they enter waters at multiple sites and their delivery is controlled by numerous environmental factors (Heckrath et al. 2007; Heathwaite et al. 2005; Schippers et al. 2006; Shigaki et al. 2007). This can make apportionment of P sources and enforcement of sustainable management policy difficult (Ærtebjerg et al. 2003). Plans to reduce and control diffuse pollution are often expensive, complex and can take a long time to design and implement. Despite this, efforts to control diffuse P pollution through land management are increasing (Ulen and Kalisky 2005; Heathwaite et al. 2005; Liu et al. 2013).

There is now growing concern that the cumulative magnitude and persistent delivery of SRP from PSS may be significantly increasing the risk of rural waters to eutrophication (Foy et al. 2003; May and Dudley 2007; Withers et al. 2011). This is especially relevant in summer months when ecological sensitivity is highest and the dilution capacity of rivers is lowest (Foy et al. 2003; Macintosh et al. 2011).

1.8 Private Sewage Systems and Treatment Levels

Properties in areas where connections to municipal sewage systems are not available must rely on PSS to treat their wastewater (Withers et al. 2012). The most common PSS system consists of a septic tank (i.e. primary treatment system) and a soakaway (i.e. soil adsorption system) (Moore 2000). The tank is often made of concrete or fibreglass and is buried beneath the ground. The main purpose of the septic tank is to remove solids from wastewater, before it drains into the soakaway. In the soils of the soakaway, clarified effluent is filtered and treated. Removing solids from the wastewater is important to ensure the soakaway does not clog causing system failure. To remove solids, septic tanks must hold wastewater for a minimum of 24 hours to allow solids to sink (making up a sludge layer at the bottom of the tank) and settlable solids float (solids with a high oil or fat content float to the surface making a scum layer) (Figure 1.7). Around 50% of the solids decompose within the tank, although if too much sludge builds up within the tank, wastewater retention time within the tank is reduced and solids may escape into the soakaway (Moore 2000). To prevent this, septic tanks must be periodically desludged (i.e. sludge must be emptied from the tank). The interval between desludging depends on the capacity of the tank, flow of wastewater and the volume of solids within the wastewater (Moore 2000).

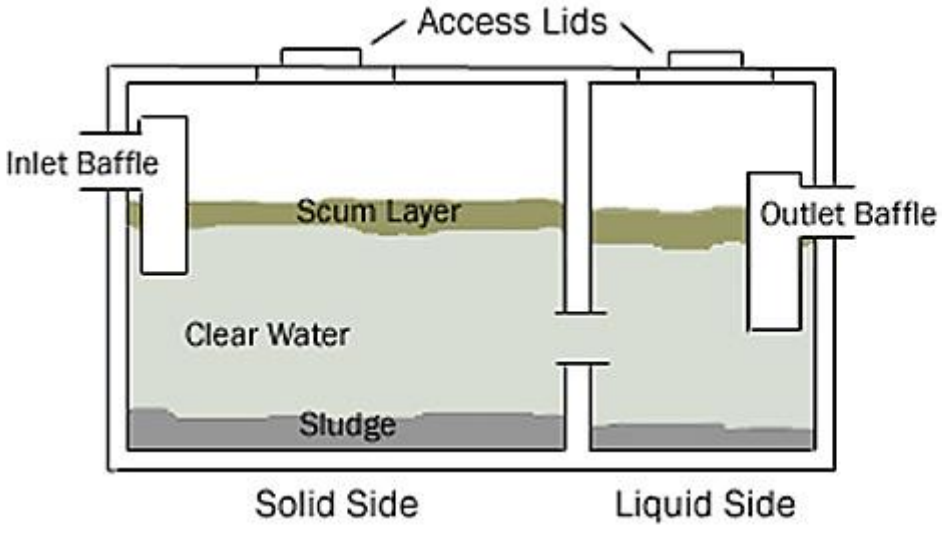


Figure 1.7 Cross section of septic tank, showing scum layer at the surface and sludge layer at the bottom of the tank (courtesy of www.aoseptic.com).

PSS may consist of further mechanical and chemical treatments (i.e. secondary and tertiary systems). The treatment levels of PSS outlined by SEPA (2011) are as follows:

- **A PSS with primary treatment is considered to have a septic tank only.** This allows the settling of solids and flotation of oils and greases, allowing the septic tank liquor to pass out into the leach field or soakaway. The volume of liquid in septic tank should remain the same; therefore pouring a litre of liquid down the drain will cause a litre of septic tank liquor to discharge into the soakaway. In Scotland, direct discharge of PSS effluent into water courses is allowed in exceptional circumstances which include a minimum dilution of >400:1 into receiving waters at the 95 percentile of river flow (SEPA 2011).

- **PSS with secondary treatment have mechanical treatment or discharge to wetlands or reed beds.** Mechanical sewage treatment systems include biological filters, rotating biological contactors, biological aerated filters, activated sludge plants or sequencing batch reactors. Discharge of effluent into constructed reed beds and wetlands is considered a passive form of secondary treatment. Combining both mechanical treatment with passive treatment would be considered a tertiary system (SEPA 2011).

- **A PSS is considered to have tertiary treatment if secondary treated effluent is further treated with a biological or chemical treatment of the following**; biological treatment to oxidise ammonia, disinfection plant or filtration plant such as sand filters, drum filters and membrane systems, designed to remove fine particulate solids. Chemical dosing of secondary treated effluent to remove P, commonly using the P binding properties of cationic divalent metal forms of iron, calcium and magnesium (SEPA 2011).

1.9 Phosphorus Pollution from Private Sewage Systems

It is estimated that 26% of the properties in Europe (Williams et al. 2012), 25% of the properties in the US (US EPA 2002b) and 20% of the properties in Australia (Beal et al. 2005) are served by PSS. When operating correctly, PSS offer an effective way of processing sewage but, if poorly installed or managed, the effluent from PSS can be a potential source of nutrients to freshwater bodies, particularly P, increasing their vulnerability to eutrophication (Ahmed et al. 2005; Arnscheidt et al. 2007; Withers et al. 2013). Recent studies estimate that 80% of the 1.5 million PSS in the UK are potentially working inefficiently with respect to P losses (Selyf-Consultancy 2002; Kirk et al. 2003). In the US one in four homes are served by a PSS. These 26.1 million properties contribute the largest volume of waste water (3.6 10^2 GL year^{-1}) to ground waters (USEPA, 2002a). The proportion of PSS failing to work correctly has been estimated in 28 states in the US and ranges from 0.4 to 70% and, although the definition of ‘failure’ varies between state, most include blockage, flooding and surface and ground water contamination (Nelson and Dix 1999).

Effective river basin management, as outlined in the Water Framework Directive (WFD) (EU 2000), requires an accurate estimation of contributions made by different P sources within the catchment and, where necessary, plans should be developed to address these sources (Edwards and Withers 2008). In properly functioning PSS, TP leaching from a PSS per person has been estimated to range between 0.24 to 0.40 kg TP yr^{-1} (Foy and Lennox 2000), whilst a conservative approximation of 0.63 to 072 kg TP person yr^{-1} has been estimated for residencies that discharge effluent directly into rivers (Pieterse et al 2003). In catchment scale TP export calculations, PSS are rarely accounted for separately (Wood et al., 2005; White and Hammond, 2006) and, if they are, they are represented by simplified export coefficients (Smith et al. 2005). These approaches may underestimate the impacts of PSS on P load to freshwaters and have limited use at a site specific level (May and Dudley, 2007).

A significant issue in monitoring P discharges from PSS is the lack of data on their location and state of repair (May et al. 2010; Withers et al. 2013) and limited research regarding the impacts of PSS on P concentrations in rivers and lakes has been reported in the literature. Despite this, in some UK rural catchments the net P contribution made to water bodies by PSS has been estimated (May and Dudley 2007), ranging from 3% in Llyn Tegid, Wales (Milliband 2002), to between 40 and 76% in Black Beck, North

England (Hall 2001) (Table 1.3).

Table 1.3 The net TP contributions made to water bodies by private sewage systems in rural catchments of Ireland and the UK.

Water body	Estimated P load from private sewage systems (tonnes yr^{-1})	Proportion of external P load attributable to private sewage systems (%)	Reference
Llyn Tegid, North Wales, UK	4.60	3%	Milliband *et al* (2002)
Lough Conn, West Ireland	1.58	5%	McGarrigle & Champ (1999)
Loch Leven, South East Scotland, UK	1.50	10%	Frost (1996)
Loch Leane, , South Ireland	1.50	12%	KMM & Pettit (2000)
Bassenthwaite Lake, North England, UK	2.30	14%	May *et al* (1996)
Loch Flemington, North Scotland, UK	0.02	18%	May (2001)
Loch Ussie, North Scotland, UK	0.03	22%	May and Gunn (2000)
Black Beck River, into Esthwaite Lake, North England, UK	0.25	40 - 76%	Hall (2001)

Spot sampling conducted in English rivers downstream of PSS have indicated increases of up to 700% in TP concentrations, with impacted concentrations of 0.4 mg P l^{-1} being reported (May et al. 2010). A study by Jordan et al. (2007) using high frequency river sampling within a 5 km^{2} Irish rural sub-catchment that had no obvious industrial or municipal point sources, indicated a chronic TP base-flow transfer between 0.25 and 0.50 mg P l^{-1}. These sources were later identified as pollution from PSS by Arnscheidt et al. (2007) by using indicators of faecal contamination in sediments and the observed positive correlations between in stream SRP concentrations and boron (B) (a marker of detergents) and in stream TP and the density of poorly maintained PSS. Pollution from these PSS were maintaining eutrophic conditions in the river during summer months (Arnscheidt et al. 2007; Jordan et al. 2007).

These studies show that the more important features of PSS P pollution may not be the magnitude of the P load, but its persistent delivery throughout the year (Withers et al. 2011; Jordan et al. 2007). The most bioavailable P form, SRP, is commonly found in high concentrations in effluent from STW and PSS effluent (Jarvie et al. 2006; Palmer-Felgate et al. 2008). It has been proposed that sewage is the primary source of SRP to ground waters (Jarvie et al. 2006; Jarvie et al. 2008). In summer months when low river flows reduce diluting capacity and ecological growth is greatest, the persistent delivery of SRP from PSS may represent a much higher eutrophication risk (Macintosh et al. 2011; Withers et al. 2011).

The impact of PSS pollution on proximal waters is site specific. Variation in the transport of P from PSS is attributed to the chemical adsorption capacity and physical texture of the soils to which the PSS discharge (unless delivered directly to the stream), as well as local hydrology, soil microbiology and the slope and distance to proximal water courses (Childs et al. 1974; Rea & Upchurch 1980; May & Dudley 2007; Beal et al. 2005). It has been assumed that the treatment type of the PSS (discussed in 1.9.1) effectively reduces P concentration of PSS effluent (Loch Leven Special Protection Area and Ramsar Site 2011), although, the validity of the assumption is examined later in this thesis.

1.9.1 Policies Regarding Phosphorus Pollution from PSS

Whilst there is a potential need to make significant reductions in P discharge from PSS, there is little legislation or guidance at a design or installation level to address this, and little regulatory control over their discharge (Withers et al. 2013).

PSS can only be sold in Europe if they have the E.U. Standard for PSS design (E.U. Standard (EN12566-1-7:2000)), although this standard does not stipulate any requirement that the design should control effluent P concentrations. Similarly, the UK Building Regulations 2010: drainage and waste disposal (HM Government 2010b) and the Building Standards (Scotland) Act 2003 (Scottish Government 2003) do not consider P removal in the guidelines for PSS installation. Individual homes connected to PSS do not need a discharge permit under the USEPA National Pollutant Discharge Elimination System (NPDES) permit program (US Goverment 2002). Although US regulations for PSS are considered the responsibility of the local state (Nelson &

Shephard 1998), only 10 states currently have regulations that mention P removal from PSS, and only 7 translate these into local plans (SORA and NESC 2012).

Under the revised Groundwater Directive (Directive 2006/118/EC), discharges from PSS are no longer exempt from groundwater protection legislation. To reflect this, regulations introduced in 2010 outlined a need for registration of PSS in England and Wales and environmental permits for those located in areas vulnerable to groundwater pollution (Bennett 2011). In England there is still debate over legislation surrounding PSS and their registration, and environmental permits for PSS are not compulsory. In contrast, in Wales, registration of PSS is legally required. In Scotland, under The Water Environment (Controlled Activities) (Scotland) Regulations 2011, owners are obliged to register their PSS with the Scottish Environment Protection Agency (SEPA), although this is only legally imposed if the property is to be sold.

The need to control P discharges from PSS has been recognised in some local development policy. The Building Regulations 2010 in Ireland (Irish Government 2010) provide an expected maximum discharge concentration of 2 mg P l^{-1} for PSS in nutrient sensitive areas. In the nutrient sensitive catchment of Loch Leven, in East Scotland, a development policy has been introduced outlining mitigation of P from PSS associated with new developments (Loch Leven Special Protection Area and Ramsar Site 2011). In general, a reliance on technological solutions (i.e. treatment level) to provide low P output from PSS has been adopted in these policies.

1.10 Water Policy

The Water Framework Directive (2000/60/EC) (WFD) is the most significant EU legislation for water management in the last 20 years (Scheuer 2000). Water legislation between 1976 and 1991 was structured around a number of fragmented directives (i.e. Urban Wastewater Directive (91/271/EEC), Bathing Waters Directive (76/160/EEC), Nitrates Directive (91/676/EEC) and the Dangerous Substances Directive (76/464/EEC)). These directives placed legal control limits and environmental quality standards on point source discharges, but did not protect aquatic ecosystems as a whole (Scheuer 2000). In 2000, the implementation of the WFD combined six directives and one regulation, with new legislation to form a single holistic policy for environmental water management across the EU.

The WFD introduced river basin level management; by dividing member states into river basins and giving responsibility of water management to one competent authority (OJC 2000). In Scotland this authority is SEPA. By integrating water quality, water resources, aquatic ecology, physical habitat and flooding, river basin management plans (RBMPs) must meet the following (Article 4 EC/2000/60/EC):

- Prevent further deterioration in the status of surface and ground water bodies.
- Protect, enhance and restore all bodies of surface and groundwater to a ‘good’ ecological status by 2015 (now derogated to 2027) (discussed in further detail in Section 1.10.1).
- Prevent or limit the input of pollutants to groundwaters and reverse any significant and sustained upward trends in the concentration of pollutants in groundwaters.
- Comply with European wide measures against priority and priority hazardous substances.
- Achieve compliance with any relevant standards and objectives for protected areas.

In the US, the equivalent legislation to protect waters is ‘The Clean Waters Act’ (CWA) and is considered the primary federal law in the US for controlling water pollution (US Goverment 2002). As the CWA does not directly relate to groundwater pollution the ‘Safe Drinking Water Act’, the ‘Resource Conservation and Recovery Act’ and ‘The Superfund Act’ work to support the CWA in protecting water quality.

The CWA outlines water quality standards (WQS), these are the allowable maximum concentrations of pollutants that will sustain healthy waters and are site specific. WQS are set by each state and are dependent on what the designated use of the water body is (e.g. water supply, agriculture, aquatic life) (US Goverment 2002). Each designation carries with it a specific set of pollutant concentration levels which must not be exceeded. Water bodies that do not meet their WQS are assigned a total maximum daily load (TMDL) for each pollutant (US Goverment 2002). A TMDL is the maximum amount of a pollutant the water body can receive and still meet its WQS. A management plan, (similar to RBMP within the EU), is then implemented to reduce pollutant inputs to meet the requirements of each TMDL until the water bodies designated WQS are reached (US Goverment 2002).

1.10.1 Current Status of Water in the UK

Under the WFD, water bodies are categorised as groundwater, rivers, lakes (i.e. lochs), transitional waters (i.e. estuaries) and coastal water bodies. Ecological status is used to describe the health of their ecosystems, in the categorical terms of, ‘high’, ‘good’, ‘moderate’, ‘poor’ and ‘bad’. The ecological status of a waterbody comprises of an assessment of general physicochemical quality elements (e.g. phosphorus, nitrogen, dissolved oxygen), assessment of water flow and water levels and the physical structure and condition of the waterbody (UK TAG 2008).

By 2015, the WFD requires all water bodies of EU member states to achieve a ‘good’ or higher status. The standards for P concentration outlined by the WFD vary dependent on the type of waterbody, its alkalinity (mg $CaCO_3$ l^{-1}), altitude (under or over 80 m), and is a measure of SRP concentration (UK TAG 2008). For example a river > 80 m, with an alkalinity < 50 mg $CaCO_3$ l^{-1}, must have an SRP concentration below 50 µg P l^{-1} to achieve ‘good’ status (UK TAG 2008). There is debate about whether these concentrations are too high (UKTAG 2012). The current status of waters within Scotland, under the WFD criteria, are summarised below in Table 1.4.

Table 1.4 Status of waterbodies in Scotland in 2009, as defined under the guidelines of the Water Framework Directive (based on SEPA status criteria http://gis.sepa.org.uk/rbmp).

Ecological Status	Rivers		Lochs		Estuaries		Coastal Waters		Groundwater	
Water Quality	Number	Area (km^2)	Number	Area (km^2)	Number	Area (km^2)	Number	Area (km^2)	Number	Area (km^2)
High	1,042	10,585	104	279	23	244	241	34,620	n/a	n/a
Good	557	5,621	117	349	11	228	203	11,054	215	55,267
Moderate	350	3,923	79	315	6	134	5	121	n/a	n/a
Poor	56	611	12	12	0	0	0	0	69	11,301
Bad	8	77	3	5	0	0	0	0	n/a	n/a
Totals	2,013	20,817	309	960	40	606	449	45,795	284	66,568
Percentage good or high	79%	78%	72%	65%	85%	78%	99%	99%	76%	83%

In 2009, of the total rivers not achieving a ‘good’ or ‘high’ status in Scotland, the greatest cause was anthropogenic pollution (18%) (SEPA 2009).

Sewage discharge and agriculture is expected to be the main source of P to these impacted rivers and, although in many catchments within Scotland there was no trend in total P concentration during the 30 year period under assessment, in the central belt, south and north-east Scotland there was decreasing loading to rivers (Anderson et al. 2010). It is suggested this is due to improvement in sewage and urban wastewater treatment. In Northern Scotland river TP concentration levels generally increased, maybe due to population growth providing greater sewage discharge through poorly managed PSS, increased agriculture, manure and fertiliser or unknown factors (Anderson et al. 2010).

A report by White & Hammond (2006) estimated annual TP and SRP load to rivers across England, Wales and Scotland by combining inventories of industrial point sources with estimated diffuse P loads (calculated with specific export coefficients for land use, human population, livestock density and atmospheric deposition). The estimated annual TP load to English, Welsh and Scottish fresh waters is estimated to be in the region of 41.6 kt TP yr^{-1}. Using TP:SRP ratios, it was further estimated that 21.1 kt of this was in the form of SRP. Households were estimated to contribute 68.70% and 67.40% of TP and SRP to British rivers, respectively (Figure 1.8).

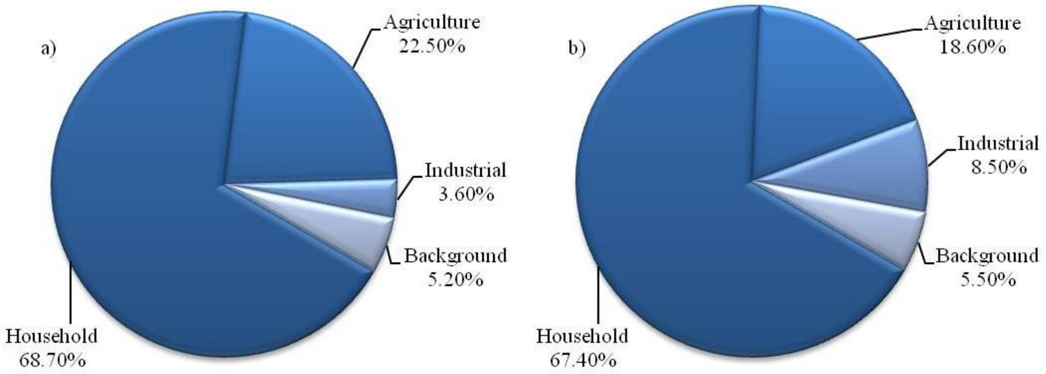


Figure 1.8 a) Annual total phosphorus (TP) load and b) soluble reactive phosphorus (SRP) load to rivers in England, Wales and Scotland (Adapted from White and Hammond 2006).

1.11 The Phosphorus Footprint

To be able to reduce a pollution source we need to be able to measure its magnitude. Life cycle assessment (LCA) is the most commonly used tool to estimate environmental impacts caused by products and processes (ISO 1997; ISO 2006a) (Reap et al. 2008a). To allow accurate comparison between different LCA, a well understood method to calculate their magnitude must be in place. The method must clearly define system boundaries, the assumptions that were made, data sources and uncertainties as well as provide transparency throughout the assessment process. This is of increasing importance as we enter a time where policy and economic decisions are often based on LCA analysis which can often contain large uncertainties (Weber et al. 2010).

The International Standards Organisation (ISO) Life Cycle Assessment framework provides a standard assessment method for stakeholders wishing to estimate the size of environmental impact of a product or process. The LCA has four phases; goal and scope definition (ISO 1998); life cycle inventory analysis (ISO 1998; ISO 2006); life cycle impact assessment (ISO 2000a); and life cycle interpretation (ISO 2000b). Despite the rapid growth in the use of LCA, it is a tool that has multiple problems within each of its four phases causing reductions in accuracy (Reap et al. 2008a; Reap et al. 2008b). The most critical causes of LCA inaccuracy lie in functional unit definition, boundary selection and allocation (Reap et al. 2008a) and local environmental uniqueness and spatial variation (Reap et al. 2008b).

The term ‘footprint’ is often used to describe an LCA with user defined boundaries, such as the ‘carbon footprint’ (an LCA with analysis limited to emissions that affect climate change) and the ‘water footprint’ (an LCA with analysis limited to the amount of water used). A criticism of the ‘carbon footprint’ has been that a lack of definition in its conceptual stages has caused the term to become ambiguous and has resulted in its diminished descriptive strength (Wright et al. 2011).

In the following work the term ‘P footprint’ is used although it assesses only ‘household P emissions of an individual’ which is only part of the human P footprint. The total P footprint of an individual would include calculating the magnitude of every P flow in the global human P cycle (as defined in Figure 1.2), allowing a final calculation of the total amount of P that had been extracted from the lithosphere to support that individual’s lifestyle requirements. In the following work an individual’s contribution is assessed to the rate at which P is emitted from the technosphere to the ecosphere (K_{em}), which is determined by P accumulation within the technosphere (T_{acc}) (Figure 1.2).

To reduce the P output to the ecosphere, domestic P emissions must be minimised. This is important not only to limit damage to freshwaters, but also to ensure P is not wasted, as an essential resource in its own right (Cordell and White 2011). PSS capture the wastewater P output of a property, and therefore provide an experimental unit that can be used to study how specific behaviours can impact domestic P emissions. This thesis focuses on understanding the physical and technical operation of PPS to underpin an assessment of individual human P emissions, and the behaviours that may be modified to reduce them.

Increasing pro-environmental behaviour of PSS users (behaviour that causes minimal damage or even benefits the environment (Steg and Vlek 2009), could potentially offer significant reduction in P discharge from PSS by 1) reducing *P input* to the PSS through modifying domestic behaviour, and 2) reducing *P output* from PSS by improving maintenance of the PSS, to reduce system failure (Figure 1.9), and ultimately reduce the human P footprint.

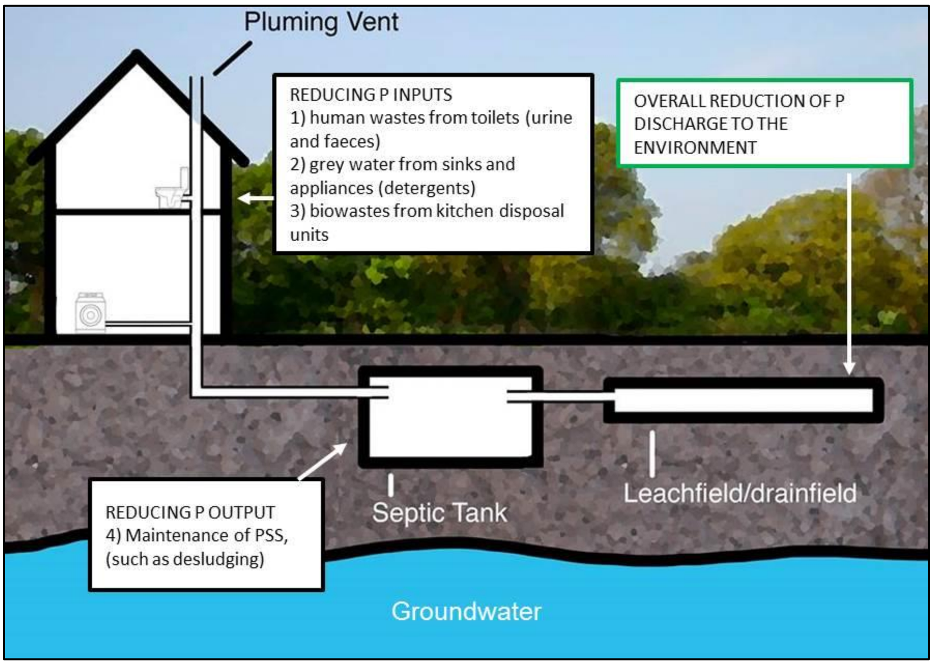


Figure 1.9 Diagram showing phosphorus sources and behaviours associated with private sewage systems.

1.12 Behavioural Change; Is Ecological Deterioration 'Psychology's Problem'?

Ecological deterioration is a problem conceptualised by an expanding population with an increasing consumption and demand for resources (e.g. water, food, energy). Maloney & Ward (1973) argue that when viewed like this technological solutions (such as increasing treatment type of PSS to reduce P discharge) are futile, and propose that solutions do not lie in traditional technological approaches but rather in the sciences that deal with modifying population behaviour, and therefore ecological deterioration is uniquely 'psychology's problem' (Maloney & Ward 1973).

The impact of human behaviour on the P discharge from PSS has not been previously examined, therefore when discussing determinants of behaviours, parallels with studies of other environmental behaviours have been made (such as recycling, water and electricity usage and waste disposal). To do this it is necessary to identify and model the controlling factors that underpin the related behaviours and to then explore ways in which such behaviours can be planned. The Comprehensive Action Determination Model (CADM) (Klöckner 2013) combines the leading behavioural models (as identified by (Sopha 2011)): these are the Theory of Planned Behaviour (TPB) (Ajzen 1991), the Norm-Activation Theory (NAT) (Schwartz and Howard 1981) and the Value-Belief-Norm Theory (VBN) (Stern 2000). These models offer the potential to identify the antecedents of related P flow behaviours, and use the results to better manage P emissions. Behavioural models are discussed in detail in Section 2.6.2.

1.13 Thesis Overview and Research Aims

It is apparent there is a pressing need to better understand and manage P flows from the technosphere to the ecosphere in order to reduce eutrophication of water bodies globally. It is proposed here that it is necessary to identify the role that individuals play in their daily lives in the delivery of P to the aquatic environment, before addressing the challenges of reducing the related P pollution at the ecosystem level. As PSS conveniently capture the wastewater P output from housing, they provide the opportunity to derive an experimental model that can be used to assess the impact different domestic behaviours have on domestic P output. Furthermore an assessment of the efficiency of different PSS designs to manage P outputs and the potential they offer to reduce them, can be conducted. To do this it was necessary to identify a suitable catchment area. The Loch Leven catchment in East Scotland, UK, was chosen because of its long and well-documented history of nutrient pollution, catchment management and recovery from eutrophication (May and Spears, 2012a, 2012b; May et al., 2012) and because it is an internationally recognized site for scientific research that has developed the understanding of the links between pollution, climate change and ecological responses in shallow lakes (May and Spears 2012a).

The aims of this thesis are to:

1) Review and measure P outputs from PSS in the chosen research catchment of Loch Leven.
2) Assess the impact of human behaviours on the quality and quantity of P compounds in PSS effluent within the catchment.
3) Review and evaluate the relative merits of local policies and strategies to regulate PSS P pollution within the catchment, in relation to evidence gathered for this thesis on the efficacy of both technical and behavioural solutions for reducing the human P footprint.

Reducing the P footprint of the individual is a multidimensional problem and therefore requires a multidisciplinary approach. The following thesis uses a combination of policy assessment, water chemistry, nuclear chemistry and human behavioural psychology.

The methodologies used to address the research aims were:

1) Colorimetric spectroscopy used to measure P concentrations of PSS effluent to answer Aim 1
2) ^{31}P nuclear magnetic resonance (NMR) spectroscopy used to assess the composition of P compounds in PSS effluent, to answer Aim 1 and 2
3) Assess human behaviours of PSS users using questionnaires, to answer Aim 2
4) Policy review using collected data, to answer Aim 3

The layout of the thesis, the hypotheses proposed for each chapter and a brief summary of the conclusions for each chapter are provided in Figure 1.10:

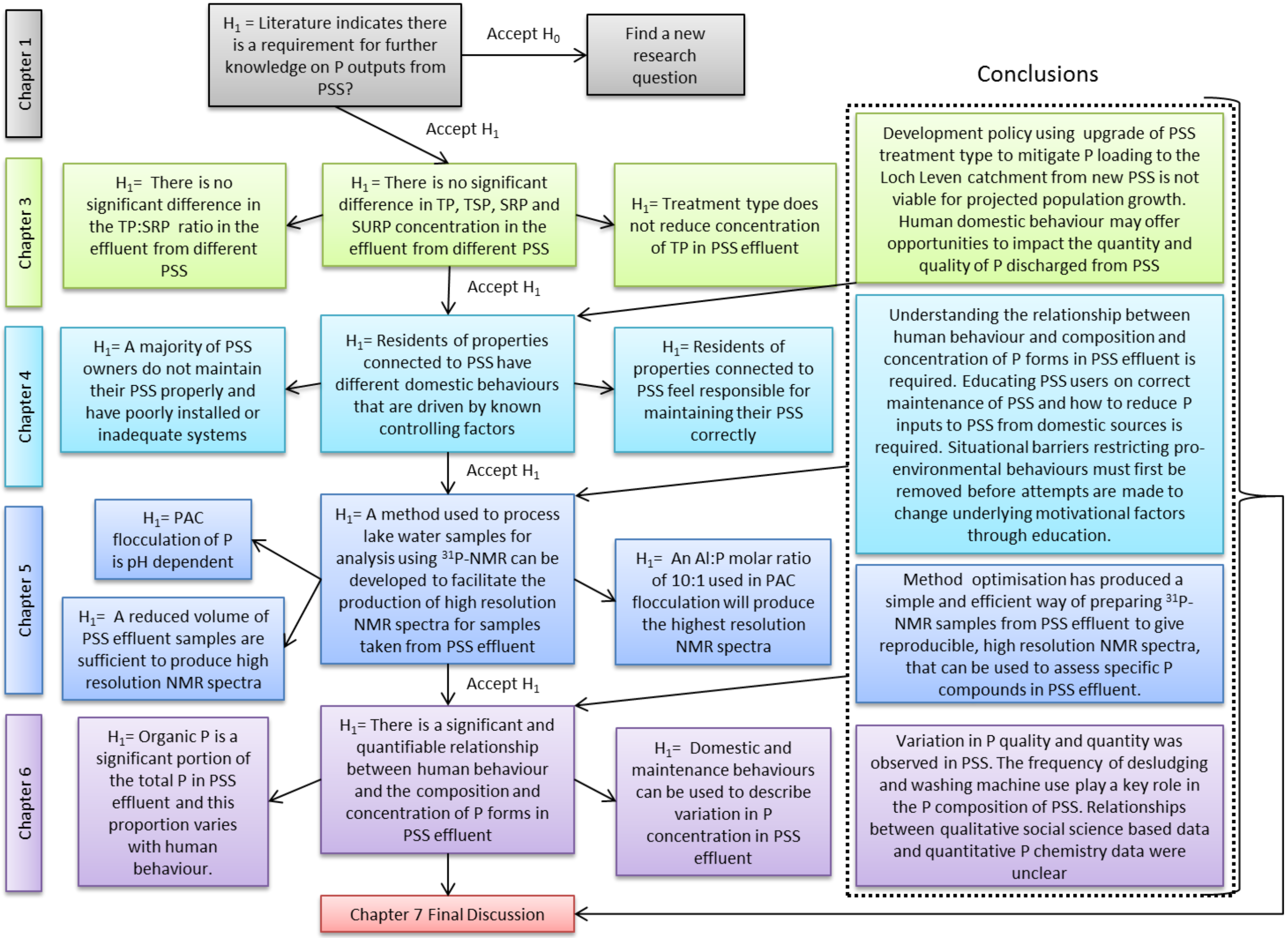


Figure 1.10 Thesis structure showing hypothesis and conclusion summary for results Chapters 3-6.

Chapter 2 Materials and Methods

2.1 Introduction

This chapter outlines the methods used in this study. In each of Chapters 3 to 6 a 'Materials and Methods' section is included that may refer to numbered sections in this chapter, whilst providing further details regarding experimental design, sampling frequency and/or the level of replication used that are specific to that chapter. A detailed preparation method for reagents and solutions mentioned in Chapter 2 is provided in Appendix A.

2.2 Site Description

Loch Leven is located to the east of Kinross, in East Scotland, UK (56^0 12'N, 3^0 22'W; altitude 107 m) (Figure 2.1). It is the largest shallow Loch in the Scottish lowlands, with a surface area of 13.3 km^2, and a mean and maximum depth of 3.9 m and 25.5 m, respectively.

Figure 2.1 Loch Leven aerial photograph, courtesy of Google Earth.

The Loch is internationally renowned for its brown trout fishery (May & Spears 2012) and as an important conservation area (May & Spears 2012), providing habitat to many waterfowl including *c*. 4000 tufted duck *(Aythya fuligula)* and 20,000 pink footed geese (*Anser brachyrhynchus)* (Carss et al. 2012). Due to its high conservation value, both nationally and internationally, it is recognised as a Site of Special Scientific Interest (SSSI), a Special Protected Area (SPA) (UK9004111), a Ramsar site (UK13033) and is part of the Natura 2000 network.

The surface water catchment of Loch Leven has an area of 145 km^2 that is dominated (80%) by agriculture (The Loch Leven Catchment Management Plan (LLCMP) 1999). To the south of the Loch, land is mainly used for grazing cattle and sheep, whilst to the north the prominent land use is arable cropping of turf, cereals and potatoes (D'Arcy et al. 2006). A population of 11,000 people live within the catchment (Frost 1996); with 60% living in the towns of Kinross, Milnathort and Kinnesswood, within properties served by mains sewerage (The Kinross Area Local Plan 2004). The number of properties not connected to mains sewerage is estimated to be 654 and, these properties are considered to be connected to private sewage systems (PSS). This figure was compiled by the Scottish Environment Protection Agency (SEPA), Scottish Natural Heritage (SNH), Perth and Kinross Council (PKC) and Scottish Water, using Ordinance Survey data to count the number of properties located in postcode areas not served by mains sewerage.

Loch Leven has a long and well-documented history of nutrient pollution, catchment management and recovery (May and Spears, 2012a, 2012b; May et al., 2012). Cyanobacterial blooms have had a direct impact on the ecology of the loch, its users and the local economy (Carvalho and Kirika 2005; Carvalho et al. 2008) (Figure 2.2). A severe single algal bloom in 1992 was estimated to cost the local economy around £1 million (LLAMAG 1993)

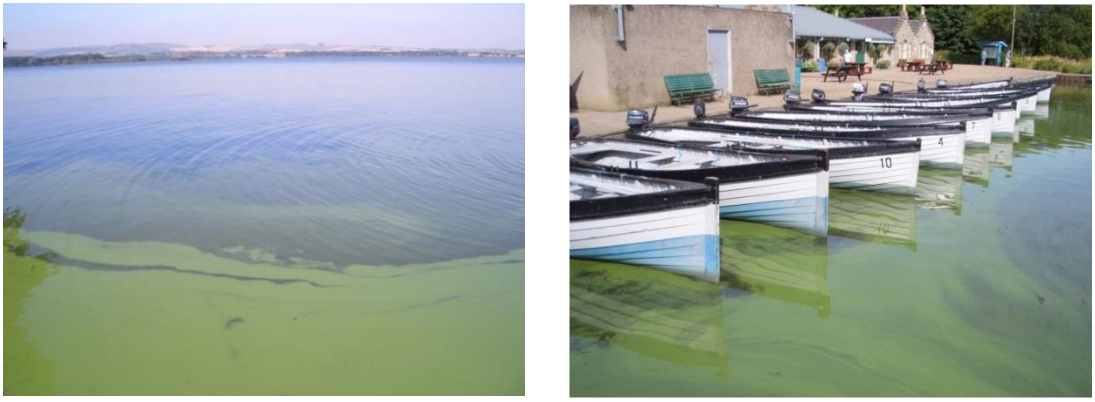


Figure 2.2 Cyanobacterial scums in Loch Leven, August 2007.

Catchment management in the 1980s to 1990s resulted in a significant (*c.* 60%) reduction in phosphorus (P) inputs to the loch. This was mainly due to reductions in P loads from sewage treatment works, industrial point sources and improvements in agricultural practices, leading to reduced diffuse P loading (May et al. 2012) (summarised in Table 2.1). This led to significant ecological improvements (Dudley et al. 2012), although ecological responses have been delayed as a result of sediment P release within the loch (Spears et al. 2011).

Table 2.1 Significant events that have reduced nutrient delivery to Loch Leven from its catchment (modified from Carvalho et al. 2004).

Year	Significant event
1973	Majority of effluent from the bleaching process from the woollen mill (located on the banks of Loch Leven) was no longer discharged into the loch and transported off-site for disposal
1985	External load measured as 20.11 t TP year^{-1} (Bailey-Watts and Kirika 1987)
1989	Discharge from the Woollen mill ended (*c.* 6.29 t TP year^{-1} reduction)
1993	Effluent from Kinross South sewage treatment works (STW) re-directed to the upgraded Kinross North STW (*c.* 1.70 t TP year^{-1} reduction)
1995	Phosphorus stripping procedures implemented at Milnathort STW (*c.* 0.59 t TP year^{-1} reduction)
1995	External load measured as 7.99 t TP year^{-1} (Bailey-Watts and Kirika 1999)
1997	Sewage from Kinnesswood STW diverted out of the catchment (*c.* 0.55 t TP year^{-1} reduction).
2005	Current measurement of TP load to Loch Leven is 7.69 t TP year^{-1} (Defew 2008)

The long term monitoring programme at Loch Leven initiated in 1967 (May and Spears, 2012a) has been facilitated by a unique and effective cooperation between researchers, policy makers and stakeholders, making it an internationally important research site (May and Spears, 2012a). Central to the success of the improvements in water quality at Loch Leven has been the LLCMP (1999), which was based on empirical relationships between P concentrations in the lake and water quality indicators.

The estimated amount of P entering the loch in 2005 was 7.69, 3.57, 2.68 and 4.11 tonnes of total phosphorus (TP), total soluble phosphorus (TSP), soluble reactive phosphorus (SRP) and particulate phosphorus (PP), respectively (Defew 2008). To restore ecological health in Loch Leven, the Loch Leven Area Management Advisory Group (LLAMAG) set water quality targets for the Loch water of 40 µg P l^{-1} (LLAMAG 1993), since then more stringent targets have been set under the WFD (EU 2000) and the new UK standards for TP for supporting 'good ecological status' under the WFD (UK TAG 2008). In 2007 and 2008, annual mean TP concentrations in Loch Leven were below the 40 µg P l^{-1} target as outlined in the LLAMAG (1993), placing Loch Leven at the UK TAG (2008) good/moderate boundary as defined in the WFD. Although encouraging, Carvalho et al. (2011) suggest extremely wet summers in 2007 and 2008 may have, in part, contributed to this reduction in TP concentrations.

2.3 Effluent Sample Collection from Private Sewage Systems

A particularly challenging and constraining feature of this study was locating suitable PSS that could be sampled easily and regularly. Sites used were those provided by volunteer residents of the Loch Leven catchment. In Chapter 3, details are given of samples that were collected from 7 PSS identified by volunteers enlisted through door to door request. For Chapters 5 and 6, 10 PSS were sampled; provided by volunteers enlisted by a written request that was added to the end of a questionnaire that was delivered to 654 properties believed to be served by PSS in the Loch Leven catchment (the details of which are provided in Chapter 4). A detailed sampling regime and description of each PSS is provided in the relevant chapters.

For Chapter 3, samples were collected in 250 ml PVC sample bottles previously cleaned with 10% hydrochloric acid and rinsed 6 times with distilled water. Samples were taken from the last or only settling tank of each PSS, accessed by opening their hatch and lowering a sample tube attached to a rod 60 cm below the surface to avoid collection of surface scum.

For Chapter 5, 0.5 l and 5.0 l effluent samples were collected, for Chapter 6, only 0.5 l effluent samples were collected. Effluent samples were taken from the last or only settling tank of each PSS, accessed by opening the inspection hatch and lowering a tube connected to a hand siphon pump into the tank. The tube was attached to a rod to ensure it was held 60 cm below the surface to avoid collection of surface scum. For samples collected in Chapter 5, septic tank liquor was siphoned into 5.0 l and 1.0 l collection bottles, for Chapter 6, only 1.0 l collection bottles were required. Sample bottles, hand pump and tubing were previously cleaned with 10% hydrochloric acid and rinsed 6 times with distilled water between each sample collection.

Discharge pipes from the final tanks of all PSS were buried underground making them inaccessible for sample collection. Hence P concentrations reported are ‘in tank’ concentrations; these systems are assumed not to leak and it is therefore considered that the samples closely resemble P concentrations of actual discharging liquor. Samples were transported to the lab in well insulated containers to maintain constant temperature and darkness. Once returned to the lab, samples were stored in darkness, at 4°C, until analysis, or further processing (in the case of NMR sample preparation).

2.4 Analysis of Samples for Different Phosphorus Forms

This project assessed P concentrations of raw effluent samples from PSS (in Chapters 3, 5 and 6) as well as samples at different stages during the P extraction procedure used to prepare samples for ^{31}P nuclear magnetic resonance (NMR) spectroscopy (in Chapter 5). To avoid repetition between chapters, a full description of the method used to analyse P concentration is provided in the following section.

2.4.1 Separation of Phosphorus Forms

P analyses used in this project involved two procedural steps; the conversion of the P forms of interest into orthophosphate (PO_4^{3-}), followed by colorimetric determination to ascertain orthophosphate concentration. The TP found in the water column can be separated into various forms that can be analytically defined for the purposes of interpretive analyses (Clesceri et al. 1998) (outlined in further detail in Section 1.4.1). TP is a measure of all the P in the sample and is composed of both particulate P (PP) and total soluble P (TSP) (Wetzel and Likens 2000). PP is an estimation of P associated with particles that do not pass through a 0.45 µm pore size filter; TSP is a measure of the soluble fraction within the sample and can be further subdivided into two categories for detailed analysis. These are soluble reactive P (SRP), which describes the bioavailable portion of dissolved P, predominantly orthophosphate, and soluble unreactive P (SURP), considered predominantly organic P.

2.4.2 Phosphorus Analysis

All samples were analysed for P concentration within 48 hours of collection. Samples for SRP and TSP analyses were filtered according to Murphy & Riley (1962), then stored with unfiltered samples for TP analysis, at 4°C in darkness. Filtration was carried out using Whatman® (GF/C) filter paper with a 0.45 µm pore size. Using this pore size may not completely filter out all fine colloidal particulate P (Clesceri et al. 1998), and some may still pass through and subsequently be hydrolysed under the acid treatment used in the colorimetric method (Sharpley 1997). This method is considered merely a gross and replicable way to separate P forms and is generally accepted to be a standard method for the separation of particulate and dissolved P forms. To ensure sample vessels were not contaminated all glassware used in the analysis steps were acid washed with 10% hydrochloric acid and then rinsed six times with distilled water before use.

All TP and TSP samples were analysed according to the methods outlined by Eisenreich et al. (1975). For TP, unfiltered 5 ml samples were first digested using potassium persulfate ($K_2S_2O_8$) acid hydrolysis digestion. This was achieved by adding 0.5 ml potassium persulfate and 0.1 ml of 30% sulphuric acid to the sample. The samples were then autoclaved at 121°C for 30 minutes. This effectively converts all soluble and particulate P into orthophosphate. The same digestion process was applied to filtered samples, allowing determination of TSP.

Analysis of SRP does not require any digestion or hydrolysis steps so samples can therefore be analysed immediately after filtration according to the methods of Murphy and Riley (1962). Colorimetric determination of orthophosphate in the sample relies on the reaction of orthophosphate with ammonium molybdate ($(NH_4)_6Mo_7O_{24}.4H_2O$) and potassium antimonyl tartrate (PAT) ($C_8H_4K_2O_{12}Sb_2$) in an acid medium (H_2SO_4). This reaction creates a yellow heteropoly acid-phosphomolybic acid complex which is reduced to a more stable complex by ascorbic acid ($C_6H_8O_6$) when in the presence of orthophosphate, producing an intense blue coloured solution. The intensity of this blue colour is proportional to the concentration of orthophosphate present in the sample, and can be measured using colorimetric spectrophotometry. P standards were used to produce absorbance readings at 882 nm for known standard P concentrations; a linear regression equation was then used to determine P concentrations in the samples of unknown P concentrations. To make P standards, a 100 mg P l^{-1} (PO_4-P l^{-1}) stock solution was first prepared by adding 0.2195 g of potassium dihydrogen orthophosphate (KH_2PO_4) to 500 ml of distilled water. Standard solutions of 50 µg P l^{-1}, 200 µg P l^{-1} and 600 µg P l^{-1} were then prepared using the 100 mg P l^{-1} stock solution at appropriate dilution volumes. All glassware was previously acid washed and thoroughly rinsed in distilled water to avoid contamination. Standards were stored at 4°C for up to one month.

Colorimetric analysis was conducted using a Varian Cary SoBio spectrophotometer (Varian, Inc. Palo Alto, CA. USA) and sample analysis was aided by a SPS-B auto sampler. The limit of detection was 3.0 µg P l^{-1}. The procedure for analysis of TP, TSP and SRP is summarised in Figure 2.3.

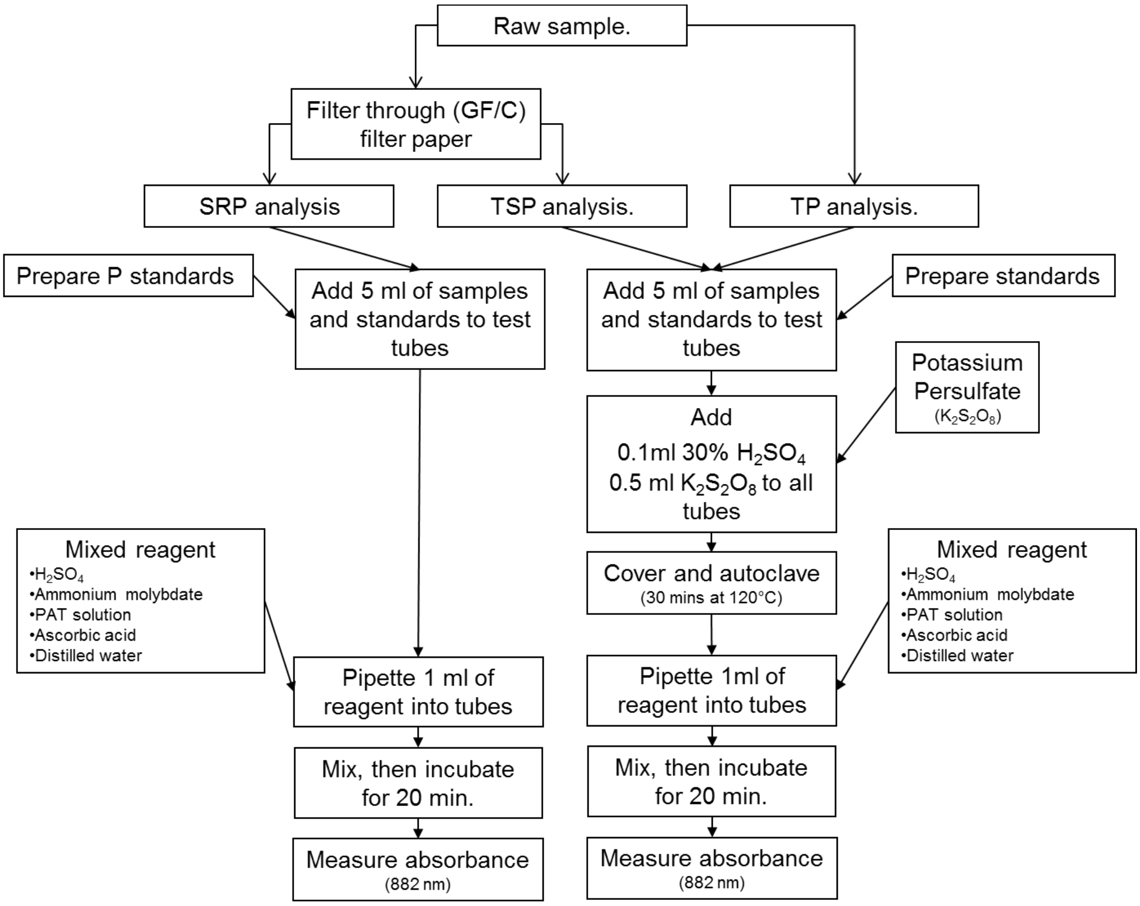


Figure 2.3 Procedure for the analysis of the concentration of total phosphorus (TP), total soluble phosphorus (TSP) and soluble reactive phosphorus (SRP), using colorimetric spectrophotometry.

2.5 Nuclear Magnetic Resonance Spectroscopy

This project assessed the composition of P compounds in raw effluent samples from PSS using solution ^{31}P NMR spectroscopy (Chapters 5 and 6). To produce high resolution spectra in solution ^{31}P NMR, the NMR sample must have concentrations of >100 mg P l^{-1} (Cade-Menun et al. 2005). As such the TP in each sample must be concentrated prior to analysis with NMR. To achieve this, P must be extracted from the sample, followed by a method of concentration, commonly lyophilisation (McDowell et al. 2008; Liu et al. 2013) or rotary vacuum evaporation (Ahlgren et al. 2006). A detailed account of the optimisation of the procedure used for sample preparation in this study is provided in Chapter 5. The following section outlines this optimised method, and was used to prepare the effluent samples for NMR analysis in Chapter 6.

2.5.1 Basic Principles of Nuclear Magnetic Resonance Spectroscopy

NMR spectroscopy has been used to identify nuclei that have magnetic properties due to an uneven number of neutrons and protons within their nuclei, such as ^{1}H, ^{13}C, ^{15}N ^{27}Al and ^{31}P (Kemp 1975). The spinning nuclei of these elements create a small magnetic dipole, analogous to a bar magnet (Cade-Menun et al. 2005). Once placed in a magnetic field these nuclei can be arranged in a low energy stable state, parallel to the magnetic field, or a high energy unstable state, perpendicular to the magnetic field (Kemp 1975; Cade-Menun et al. 2005). A radio frequency pulse will cause the nuclei to flip from low to high energy states; once the nuclei relax back to their low energy state, the energy absorbed is emitted (Cade-Menun et al. 2005). Due to electron cloud shielding of different compounds, different nuclei will emit signature emission signals. Compounds with less shielding require less energy to ‘flip’ and therefore produce a peak with a lower energy reading (for example polyphosphates emit higher energy signals than the less shielded nuclei found in phosphonates) (Cade-Menun et al. 2005). Peaks are therefore observed at different positions within the spectra. The strength of signal (and therefore size of the peak) can be used to give quantitative information on the proportional composition of compounds present, if the TP concentration of the raw sample is known (Reitzel et al. 2006). Spectra can be used to describe the type and ratio of P compounds present in the sample.

Seven groups of phosphorus compounds are readily detected within solution ^{31}P NMR spectra: phosphonate (phospho-P); orthophosphate (ortho-P); orthophosphate monoesters (mono-P); orthophosphate diesters, phospholipid P (PL-P) and deoxyribonucleic acid P (DNA-P); pyrophosphate (pyro-P), and polyphosphates (poly-P) (Ahlgren et al. 2007) (summarised in Figure 2.4).

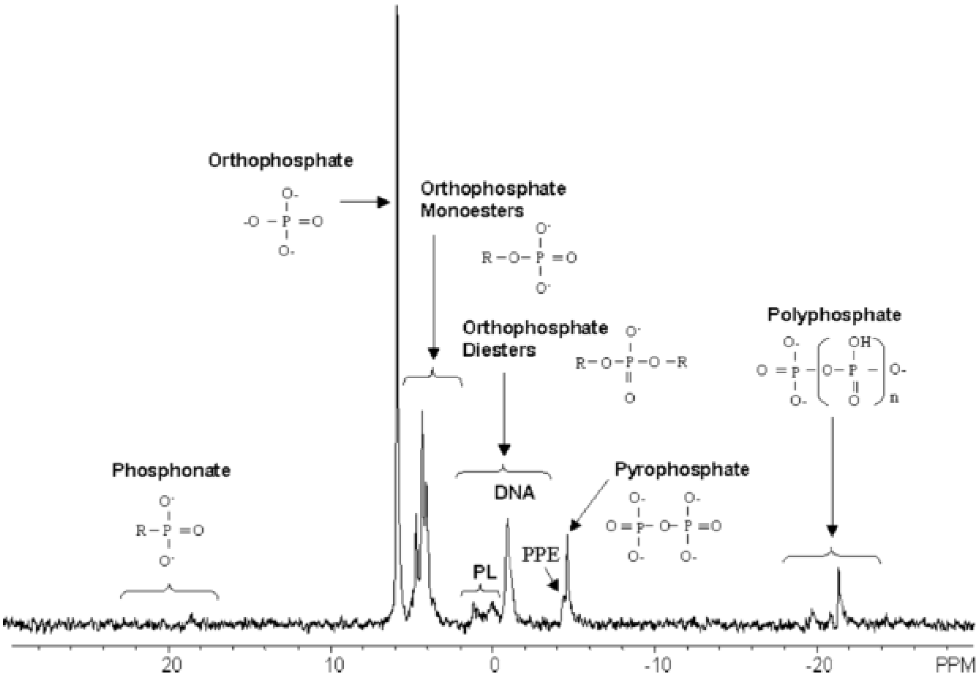


Figure 2.4 A solution ^{31}P NMR spectra of a forest floor soil sample, showing all phosphorus groups that can be identified (modified from Cade-Menun, 2005).

An expansion of the orthophosphate monoester region reveals peaks identified as the P groups of *myo*-inositol hexakisphosphate (commonly known as phytic acid), named according to Turner et al., (2003) (Figure 2.5).

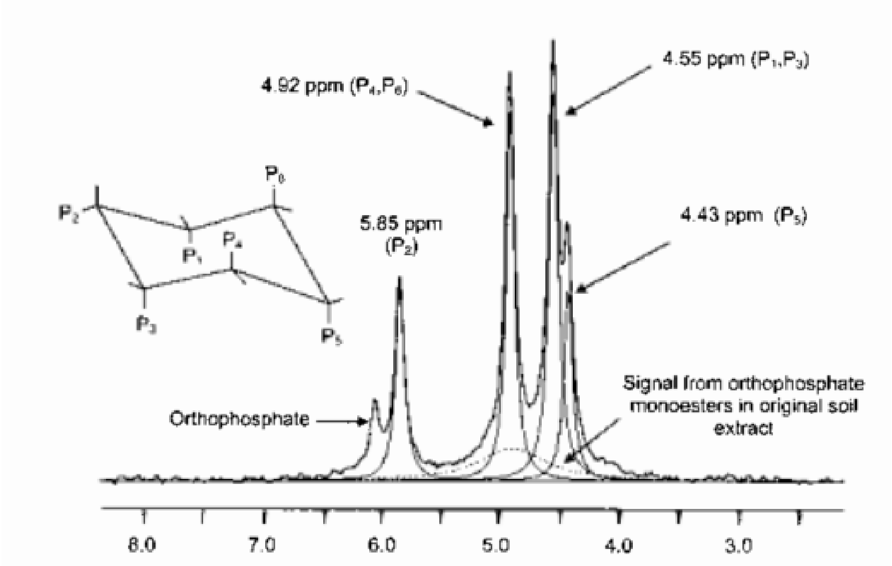


Figure 2.5 Plot showing an expansion of the monoester region of a solution ^{31}P NMR spectra with a myo-inositol hexakisphosphate standard added as a spike to an NaOH-EDTA soil extract. Peaks for phosphorus groups of myo-inositol hexakisphosphate are shown (figure taken from Turner et al. (2003).

2.5.2 Preparation of Effluent Samples for Analysis using NMR Spectroscopy

To extract P from PSS effluent, 0.5 l samples were first treated with PAX-18 (a poly aluminium chloride solution with an active substance of 26.98 g l^{-1}, Kemira™) at an Al:P molar ratio of 10:1, assuming an effluent TP concentration of 9.28 mg l^{-1} (based on the median TP concentration of 47 PSS effluent samples taken from seven PSS over five months, outlined in 3.2.2). Samples were then well shaken by hand for *c.* 5 minutes each, to ensure thorough mixing and aid flocculation. The pH was then adjusted to between 6.5 and 7.0 using 1 M NaOH and left in darkness and 4^{0}C for 12 hours with a yellow floc collecting at the bottom of the container (Stage 1, Figure 2.6).

As much 'residual' water ((B) Figure 2.6) was siphoned off as possible without disturbing the settled floc (*c.*250 ml), leaving the floc suspended in *c.* 250 ml of water (Stage 2, Figure 2.6). The floc was then decanted into 50 ml centrifuge tubes and centrifuged at 5000 g for 5 minutes to isolate the floc from any remaining water ((C) Stage 3, Figure 2.6). The supernatant ((C) Figure 2.6) was discarded and the pellets ((p) Figure 2.6) combined and dissolved into 50 ml of 1M NaOH and placed on over-end shakers for 17 hours (this process 'washes' the P compounds from the precipitate) (Stage 4, Figure 2.6). Tubes were then centrifuged again at 5000 g for 5 minutes, to remove any excess sediment (Stage 5, Figure 2.6). The supernatant of each tube ((D) Figure 2.6), now containing the TP, were then combined and further concentrated by vacuum rotary evaporation at 35°C until the samples were reduced to a volume of *c.* 5 ml ((E) and Stage 6, Figure 2.6). This highly concentrated 5 ml sample was then centrifuged at 5000 g (Stage 7, Figure 2.6) and 630 µl of the supernatant removed and added to 70 µl of D_2O and 50 µl 0.5 M ethylenediaminetetraacetic acid (EDTA) within a 5 ml NMR tube. Samples were stored at -18^{0}C until ^{31}P NMR analysis at a later stage (Stage 8, Figure 2.6). All NMR analysis was done with 31 days of sample collection.

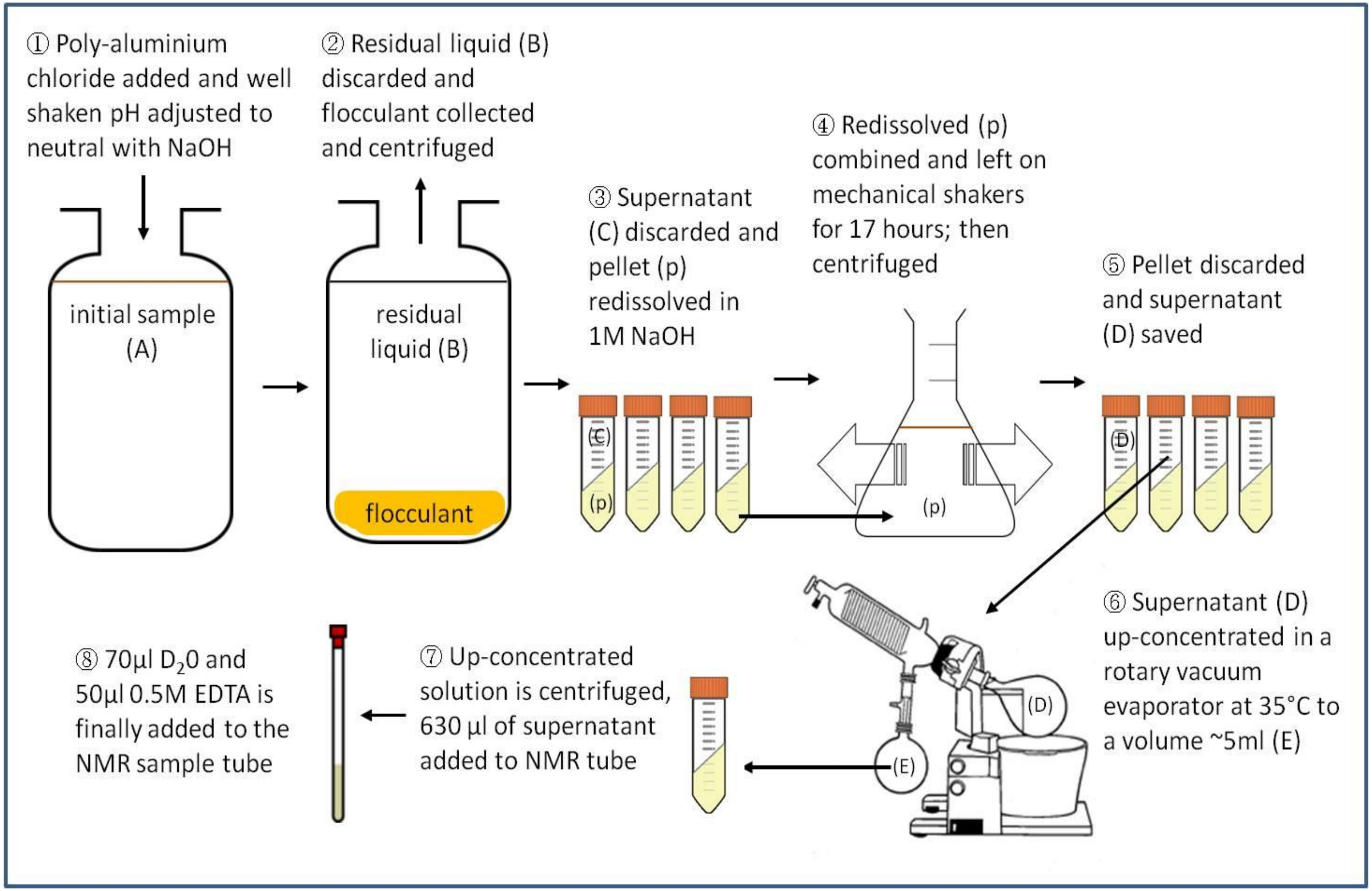


Figure 2.6 Diagram outlining the stages of the procedure used to prepare effluent from private sewage systems for analysis using ^{31}P NMR spectroscopy.

2.5.3 Settings for the Analysis of Effluent Samples with NMR Spectroscopy

The NMR was recorded on a Bruker AVIII, operating at 161.98 MHz for ^{31}P, at 25˚C. Spectra were recorded using a 30˚ observation pulse, acquisition time of 1.01 seconds and a relaxation delay of 0.5 seconds. The final NMR sample volume, magnetic field strength and probe temperature were constant for each analysis. Run times varied from 3 hours 0 minutes to 14 hours 21 minutes, and were stopped by an NMR technician, (Dr Dave Ellis, of Heriot Watt University) when the NMR spectra produced was of a sufficient quality and resolution. Chemical shifts were indirectly referenced to D_2O for signal lock. The areas of peaks are proportional to the number of nuclei present in the sample. The percentage area of each peak was assigned based on their proportional area relative to the largest peak. Compound concentrations were then calculated using the TP concentration of the raw sample. Although it is acknowledged that P compound concentrations calculated in this way are based on percentage compositions of compounds within the final NMR sample only, it is believed to be an accurate representation of the P compound composition of the raw sample. This assumption is made in similar studies of Jørgensen et al. (2011), Ding et al. (2010) and Reitzel et al. (2006). Peaks were assigned by comparison with the literature (Cade-Menun, 2005) (Figure 2.4).

2.6 Assessment of Human Behaviour

This project used a questionnaire to assess human behaviours that may be potentially modified to reduce domestic P emissions from homes to the environment. To increase such behaviours, important antecedents to relevant behaviour must be identified so those promoting behaviours can be supported and those inhibiting behaviours removed (Steg and Vlek 2009).

2.6.1 Identifying the Controlling Factors that Underpin Behaviours

The assumption that simply informing individuals about environmental issues to increase environmental concern will lead to pro-environmental behaviour is incorrect (Kollmuss and Agyeman 2002; Bamberg 2003). Bamberg (2003) showed environmental concern accounted for less than 10% of the variance in environmental behaviour in the combined meta analyses of Hines et al. (1987) (128 studies) and Eckes (1994) (17 studies). Government agencies often sideline these requirements with a perceived necessity to simply tell individuals there is an environmental problem, which demands individual action (Barr 2004). The EPA consider educating users on correct maintenance of PSS an essential part of wastewater management programs designed to change behaviour (US EPA 2002b). In a study Silverman (2005) showed door to door delivery of information outlining better PSS management does successfully educate individuals about PSS management, but does not result in any significant change in personal PSS management.

To design a questionnaire that not only assesses relevant behaviours but also the factors that control those behaviours, the leading behavioural models used in environmental psychology to predict behaviours were compared. These models are outlined in the following sections.

2.6.2 Modelling Environmental Behaviour

Three main models are used in environmental psychology to describe the factors that control environmental behaviours; the Theory of Planned Behaviour (TPB) (Ajzen 1991), the Norm-Activation Theory (NAT) (Schwartz and Howard 1981) and the Value-Belief-Norm Theory (VBN) (Stern 2000) (Sopha 2011). These models provide a valuable insight into the potential changes that can be made to promote a behavioural choice. A literature review of 99 studies (focused on household energy use) showed 39% used the TPB, 15% used the NAT, 15% used the VBN and 13% used variables from two or more of the models to describe environmental behaviour (Sopha 2011).

The TPB, NAT and VBN have all been shown to empirically predict environmental behaviour in multiple studies (De Groot and Steg 2007; Hansla et al. 2008). The TPB has been criticised for under representing the impact of morality on behaviour. The NAT and VBN have been used to successfully explain low cost environmental behaviour (Steg and Vlek 2009), but have been less effective at explaining behaviours with high cost or strong behavioural constraints (Bamberg & Schmidt 2003). All three models show significant weakness in predicting repeated behaviours and formation of habit (Klöckner 2013) .

To address this, The Comprehensive Action Determination Model, (CADM) (Klöckner 2013) integrates the TPB, NAT and VBN, as well as the influence of habit strength on modelled relationships, into a single framework outlining controlling factors that drive a broad range of individual environmentally relevant behaviours. The predictive capacity of the CADM was successfully tested using the meta-data from 56 studies (Klockner 2013), and is used in this report to assess factors that influence human behaviours that potentially impact P discharge from PSS in the Loch Leven catchment. The following section describes the basis of the TPB, NAT and the VBN and the integration of these models into the CADM.

2.6.3 Theory of Planned Behaviour

The TPB proposes that the likelihood an individual will perform a general behaviour is directly related to intention to act, which in turn is modified by 1) social norms, 2) attitude and 3) personal behavioural control (Ajzen 1991) (Figure 2.7). Social norms are the combination of the social pressure perceived by an individual to perform a behaviour multiplied by their willingness to do so. Chan (1998) demonstrates how the mass media play an important role in establishing social norms for pro-environmental behaviour. Attitude towards the behaviour is a measure of an individual's belief that the action will produce a desired outcome, and that this outcome is favourable. Perceived behavioural control is a combination of how accessible the behaviour is and how capable the individual feels (Schahn and Holzer 1990; Klöckner 2013). The provision of a range of facilities that can be easily accessed by individuals to perform the relevant pro-environmental behaviour is essential (Barr 2004). The TPB has been used to successfully explain general pro-environmental behaviour (Kaiser et al. 1999) as well as specific change towards pro-environmental behaviours concerning water use, meat consumption, purchase of energy saving light bulbs (Harland et al. 1999) and waste composting (Mannetti et al. 2004). The TPB explains general behaviour based on cost benefits; studies have found individuals chose pro-environmental behaviour that provide the highest benefits against lowest costs (Steg and Vlek 2009). The NAT and VBN, which are closely related, consider environmental behaviour as a form of altruism.

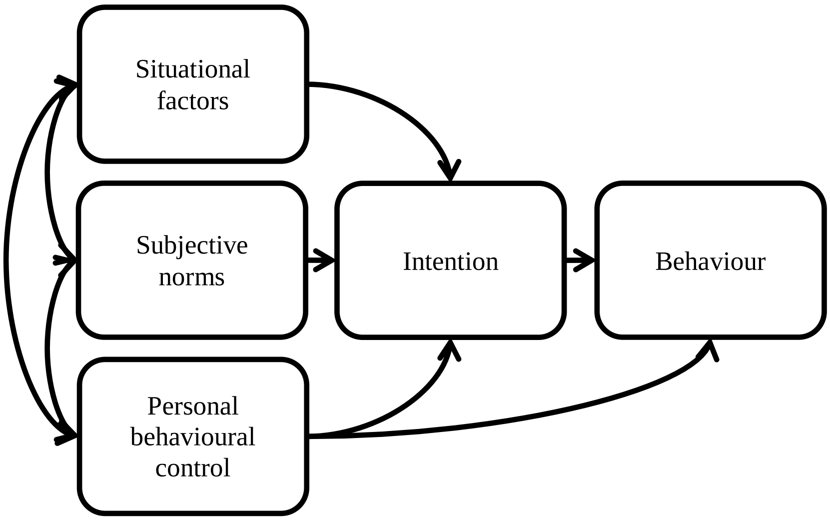


Figure 2.7 The Theory of Planned Behaviour (TPB) (Ajzen 1991).

2.6.4 Norm-Activation Theory

The NAT was developed to define conditions that cause people to act altruistically in a given situation, with a core assumption that moral obligation will induce helping behaviour, a status referred to as an activated personal norm (Schwartz and Howard 1981). To activate a personal norm, the individual needs to be 1) aware of the problem, 2) know that the problem can be alleviated through their action, 3) perceive they are capable of performing the behaviour, and 4) accept responsibility for their actions (Figure 2.8). Personalisation or localisation of the environmental problem may trigger egoistic concern and can be used to drive pro-environmental behaviour (Eden 1993).

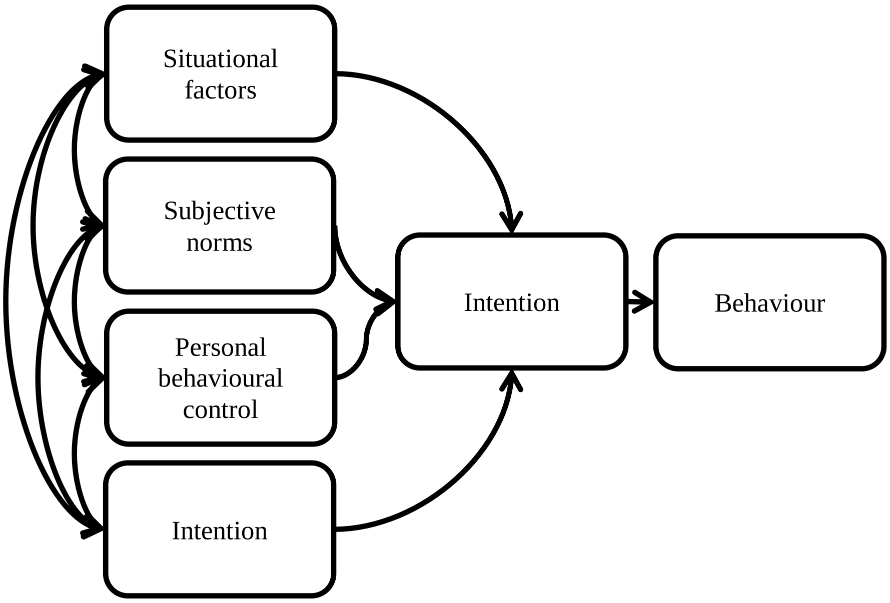


Figure 2.8 The Norm-Activation Theory (NAT) (Schwartz & Howard 1981).

2.6.5 The Value Based Norm Theory

The VBN is similar to the NAT in as much as it states behaviour is directly determined by personal norms, but proposes the determinants follow a causal linear chain framework (Figure 2.9). The VBN states that if an individual 1) has an ecological worldview then they are likely to 2) display awareness that an environmental problem can be alleviated through their behaviour, which can lead to 3) ascription of responsibility and the subsequent activation of personal norms directly leading to behaviour (Stern 2000). An individual with an ecological worldview accepts there are limited resources, understands human activity affects natural equilibriums and believes humans should not dominate nature (Klöckner 2013), a mindset that can be measured by the New Environmental Paradigm (NEP) (Dunlap et al. 2000). General values such as biospheric values (belief the environment has an intrinsic value), altruistic and self-transcendence values (i.e. universalism and benevolence) can predispose individuals towards an ecological worldview (De Groot and Steg 2008), whilst egoistic and self-enhancement values (i.e. hedonism and value of power) inhibit an ecological worldview. Deyoung & Kaplan (1985) have shown some individuals find an intrinsic satisfaction from pro-environmental behaviour, whilst (Selman 1996) states the importance of individual environmental citizenship in explaining pro-environmental behaviour. Socio-demographics have been related to environmental values (Barr 2004). However, Saphores et al. (2012) found that education, age and ethnicity played only minor roles in an individual’s tendency to recycle and that recycling convenience, knowledge of potential hazards of not recycling and prior experience of recycling were more important, as were marital status and gender.

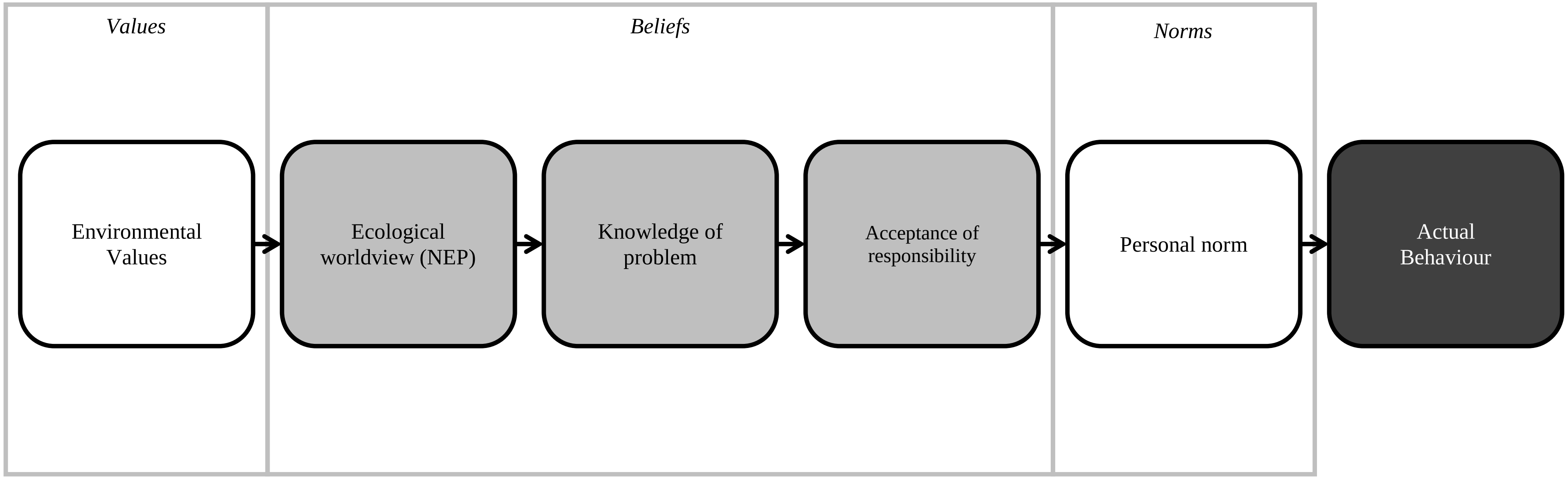


Figure 2.9 The Value-Belief-Norm Theory (VBN) (Stern 2000).

2.6.6 The Influence of Habits

In many cases, an individual’s behaviour is not preceded by intricate reasoning and is often habitual, directed by automated cognitive processes. Therefore to change an individual’s behaviour consideration of how habits are created, reinforced and continued is necessary. In situations when a behaviour is repeated frequently the relationship between intention and behaviour (Verplanken et al. 1998), and personal norms and behaviour (Klöckner and Matthies 2004), is weakened and a growing importance is assigned to habit strength in predicting behaviour (Klöckner 2013). Ouellette and Wood (1998) found behaviour repeated annually or bi-annually is greatly determined by intention, whilst weekly behaviour is influenced by habit strength.

2.6.7 The Comprehensive Action Determination Model

As the CADM is designed to predict general environmental behaviours, degree of habitualization is assessed in terms of characteristics of the individual (the degree to which they adopt habit in comparison to another person within the same situation) rather than the characteristic of the behaviour (frequency) (Klöckner 2013).

The CADM assumes perceived behavioural control, habit strength and intentions are direct predictors of behaviour. Habit strength also works as a moderator of the relationship between intention and behaviour. As habit strength increases the importance of intention on the decision to perform the behaviour decreases. Intentions combine the influences of attitudes, social norms, perceived behavioural control (as assumed in the TPB), but also incorporate the impact of personal norms. The determinants of personal norms assumed in the NAT, (i.e. an individual’s knowledge of the problem, awareness the individual can alleviate it, social norms and perceived behavioural control) are integrated with the additional influencing factor of whether the individual has an ecological worldview (as assumed in the VBN) defined by the NEP. The positive influence of self-transcendence and the negative influence of self-enhancement on the NEP are included (Figure 2.10).

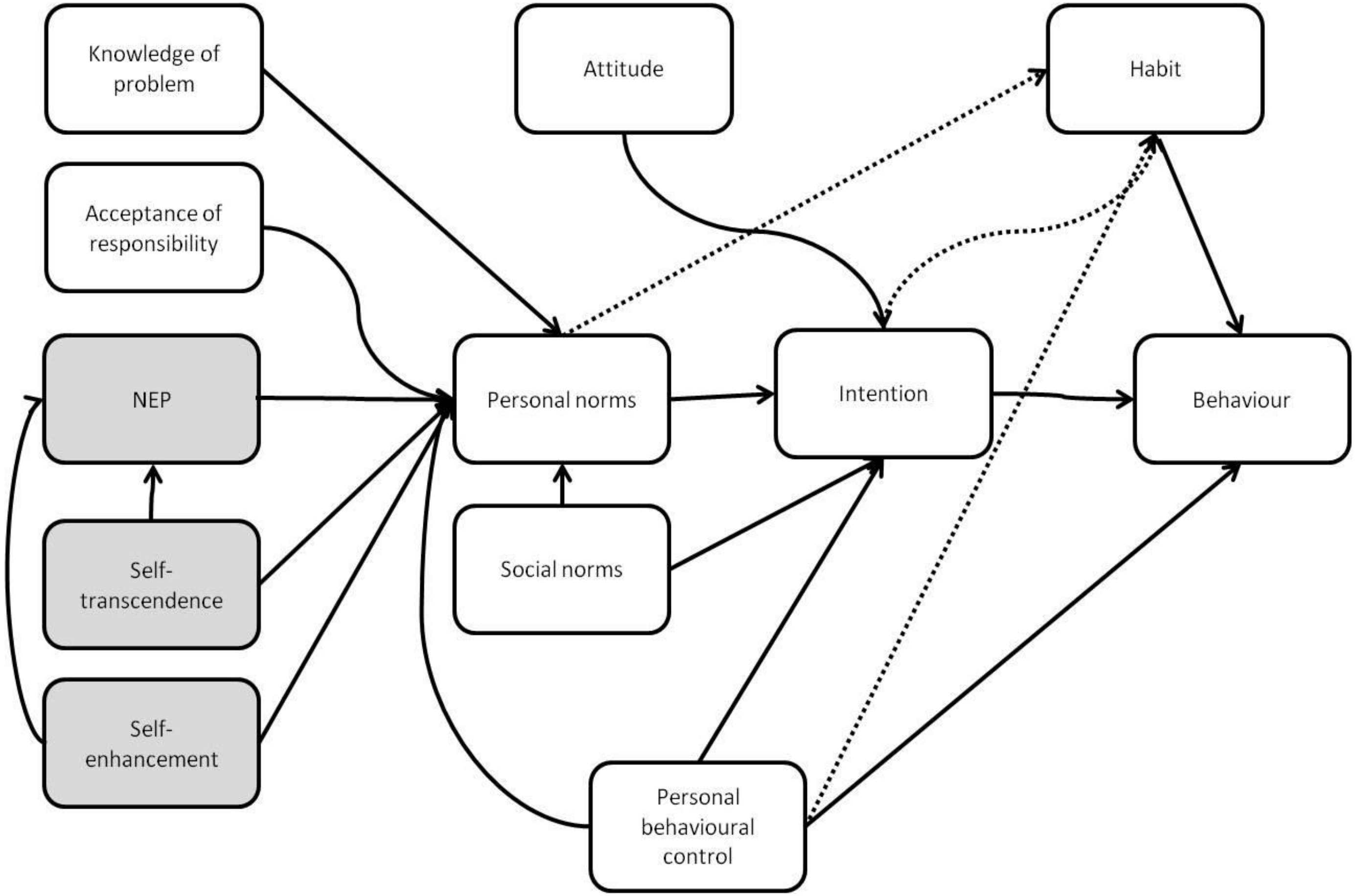


Figure 2.10 The Comprehensive Action Determination Model (CADM) (Klöckner 2013).

2.6.8 Identifying Behaviours to be Changed

To assess which behaviours most impact domestic P emissions to the environment, domestic P sources were identified from the peer reviewed literature in which the P contribution to wastewater from different sources in the UK (Comber et al. 2012), Sweden (Jonsson et al. 2006) and the US (US EPA 2002b) had been assessed (summarised in Table 2.2)

Three main sources of domestic P were identified; human wastes, grey waters from sinks and appliances, and bio-wastes from kitchen disposal units. Those providing the greatest contribution of P to wastewaters that could feasibly be reduced were selected as the main focus of the questionnaire for this study. As such, questions were designed to collect data regarding behaviours that impact on P in grey waters; and also regarding PSS maintenance. Maintenance of PSS (such as desludging) is considered a behavioural group that could be potentially modified to reduce P output from PSS. Dietary behaviours were excluded from the survey due to the well documented complexities involved in changing such behaviour (Vieux et al. 2012). Biowastes (i.e. food-scraps and carbonated drinks poured down the sink) are considered to be such a minor and largely unavoidable source of P (Comber et al. 2012) that they were also excluded from the survey.

Table 2.2 Phosphorus (P) contribution of different domestic sources to wastewaters from households in the UK, Sweden and the US.

	UK study (Comber *et al* 2012)		Swedish study (Jonsson *et al* 2006)		US study (US EPA 2002)	
Phosphorus Sources	P contribution to wastewater (g P capita^{-1} day^{-1})	% total	P contribution to wastewater (g P capita^{-1} day^{-1})	% total	P contribution to wastewater (g P capita^{-1} day^{-1})	% total
Human Waste						
Food additives	0.59	28%	-	-	-	-
Faeces	0.21	10%	0.49	21%	-	-
Urine	0.61	29%	0.90	38%	-	-
Total from human waste	1.41	67%	1.39	59%	1.60	59%
Grey waters						
Washing machines	0.28	13%	-	-	-	-
Dishwashers	0.18	8%	-	-	-	-
P dosing of tap water	0.13	6%	-	-	-	-
Personal care products	0.02	1%	-	-	-	-
Total from grey waters	0.60	28%	0.68	29%	1.00	37%
Biowaste						
Total from biowaste	0.1	5%	0.27	12%	0.10	4%
Overall Total	2.11	-	2.34	-	2.70	-

The factors that control behaviours relating to domestic P inputs to grey waters and PSS maintenance behaviours have not been examined previously. A simplified framework of the variables that influence both an individual's behavioural intention and their actual behaviour was constructed, based on the work of Barr (2004).

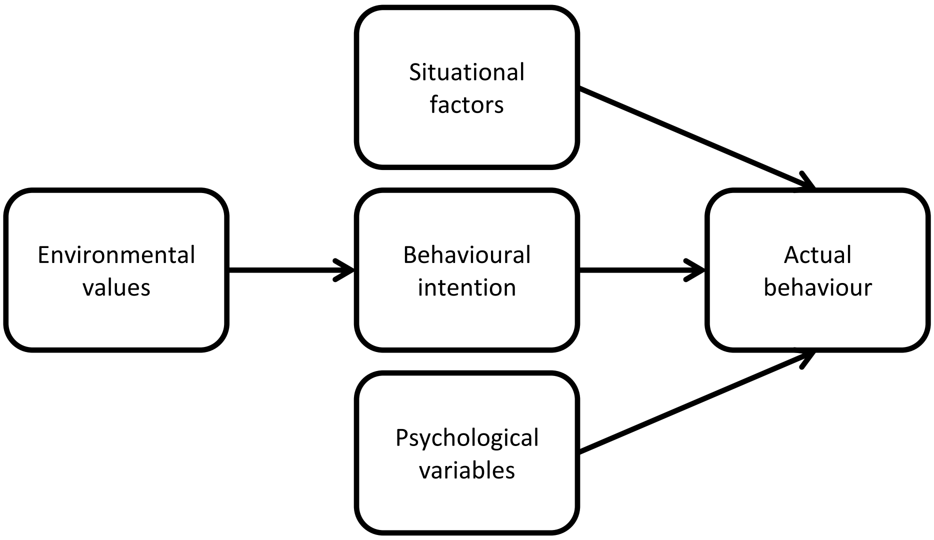


Figure 2.11 Framework explaining the variables which influence behaviour and modify the relationship between behavioural intention and actual behaviour (modified from Barr 2004).

Using this framework, variables were grouped into situational factors, psychological variables and environmental values, and using the behavioural models outlined earlier in this chapter and current literature (summarised in Table 2.3), a number of 'controlling factors' that are known to be important in predicting behaviour were assigned to each (Table 2.3). Questions were designed to collect information about factors known to facilitate environmental behaviours (Table 2.3), but in the context of behaviours related to domestic P output and PSS maintenance regime. Questions designed to collect information about the controlling factors of behaviours were focused upon 'situational factors' and 'psychological variables' only, as 'environmental variables' were deemed less feasible to modify (as they are based on personality traits and therefore beyond the scope of this study).

Table 2.3 Controlling factors that influence behaviour and behavioural intention, based on the proposed framework of Barr (2004).

Variable Group	Controlling factor	References
Situational Factors	Provision of a range of facilities to perform behaviour	(Barr 2004)
	Socio-demographic variation	(Stern et al. 1993; Schultz et al. 1995; Saphores et al. 2012)
	Low cost-high benefit	(De Groot and Steg 2008; Ajzen 1991)
	Knowledge of the problem	(Schahn and Holzer 1990; Barr 2004)
	Knowledge of how the problem can be solved	(Barr 2004)
Psychological Variables	Perceived behavioural control: • self-efficacy to perform the behaviour • responsibility to perform the behaviour • optimism the result is successful	(Ajzen 1991; Klöckner 2013; Schwartz & Howard 1981; Stern 2000)
	Personalisation and localisation of the problem	(Eden 1993)
	Social Pressure	(Tucker 1999; Baca-Motes et al. 2013; Chan 1998)
Environmental Values	Ecological world view • Higher score on the NEP (Dunlap et al. 2000)	(Steel 1996; Thompson & Barton 1994; Klöckner 2013; Dunlap et al. 2000)

2.6.9 Questionnaire Design

The resulting questionnaire was designed to collect information on 1) human behaviours that impact the amount of P entering a PSS from domestic sources, 2) human behaviours regarding the maintenance of PSS, and 3) potential controlling factors that underpin those behaviours, and 4) background information about the household, property and PSS. A trial questionnaire was sent out to a subset of six people, to test length and ease of use. The feedback was that the length of the questionnaire was too long, some questions were too personal, whilst others were open to multiple interpretations. Consequently the questionnaire was reduced from 35 to 27 questions. Those questions removed were considered potentially too personal (i.e. what is your annual salary?) or too vague (i.e. is the health of the environment important to you?).

To encourage a maximal response the questionnaire was kept short (27 questions), anonymous (sex, age and gender only) and simple to answer (predominantly tick box answers). Care was taken to present non-leading and unbiased questions. Questions used in the final questionnaire are provided in Table 2.4 and
Table 2.5.

Table 2.4 Survey questions concerning socio-demographic variation and domestic behaviour, the controlling factors they address and explanatory statistics describing responses, and the unit of responses.

Questions	Controlling factor or behaviour investigated	Unit
Socio-Demographic Characteristics		
1. What sex are you?	socio-demographic variable	sex
2. How many people live in your house?	socio-demographic variable	people
3. How old are you?	socio-demographic variable	years
4. How old is your property?	housing demographic	years
5. How old is your PSS?	housing demographic	years
6. How long have you lived at your address?	housing demographic	years
7. How many properties are connected to your PSS?	responsibility, personal behavioural control	properties
8. Where does your PSS drain to?	housing demographic, knowledge of the problem,	drainage destination
Domestic behaviour		
9. How many dishwasher cycles do you run per week?	behavioural response	no. person^{-1} week^{-1}
10. How many washing machine cycles do you run per week?	behavioural response	no. person^{-1} week^{-1}
11. How many baths are run in your house per week?	behavioural response	no. person^{-1} week^{-1}
12. How many showers are run in your house per week?	behavioural response	no. person^{-1} week^{-1}
13. How many times do use a disposal unit in your house per week?	behavioural response	no. person^{-1} week^{-1}
14. When buying washing machine detergent which of the following, influence which detergent you buy? (multiple ticks allowed)	behavioural response, low cost-high benefit, knowledge of the problem, knowledge of how to solve the problem	influence factor
15. When buying dishwashing machine detergent which if the following influence which detergent you buy? (multiple ticks allowed)	behavioural response, low cost-high benefit, knowledge of the problem, knowledge of how to solve the problem	influence factor
16. Do you feel adequate information is available on how to change your domestic habits to improve the performance of your PSS (i.e. change of household detergent)?	knowledge of the problem, knowledge of how to solve the problem, perceived behavioural control	yes or no

Table 2.5 Survey questions concerning maintenance behaviour and the public perception of the problem, the controlling factors they address and explanatory statistics describing responses, and the unit of responses.

Questions	Controlling factor or behaviour investigated	Unit
Maintenance behaviour		
17. Has your septic tank or PSS ever failed to work correctly (i.e. blocked, overflowed or produced a bad smell)?	behavioural response	yes or no
18. Have you ever emptied/desludged your septic tank? And if so, when was the last time you did?	behavioural response	months
19. Does your septic tank have any cracks?	responsibility, knowledge of the problem, knowledge of how to solve the problem	yes or no
20. Does your septic tank receive roof runoff?	responsibility, knowledge of the problem, knowledge of how to solve the problem	yes or no
21. Who is responsible for correctly maintaining a PSS? (multiple ticks allowed)	Responsibility	n/a
22. Who is responsible for fixing a PSS known to be working incorrectly? (multiple ticks allowed)	Responsibility	n/a
23. Do you feel adequate information is available on how to correctly maintain your PSS?	knowledge of the problem, knowledge of how to solve the problem, perceived behavioural control	yes or no
24. Do you feel adequate information is available on measures to reduce pollution from your PSS?	knowledge of the problem, knowledge of how to solve the problem, perceived behavioural control	yes or no
Public Perception of the problem		
25. How many PSS in the Loch Leven catchment do you think are working inefficiently?	personalisation and localisation of the problem	percentage range of tanks failing
26. Do you feel informed about the current legislation in relation to PSS?	social pressure, knowledge of the problem	yes or no
27. Do you think PSS should be registered?	social pressure	yes or no

Questionnaires were posted to all addresses within the catchment believed to be served by PSS. This address list was compiled by the Scottish Environment Protection Agency (SEPA), Scottish Natural Heritage (SNH), Perth and Kinross Council (PKC) and Scottish Water using Ordnance Survey data to count the number of properties located in postcode areas not served by mains sewerage. ArcGIS 3.2 was used to visualise the distribution of these addresses in the Loch Leven catchment (Figure 2.12). The following datasets were used to create a GIS map of the Loch Leven catchment, its rivers and lochs and the estimated density of PSS within the catchment; 'The National River Flow Archive' hosted by the Centre of Ecology information Gateway and 'Aerial Imagery at a 1:250,000 scale' provided by Ordnance Survey.

Questionnaires were delivered to 654 addresses on the 5th of September 2012, with self-addressed postage paid envelopes to make it easy for individuals to return completed forms by the deadline of the 5th of October 2012. A covering letter explaining the purpose of the study (i.e. PhD research project), the institution involved (i.e. Heriot Watt University) and the contact information of the project leader (i.e. the author) was also included, both cover letter and questionnaire are provided in Appendix B. A return of 156 (24%) of the questionnaires were completed by the deadline and used in analysis.

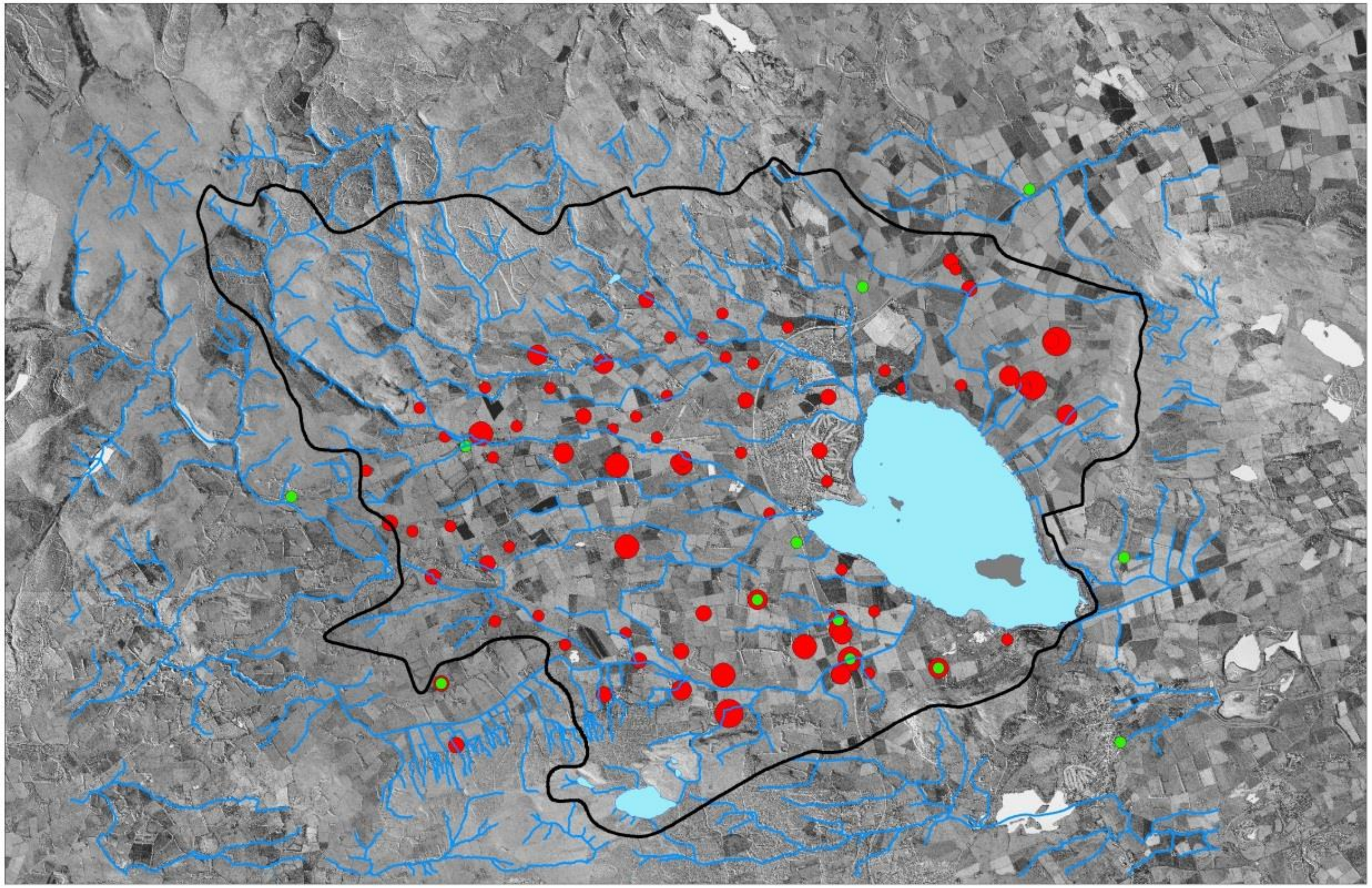


Figure 2.12 The estimated density of PSS in the Loch Leven catchment; the black line indicates the catchment boundary, red spots indicate the geographic centre of postcodes, size is proportional to PSS density. Green dots represent addresses that have registered PSS with the Scottish Environment Protection Agency (as of October 2012).

2.7 Conclusion

In this chapter, the research catchment has been described, as have the two physical measurement methods used, followed by a fuller description of the behavioural theory that underpins the described questionnaire approach developed for the thesis. The following four chapters describe the research work undertaken using these methodologies, whilst Chapter 7 provides an overall discussion of the results in relation to the aims of the thesis.

Chapter 3 Measuring the Effectiveness of Legislation for the Control of Phosphorus Emissions from Housing, A Case Study of Private Sewage Systems in the Loch Leven Catchment, Scotland, UK

The work in this chapter is published in: Brownlie, W., May, L., McDonald, C., Roaf, S. and Spears, B.M. 2014. Assessment of a novel development policy for the control of phosphorus losses from private sewage systems to the Loch Leven catchment, Scotland, UK. Environmental Science & Policy 38, pp. 207–216.

Abstract

Legislation to control nutrient enrichment of inland waters has been developed and implemented across local, regional and international scales. In the EU, measures must be identified to ensure that all inland water bodies meet ecological guidelines as set by the Water Framework Directive (WFD) by 2015 or 2027. However increasing demand for rural development, associated with projected population increase, confound existing nutrient management approaches. This highlights two questions, 1) how can the effectiveness of P management approaches be reliably measured and 2) are novel rural development policies working well in ensuring the private sewage systems (PSS) of new developments do not increase the phosphorus (P) load to the environment within a lake catchment. The chosen case study policy in Loch Leven, referred to as ‘the 125% rule’, involves mitigating 125% of their calculated P output of a development by modifying an existing, third party PSS. The assumption that PSS discharge a hierarchal reduction in P output with increasing treatment level (i.e. primary treatment (10 mg l^{-1}) > secondary treatment (5 mg l^{-1}) > tertiary treatment (2 mg l^{-1})) lies at the core of this policy. In this chapter standard methods of measuring P concentration of samples are employed to evaluate the effectiveness of the 125% rule (Loch Leven Special Protection Area and Ramsar Site 2011) in achieving a reduction in P discharge from PSS to the catchment. To do this, seven PSS (four with primary, one with secondary and two with tertiary treatment) were monitored over a five month period to provide a range of P discharge concentrations across treatment types. These data were used to assess the potential impact of future rural development on P losses to the catchment using the expected, and the hypothetical, population increase rate of 1.3% yr^{-1} over a 90 year projection. No significant differences in TP concentration of effluent were observed among PSS or between the treatment levels of PSS sampled. To ensure this policy meets its aim, improvement in technology and management of PSS along with alternative mitigation measures are required. The effectiveness of the measurement regime is also discussed in the conclusions.

3.1 Introduction

Properties in areas where connections to municipal sewage treatment works are not available must rely on private sewage systems (PSS) to treat their wastewater (Withers et al. 2012). It is estimated that 26% of the properties in Europe (Williams et al. 2012), 25% of the properties in the US (US EPA 2002b) and 20% of the properties in Australia (C.D. Beal et al. 2005) are served by PSS. Recent studies estimate that 80% of the 1.5 million PSS in the UK are potentially working inefficiently with respect to phosphorus (P) losses (Selyf-Consultancy 2002; Kirk et al. 2003). In some UK rural catchments the net P contribution made to water bodies by PSS has been estimated (May and Dudley 2007); ranging from 3% in Llyn Tegid, Wales (Milliband 2002) and 40 to 76% in Black Beck, North England (Hall 2001). In the US, the estimated 26.1 million PSS contribute the largest volume of waste water ($3.6\ 10^2$ GL $year^{-1}$) to the subsurface (USEPA, 2002a). In 28 US states, estimates have been made of the proportion of PSS failing to work correctly have been made, and range from 0.4 to 70%, (although the definition of ‘failure’ varies between state, most include blockage, flooding and surface and ground water contamination) (Nelson and Dix 1999). The cumulative magnitude and temporal persistence of phosphorus (P) pollution from private sewage systems (PSS) can significantly increase eutrophication risk of fresh waters (Ahmed et al. 2005; Arnscheidt et al. 2007; Withers et al. 2013). Studies suggest the more important feature of PSS P pollution may not be the magnitude of the P load, but the high proportion of bioavailable P in its composition (bioavailable P is of particular concern to the immediate onset of eutrophication) (Withers et al. 2011; Jordan et al. 2007).

In east Scotland, UK, a novel planning policy has been put in place to address the potential increase in P discharges to the Loch Leven catchment from new developments with PSS. Under the Town and Country Planning (Scotland) Act 1997; as amended by the Planning etc. (Scotland) Act 2006 (amended in 2009) (Scottish Government 2009), councils and national park authorities must construct a Development Plan (DP) to manage building development. The Loch Leven Catchment is covered by the TAYplan Strategic Development Plan (TAYplan 2012), which provides guidance for an area of 8,112 km^2 with over half a million inhabitants. Local planning authorities must convert these broad DPs into a more detailed local development plan (LDP) that details land use policies and proposals for their area (Figure 3.1). DPs and LDPs may also accept supplementary guidance. For example, the Kinross Area Local Plan (2004) adopts the principles of the the Loch Leven Catchment Management Plan (1999) (LLCMP) for the control of pollution to Loch Leven (Figure 3.1).

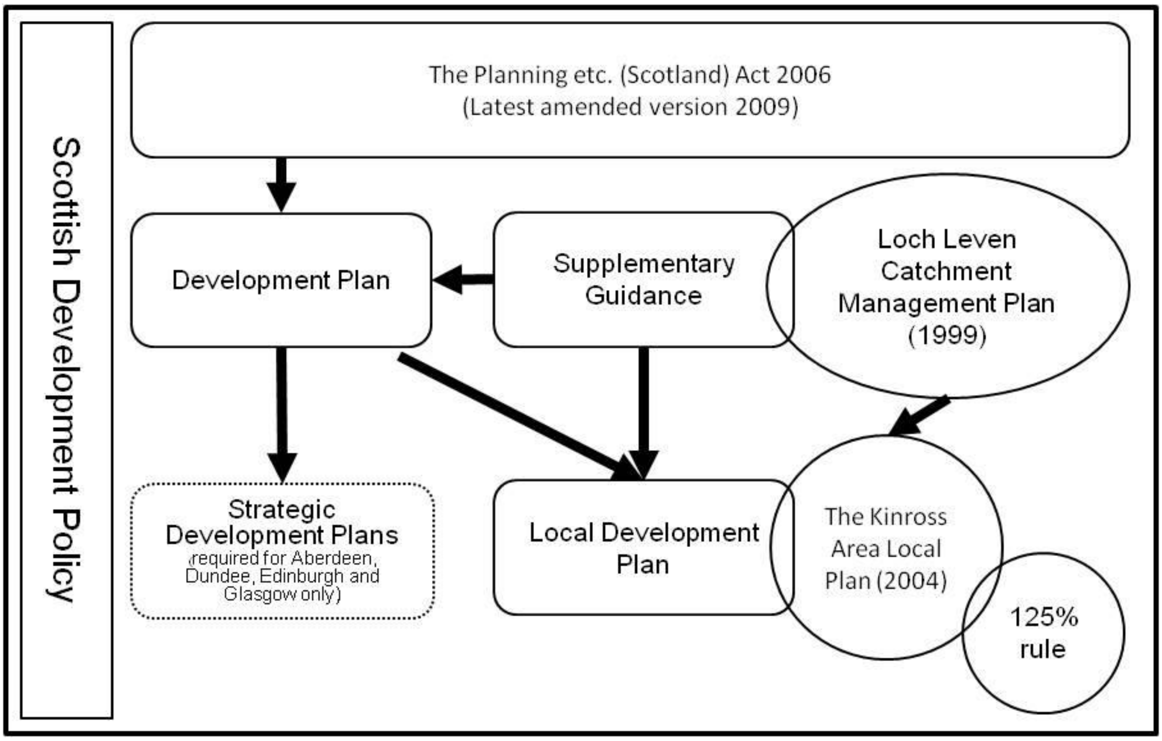


Figure 3.1 The current structure of planning and development legislation in Scotland, including the 125% rule.

The Kinross Area Local Plan (2004) contains novel rural policies that aim to ensure that new developments do not increase P loading to the Loch Leven catchment. The policies are aimed at individuals proposing any form of rural development within the catchment that require a PSS (policy 10). It states that the future P output from the PSS must be estimated (policy 11) and that measures to mitigate the estimated output to the catchment by 125% must be proposed (policy 12). This should be achieved by upgrading third party primary treatment PSS to systems with secondary or tertiary treatment (Loch Leven Special Protection Area and Ramsar Site, 2011). In the following text, these policies are, collectively, termed ‘the 125% rule’. The 125% rule assumes that PSS with secondary treatment (i.e. wetlands, reed beds and mechanical treatment plants) or tertiary treatment (i.e. sand filters, drum filters, membrane systems or chemical dosing) will produce lower TP discharge concentrations than PSS with primary treatment (single septic tank treatment, only) (SEPA 2011), thereby reducing the P discharge to the environment. The efficacy of this new legislation relies on the accuracy of the desk based TP load estimation for proposed PSS and requires validation in the context of potential benefits or threats to the net TP load to the Loch.

3.1.1 Research Aims

In order to better understand the effectiveness of the 125% rule, we quantified potential uncertainty using the current desk based calculation procedure and compared it to actual measured TP concentrations from seven PSS within the Loch Leven catchment. The potential change in P output from projected developments over the next 90 years was forecast using both of these approaches. The results are compared and discussed in relation to potential policy appraisal. Specific hypothesis are as follows:

- There is no significant difference in TP, TSP, SRP and SURP concentration in the effluent from different PSS
- There is no significant difference in the TP:SRP ratio in the effluent from different PSS
- Treatment type does not reduce concentration of TP in PSS effluent

3.2 Methods

3.2.1 Implementation of the '125% Rule'

The 125% rule assessment calculations use pre-defined TP effluent concentrations of 10.00 mg P l^{-1}, 5.00 mg P l^{-1} and 2.00 mg P l^{-1}, for PSS with primary, secondary and tertiary treatment, respectively (SEPA 2011; Loch Leven Special Protection Area and Ramsar Site 2011), a people equivalence (P.E.) value based on the number of bedrooms (n) (P.E. = n + 2) and an estimated per capita waste water production rate of 180 l day^{-1} (British Water: Flows and Loads 3. 2009). Phosphorus output (mg P day^{-1}) is calculated by multiplying the P.E. by the estimated water usage (l) and the TP discharge concentration according to the treatment type (Figure 3.2).

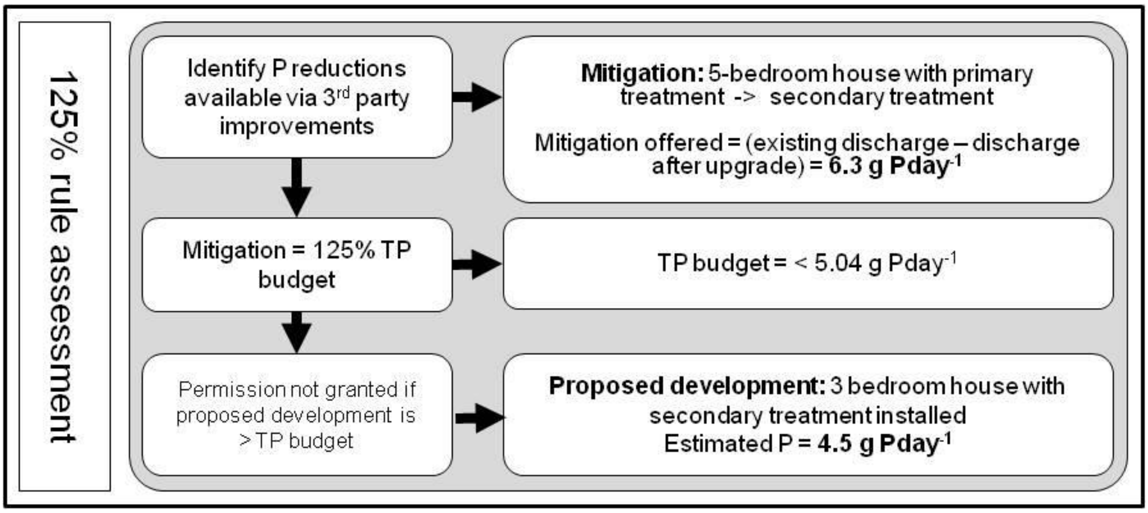


Figure 3.2 The assessment calculation of the "125 rule", a case study example is also shown (with assumptions used).

A case study for rural development in the Loch Leven catchment using these recommended guidelines is presented in Figure 3.2. All available mitigation options are first identified and potential TP load 'savings' estimated. Such 'savings' must be greater than 125% of the estimated TP load from the proposed development. Therefore the number of bedrooms allowed in the proposed development is reliant on how much the net TP load can be reduced. In this case study, the mitigation scheme proposes an upgrade to the PSS of a five bedroom house with secondary treatment, resulting in an estimated reduction in TP discharge to the catchment of 6.30 g P day^{-1}. This figure must equate to 125% of the PSS TP load from the proposed development. Therefore, to meet the requirements of the 125% rule, the proposed development must produce < 5.04 g P day^{-1}.

In this way, mitigation options provide guidance on the scale of proposed developments. In keeping with the 'TP budget,' development of a three bedroom house (P.E. = 5 people) with secondary treatment, discharging an estimated 4.5 g P day^{-1} would be allowed. If accurate, this development and associated mitigation activities would reduce the TP load to the catchment by 0.54 g P day^{-1}.

3.2.2 Septic Tank Sampling Methods

To explore the uncertainty of the assumptions for P effluent concentrations from PSS with different treatment levels, discharges from seven PSS within the Loch Leven catchment were analysed for TP, soluble reactive phosphorus (SRP) and total soluble phosphorus (TSP) content over a 5 month period. From these data, particulate phosphorus (PP=TP-TSP) and soluble un-reactive (organic) phosphorus (SURP=TSP-SRP) were calculated (as described in Section 1.4.1). A particularly challenging and constraining feature of this experimental design was locating suitable PSS that could be sampled easily and regularly; those chosen represent systems with primary, secondary and tertiary treatment. Four primary systems were selected to represent systems eligible for modification under mitigation scenarios; two constructed from concrete tanks (PSS 1 and 2) and two from fibreglass tanks (PSS 3 and 4). One tank with secondary treatment (mechanical mixing) (PSS 5) and two with tertiary treatments, one injected daily with 5ml of concentrated iron chloride to bind orthophosphate (PSS 6) and one fitted with an aeration system and filter system using Bauxsol^{TM} pellets (containing Al and Fe compounds) to bind P (PSS 7), were sampled. Samples were collected between October 2011 and February 2012. Restricted access to some sites, lead to less frequent sampling with PSS 3 and 4 sampled eight times; PSS 1, 2, and 6 sampled seven times and PSS 5 and 7 sampled five times.

Samples were collected as described in Section 2.3. Samples for SRP and TSP analyses were filtered through a Whatman® GF/C filter paper then stored with unfiltered samples for TP analysis at 4°C in darkness, overnight. All samples were analysed within 48 hours of collection. TP and TSP samples were digested using potassium persulfate ($K_2S_2O_8$) acid hydrolysis digestion based on methods by Eisenreich et al. (1975). Samples were then analysed for orthophosphate-P according to the methods of Murphy and Riley (1962).

3.2.3 Statistical Analysis

Data were analysed using the statistical software R version 2.15.1 (R-Core Team, 2012). Linear models were used to test for the significant differences in TP, SRP and SURP effluent concentrations of individual PSS and between treatment types. A linear model with a Gaussian error structure was fitted to the data using a separate model with TP, SRP and SURP as the response variables and PSS and treatment as the fixed variables. However, the assumption of homogeneity was not met, with the spread of the residuals differing between each individual PSS and treatment type. This is probably due to the unequal sample sizes for each PSS and treatment type. Due to this, a linear model with a variance structure which could account for this difference was fitted. This was achieved using a generalised least squares model (‘gls’ function) with a ‘varIdent’ variance structure from the ‘nlme’ package (Pinheiro et al. 2012) in R. To test for significant differences in SRP:TP and SURP:TP concentration ratios between PSS and between treatments, data were transformed using the arcsin square root transformation to meet the assumption that the response variable needs to be normally distributed. A linear model with a Gaussian error structure was then fitted to the data.

3.2.4 Modelled Scenarios and Uncertainty Analysis

Uncertainty analysis of the modelled TP discharge concentration from PSS using the 125% rule assessment procedure was conducted. The following analysis is based on the assumption that all P discharged from PSS represents an increase in the P load to the Loch Leven *catchment*, and is therefore *potentially* delivered to Loch Leven. In this study, no significant difference in TP concentration between treatments was observed, therefore all samples irrespective of treatment type were combined to give a median TP concentration (9.28 mg l^{-1}). The net TP load from PSS to the catchment was calculated using assumed (i.e. by the 125% rule) TP discharge concentrations for those with primary, secondary and tertiary treatment as well as the median TP concentration of all ‘in tank’ samples collected in this survey. A projected population increase of PSS users within the Loch Leven catchment allowed comparison of the increase in net P discharge from PSS to the catchment using each modelled scenario between 2010 and 2100.

3.2.5 Population Projections

The number of properties not connected to mains sewerage in the Loch Leven catchment in 2001 was estimated to be 654. This figure was compiled by the Scottish Environment Protection Agency (SEPA), Scottish Natural Heritage (SNH), Perth and Kinross Council (PKC) and Scottish Water using Ordnance Survey data to count the number of properties located in postcode areas not served by mains sewerage. Assuming that these properties are served by PSS, and using 2.22 as the average number of people per household (2010 estimate in The National Records of Scotland, 2012), 1452 people were estimated to be served by PSS in 2001. Population growth within the Perth and Kinross area is projected to be 1.28% per annum between 2010 and 2035 (National Records of Scotland 2012); assuming that growth in PSS users occurs at the same rate, an estimated 5114 people will be served by PSS in 2100. This figure is used to demonstrate the scale of uncertainty in predicting phosphorus discharge from PSS in line with potential population increases.

3.3 Results

3.3.1 Loch Leven Catchment Private Sewage System Survey

TP concentrations of all samples taken from PSS with primary treatment (PSS 1 to 4) ranged from 4.45 to 18.01 mg l^{-1} with a median 9.06 mg l^{-1}. The median TP effluent concentration of individual PSS across the sample period ranged from 6.19 to 12.81 mg l^{-1}. SRP concentrations in all samples taken from PSS with primary treatment ranged from 0.32 to 10.56 mg l^{-1}, with a median of 4.83 mg l^{-1}. The SRP median concentration of individual PSS ranged from 1.83 to 8.82 mg l^{-1}. For SURP, concentrations of all samples taken from PSS with primary treatment ranged 0.04 to 6.14 mg l^{-1} with a median of 0.67 mg l^{-1}, whilst the median SURP discharge concentration of individual PSS ranged from 0.12 to 0.94 mg l^{-1} (Figure 3.3).

TP concentrations from all samples taken from the PSS with secondary treatment (PSS 5) ranged from 5.79 to 14.43 mg l^{-1}, with a median concentration of 11.86 mg l^{-1} (as only one PSS with secondary treatment was accessible in this trial no range of median concentrations could be calculated). SRP concentrations ranged from 2.26 to 11.91 mg l^{-1} with a median concentration of 8.82 mg l^{-1}, whilst SURP concentrations ranged from 0.41 to 1.44 mg l^{-1} with a median of 0.86 mg l^{-1} (Figure 3.3).

Total phosphorus concentrations of all samples taken from PSS with tertiary treatment (PSS 6 and 7) ranged from 1.91 to 14.44 mg l^{-1}, with a median concentration of 9.31 mg l^{-1}. The median concentration of PSS 6 and 7 was 10.57 mg l^{-1} and 8.26 mg l^{-1}, respectively. The SRP concentration of all samples taken from PSS with tertiary treatment ranged from 1.42 to 10.60 mg l^{-1}, with a median of 5.54 mg l^{-1}. The median SRP discharge concentration of PSS 6 and 7 was 7.28 and 3.76 mg l^{-1}, respectively. Soluble unreactive phosphorus concentration of all samples taken from PSS with tertiary treatment ranged from 0.10 to 1.71 mg l^{-1} with a median of 0.36 mg l^{-1}. The median SURP concentration of PSS 6 and 7 was 0.29 and 0.44, respectively (Figure 3.3).

No significant difference was observed in TP concentrations (linear model, $F_{(6,40)} =$ 1.36 P = 0.25, n = 47) or SURP concentrations (linear model, $F_{(6,40)} =$ 1.80 P = 0.12, n = 47) among PSS, although SRP concentrations were significantly different (linear model, $F_{(6,40)}$ = 12.91, P = < 0.001, n = 47). No significant differences were observed in TP (linear model, $F_{(2,44)}$ = 0.27, p = 0.76, n = 47), SRP (linear model, $F_{(2,44)}$ = 0.99, p = 0.38, n = 47) or SURP concentrations (linear model $F_{(2,44)}$ = 2.11, P = 0.13 n = 47, respectively) among treatment types (Figure 3.3).

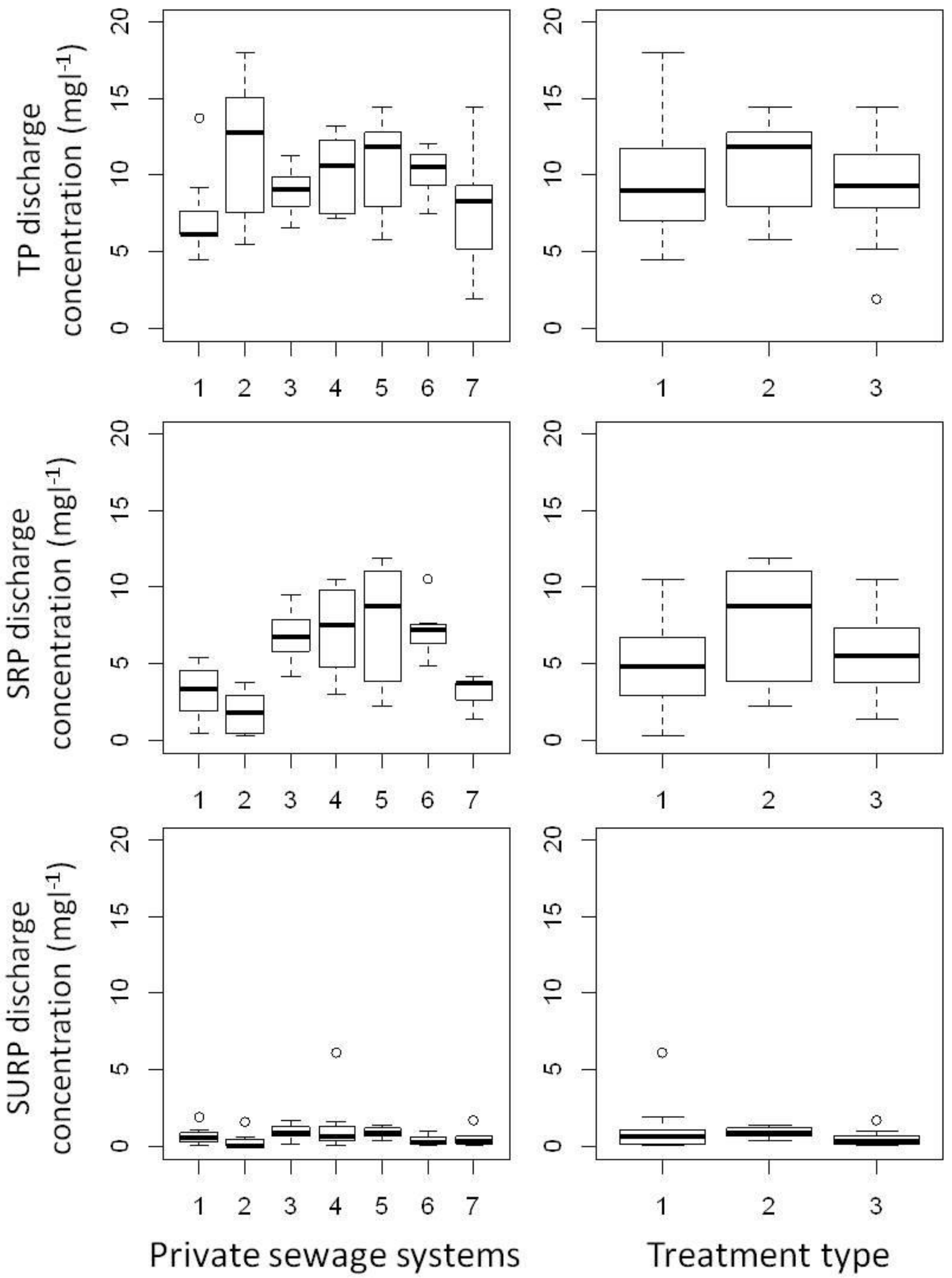


Figure 3.3 Box plots showing total phosphorus (top panel), soluble reactive phosphorus (middle panel) and soluble unreactive phosphorus (bottom panel) discharge concentrations (mg l^{-1}) between individual PSS and between primary, secondary and tertiary treatments of 7 private sewage systems within the Loch Leven Catchment. Whiskers show the lowest datum still within 1.5 interquartile range (IQR) of the lower quartile, and the highest datum still within 1.5 IQR of the upper quartile, dots represent outliers outside of this range.

The ratio of SRP:TP was significantly different among individual PSS (linear model $F_{(6,40)} = 6.20$, p = <0.001, n = 47), but not among treatments (linear model, $F_{(2,44)} = 0.98$, p = 0.38, n = 47). The median SRP contribution to TP was 68.48% (from a range of 2.36 to 91.32%). The ratio of SURP:TP did not show significant differences among individual PSS (linear model $F_{(6,40)} = 1.74$, p = 0.14, n = 47), or treatments (linear model, $F_{(2,44)} = 1.57$, p = 0.22, n = 47). The median SURP contribution to TP was 7.24% (from a range of 0.25 to 47.53%) (Figure 3.4).

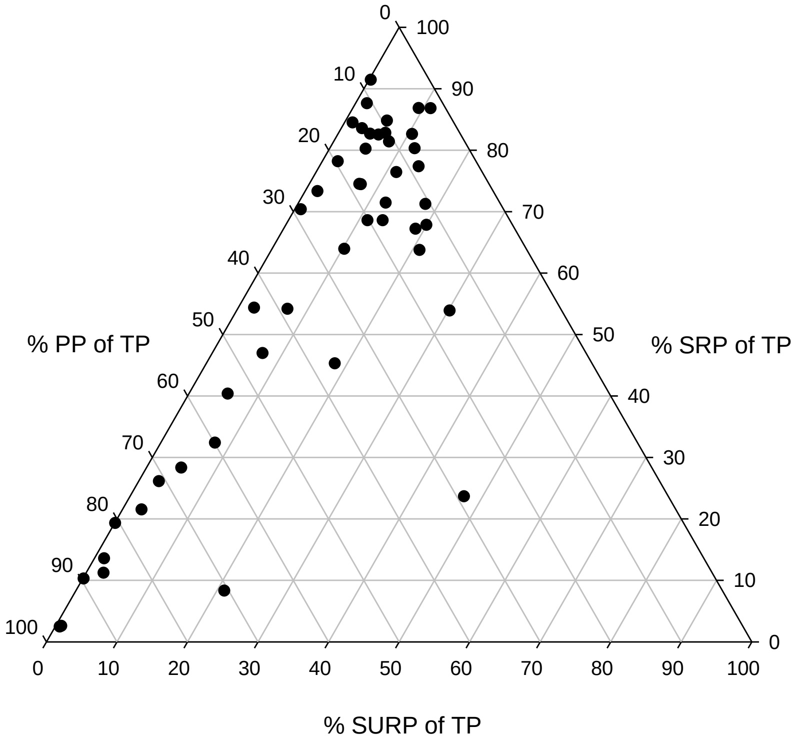


Figure 3.4 Ternary plot showing the proportion of soluble reactive phosphorus (SRP), soluble unreactive phosphorus (SURP) and particulate phosphorus (PP) found in all samples taken from 7 private sewage systems in the Loch Leven catchment during this study.

3.3.2 Uncertainty Analysis of the '125% Rule' with Future Population Growth

Using the assessment methods outlined by the 125% rule, if the 3486 extra people served by PSS between 2010 and 2100 are connected to PSS with primary, secondary or tertiary treatment an additional TP discharge to the catchment of 3.36, 1.68 or 0.67 t TP yr^{-1} is expected, respectively (Figure 3.5). Using the median TP discharge concentration from PSS sampled an increase of 3.12 t TP yr^{-1} is estimated, with a range of 1.78 to 4.94 t TP yr^{-1} (based on the 5th and 95th percentile) (Figure 3.5).

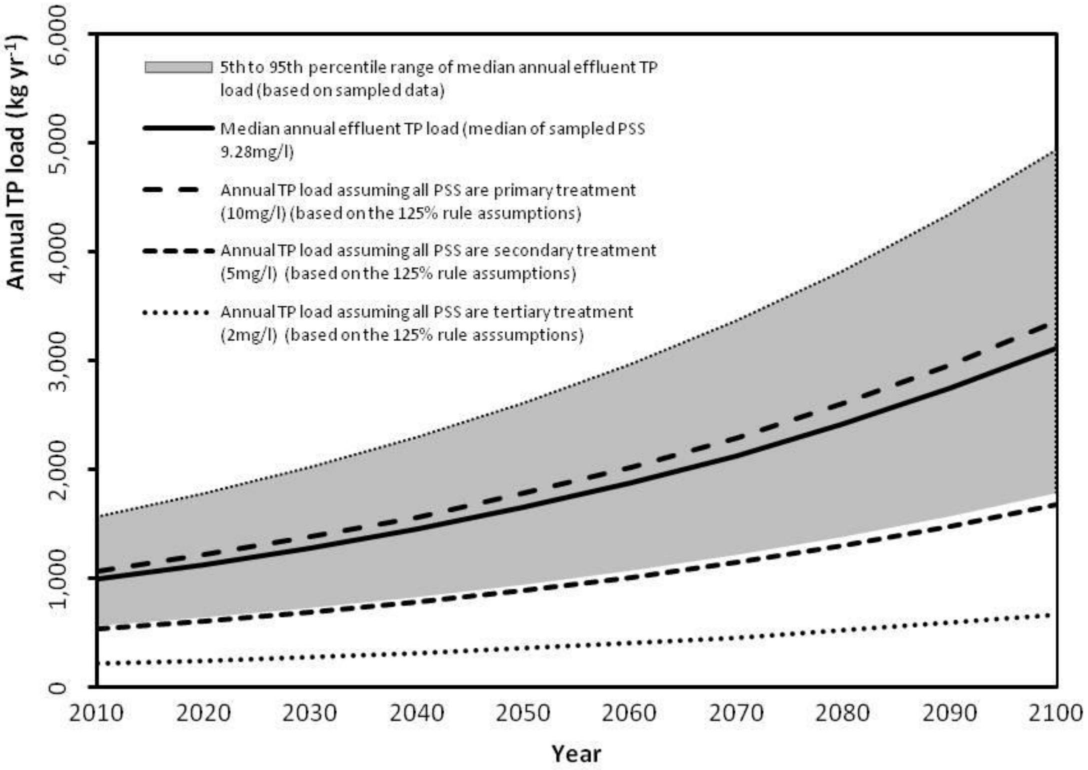


Figure 3.5 Graph showing additional total phosphorus (TP) load from septic tanks to the Loch Leven catchment under the projected population increase until 2100.

3.4 Discussion

3.4.1 Variation in Phosphorus Concentrations in PSS

No significant difference in TP concentration was observed between PSS or between treatment types of PSS in this study. The median TP concentration of all samples (9.28 mg P l^{-1}) most closely resembled concentrations expected from PSS with primary treatment (10 mg P l^{-1}) under the 125% rule assumptions (SEPA 2011; Loch Leven Special Protection Area and Ramsar Site 2011). These results indicate that secondary and tertiary treatments do not significantly reduce TP concentration in the sampled tanks, suggesting that the assumptions used in the 125% rule may not reflect reality.

P reduction is not required for the E.U. Standard for PSS (E.U. Standard (EN12566-1-7:2000). Gill et al. (2009) states that package treatment plants (septic tanks with secondary or tertiary treatment) are not specifically designed to remove P. It has been reported that the aerobic environment provided by secondary treatment aeration can cause c. 15% reduction in PSS effluent P via assimilation, precipitation and adsorption (Metcalf and Eddy, 2003). In this study, reductions were not observed and this would not be enough to accommodate the TP reduction assumed in the 125% rule from upgrading from primary to secondary treatments. Gill (2009) reported similar (12%) reduction in SRP through biological assimilation under secondary treatment and, although SRP concentration did vary significantly between PSS sampled in this study, this was not significantly related to treatment type. Human domestic behaviour such as detergent choice (sodium tri-polyphosphate (STPP) is a common source of SRP from detergent), water usage and maintenance regime of PSS (i.e. desludging interval) may account for this observed variation. Quantifying the impacts of human behaviour on SRP discharge concentration may identify options that can be used to reduce P discharge concentration.

The ratio of SRP:TP varied significantly between PSS but not among treatment levels, with no significant difference being observed in SURP:TP ratio between PSS or treatment. In samples analysed, a median of 68.48% of TP was present in the form of SRP whilst 7.24% was present as SURP. Bouma (1979) reported studies that found more than 85% of TP in septic tanks was SRP whilst Whelan and Titamnis (1982) found 93-100% of TP was SRP. Although delivery of P from PSS to aquatic systems may be relatively small (in comparison to other sources), PSS have the potential to cause persistent inputs (Arnscheidt et al. 2007), raising concern that, during low flow summer months when dilution capacity is reduced and ecological sensitivity is greatest, such SRP delivery could promote eutrophication (Macintosh et al. 2011). It is unclear whether high domestic SRP input or in-tank biological conversion of organic P to SRP is responsible for this SRP dominance. What is evident is that treatment aimed at reducing TP discharge concentration will be most effective if designed to target SRP as this is the major component of P in PSS effluent. Flocculation of soluble P and particulate P compounds by adding alum to primary settling tanks in PSS can reduce SRP in septic tank effluent by 96% (Brandes 1977). This could provide SRP reductions that meet the required P reduction targets outlined in the 125% rule, but difficulty in creating flocculant in ‘real life’ systems (i.e. pH can affect flocculation (Reitzel et al. 2009)) and the implications that aluminium delivery has for the environment may make safe and effective application challenging.

3.4.2 Relative Contribution of PSS to Catchment Phosphorus Load

Variation in the transport of P from PSS can be attributed to site characteristics such as the chemical adsorption capacity and physical texture of draining soils, hydrology, soil microbiology and the slope and distance to proximal water courses (Rea and Upchurch, 1980; Harper, 1992; Beal et al., 2005). Currently site characteristics are not specifically considered in the 125% rule, although building regulations deem that new PSS must be 10 m from a water course, with soakaways constructed in free draining soils (HM Government 2000). Much of the soil in the Loch Leven catchment is not suited to soakaway construction and many older installations discharge directly to a water course (Frost 1996). In older soakaways, long term P laden discharge can fully saturate soils, over-riding their P buffering capacity (Heathwaite et al. 2006). Improvement and management of soil adsorption systems (i.e. soakaways) may yield a greater percentage reduction in the delivery of PSS P to the Loch. Evidence of irreversible sorption in a long term monitoring site has been questioned and suggests that P in groundwater may not be permanently immobilised (Robertson 2008). This highlights the need to include an assessment of soakaway system efficiency in the diagnostic monitoring of PSS. Such considerations should be included in policies aimed at reducing P delivery from PSS to aquatic systems.

3.4.3 Implications for Local Policy Development and Implementation

The 125% rule invokes ‘The Precautionary Principle’ (EU 2010; Commission of the European Communities 2000) allowing rapid preventative decision-taking in the face of a possible threat to the environment where scientific data does not allow full risk assessment, and carries a ‘polluter must pay’ policy. The use of a ‘125%’ reduction offers a buffer against a net increase of P to the catchment from development where data are lacking, acknowledging uncertainty in estimation of PSS P load. At the core of the assessment procedure is the assumption that P output from PSS decreases with increasing treatment level. Whilst the 125% rule is conceptually strong, the PSS sampled here do not display any significant reduction with increasing treatment level, albeit we are considering a small population of tanks. A larger number of PSS need to be sampled and a better understanding of P processing within PSS is required to reveal whether such policy instruments can cause nutrient loss reduction.

Using the 125% rule assumptions and substituting the median effluent TP concentration of PSS sampled (9.28 mg l^{-1}), to offset 125% of the P from the 3486 extra people predicted to be connected to PSS by 2100, developers would be required to mitigate 2.19 t TP yr^{-1}. Currently this must come from improvement to third party PSS. This exceeds the current estimate of 0.99 t TP delivered annually to the catchment from PSS, capping mitigation potential. If increasing treatment level does not make suitable reductions, future developments will need to rely on improved technology and management of PSS (to significantly reduce TP), reduction of domestic P loading and/or alternative mitigation measures such as change in land use (Abell et al. 2011) or removal of PSS systems into municipal waste water treatment works.

The 125% rule aims to ensure that new developments do not increase P load to the catchment (Loch Leven Special Protection Area and Ramsar Site 2011). Although Wakida and Lerner (2002) observed greater transfers of nitrates (N) as a result of soil disruption during housing construction (65 kg ha^{-1}) than ploughing temporary grassland (50 kg ha^{-1}) (Cameron and Wild, 1984), little or no research has addressed equivalent P losses (Lubliner 2007). Other potential P sources associated with development (non-PSS associated) may also need to be assessed, such as garden fertiliser, car washing detergents and domestic livestock waste.

To improve the efficacy of this policy further information is required, with improvements including:

- high frequency monitoring of PSS at all stages of effluent treatment to ascertain process P reduction profiles (i.e. primary septic tank, after secondary and tertiary treatment, soakaway etc.),
- site specific risk analysis of proposed and existing PSS,
- identification and quantification of domestic behaviours that reduce P load to PSS,
- quantification of alternative mitigation options, and
- regular policy auditing based on monitoring data.

To aid monitoring, future installation and retrofitting of PSS should incorporate easily accessible sample collection points at each stage of treatment.

3.4.4 Implications for Wider Policy Development and Implementation

In terms of wider policy development there is a well-recognised lack of information surrounding PSS, such as number, location, age, condition, efficiency, maintenance and frequency of desludging of PSS, downstream processing of P in soils, hydrological variation and proximity of watercourses at a site level, and the impacts of human domestic behaviour on P loading (Harper 1992; Withers et al. 2012). Without such information, estimation of the relative contribution PSS make to catchment TP loads will suffer potential inaccuracies whilst policy aiming to reduce such contributions may misrepresent the problem and the solution. Where data are limited and problems are complex, normal planning and policy making processes may not be equipped to offer timely intervention. Reducing P output with expensive engineering solutions (treating the effects of the problem) may be less effective than reducing domestic P inputs to PSS in the first place (reducing the causes of the problem). Detergent P forms between 9% and 50% of P in wastewater (Morse et al. 1993). Sale of detergents with more than 0.5% P is banned in sixteen states in the US due to the risks they pose to freshwaters (Lusk et al. 2011), resulting in a reduction of P in wastewaters by 40-50% (US EPA 2002b). In June 2013, similar bans in the E.U. will prohibit sale of consumer laundry detergents that provide ≥ 0.5 g P per standard dosage and bans on sale of dishwasher detergents with ≥ 0.3 g P per standard dosage are planned for 2017 (EC 2011). Use of low P detergents and reductions in the volume of detergents used will reduce P entering PSS. In the UK this could potentially offer a < 28% reduction of wastewater P (Comber et al. 2012) and is a positive step towards reducing our human P footprint.

To make significant reductions in TP discharge concentration from PSS (as required by policies such as the 125% rule), a holistic approach covering user inputs, PSS outputs and downstream processing is required. With a better understanding of the risks PSS pose to the environment, pioneering policies such as the 125% rule can be further developed using more quantitative approaches to provide a means of supporting impending rural development.

3.5 Discussions on the Effectiveness of the Measurement Method

Colorimetric spectrophotometry is a commonly used and standardised method to analyse the concentration of different forms of P within a sample (different P forms are defined based on size (soluble P forms are considered those P compounds that pass through a filter with a 0.45 µm pore size (Mckelvie et al. 1995)), and orthophosphate content before and after acid digestion (as outlined in Eisenreich et al. (1975)). A shortfall of this method is that specific P compounds cannot be identified directly. In future work analysis of a larger number of PSS, with a better representation of PSS with secondary and tertiary treatment, would improve the statistical robustness of conclusions.

3.6 Conclusions

In this chapter we first looked at an innovative development policy, and then in order to assess its effectiveness in practice, P concentrations of effluent from the PSS of 7 homes in the Loch Leven catchment were measured using standard colorimetric spectroscopic techniques. The following conclusions were drawn from the study:

- The range of TP, SURP and PP in all seven PSS sampled were 1.91 to 18.01 mg l^{-1}, 0.04 to 6.14 mg l^{-1} and 0.23 to 16.13 mg l^{-1}, respectively.
- No significant differences in TP concentration between PSS with primary, secondary or tertiary treatment were observed in the PSS sampled in this study.
- Our results indicate that PSS treatment type may not be an accurate indicator of TP discharge.
- Policy changes should be made to encourage efficient and routine monitoring of all PSS.
- The importance of human domestic behaviour and tank treatment type and design should be combined to assess the drivers of variability in the quantity and quality of P discharged from PSS.

Building on the results above, that indicate technical improvements are not achieving the required reductions in P flows from the PSS in the Loch Leven catchment, the focus now turns to the theoretical idea that human behaviours may be of key importance in the management and reduction of P flows from homes. Chapter 4 looks at how behaviours may be dictating the recorded P flows from the PSS and, if so, how they can be manipulated to reduce domestic P emissions.

Chapter 4 Assessing Human Behaviour in Relation to the Management of Phosphorus Losses from Private Sewage Systems: the Loch Leven Experience

Abstract

Recent studies suggest that 80% of the estimated 1.5 million private sewage systems (PSS) in the UK are working inefficiently and represent a significant source of phosphorus (P) to freshwater bodies, increasing their vulnerability to eutrophication. Having established in Chapter 3 that increase in private sewage system (PSS) treatment level may not be currently achieving required reductions in P effluent concentrations, the focus of this thesis now turns to the potential to use behaviours to reduce phosphorus (P) emissions from homes to the ecosphere. Promoting pro-environmental behaviour of PSS users potentially offers a significant reduction in P discharge from these systems by 1) reducing P input to the PSS by modifying domestic behaviour, and 2) reducing the risk of P output from PSS failure by improving maintenance of the PSS. To explore the factors that control these behaviours a detailed questionnaire was delivered to all PSS users in the catchment of Loch Leven, Scotland, UK. A return of 156 (24%) revealed over 70% of users feel responsible for maintaining their PSS, 46% are potentially maintaining them ineffectively (i.e. not desludging annually), nearly 30% have poorly installed systems (PSS still receive roof runoff) and 45% reported that their PSS has, at some point, blocked or overflowed. Sixty eight percent of respondents felt that they did not have access to adequate information on PSS maintenance or options for reducing their domestic P production. The results indicate that the most effective action for the improvement of PSS operation could be to provide better guidance on the use of low P detergents and correct PSS maintenance with an improvement in the provision of facilities to support these pro-environmental behaviours.

4.1 The Role of Behaviours on Household Phosphorus Emissions

In the UK and Ireland, the need to control P discharges from PSS has been recognised in recently developed policy. The Building Regulations 2010 in Ireland (Irish Government 2010) provide an expected maximum discharge concentration of 2 mg P l^{-1} for PSS in nutrient sensitive areas. And, in the P sensitive catchment of Loch Leven, in east Scotland, a development policy has been introduced outlining mitigation of P from PSS associated with new developments (Loch Leven Special Protection Area and Ramsar Site 2011). In general, a reliance on technological solutions (i.e. treatment level) to provide low P output from PSS has been adopted in these policies. In a comparative study of nutrient loading to subsoils from PSS with either primary or secondary treatment, Gill et al. (2009) observed that reducing P output by increasing the treatment level of PSS is challenging and most PSS are not specifically designed to reduce P discharge. In those tanks studied in Chapter 3, no significant difference in TP concentration between PSS with primary, secondary or tertiary treatment was observed; indicating PSS treatment type may not be an accurate indicator of TP discharge (Brownlie et al. 2014). To make significant reductions in P discharge from PSS, such technological solutions may not be sufficient when conducted in isolation and increased pro-environmental behaviour of PSS users may also be required to meet required reductions (Comber et al., 2012; Maloney & Ward, 1973).

4.1.1 Understanding Environmental Behaviour

Geller (2002), later assessed by Steg & Vlek (2009), recommends the use of the following research framework when promoting behaviour change:

1. identify behaviours to be changed,
2. identify the controlling factors that underpin those behaviours,
3. design interventions to change those behaviours, and
4. evaluate the effects of those interventions.

We gathered data from 156 PSS users in the Loch Leven catchment to address stages (1) to (3) of this framework and to address the following objectives: (1) to describe socio-demographic aspects of respondents; (2) to assess the perception that PSS users believe there to be a lack of available information regarding best practice on domestic and maintenance behaviours; (3) to assess interactions between controlling factors and behavioural responses (in relation to PSS maintenance and domestic behaviours); and (4) to discuss the results of this study in the context of encouraging pro-environmental behaviour to reduce P discharge from PSS. Specific hypotheses were:

- Residents of properties connected to PSS have different domestic behaviours that are driven by known controlling factors.
- Residents of properties connected to PSS feel responsible for maintaining their PSS correctly.
- A majority of PSS owners do not maintain their PSS properly and have poorly installed or inadequate systems.

4.2 Methods

4.2.1 Questionnaire Design

Questions were designed to collect information about factors known to facilitate environmental behaviours (outlined in Section 2.6.1, Table 2.3), but in the context of behaviours related to domestic P output and PSS maintenance regime (outlined in Section 2.6.1, Table 2.2). Background information about the households, properties and PSS was also collected (Full question summary is provided in 2.6.9). A full account outlining the process used to design the questionnaire is provided in Section 2.6.

To encourage a maximal response, the questionnaire was kept short (27 questions), anonymous (sex, age and gender only) and simple to complete (predominantly tick box answers). Care was taken to present non-leading and unbiased questions. Questionnaires were delivered on the 5th of September 2012, with self-addressed postage paid envelopes to make it easy for individuals to return completed forms by the deadline of the 5th of October 2012. Questionnaires were distributed to 654 addresses within the catchment that were believed to be served by PSS; 156 (24%) were returned. The address list was compiled by the Scottish Environment Protection Agency (SEPA), Scottish Natural Heritage (SNH), Perth and Kinross Council (PKC) and Scottish Water, using Ordnance Survey data to estimate the number of properties located in postcode areas not served by mains sewerage schemes.

4.2.2 Statistical Analysis

Using the statistical software R version 2.51.1 (R-CORE-TEAM 2012), multidimensional categorical data were analysed to test for relationships between controlling factors and, mosaic plots used to visualise significant results. A mosaic plot (Hartigan and Kleiner 1984) is a method of visualising multi-way contingency tables as an area-proportional visualization of frequencies, composed of tiles (corresponding to the cells). They are created by recursive vertical and horizontal splits of a rectangle, thus, the area of each rectangle is proportional to the corresponding cell entry given the dimensions of previous splits. Mosaic plots were used to assess whether:

- respondents who stated that ‘impact on the environment’ influenced the detergent that they bought, also considered ‘low P content’ to be important,
- PSS failures (i.e. becoming blocked, overflowing or producing a bad smell) were affected by the time since the septic tank had last been desludged,
- perception of the degree of personal responsibility to maintain a PSS correctly was related to the time since the septic tank had last been desludged, and
- availability of adequate information on correct PSS maintenance affected perception of the level of personal responsibility to correctly maintain a PSS.

Plots were created in R, using the ‘mosaic’ function within the Visualizing Categorical Data (‘vcd’) package (Meyer et al. 2012) and strucplot framework (Meyer et al. 2006a) with ‘hcl’ residual-based shading (Zeileis et al. 2007). The Pearson Chi-Square Test was used to test if the pattern of data observed (in plots) was significant (i.e. is the pattern of data visualised in the mosaic plot representative of the population as a whole). Only those plots that were significant (i.e. $p \leq 0.05$) are reported, and are considered an accurate representation of the entire population.

Cell shading was used to represent the sign and magnitude of Pearson residuals (standardised deviations of observed from expected values) (Zeileis et al. 2007; Meyer et al. 2006b). Cells with a Pearson residual of >2 or <2 represent a significant departure from independence at the 95% confidence level and are shaded. Shading is not used to visualize significance, but the pattern of dependence (Zeileis et al. 2007). Only responses from users that provided answers to both questions in each mosaic plot were used (accounting for variation between the n-value of the mosaic plot and its two individual questions).

4.3 Results

4.3.1 Socio-Demographic Variation

Respondents were asked how many properties shared their PSS. Sixty percent of respondents stated that no other property shared their PSS, whilst 18% shared their PSS with more than five other properties (range of 0-60, SD = 8.72) (Figure 4.1 (a)). When asked where their PSS drains to, 62% of respondents stated ‘soakaway’, 15% stated ‘direct to river’, 4% selected ‘open drainage ditch’ (Figure 4.1 (b)). The responses to questions regarding the socio-demographic characteristics of respondents (questions 1-8) are summarised in Table 4.1

4.3.2 Domestic Behaviour and PSS Maintenance and their Controlling Factors

The mean number of dishwasher cycles, washing machine cycles, showers and baths taken per person per week was 1.72 (range of 0-7, SD = 1.45), 2.12 (range 0-10, SD = 1.39), 4.62 (range 0-14, SD = 2.58) and 0.95 (range 0-7, SD = 1.62), respectively (Figure 4.1(c)). Respondents were asked to estimate the percentage of PSS in the Loch Leven catchment not operating correctly; 16% considered ‘0-25%’, 25% considered ‘26-50%’, 6% considered above 51%, whilst 52% did not provide an answer (Figure 4.1 (d)). The responses to questions regarding P producing domestic behaviours and the factors that control them (questions 9-16), and those regarding PSS maintenance and the factors that control them (questions 17-23) are summarised in Table 4.1 and Table 4.2.

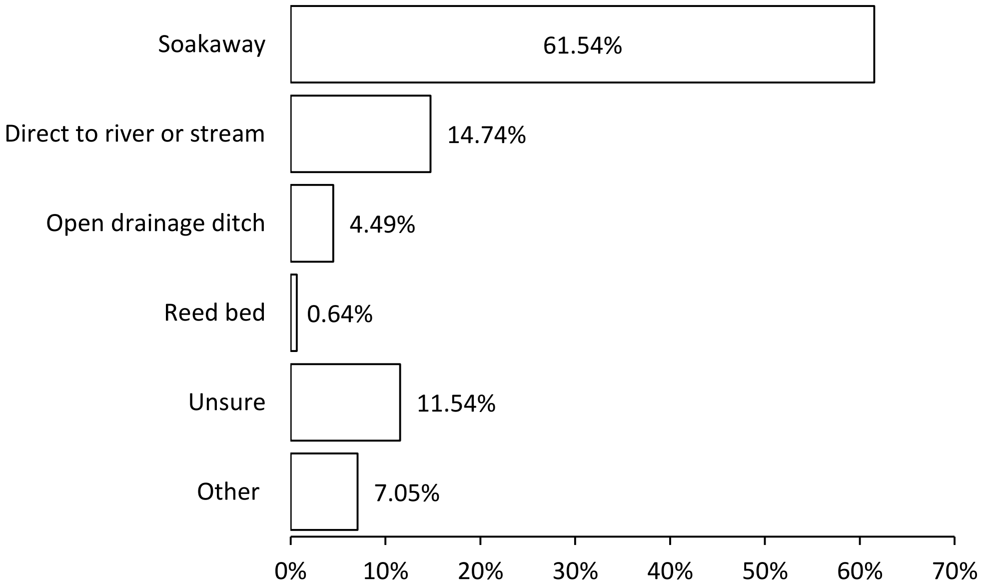


Figure 4.1 (a)

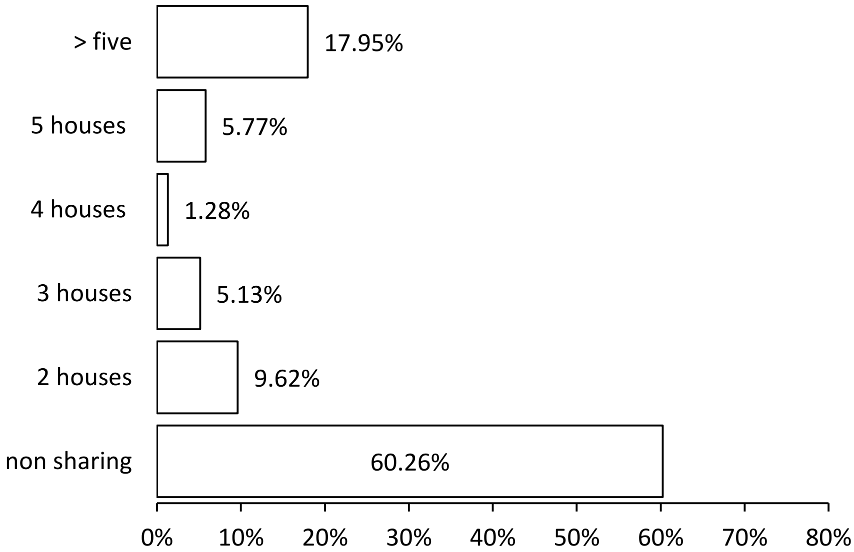


Figure 4.1 (b)

Figure 4.1 (a) The proportion of private sewage systems (PSS) in Loch Leven that drain to soakaways, rivers or streams, drainage ditches, reed beds, other or unknown destinations (n=156), (b) the proportion of households in Loch Leven that share PSS with other households (n=156)

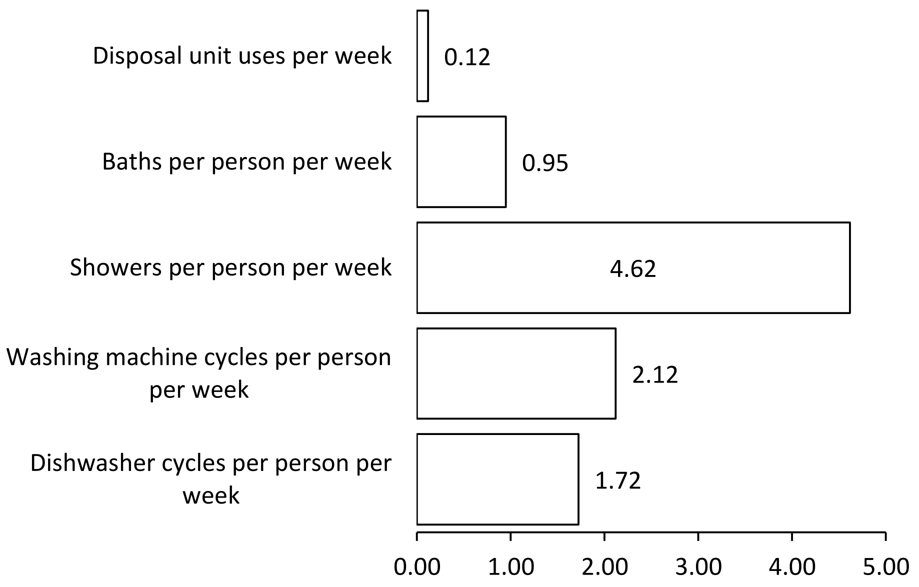


Figure 4.1 (c)

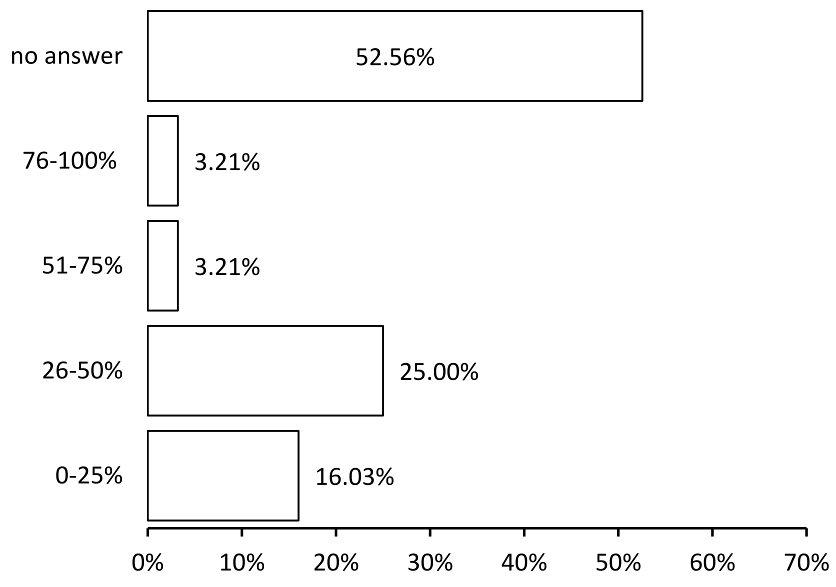


Figure 4.1 (d)

Figure 4.1 (c) The mean water appliance use (disposal units, baths, showers, washing machine and dishwashing machine cycles), per person per week (n=156), (d) the proportion of respondents who estimate the percentage range of PSS that work inefficiently in the Loch Leven catchment was 0-25%, 26-50%, 51-75%, 76-100% and those who didn't provide an answer (n=156).

Table 4.1 Survey questions concerning socio-demographic variation and domestic behaviour, the controlling factors they address and explanatory statistics describing responses.

Questions	Controlling factor or behaviour investigated	Response	Unit
Socio-Demographic Characteristics			
1. What sex are you?	socio-demographic variable	Male (61%), female (35%), no answer (4%)	sex
2. How many people live in your house?	socio-demographic variable	2.52 (mean), (SD = 1.19, n = 156)	people
3. How old are you?	socio-demographic variable	56.55 (mean), (SD = 12.80, n = 146)	years
4. How old is your property?	housing demographic	90.78 (mean), (SD = 83.10, n = 151)	years
5. How old is your PSS?	housing demographic	29.52 (mean), (SD = 32.80, n = 122)	years
6. How long have you lived at your address?	housing demographic	15.00 (mean), (SD = 83.10, n = 150)	years
7. How many properties are connected to your PSS?	responsibility, personal behavioural control	1 = 60.26%, 2 = 9.62%, 3 = 5.13%, 4 = 1.28%, 5 = 5.77%, > 5 = 17.95%, (n = 122)	properties
8. Where does your PSS drain to?	housing demographic, knowledge of the problem,	soakaway = 61.54%, direct to river = 14.74%, open drainage ditch = 4.49%, reed bed = 4.49%, unsure = 11.54%, other = 7.05%, (n = 156)	drainage destination
Domestic behaviour			
9. How many dishwasher cycles do you run per week?	behavioural response	1.72 (mean) (range 0-7, SD = 1.45, n = 156)	no. person^{-1} week^{-1}
10. How many washing machine cycles do you run per week?	behavioural response	2.12 (mean) (range 0-10, SD = 1.39, n = 156)	no. person^{-1} week^{-1}
11. How many baths are run in your house per week?	behavioural response	0.95 (mean) (range 0-7, SD = 1.62, n = 156)	no. person^{-1} week^{-1}
12. How many showers are run in your house per week?	behavioural response	4.62 (mean) (range 0-14, SD = 2.58, n = 156)	no. person^{-1} week^{-1}
13. How many times do use a disposal unit in your house per week?	behavioural response	0.12 (mean) (range 0-7, SD = 0.71, n=156)	no. person^{-1} week^{-1}
14. When buying washing machine detergent which of the following, influence which detergent you buy? (multiple ticks allowed)	behavioural response, low cost-high benefit, knowledge of the problem, knowledge of how to solve the problem	price' = 69.23%, 'cleaning performance' = 53.21%, 'impact to the environment' = 30.90%, 'allergies' = 26.92%, low P content' = 8.97%, 'other' = 4.49%, (n=156)	influence factor
15. When buying dishwashing machine detergent which if the following influence which detergent you buy? (multiple ticks allowed)	behavioural response, low cost-high benefit, knowledge of the problem, knowledge of how to solve the problem	price' = 69.23%, 'cleaning performance' = 53.21%, 'impact to the environment' = 30.90%, 'allergies' = 26.92%, 'low P content' = 8.97%, 'other' = 4.49%, (n=156)	influence factor
16. Do you feel adequate information is available on how to change your domestic habits to improve the performance of your PSS (i.e. change of household detergent)?	knowledge of the problem, knowledge of how to solve the problem, perceived behavioural control	71.33% = no, 28.67% = yes, 9.09% = no answer (n = 156)	yes or no

Table 4.2 Survey questions concerning maintenance behaviour and the public perception of the problem, the controlling factors they address and explanatory statistics describing responses.

Maintenance behaviour			
17. Has your septic tank or PSS ever failed to work correctly (i.e. blocked, overflowed or produced a bad smell)?	behavioural response	yes = 42.31%, no = 51.92%, no answer = 5.77%, (n=156)	yes or no
18. Have you ever emptied/desludged your septic tank? And if so, when was the last time you did?	behavioural response	≤12 = 44.23%, >12 ≤24 = 9.62%, >24 ≤36 = 4.49%, >36 ≤48 = 8.33%, >48 = 10.26%, never = 23.08%, (n=156)	months
19. Does your septic tank have any cracks?	responsibility, knowledge of the problem, knowledge of how to solve the problem	yes = 28.85%, no = 56.41%, no answer = 14.74% (n=156)	yes or no
20. Does your septic tank receive roof runoff?	responsibility, knowledge of the problem, knowledge of how to solve the problem	yes = 17.96%, no = 71.16%, no answer = 9.60 % (n=156)	yes or no
21. Who is responsible for correctly maintaining a PSS? (multiple ticks allowed)	Responsibility	private property owner = 69.48%, local council = 22.08%, Scottish Water = 21.43%, SEPA = 11.69%, other = 3.25%, (n = 154)	n/a
22. Who is responsible for fixing a PSS known to be working incorrectly? (multiple ticks allowed)	Responsibility	private property owner = 69.87%, local council = 18.59%, Scottish Water = 17.95%, SEPA = 14.74% other = 5.13%, (n = 155)	n/a
23. Do you feel adequate information is available on how to correctly maintain your PSS?	knowledge of the problem, knowledge of how to solve the problem, perceived behavioural control	67.61% = no, 32.39% = yes, 9.86% = no answer (n = 156)	yes or no
24. Do you feel adequate information is available on measures to reduce pollution from your PSS?	knowledge of the problem, knowledge of how to solve the problem, perceived behavioural control	61.87% = no, 38.13% = yes, 12.23% = no answer (n = 156)	yes or no
Public Perception of the problem			
25. How many PSS in the Loch Leven catchment do you think are working inefficiently?	personalisation and localisation of the problem	0-25%' = 16.03%, '26-50%' = 25.00%, '51-75% = 3.21%, '76-100%' = 3.21%, no answer = 52.56% (n=156)	percentage range of tanks failing
26. Do you feel informed about the current legislation in relation to PSS?	social pressure, knowledge of the problem	yes = 26.28, no = 70.51%, no answer = 3.21% (n=156)	yes or no
27. Do you think PSS should be registered?	social pressure	yes = 67.31%, no = 32.69%, no answer = 7.05% (n=156)	yes or no

4.3.3 Interaction between Behaviours

Of the respondents, 36% considered ‘impact to the environment’ an influencing factor when buying detergent, whereas only 6% considered both ‘low P content’ and ‘impact to the environment’ to be an influence. In contrast, 61% of respondents felt neither had any influence on the detergents they purchased. This data significantly represents the population ($p = 0.020$, $n = 156$) (Figure 4.2 (a)).

Respondents were asked if their PSS had, at some point, failed to work properly (i.e blocked, over-flowed or produced a bad smell), and how long it had been since they had last desludged their septic tank. Of the respondents, 47% had desludged their septic tank within the last 12 months, 27% had both reported failure, and had desludged their septic tank within the last 12 months. Conversely, 17% of respondents that had never desludged their tank, and 12% that stated their septic tank had not failed and had never desludged their septic tank ($p = 0.042$, $n = 129$) (Figure 4.2. (b)).

Of the respondents, 53% had not desludged their tank within the last 12 months. 40% had not desludged their tank within the last 12 months whilst feeling correctly maintaining a PSS was the responsibility of the private property owner ($p = 0.0075$, $n = 129$) (Figure 4.2 (c)). Of the respondents, 69% felt correctly maintaining a PSS was the responsibility of the private property owner; whilst 43% felt that although the private property owner was responsible to maintain their PSS correctly there was not adequate information available with which their behaviours could be informed ($p = 0.049$, $n = 141$) (Figure 4.2 (d)). The data for PSS failure and connection of PSS to roof run-off or reports of cracks in PSS was not sufficient to significantly represent the population ($p = 0.27$, $n = 126$).

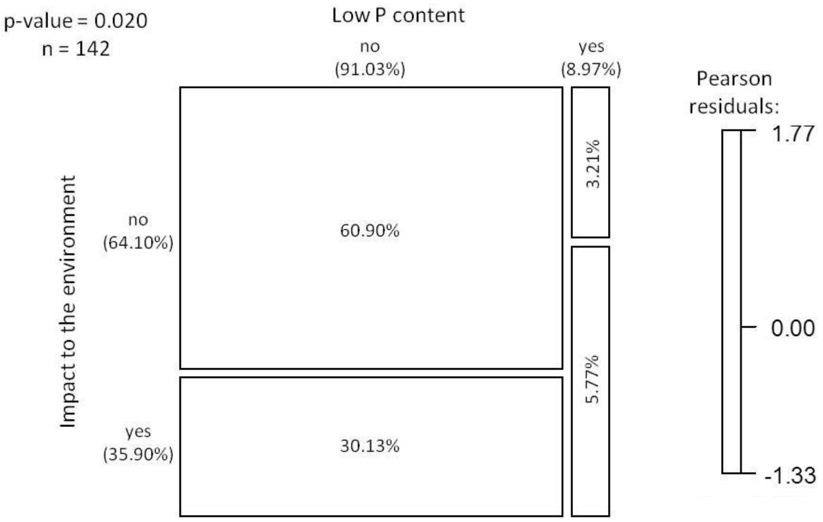


Figure 4.3 (a)

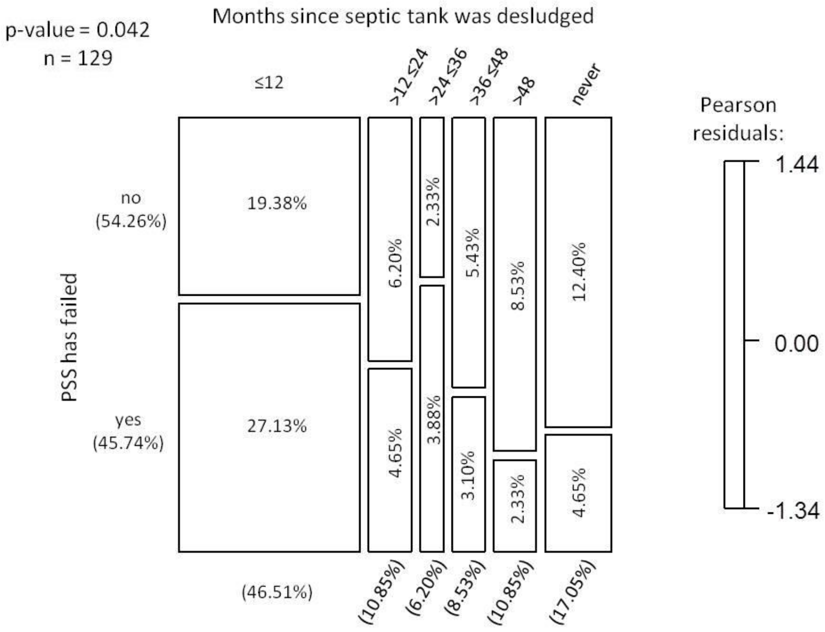


Figure 4.3 (b)

Figure 4.2 Mosaic plots showing the relationships between respondents that state 'low phosphorus content' and 'impact to the environment' influence their washing machine purchasing decisions, and b) the relationships between respondents who reported their septic tank to have failed to work correctly and the time since their private sewage system had last been desludged.

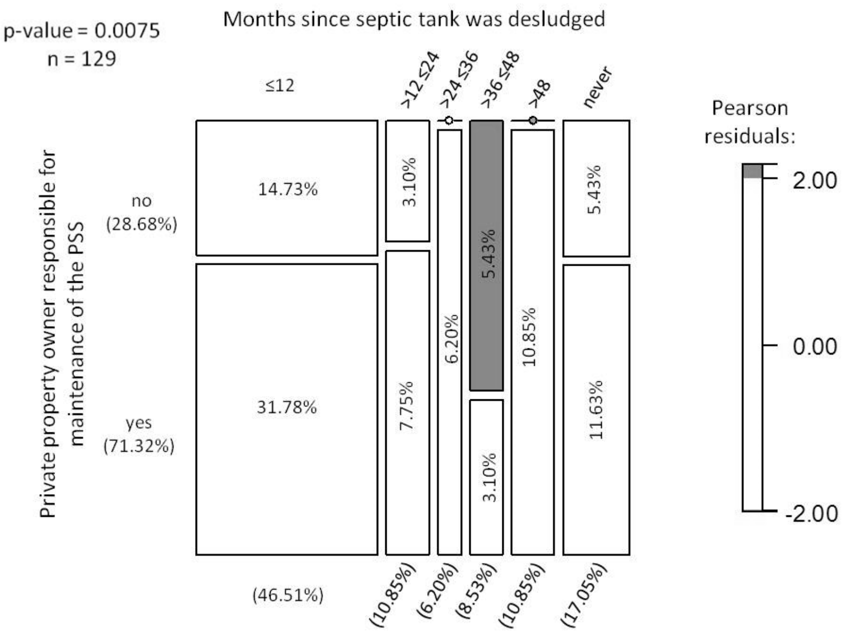


Figure 4.3 (c)

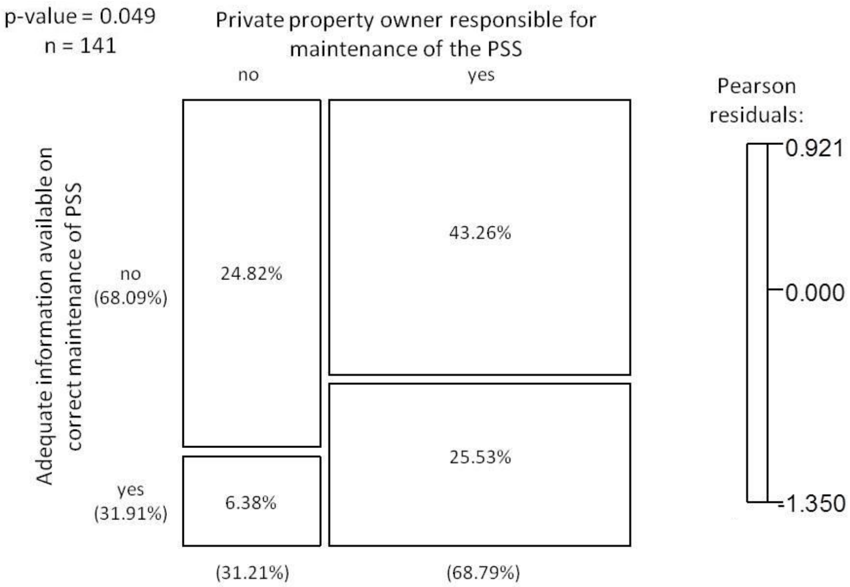


Figure 4.3 (d)

Figure 4.2 Mosiac plots showing c) the relationships between respondents who believe the private property owner is responsible for maintenance of the private sewage system (PSS) and the time since their septic tank had last been desludged, and d) the relationships between respondents who believe there is or is not adequate infromation available on correct maintenance of PSS and those who believe the private property owner is responsible for maintenance of the PSS.

4.4 Discussion

4.4.1 Factors that Affect Domestic Phosphorus Input to PSS

In this survey, purchasing choice of detergent was influenced most by price, followed by cleaning performance. Although in the UK, use of low P detergents and reduction in the volume of detergents used could potentially offer < 28% reduction in P entering PSS (Comber et al. 2012), respondents did not consider 'impact on the environment' when buying detergent and, of those that did, most did not identify 'low P content' as important. Results indicate that individuals consider that the P content of detergents does not impact the environment or consider this impact minimal or unavoidable. Assuming that individuals want to behave in a manner that does not cause harm to the environment, this survey shows respondents do not have knowledge of the problem or potential solutions. This corresponds to low 'perceived behavioural control', (i.e. an individual's perception of responsibility and of their competence to change behaviours that will achieve a desired outcome) a known prerequisite to choosing pro-environmental behaviour (Klöckner 2013).

The perceived value of using a low P content detergent (i.e. reducing P output of PSS) must outweigh the perceived value of a detergent that is cheap and cleans well. The Theory of Planned Behaviour states that individuals will choose low cost-high benefit behaviour (Barr 2004; Ajzen 1991). Currently this may not be satisfied; greater information on detergent packaging may raise awareness. Köhler (2001) highlights that 'ecolabels' highlighting detergent P content are inherently complex to produce, due to the general lack of clarity in the necessary message that would need to be included.

In the US, environmental policy has been implemented to reduce the impact of P from detergents; the sale of detergents with more than 0.5% P has been banned in sixteen states due to the risks that they pose to freshwaters (Lusk et al. 2011). This has resulted in a reduction of P in wastewaters by 40-50% (US EPA 2002b). Since June 2013, the EU has prohibited the sale of consumer laundry detergents that provide ≥ 0.5 g of P per standard dosage (for a single cycle). By 2017 the sale of dishwasher detergents with ≥ 0.3 P g per standard dosage (for a single cycle) will also be banned (EU 2012). This is encouraging, but it regulates only P 'concentrations' in detergent; the 'amount' (or P load) of detergent used is still determined by individual behavioural choice. Providing accurate measuring cups for liquid detergents and the use of detergent in tablet form are effective measures for controlling the quantity of P used in each wash (Köhler 2006).

Habitual behaviour, such as dishwasher, washing machine and detergent use, is often not preceded by intricate reasoning and is directed by automated cognitive processes. Behaviour repeated annually or bi-annually is greatly determined by intention (i.e. desludging a septic tank), whilst weekly behaviour (i.e. detergent purchase and use) is influenced by habit strength (Ouellette & Wood 1998). Such behaviours can be difficult to change (Wood et al. 2005). Interventions that disrupt the context that maintain habits use regular reminders (Nilsen et al. 2012); Chan (1998) demonstrates how the mass media play an important role in establishing social norms.

Although not explored within this survey, it should be noted that 30-70% of P in wastewater can come from urine and faecal derived nucleic acids and tri-phosphates (Lusk et al. 2011) and may exceed detergent P load from domestic sources. Additives in processed foods can add an extra 0.47-1.00 g P day^{-1} to diets and are often 'non-essential' (i.e. added for aesthetic and preservative reasons) (Comber et al., 2012; Uribarri & Calvo, 2003). Reduction in the use of such additives at an industry level may be required if significant domestic P reductions are to be made.

4.4.2 Factors that Impact Maintenance Behaviour

Regular septic tank desludging is recommended as good maintenance practice (University of Minnesota 1998; SEPA et al. 2006; US EPA 2002b). However, there is a general public perception that PSS are self-maintaining and tanks do not need regular emptying (Moelants et al. 2008). In this survey, the number of PSS running inefficiently is greatly underestimated by the public, only 3% of respondents considered 75-100% of the PSS in the Loch Leven catchment were operating inefficiently (current UK estimates suggest 80% of PSS in the UK are working inefficiently; in this study 42% of PSS described by respondents were connected to roof runoff or/and had not been desludged in the last year). Without such knowledge, moral obligations to address the issue are diminished and social norms (the combination of the social pressure perceived by an individual to perform the behaviour, multiplied by their willingness to do so) are reduced. From the large variation in responses, it is suggested that there is no established social norm with regards to the regularity of septic tank desludging and, therefore, little social pressure to do so. This is confounded by the variety of different information available regards suitable desludging frequency, ranging from 1-6 years (SEPA 2006; Angus Council 2012; Aberdeenshire Council 2012; US EPA 1999), whilst others state septic tanks should be emptied in accordance with the manufacturers specifications (HM Government 2010a), although the manufacturers details may not be known by many PSS owners.

The required frequency of desludging of a PSS depends on the capacity of the tank and the volume and type of waste that it receives, and may, therefore, be considered PSS specific (Withers et al. 2012). Moore (2000) provides a matrix in which household size and tank capacity can be used to estimate desludging frequency (i.e. a family of two with a 500 gallon (2273 l) tank should empty their tank every 2.6 years). In the UK, a lack of data on PSS (Withers et al. 2012) could make such calculations difficult. It is, therefore, challenging for users to determine the correct maintenance practices for their PSS.

In our survey, of those respondents that had desludged their septic tank within the last 12 months, the majority reported that their PSS had, at some point, also failed to work correctly. Conversely, the majority of respondents that had never desludged their tank did not report failure. This suggests that septic tanks may be commonly emptied as a response to failure as opposed to as a preventative step to avoid failure, and/or that some PSS are poorly installed or inadequately sized causing failure despite regular emptying. A comprehensive field survey of PSS is needed to identify those tanks that are working incorrectly and greater public information is required to raise awareness of the importance of desludging regimes in reducing P discharges to the environment from PSS.

In shared systems, responsibility for tank emptying can be unclear (Withers et al. 2012). Although, in this survey, nearly 40% of respondents reported a shared PSS, we found that nearly 70% of respondents felt that it was their personal responsibility to correctly maintain their PSS. Although responsibility is a core controlling factor of behaviour, it did not equate to the behaviour of regular annual desludging (i.e. less than half had desludged their septic tanks within the last 12 months). Nearly 70% of respondents felt that there was inadequate information to inform their PSS maintenance regime leading to the suggestion that perception of responsibility coupled with the provision of sufficient information may result in improved overall behaviour. However, nearly a third of respondents denied any responsibility for maintaining or fixing their PSS, a perception that clearly needs to be addressed.

4.5 Discussion on the Methods Used

Despite the survey being reliant on volunteer participation, a response rate of 24% was observed is comparable with similar studies (i.e. a 24% response rate in a postal survey of the public was observed in a similar behavioural study by Miao & Wei (2013)). Monetary incentives are shown to double the response rate to postal questionnaires (Edwards et al. 2002). Although the incentive of a small donation to a charity for each response received was considered, this was beyond the funding budget for the study. A careful balance between a) number of questions asked (too many questions could potentially deter respondents from returning questionnaires) and b) the need to obtain as much information as possible, was required. It is emphasised that the questionnaire used in this report was an exploratory study to assess relevant behaviours (Table 2.2) and known factors that control environmental behaviours (Table 2.3), and was not designed to be used to fully describe or fully predict domestic behaviours. A much more in depth analysis of personal characteristics of each respondent would be required to achieve this. The complexity of behavioural models (as outlined in section 2.6) highlight the amount of information required to predict behaviours (i.e. information detailing personal beliefs, attitudes, degree of personal behavioural control and behavioural intention). The acquisition of such information was beyond the scope of this questionnaire.

4.6 Conclusions

In this chapter, an exploratory study was conducted focusing on the behaviours that contribute to P emissions from PSS, with the aim to assess the potential to reduce P emissions from homes through behavioural change. A survey of 156 participants was undertaken and the conclusions of statistical analysis and review of the resulting data is as follows:

- A large proportion of PSS users feel responsible for correctly maintaining their PSS, but are potentially not maintaining them effectively (i.e. lack of regular annual desludging) or have poorly installed or inadequate systems (i.e. unaddressed cracks in PSS with some still receiving roof runoff).
- There is a need for better education and information on PSS maintenance and the input of P to these systems from domestic sources.
- It is suggested that in order to change target behaviours, situational barriers such as the provision of cheap, accessible behavioural alternatives that are considered the social norm must first be addressed before attempts are made to change underlying motivational factors through education.

This study does suggest that considerable reductions in P flows could be achieved through behaviour changes. A problem in measuring the extent of individual reductions resulting from a particular behaviour, lie in the fact that traditional methods of measuring P (i.e. colorimetric spectroscopy) do not enable identification of specific P compounds, that may be associated with a particular domestic source. Certain behaviours may result in the emission of specific P compounds. To further understand the link between human behaviour and domestic P emissions to the ecosphere, a full analysis of survey data against the composition of P compounds found in corresponding PSS effluent is required. It is for this reason that the next chapter focuses on the development of a new method to enable analysis of PSS effluent with ^{31}P nuclear magnetic resonance spectroscopy, which can be used to identify the composition of specific P compounds within a sample.

Chapter 5 Optimisation of a Novel Method to Prepare Private Sewage System Effluent Samples for Analysis Using 31-Phosphorus Nuclear Magnetic Resonance Spectroscopy.

Abstract

As discussed and studied in Chapter 4, human domestic behaviours have the potential to determine the forms, quantities and transport routes of phosphorus (P) from domestic sources (i.e. detergents, dietary P and personal products) to sewerage systems. But to accurately track the sources of private sewage system (PSS) pollution, it is necessary to identify the types of P compounds that persist within the liquor of a PSS and link them to their sources within the home. In the following chapter we use ^{31}P nuclear magnetic resonance (NMR) spectroscopy to achieve this. ^{31}P NMR is a non-destructive, non-invasive method that can be used to detect both inorganic and organic P compounds from samples simultaneously, effectively ‘fingerprinting’ the P composition of a sample. To produce high resolution spectra in solution ^{31}P NMR, the final sample must have concentrations of > 100 mg P l^{-1}. To achieve this, P must be extracted from the raw sample and concentrated. Here we report the development and optimisation of a simple and efficient way of preparing ^{31}P NMR samples from PSS effluent to give reproducible, high resolution NMR spectra. This method uses the addition of poly-aluminium chloride (PAC) to a raw sample (which is then adjusted to between pH 6.5-7.0) to flocculate P compounds. P compounds are subsequently recovered and dissolved by NaOH, before samples are concentrated by rotary vacuum evaporation. The development of this method revealed that PAC flocculation of P from PSS effluent is highly pH dependent. Adjustment of pH to 6.5-7.0 during the flocculation stage is necessary, and can achieve > 99% TP flocculation. Optimisation of the method reveals that 0.5 l sample volumes of PSS effluent extracted with PAC added at an Aluminium:P molar ratio of 10:1 will produce spectra of high signal to noise ratio (S:N). Spectra produced from PSS effluent showed presence of phosphonate, orthophosphate, orthophosphate monoesters, phospholipid P, deoxyribonucleic acid P and pyrophosphate, as well as multiple P groups of myo-inositol hexakisphosphate. The successful analysis of PSS effluent with ^{31}P NMR spectroscopy, demonstrated in this work, opens the way to more detailed study of PSS effluent P composition (and the domestic sources that contribute to it), and has the potential to enable identification of links between human domestic behaviours and the quantity and quality of P compounds in PSS effluent. Such information may be valuable in the implementation of strategies aimed to manage P flows from the built environment.

5.1 Introduction

Human domestic behaviour may regulate forms and transport of P from domestic sources (i.e. detergents, dietary P and personal products) to sewerage systems. But to further understand this link and substantiate the risk of PSS pollution, identification of the types of P compounds that persist within the liquor of the last or only septic tank within a PSS is required. Such P compounds will ultimately be delivered to the aquatic environment via soakaway, drainage ditch, or in some cases directly to the river channel itself (the proportions of which are discussed in Section 4.3.1). Little research has been conducted to identify the types of P compounds that persist within a septic tank, in part due to the complexities surrounding suitable analytical techniques.

5.1.1 Analysing the Inorganic and Organic Phosphorus Compounds in Environmental Samples

Techniques used to directly identify specific P compounds include enzyme hydrolysis, high performance liquid chromatography (HPLC), mass spectroscopy and ^{31}P nuclear magnetic resonance (NMR) spectroscopy (O'Halloran and Cade-Menun 2007). Such methods can be complex, laborious and expensive (Cade-Menun 2005). Of all the techniques available, since its first use by Newman and Tate (1980), ^{31}P NMR spectroscopy has advanced the knowledge of organic P in environmental samples more than any other technique (Cade-Menun 2005). For a full description of ^{31}P NMR, see Section 2.5.

The P in environmental samples is rarely of high enough concentration to be detected using NMR spectroscopy, and therefore must be concentrated. A major difficulty involved in preparing samples for ^{31}P NMR, is how to extract, recover and concentrate the P in the sample without damage or alteration in P compounds present (Peng et al. 2010). Although the methods of ^{31}P NMR spectroscopy are often challenging, the results provide a far higher resolution in the chemical analysis of P compounds in an environmental sample, in comparison to common fractionation techniques, such as Hedley fractionation (Hedley et al. 1982) and Psenner fractionation (Psenner et al. 1988).

5.1.2 Preparation of Sample for Use in Solution ^{31}P NMR

Although solid samples can be used ^{31}P NMR, solid-state ^{31}P NMR is limited to those samples that have the minimum concentration of 1 mg P g^{-1} required to produce a detectable signal (Magid et al. 1996). Even in solids that meet this criteria, spectral resolution of solid state ^{31}P NMR is very poor in comparison to solution ^{31}P NMR (Cade-Menun et al. 2005). The following work discusses sample preparation for use in solution ^{31}P NMR only.

To maximize useful information from NMR spectra, a high spectral resolution (the sharpness and separation of peaks) and signal to noise ratio (S:N) (the height of peaks in relation to baseline noise) are required (Cade-Menun 2005). To produce such spectra in solution ^{31}P NMR, the final sample must have concentrations of >100 mg P l^{-1} (Cade-Menun et al. 2005). To achieve this, P must be extracted from the raw sample if solid (i.e. soil) or precipitated from the solution if liquid (i.e. PSS effluent or lake water). This is followed by a method of concentration, commonly lyophilisation or rotary vacuum evaporation. It is argued that such processes may reduce reliability of spectra to represent the types of compounds present in the initial environmental sample (Cade-Menun 1996). Problems with incomplete P extraction can result in misleading results and poor detection of P forms. NMR is an expensive procedure; samples with low P concentration are more expensive to process as longer run times are required to produce readable spectra. As well as this, the longer time a sample is held at ambient temperature (within the NMR machinery), the greater the risk that P compounds may degrade within the sample (Leytem and Mikkelsen 2003). Compounds must therefore be extracted and concentrated efficiently and without damage (Peng et al. 2010). S:N can be enhanced by raising the number of nuclei in the sample (i.e. increasing the sample P concentration), increasing the sample volume (of the final NMR sample volume used within the NMR apparatus), increasing the magnetic field strength (James 1998) or increasing the NMR probe temperature (Turner et al., 2003).

Although ^{31}P NMR analysis has successfully been used in the analysis of P compounds in soils (Turrion et al. 2010; Xu et al. 2012; Cade-Menun 1996) and sediments (Xu et al. 2012; Ahlgren et al. 2006), the analysis of sewage sludge using ^{31}P NMR is in its infancy (Peng et al. 2010) and, to the knowledge of the author, the work presented here is the only known use of ^{31}P NMR to analyse P compounds in PSS effluent. Currently no standard method to prepare samples for NMR analysis is used (Xu et al. 2012), which potentially confounds comparisons between the results of studies using different sample preparation methods. Different reagents have been successfully used to extract P compounds from an array of different environmental samples, although a 1:1 mixture of 0.25 M NaOH and 0.05 M sodium ethylenediaminetetraacetic acid (EDTA) has been most widely used (Reitzel et al. 2006; Zhang et al. 2012; Peng et al. 2010; McDowall et al. 2009) (summarised in Table 5.1).

Table 5.1 Studies of different environmental samples that have been analysed using solution ^{31}P NMR spectroscopy and the extraction reagents and the method of concentration used

Environmental sample	**Extraction Reagents**	**Concentration Procedure**	**Reference**
Lake sediments	0.25 M NaOH 0.05 M Na_2EDTA	Lyophilisation and rotary vacuum extraction	(Xu et al. 2012)
Lake Sediments	0.25 M NaOH 0.05 M Na_2EDTA	Rotary vacuum evaporation	(Ahlgren et al. 2006)
Forest floor soils	0.5 M NaOH 0.1 M Na_2EDTA	Lyophilisation	(Turrion et al. 2010)
Forest floor soils	0.25 M NaOH 0.05M Na_2EDTA	Lyophilisation	(Zhang et al. 2012)
Marine particulates	0.25 M NaOH 0.05 M Na_2EDTA	Lyophilisation	(Paytan et al. 2003)
Cattle feed and faeces	0.25 M NaOH 0.05 M Na_2EDTA	Lyophilisation	(McDowell et al. 2008)
River sediments	0.4 M NaOH	Rotary vacuum evaporation	(Wang and Pant 2010)
Sewage sludge	0.25 M NaOH 0.05 M Na_2EDTA	Lyophilisation	(Peng et al. 2010)
Volcanic soils	0.25 M NaOH Chelex	Lyophilisation	(Briceno et al. 2004)

A disadvantage of using such methods (outlined in Table 5.1) is that paramagnetic ions, such as manganese, iron and calcium are also extracted along with P compounds which can cause line broadening and distortion of NMR spectra (Cade-Menun 1996; Reitzel et al. 2009).

The following work focuses on a novel, and to date little used, sample preparation technique that has been shown to successfully extract P compounds without extracting paramagnetic ions, successfully concentrate P in samples by up to 5500 times, and cause minimal degradation to P compounds (Reitzel et al. 2009). This method uses the addition of poly-aluminium chloride (PAC) to a raw sample (which is then adjusted to between pH 6.5-7.0) to flocculate P compounds. P compounds are subsequently recovered and dissolved by NaOH, before samples are concentrated by rotary vacuum evaporation (Reitzel et al. 2009). Reitzel et al. (2009) demonstrated that, using this method, 20 l samples of lake water with TP concentrations ranging from 19 to 531 µg P l^{-1} can be concentrated to between 131 to 1135 mg P l^{-1}, and used to produce high resolution ^{31}P NMR spectra. This method provides a sensitive and simple procedure to process environmental samples for ^{31}P NMR analysis.

5.1.3 Research Aims

Here we report the development and optimisation of a method to prepare PSS effluent samples for ^{31}P NMR analysis, (based on the method outlined in Reitzel et al., (2009)). Optimal method selection was based primarily on improvement to the S:N of the NMR spectra followed by improvement to the simplicity and ease of use of the procedure.

Method development involved an assessment of the proportion of TP extracted using PAC flocculation, and the effect pH has on this process, and an assessment of the proportion of TP dissolved from the flocculent during the NaOH ‘wash’ stage. Method optimisation involved assessing if the S:N of the spectra can be improved by adjusting the volume of raw sample used, and altering the Al:P molar ratio used to calculate the volume of PAC to be added in the flocculation step. Specific hypotheses are as follows:

- A method used to process lake water samples for analysis using ^{31}P-NMR (Reitzel et al. (2009) can be developed to facilitate the production of high resolution NMR spectra for samples taken from PSS effluent.
- PAC flocculation of P from samples is pH dependent.
- A reduced volume of PSS effluent sample (in comparison to lake water sample volumes used in the methodology of Reitzel et al. (2009)) is sufficient to produce high resolution NMR spectra.
- An Al:P molar ratio of 10:1 used in PAC flocculation will produce the highest resolution NMR spectra.

5.2 Methods

Samples were collected from three PSS. PSS 1 had a tertiary treatment consisting of an aeration system and a filter system using Bauxsol^{TM} pellets (containing Al and Fe compounds) to bind P. PSS 2 and PSS 3 were both primary treatment systems constructed from single fibre glass tanks.

Samples were collected from each PSS as outlined in Section 2.3. Samples were then transported back to the lab and stored in darkness at 4°C until preparation of samples for NMR was started; this was within 12 hours of sample collection for all samples. All samples were collected between November and December 2012.

5.2.1 Phosphorus Extraction Method

Phosphorus was extracted from effluent samples using PAC flocculation at an Al:P molar ratio of 10:1, and an adjusted pH of 6.5-7.0. Samples were concentrated using rotary vacuum evaporation. A full description of the method is provided in Section 2.5.2.

To test that a single NaOH ‘wash’ had effectively dissolved all P from the Al floc, the pellets remaining after the second centrifugation (Stage 5, Figure 2.6), were dissolved in 50 ml of 1 M NaOH and placed on an end-over-end shaker for a further 17 hours. After which samples were centrifuged (at 5000 g) and the P concentration of the supernatant determined using colorimetric spectroscopy. Presence of P would indicate a single NaOH ‘wash’ does not dissolve all P contained within the Al floc.

5.2.2 Modification of the Method

Modifications of the method, as outlined by Reitzel et al. (2009), are written into the method procedure in Section 2.5.2 and highlighted in the following passage. Firstly the initial sample was not filtered since this was not feasible due to the viscosity and volume of the sample. Secondly, an extra centrifuge stage (at 5000 g) was added after the Al floc was removed from the over-end shaker (Stage 5, Figure 2.6) in order to remove excess sediment/suspended precipitate. Thirdly, after rotary evaporation the sample was centrifuged again at 5000 g as opposed to 59,860 g due to a lack of access to a centrifuge capable of performing this. Reitzel et al. (2009) prepared samples for ^{31}P

NMR from 20.0 l volumes of lake water. Here we use effluent with a TP concentration more than a factor of 10 greater so a sample volume of 0.5 l and 5.0 l was used.

5.2.3 NMR Settings

The NMR was recorded on a Bruker AVIII, operating at 161.98 MHz for ^{31}P, at 25˚C. Spectra were recorded using a 30˚ observation pulse, acquisition time of 1.01 seconds and a relaxation delay of 0.5 seconds. To ensure comparability, all samples were run for 7 hours and 10 minutes, acquiring around 16,000 transients. The final NMR sample volume, magnetic field strength and probe temperature were constant for each analysis. Chemical shifts were indirectly referenced to D_2O for signal lock. The areas of peaks are proportional to the number of nuclei present in the sample. The percentage area of each peak was assigned based on their proportional area distribution as a percentage of the largest peak. Peaks were assigned by comparison with literature (Cade-Menun, 2005).

5.2.4 Analysis of Phosphorus Concentration of PSS Effluent Samples

To track movement of P during the P extraction procedure, sub-samples were taken at various stages (as discussed in Section 5.2.5) and P concentration determined using colorimetric spectrophotometry as outlined in Section 2.4.

5.2.5 Assessing the Effect of pH on Poly Aluminium Chloride Flocculation of Phosphorus

To test whether pH adjustment has an effect on PAC flocculation, six 0.5 l samples were taken from both PSS 1 and PSS 2. A volume of PAX-18 at an Al:P molar ratio of 10:1 was then added to all twelve samples. After the addition of PAX-18, the pH of the effluent samples taken from PSS 1 was 11.2-11.4, whilst the pH of the effluent samples from PSS 2 was 10.6-10.9. The pH of three of each set was then adjusted to between pH 6.5-7.0 with drop wise addition of 1 M NaOH.

To track the movement of P during the extraction, 5 ml sub-samples were taken from each sample at the following key stages, and the TP, TSP and SRP concentration determined using colorimetric spectroscopy.

- the initial sample ((A) Figure 2.6),
- the residual water after flocculation ((B) Figure 2.6),
- the supernatant after the first centrifuge stage ((C) Figure 2.6),
- and the supernatant of the Al floc after the second NaOH wash (shaken for 17 hours and then centrifuged).

5.2.6 Assessing the Volume of Raw Sample Required for the Preparation of PSS Effluent Samples for ^{31}P NMR Analysis

To test if spectral resolution is impacted by the volume of the PSS effluent sample, one 5.0 l and one 0.5 l sample was collected from PSS 1 and PSS 2, and prepared for NMR analysis. A volume of PAX-18 at an Al:P molar ratio of 10:1 was added to all four samples and the pH adjusted to between 6.5 and 7.0. The method was then followed as outlined in Section 2.5.2. Each sample was analysed using ^{31}P NMR spectroscopy, and the plots of each assessed for differences in S:N and compound distribution.

5.2.7 Assessing the Amount of Poly Aluminium Chloride used in Phosphorus Extraction

To optimise the volume of PAX-18 to be added, nine 0.5 l samples were taken from PSS 3. Three samples were treated with PAX-18 at an Al:P molar ratios of 10:1 (0.516 ml of PAX-18), three at an Al:P molar ratio of 50:1 (2.58 ml of PAX-18), and three at an Al:P molar ratio of 100:1 (5.16 ml of PAX-18). In the following report these three treatment types are referred to as Al:P 10:1, Al:P 50:1 and Al:P 100:1. All other stages of sample preparation were followed as outlined in Section 2.5.2. Each sample was then analysed using ^{31}P NMR spectroscopy, and the plots of each assessed for differences in S:N and compound distribution.

5.2.8 Method Optimization Selection Criteria

The measure of improvement used in the method optimization was based on improvement made to the S:N of the NMR spectra. If little or no improvement to S:N was observed, the method with the simplest procedure was selected. Visual comparison of the spectra was aided by S:N calculated by the Bruker AVIII software. S:N increases as the square root of the number of acquisitions (i.e. scans), therefore four times the number of acquisitions are needed to double the S:N. The final NMR sample volume, magnetic field strength, probe temperature and run time were kept constant for each analysis (known to impact S:N). It is assumed that change in S:N and spectral resolution was predominantly due to an increase in the concentration of nuclei. It is acknowledged that factors such as viscosity and variation in local magnetic field surrounding NMR apparatus can also affect S:N. Therefore S:N is used as a qualitative indication of signal improvement rather than a quantitative scale of improvement.

5.2.9 Statistical Methods

To assess if adjusting the pH to 6.5-7.0 had a significant effect on P flocculation, the Mood's Median test was used to test if the median TP, TSP and SRP concentration (response variables) in the residual water ((B) Figure 2.6) of samples, differed significantly in those samples that were pH adjusted after PAC addition, and those samples that were not pH adjusted after PAC addition (treatment variables).

To assess if increasing the amount of PAC used during sample preparation had an impact on spectra S:N, the Mood's Median test was used to test for significant difference between the median S:N of spectra (response variables) for samples treated with PAC at different Al:P molar ratios (i.e. Al:P 10:1, Al:P 50:1 and Al:P 100:1 (treatment variables)).

5.3 Results

5.3.1 The Effect of pH on Poly Aluminium Chloride Flocculation of Phosphorus

After PAC addition, flocculation was visibly reduced in samples without pH adjustment (Figure 5.1). Concentrations of TP, TSP, SRP and PP of raw samples taken from PSS 1 were 19.36, 15.81, 14.24 and 3.54 mg l^{-1}, respectively (Figure 5.2 a)). Initial concentrations of TP, TSP, SRP and PP of samples taken from PSS 2 were 12.61, 5.77, 5.47, and 6.84 mg l^{-1}, respectively (Figure 5.2 c)).

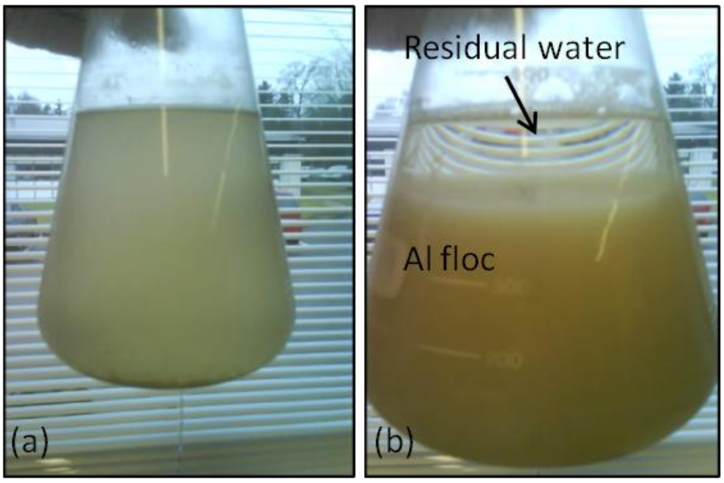


Figure 5.1 Effluent samples taken from a private sewage system with primary treatment c. 30 minutes after addition of PAX-18; (a) sample without pH adjustment and (b) sample with pH adjusted to between 6.0 and 7.5.

In both of the samples that were adjusted to pH 6.0 to 7.5, after addition of PAX-18, a 99% to 100% reduction in TP concentration was observed in both residual liquid ((B) Figure 2.6) and supernatant ((C) Figure 2.6), in comparison to initial sample TP concentrations (Figure 5.2 b) and d)).

In those PSS samples without pH adjustment, a reduction in TP concentration in residual liquid (B) and supernatant (C) 17% and 2% was observed in the sample taken from PSS 1 (Figure 5.2 a)) and 34% and 41% in the effluent sample taken from PSS 2 (Figure 5.2 c)). The reduction observed in TP concentration in the sample taken from PSS 2 was mainly composed of a decrease in PP concentration; a reduction by 4.17 mg l^{-1} in the residual liquid (B) and 4.27 mg l^{-1} in the supernatant (C). The PP concentration of the sample taken from PSS 1 increased from 3.54 in the residual liquid (B) to 4.51 mg l^{-1} in the supernatant (B). In those samples without pH adjustment a minimum reduction in SURP concentration of 83% was measured between the raw sample (A), and both the residual liquid (B) and the supernatant (C) samples (Figure 5.2 a) and c)).

In both PSS 1 and PSS 2 samples, significant difference in the median TP, TSP and SRP concentrations were observed between the residual liquid (B) of the samples with pH adjustment and the residual liquid of the samples without pH adjustment ($p = 0.01$, $n = 6$).

The TP concentration in the jsupernatant of the floc after a second ‘wash’ with 1 M NaOH was below 2.0 mg l^{-1} in all samples, and for those with pH adjustment, concentrations of less than 1.10 mg l^{-1} were observed (Figure 5.2).

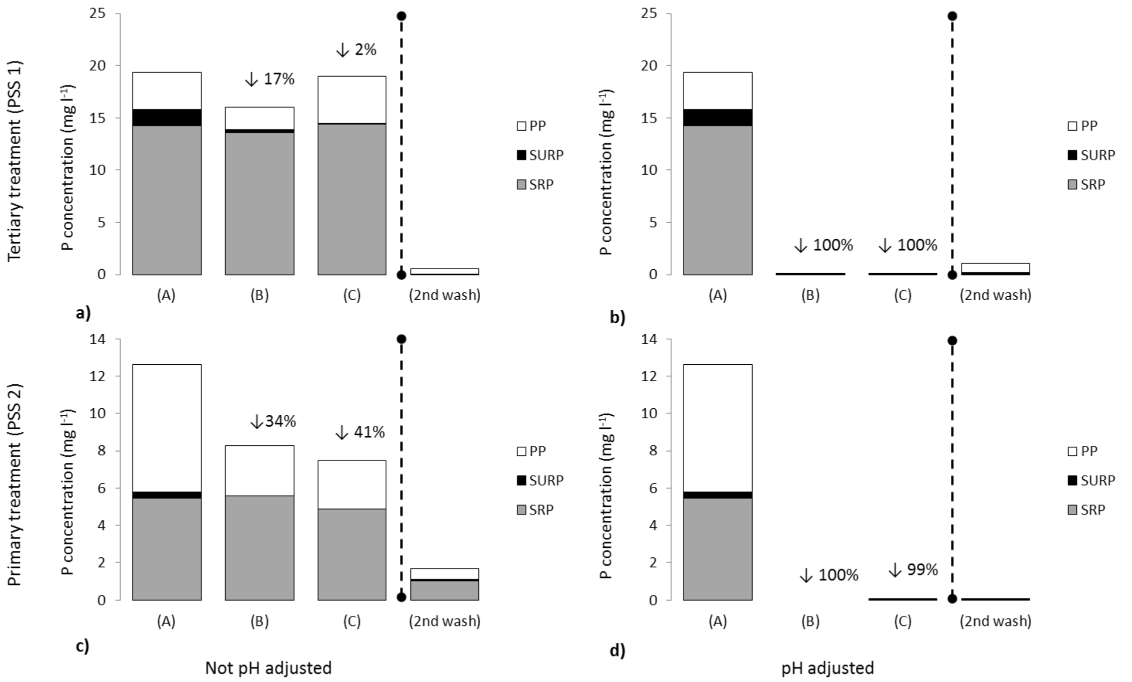


Figure 5.2 Plots showing the mean concentration (n=3) of soluble reactive phosphorus (SRP), soluble unreactive phosphorus (SURP) and particulate phosphorus (PP) that make up the total phosphorus (TP) concentration of private sewage system effluent in, (A) the raw sample, (B) the residual liquid after addition of PAX-18 and (C) the supernatant after centrifuging flocculant, and (2nd wash) the supernatant of the Al floc after a second NaOH ‘wash’ (dotted lines represents sample at this stage has had residual water removed). The % decrease in TP concentration from A to B and A to C is also shown. Plot a) shows results for the PSS 1 without pH adjustment, b) PSS 1 with pH adjustment, c) PSS 2 without pH adjustment, and d) PSS 2 with pH adjustment.

5.3.2 Optimising the Volume of Raw Sample Required for the Preparation of PSS Effluent Samples for ^{31}P NMR Analysis

The NMR samples prepared from both 0.5 and 5.0 l sample volumes from PSS 2, produced high resolution spectra, with a S:N of 31.94 and 19.29 for the 0.5 l and 5 l samples, respectively. Both spectra show presence of orthophosphate (ortho-P) and orthophosphate monoester (mono-P), although the proportion of mono-P detected using a 5 l volume was greater (Figure 5.3 a) and b)). A small concentration of pyrophosphate (pyro-P) was potentially observed in the spectra of the 5 l sample, although this was unclear due to S:N in this plot (Figure 5.3 b). The expansion of the mono-P peak shows the presence of the P1 and P3 peaks of *myo*-inositol hexakisphosphate in both samples, although peaks are larger in the plot of the 5.0 l volume sample. The TP concentration of the initial PSS 2 sample was 11.24 mg P l^{-1}.

High resolution spectra were produced from NMR samples prepared from both 0.5 and 5.0 l volumes of effluent taken from PSS 1, with an S:N of 233.71 and 522.62 for the 0.5 l and 5 l samples, respectively. Both show presence of phosphonate (phospho-P), ortho-P, mono-P, deoxyribonucleic acid P (DNA-P) and phospholipid-P (PL-P). At such high S:N little difference in clarity of information provided by spectra is observed (Figure 5.3 c) and d)). Expansion of the orthophosphate-monoester region in spectra from both sample volumes show peaks for P1 and P3, P2, P4 and P6, and P5 groups of myo-inositol hexakisphosphate. The TP concentration of the initial PSS 1 sample was 15.78 mg P l^{-1}.

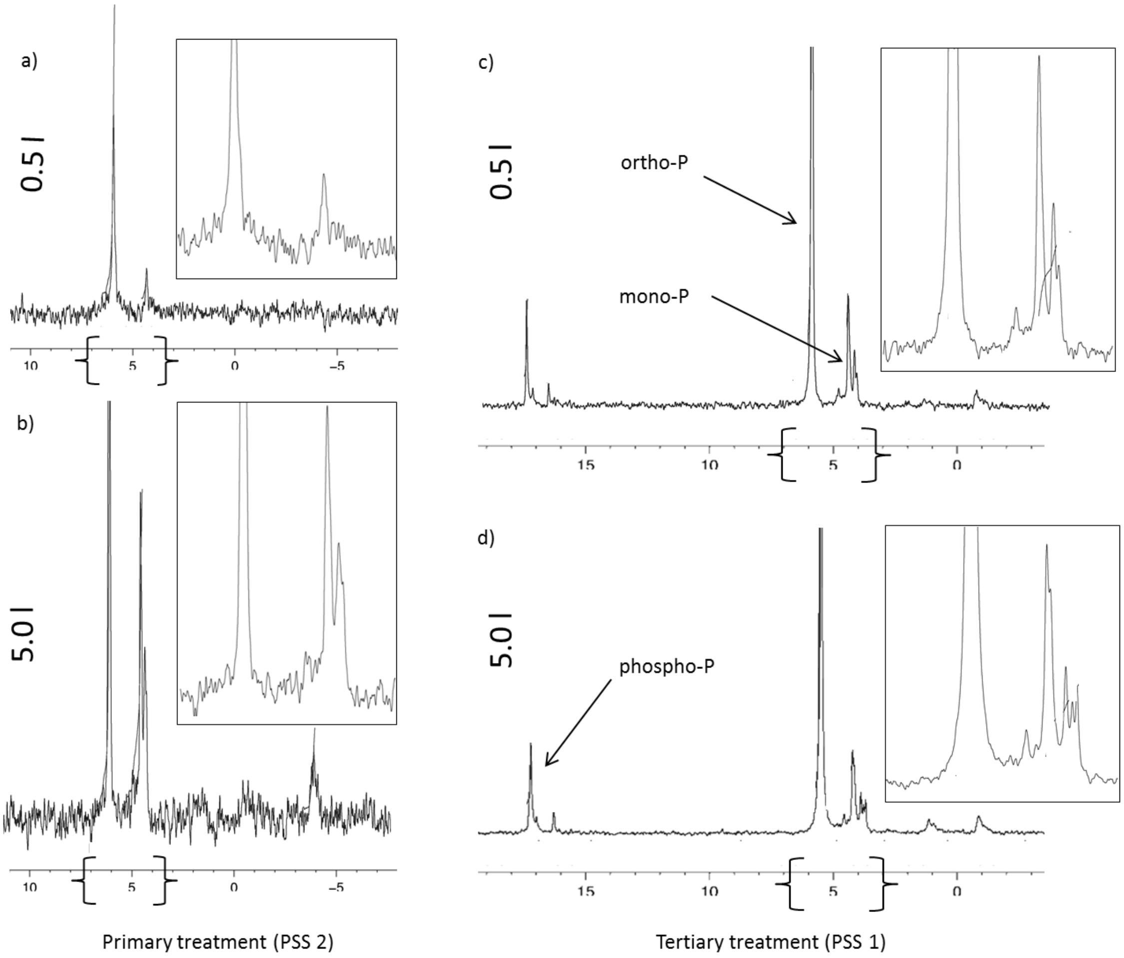


Figure 5.3 ^{31}P NMR spectra of a) 0.5 l (signal to nosie ratio (S:N) 31.94) and b) 5.0 l (S:N 19.29) samples taken from a private sewage system (PSS) with primary treatment (PSS 2) and c) 0.5 l (S:N 233.71) and d) 5.0 l (S:N 522.62) samples taken from a PSS with tertiary treatment (PSS 1). Expansion of orthophosphate (cropped) and orthophosphate monoester peaks are shown inset within each plot (expansion of regions in bracketed areas of the x axis).

5.3.3 Optimising the Amount of Poly Aluminium Chloride Used in Phosphorus Extraction

In samples with Al:P 10:1 treatment, the median (n = 3) percentage of TP that was ortho-P was 58.17% (SD = 7.63%), with 27.36% as mono-P (SD = 5.67%), 2.04% as PL-P (SD = 1.04%), 2.27% as DNA-P (SD = 1.21%) and 5.02% as pyro-P (SD = 2.14%). In one sample a single measurement of poly-P was observed, at 0.80% of the TP of that sample.

In samples with Al:P 50:1 treatment, the median percentage of TP that was ortho-P was 30.87% (SD = 4.68%), with 63.09% as mono-P (SD = 4.07%), 3.81% as PL-P (SD = 2.20%) and 1.90% DNA-P (SD = 1.27%).

In samples with Al:P 100:1 treatment, the median percentage of TP that was ortho-P was 24.00% (SD = 1.81%), with 65.38% as mono-P (SD = 2.60%), 4.21% as PL-P (SD = 1.16%), 3.70% as DNA-P (SD = 1.75%) and 4.61% as pyro-P (SD = 3.44%).

Within each group of treatments (Al:P 10:1, Al:P 50:1 and Al:P 100:1) compound distribution was highly replicable and low standard deviation was observed in all groups (≤ 0.08) (Figure 5.4 and Table 5.2). Ortho-P and mono-P were the main P compounds found in all samples with trace concentrations of PL-P observed. As the Al:P molar ratio was increased, the proportion of TP detected as ortho-P decreased and the proportion of mono-P increased.

Table 5.2 Percentage composition of phosphorus (P) compounds in private sewage system effluent samples prepared for ^{31}P NMR analysis using PAC flocculation at Aluminium:Phosphorus (Al:P) molar ratios of 10:1, 50:1 and 100:1. P compounds identified in corresponding spectra were orthophosphate (ortho-P); orthophosphate monoesters (mono-P); phospholipid P (PL-P) and deoxyribonucleic acid P (DNA-P); pyrophosphate (pyro-P), and polyphosphates (poly-P). Signal to noise ratio (S:N) of each spectra is provided.

Al:P treatment ratio	ortho-P (% of TP)	mono-P (% of TP)	PL-P (% of TP)	DNA-P (% of TP)	pyro-P (% of TP)	poly-P (% of TP)	S:N
10:1	57.55%	31.55%	1.38%	1.21%	8.30%	0.00%	109.98
10:1	71.07%	20.33%	2.04%	2.27%	4.29%	0.00%	399.19
10:1	58.17%	27.36%	3.42%	3.62%	5.02%	2.39%	171.38
50:1	38.34%	56.21%	3.04%	2.42%	0.00%	0.00%	25.09
50:1	29.73%	63.09%	7.18%	0.00%	0.00%	0.00%	23.84
50:1	30.87%	63.42%	3.81%	1.90%	0.00%	0.00%	19.64
100:1	25.03%	66.00%	5.27%	3.70%	0.00%	0.00%	21.43
100:1	21.50%	61.22%	4.21%	6.35%	6.72%	0.00%	25.98
100:1	24.00%	65.38%	2.96%	3.05%	4.61%	0.00%	25.24

Increasing the amount of PAX-18 used in the P extraction procedure does not increase the S:N of the spectra. Those samples treated with PAX-18 at an Al:P molar ratio of 10:1 (Figure 5.4a) b) and c)), 50:1 (Figure 5.4 d) e) and f)) and 100:1 (Figure 5.4 g) h) and i)) produced a median S:N of 226.85 (SD = 152.38), 22.86 (SD = 2.85) and 24.22 (SD = 2.44) respectively (Figure 5.4 a) b) and c)). A Mood’s Median test revealed a significant difference between median S:N for spectra of each treatment type (p = 0.04, n = 9). The median S:N for the spectra of the three samples treated with Al:P at molar ratio of 10:1 were significantly higher than the median S:N of the spectra produced from samples treated with Al:P at a molar ratio of 50:1 and 100:1.

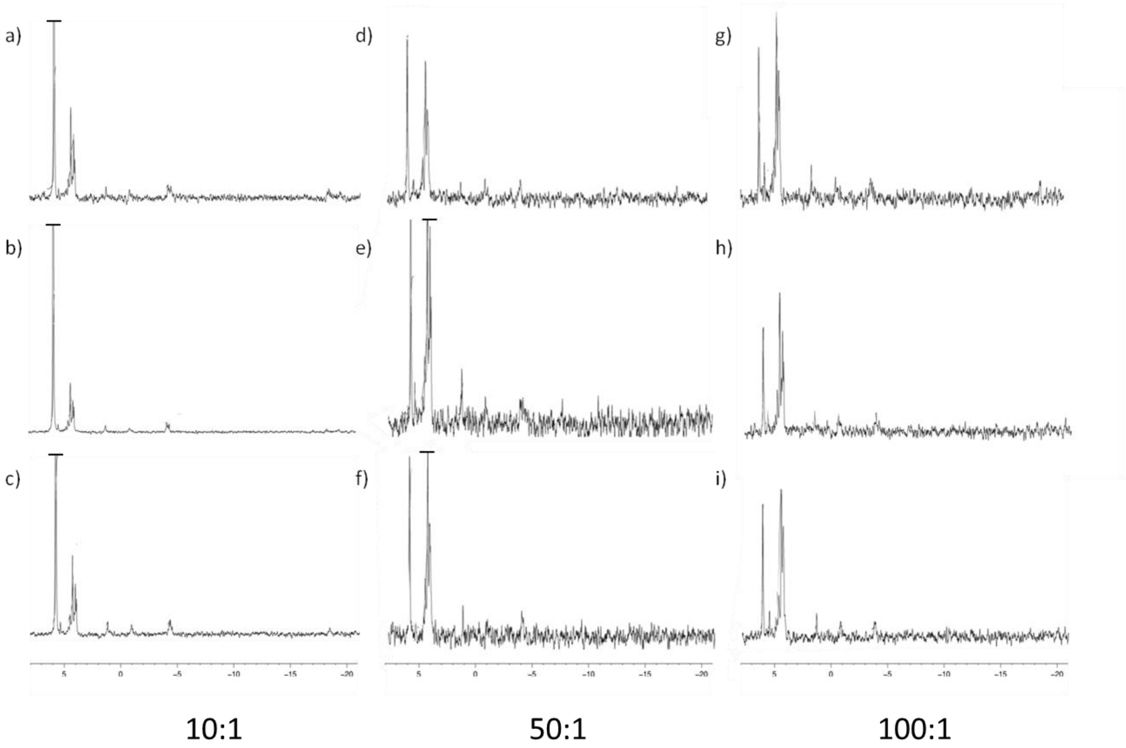


Figure 5.4 ^{31}P NMR spectra showing spectra of nine private sewage system (PSS) effluent samples (collected from PSS 3 at the same time), extracted with different volumes of poly aluminium chloride (PAC) based on aluminium:phosphorus (Al:P) molar ratios. An Al:P molar ratio of 10:1 was used for a) b) and c); 50:1 was used in d) e) and f); and 100:1 was used in g) h) and i). Orthophosphate peaks in a) b) c) and orthophosphate monoester peaks in e) and f) are cropped).

5.4 Discussion

The use of PAC to extract P from PSS effluent was successfully used to prepare samples for ^{31}P NMR analysis. This method can be used to identify the types of P compounds in PSS effluent and help further understand the link between domestic behaviour and the domestic P emissions. Such information has potential importance in substantiating the risk to the aquatic environment of PSS P pollution, and can potentially be used to isolate behaviours that can be altered to reduce domestic P output.

5.4.1 Modification of the Method

Modification of the method of sample preparation outlined in Reitzel et al., (2009) involved the removal of sample filtration. The viscosity and volume of PSS effluent samples made this unfeasible. Additional stages of centrifugation were considered sufficient to remove suspended sediment. Modifications to the method were driven by the importance of efficient and quick sample preparation in order to minimise potential sample degradation, as highlighted by Cade-Menun (2005) and Peng et al. (2010).

The development and optimization of this method show that addition of PAC at a molar ratio of 10:1 followed by adjustment of pH to 6.5-7.0 will extract $\geq$ 99% of the TP from PSS effluent samples. It was also shown that ‘washing’ the flocculant in 1 M NaOH for 17 hours on an end-over-end shaker is sufficient to release all P from the flocculent (a second wash in fresh NaOH did not cause release of further P from the flocculant). Optimisation of this method revealed PAC extraction of P from PSS effluent at an Al:P molar ratio of 10:1 produced spectra of highest S:N (S:N > 110), in comparison to Al:P molar ratios of 50:1 (S:N < 26) and 100:1 (S:N < 26). Furthermore, 0.5 l volumes of raw effluent are sufficient to produce spectra with sufficient S:N to identify presence of P compounds in the sample.

Using this method, a range of distinct P groups including phospho-P, ortho-P, mono-P, DNA-P, PL-P and poly-P were identified by ^{31}P NMR spectroscopy. Sample preparation of three samples taken from the same raw effluent produced spectra of highly replicable P compositions (Figure 5.6 a) b) and c)). The median percentage of TP for each compound had low standard deviation ($\leq$ 7.63%), demonstrating this method produces replicable results. Resolution of spectra was also sufficient to identify peaks within the orthophosphate monoester range that have been identified as the P1 and P3, P2, P4 and P6, and P5 groups of myo-inositol hexakisphosphate, as identified in Turner et al. (2003b). The following section discusses these findings in greater detail.

5.4.2 Assessing the Effect of pH on Poly Aluminium Chloride Extraction of Phosphorus

Tracking the movement of P throughout the extraction procedure showed that reduction of pH to between 6.5 and 7.0, post application of PAC is vital if all P compounds are to be flocculated. Unless all the P in the raw sample is extracted, (and later dissolved into the final NMR sample), potential differences in Al affinity of P compounds may produce an NMR sample that does not accurately represent the P compounds in the initial sample (Peng et al. 2010). In addition, tracking P concentrations throughout the extraction procedure revealed that a single NaOH wash on end-over-end shakers for 17 hours was sufficient to recover all P compounds from the Al floc. This was demonstrated after minimal P was dissolved into NaOH solution after a second ‘wash’.

After PAC addition the pH of samples without pH adjustment, was between 10.7 and 11.2. In these samples, 59 to 83% of the TP in the initial sample was still detected in the residual and supernatant waters. Reduction in TP was dominated by a decrease in organic P and PP, whilst minimal change was observed in SRP concentration.

Similar patterns in P flocculation efficiency at different pHs have been reported in studies using alum ($KAl(SO_4)_2 \cdot 12H_2O$) to precipitate TP from secondary effluent in wastewater treatment. Significantly higher removal of TP was observed when the initial pH of the effluent was adjusted to 6.0 in comparison to 8.0 (Malhotra et al. 1964). In sub-soil systems attenuation of ortho-P is dominated by Al (and iron) when pH is < 6 (Arias et al. 2001), but when pH rises > 6, ortho-P precipitation shifts to a combination of physical adsorption onto iron, Al oxides and calcium phosphates in calcareous sands (Erickson et al. 2007).

Iron and manganese can cause line broadening in NMR spectra and calcium plays a role in the breakdown of poly-P (Reitzel et al. 2009). A major advantage of this method is that PAC extraction does not extract these paramagnetic ions. Reitzel et al. (2009) observed that less than 8% of the iron and 7% of the manganese and 0% of the calcium present in the initial lake water sample, were recovered in the final NMR sample. As the spectra produced in this study contained sharp peaks we would assume paramagnetic ions in the final NMR sample are in such low concentrations that they do not cause significant interference.

In the samples not pH adjusted during flocculation, the PSS with primary treatment (PSS 2), showed a 0.09 mg P l^{-1} increase in SRP concentration in the residual water ((B) Figure 5.2); similarly in the supernatant of the sample taken from the PSS with tertiary treatment (PSS 1), a 0.15 mg P l^{-1} increase in SRP concentration was observed in the supernatant ((C) Figure 5.2). This is potentially explained by the conversion of organic P or PP to inorganic P. It is documented that an increase in pH can cause conversion of sediment bound P to inorganic soluble P in the water column (Moss 1998). The increase in SRP concentration is small and is not observed in all SRP concentration measurements of residual and supernatant water, without further study it is unclear whether this finding is a result of analytical error.

Morse et al. (1998) and Donner et al. (2009) reviewed leading technologies in P removal and recovery from wastewaters. The use of PAC in P precipitation from wastewater is recognized, although the important role pH plays in flocculation efficiency is not mentioned. The importance pH has on TP precipitation by PAC should be considered when assessing efficiency of such methods in chemical tertiary treatments for PSS. Furthermore, it is of note that when aluminium is applied in solution to flocculate P in lakes, it is considered critical to maintain a pH > 6.5 to prevent the formation of highly toxic Al^{3+} ions (Cooke et al., (2005). This may be of concern in maintaining healthy ecosystems in waters receiving direct input from aluminium treated PSS effluent.

5.4.3 Raw Sample Volume Requirements for the Preparation of PSS Effluent Samples for ^{31}P NMR Analysis

Little difference in either the distribution of P compounds or the spectral resolution of the NMR plot was observed in samples prepared from either 5.0 l or 0.5 l volumes (Figure 5.3). Potentially, a marginal increase in diversity of P compounds was observed when using a larger sample volume from PSS 2. Pyro-P was potentially visible in the spectra of the 5.0 l sample, but due to the lower S:N in the spectra of the 5.0 l sample (S:N of the spectra for the 5.0 l and 0.5 l was 19.29, and 31.94, respectively), it is unclear whether this is a product of noise or an actual peak.

Because of the high P concentration found in PSS effluent, and the high degree of up-concentration achieved, NMR samples of sufficient concentration (> 100 mg P l^{-1}) to produce high resolution spectra can be prepared from 0.5 l of effluent. The TP concentration of the final NMR sample is likely to be > 1 g P l^{-1}. The required dilution factors needed to determine such high P concentrations using colorimetric spectroscopy produce high analytical errors, due to the propagation of error (dilution factor is directly multiplied by the instrumental error to calculate total error of analysis) (Drolc and Ros 2002), as such these data are not presented.

Using 0.5 l samples is of great practical importance when processing multiple samples. In terms of sample collection and extraction working with 0.5 l sample is easier, cheaper and potentially less hazardous in terms of storing and sample processing of raw effluent.

5.4.4 The Impact of Increasing the Amount of Poly Aluminium Chloride Used in Phosphorus Flocculation of PSS Effluent Samples

Method optimisation showed PAC extraction of P when conducted at an Al:P of 10:1 produced spectra of high S:N (> 110). Contrary to findings by Reitzel et al., (2009) increasing Al concentration in P flocculation did reduce spectrum quality. Al:P addition at a molar ratio of 50:1 and 100:1 caused line broadening and visibly lower S:N (< 26). Although the reason for this is unclear, low spectral resolution suggests a lower concentration of P compounds in the final NMR sample. A shift in the dominance of ortho-P to mono-P in samples treated with higher volumes of PAC was also observed, although further work is needed to identify the mechanisms behind this.

5.5 Conclusions

In the quest to develop reliable and replicable methods to track P flows from homes via PSS into the environment the potential for using NMR techniques has been tested and assessed with the following conclusions:

- The method presented here (modified from Reitzel et al. (2009)) offers a simple and efficient way of preparing ^{31}P-NMR samples from PSS effluent to give reproducible, high resolution NMR spectra.
- Spectra produced from PSS effluent showed presence of pyro-P, phospho-P, ortho-P, mono-P, DNA-P and PL-P and poly-P, as well as multiple P groups of myo-inositol hexakisphosphate.
- PAC flocculation of P from PSS effluent is pH dependent; adjustment of pH to 6.5-7.0 during the flocculation stage is necessary to achieve > 99% TP flocculation.
- Optimisation of the method revealed that 0.5 l sample volumes of PSS effluent extracted with PAC added at an Al:P molar ratio of 10:1 will produce spectra of S:N that can be used to detect all P compounds present in the sample.
- The successful analysis of PSS effluent with ^{31}NMR spectroscopy, demonstrated in this work, opens up the door to more detailed study of PSS effluent composition. This has potential importance in understanding the link between human domestic behaviour and the quantity and quality of P compounds in PSS effluent.

Relating these results to the aims of the thesis, one of which was to ‘assess the impact of human behaviours on the quality and quantity of P compounds in PSS effluent within the catchment’, there is no doubt that NMR can be used as an effective method to enhance our understanding of the quantity and quality of P compounds in PSS effluent. To fully answer this aim, an assessment of composition of P in PSS effluent must be combined with an assessment of the impact that user behaviours have on the P composition observed. In the next chapter, NMR is used as a method to assess the PSS effluent of ten PSS users that have provided behavioural data by answering the questionnaire outlined in Section 2.6.9. Another aim of this thesis was to ‘review and evaluate the merits of local policies and strategies to regulate PSS P pollution within the catchment, in relation to evidence gathered for this thesis on the efficacy of both technical and behavioural solutions for reducing the human P footprint'. Here it is necessary to raise the issue of how usable NMR is by regulating authorities in assessing the efficacy of their policies at reducing PSS emissions to their catchment, and what use is it in the future, in terms of the practical application of P reduction policies. The answer most likely is none, since NMR is a highly specialist tool and is expensive and time consuming to use. That withstanding, academic studies using NMR as a tool can potentially advance the understanding of behavioural impacts on P emissions, and this may well influence policy and decision makers. Chapter 6 looks at how such academic research may contribute to policy making, by assessing the impact domestic behavioural choices have on the P chemistry of PSS effluent, assessed using NMR analysis.

Chapter 6 An Assessment of the Impact of Human Domestic Behaviour on Phosphorus Compounds in Private Sewage Systems in the Loch Leven Catchment (Scotland, UK) using 31-Phosphorus Nuclear Magnetic Resonance Spectroscopy

Abstract

As discussed in the previous chapters, human domestic behaviour can regulate forms and transport of phosphorus (P) to aquatic ecosystems. Private sewage systems (PSS) provide an opportunity to assess these links in a replicated manner. The work presented here combines an assessment of human domestic behaviour and PSS maintenance of 10 PSS users within the Loch Leven catchment (Scotland, UK), with an assessment of the composition of P compounds present in the effluent from the PSS connected to their homes. Human behaviour was assessed using questionnaires focussing on domestic habits and maintenance of PSS. Colorimetric spectrophotometry was used to assess concentration of P forms and 31-phosphorus nuclear magnetic resonance (^{31}P-NMR) spectroscopy was used to identify the composition of P compounds in the effluent of each PSS. One-way ANOVA revealed significant variation between concentrations of P compounds in PSS effluent ($F_{5,54}$ = 85.54, p = 0.00, n = 60). Samples contained a median of 93.57% orthophosphate and 4.48% orthophosphate monoesters, with trace levels of phosphonates, orthophosphate diesters (phospholipid-P and DNA-P) and pyrophosphonates. The length of time a PSS had not been emptied for plays a key role in the P composition of PSS, possibly due to microbial conversion of organic compounds to orthophosphate. In this study 85.4 % and 84.5% of the variation in soluble reactive P (SRP) (p = 0.001), and total soluble P (TSP) (p = 0.001) was explained by a combination of desludging frequency and washing machine use, revealed using stepwise multiple regression.

6.1 Introduction

The value of integrating social science with the natural sciences is widely recognised, both in terms of general environmental impacts, sustainability and natural resource use (Wilson 1998; Holm et al. 2013; Reboratti 1999), as well as specifically in terms of the sustainable use of P (Ulrich 2010; Ulrich et al. 2013). In Chapter 3 it is demonstrated that current policies that rely on technological means to achieve reductions in P outputs from PSS are inefficient. In Chapter 4, a study of human behaviour of 156 PSS users suggested that reductions in P output from PSS could be achieved by changing behaviours. A problem in measuring the extent of individual P reductions resulting from a particular behavioural alternative is that traditional methods of measuring P (i.e. colorimetric spectroscopy) do not identify specific P compounds that could potentially allow the tracking of a P compound to a unique domestic source. In Chapter 5 we optimised a method to allow such analysis, through the use of ^{31}P-NMR spectroscopy. In the following chapter the methodologies of all previous chapters are combined, integrating social science with natural sciences and combining data from both fields to use in a predictive analysis of the behavioural impacts of PSS users on domestic P emissions to the ecosphere.

6.1.1 Research Aims

The work presented here assesses the potential impact domestic and PSS maintenance behaviours have upon the concentration and speciation of P compounds in effluent. To achieve this, an assessment of human domestic behaviour and PSS maintenance of 10 PSS users within the Loch Leven catchment (Scotland, UK) is combined with an assessment of the P compounds present in the effluent from their PSS. Human domestic behaviour was assessed using questionnaires focussing on domestic habits and maintenance of PSS. The composition of P compounds in PSS effluent was identified by ^{31}P-NMR spectroscopy and the concentration of P forms assessed by colorimetric spectrophotometry.

Specific hypotheses are as follows:

- There is significant variation in the composition of phosphorus compounds found in the effluent of PSS.
- There is a significant and quantifiable relationship between human behaviour and the composition and concentration of P forms in PSS effluent.
- Domestic and maintenance behaviours can be used to describe variation in P concentration in PSS effluent.
- Organic P is a significant portion of the total P in PSS effluent and this proportion varies with human behaviour.

6.2 Methods

The following section provides details regarding experimental design that are specific to this chapter. Although this section does provide an outline of common methods used, reference is made to sections in Chapter 2 that provide fuller and more detailed descriptions of the procedures used.

6.2.1 Questionnaire Design and Distribution

A questionnaire was designed to collect information on 1) human behaviours that impact the amount of P entering a PSS from domestic sources, 2) human behaviours regarding the maintenance of PSS, and 3) potential controlling factors that underpin those behaviours. Questions are summarised in Section 2.6.9. Questionnaires were delivered to 654 addresses within the catchment that were believed to be served by PSS on the 5th of September 2012; 156 (24%) were completed and returned (further details are provided in Section 2.6.9.

Each questionnaire provided an option for respondents to provide contact information if they were willing to participate in a follow up study involving collection of effluent samples from their PSS. Nineteen respondents provided contact details. After a site inspection of each property, ten PSS were deemed suitable for sample collection. Of the nine PSS excluded, seven sites were excluded because the PSS was not accessible and/or effluent samples could not be collected safely and two sites excluded because the PSS were connected to multiple properties and behavioural data was only available for one of the properties served by the PSS and/or residents of other connected properties did not provide permission to collect effluent samples. The locations of the selected sample sites are shown in Figure 6.1.

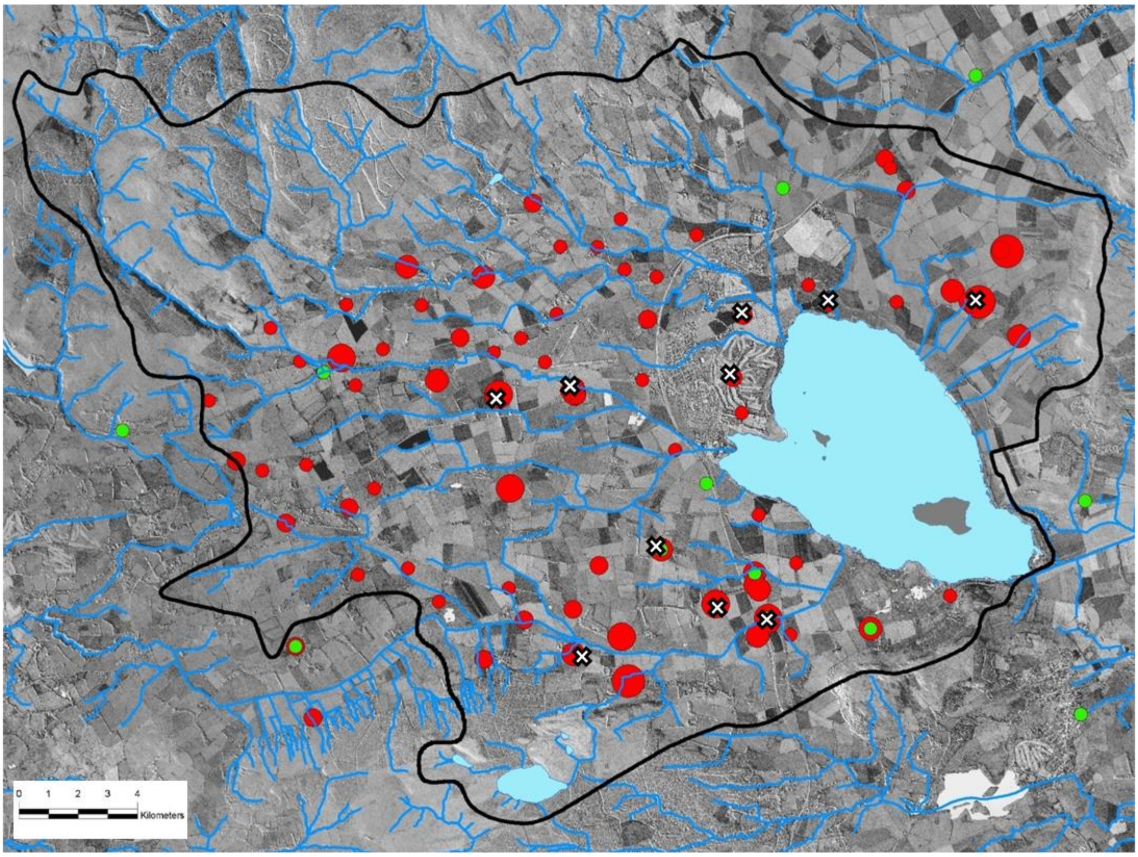


Figure 6.1 Image showing Loch Leven catchment and location of PSS, red spots indicate the geographic centre of postcodes, size is proportional to PSS density; green dots represent PSS registered with the Scottish Environment Protection Agency. Crosses indicate PSS sampled sites.

6.2.2 Sample Collection and Description of Sites

Details of sample collection are provided in Section 2.3. Of the ten PSS selected, eight had primary treatment; three of which were constructed from concrete tanks (PSS 2, 3 and 9) and five constructed from fibre glass tanks (PSS 4, 5, 7, 8 to 10). PSS 1 had secondary treatment (mechanical mixing) and PSS 6 had tertiary treatment, fitted with an aeration system and a filter system using Bauxsol^{TM} pellets (containing Al and Fe compounds) to bind P. All PSS, except PSS 6, were connected to a single residential property, with between two to four residents. PSS 6 was connected to a café/restaurant that had no permanent resident but received between 8000-10,000 visitors monthly. Samples were collected between January 2013 and February 2013. Due to time constraints, financial budgets and access permission from volunteers, each PSS was sampled only once.

6.2.3 Analysis of Phosphorus Concentration of Effluent Samples

Samples were tested for TP, SRP and total soluble phosphorus (TSP) concentrations using colorimetric spectrophotometry analyses (as described in Section 2.4). All samples were analysed within 48 hours of collection.

6.2.4 Preparation of Samples for ^{31}P NMR Spectroscopy

The composition of P compounds in samples was assessed using ^{31}P NMR spectroscopy (as described in detail in Section 2.5).

6.2.5 Settings for the Analysis of Effluent Samples with NMR Spectroscopy

The NMR spectra were recorded on a Bruker AVIII, as described in Section 2.5. Run times varied from 3 hours 0 minutes to 14 hours 21 minutes, and were stopped by an NMR technician when the NMR spectra produced was of a sufficient quality and resolution. The percentage area of each peak was based on their proportional area distribution as a percentage of the largest peak. Compound concentrations were then calculated using the TP concentration of the raw sample. As shown in Section 5.3.1, the extraction method extracts ≥99% of the P within the sample. Although it is acknowledged that P compound concentrations reported are based on percentage compositions of compounds within the final NMR sample only, this is believed to be an accurate representation of the P compound composition of the raw sample, as also assumed in the studies of Jørgensen et al. (2011), Ding et al. (2010) and Reitzel et al. (2009). Peaks were assigned to specific P compounds by comparison with the literature (Cade-Menun, 2005) (Figure 2.4).

6.2.6 Assessing Variation in Phosphorus Composition of PSS Effluent and User Behaviours

All dependent variables (i.e. P concentration data) and continuous independent variables (non-categorical behavioural data) were tested for normal distribution using an Anderson-Darling test.

Non-normally distributed data were transformed using a base 10 logarithmic transformation (log n+2); this approach was retained in all further analyses. Statistical analyses were carried out using Minitab statistical software, version 14 (Minitab Ltd., Coventry, UK).

One way ANOVA was used to test for significant differences between the concentrations of different P compounds found within the ten PSS effluents sampled. Following this, linear relationships between paired variables were assessed using the Pearson product moment correlation coefficient.

6.2.7 Assessing the Interaction between Domestic and PSS Maintenance Behaviour and Phosphorus Composition of PSS Effluent

To visually assess inter correlation between variables, principal components analysis (PCA) (using correlation, as the variables were measured with different scales) was used to produce two synthetic axes that best displayed variation in the following variables; concentrations of TSP, SRP and ortho-P, desludging frequency, dishwasher and washing machine uses per week, showers and baths per week and the age of the PSS. TP was not included in the PCA as it displayed strong covariation with TSP, SRP and ortho-P ($p = \leq 0.05$). Variables with two or less readings were left out of analysis resulting in the exclusion of domestic waste disposal unit use and DNA-P, PL-P, pyro-P and phospho-P concentration. It is acknowledged that PCA analysis is subjective and a the limited data compromises this analysis.

Multiple linear regression analysis was used to explain variation in the concentration of P compounds in the PSS effluents sampled. Stepwise multiple regression analysis was used to identify which of the continuous independent variables (behavioural and maintenance data) best explained dependent variables (P concentrations). Stepwise linear multiple regression models were calculated using an in-F and out-F criteria of 0.05 for each predictor tested. Using these criteria, variables were only added to the model if the subsequent improvement was statistically significant at $p < 0.05$, similarly a term was removed if the resulting deterioration was not significant at $p < 0.05$. A linear regression equation was then calculated to describe significant ($p \leq 0.05$) relationships between variables.

6.2.8 Using Qualitative PSS User Opinion Based Data as a Predictor of the Phosphorus Composition of PSS Effluent

Main effect factorial plots were created to visualise whether qualitative binomial data (i.e. yes or no responses to questions regarding user opinions and PSS system characteristics) had any impact on the continuous variables (i.e. phosphorus composition of PSS effluent and desludging frequency). From these plots, the magnitude each effect had on the mean of the response variable was compared (Figure 6.6 and Figure 6.7). Statistical relationships between those predictor variables which displayed an effect were then tested for; those that were shown to not have an effect were excluded. To account for unbalanced data due to small sample size, a general linear model (GLM) was used to perform an ANOVA between binomial data sets and continuous variables. Those factors identified as having an effect by main effect factorial plots were included in the model. These were the answers to the following questions:

1) Is your washing machine detergent buying choice influenced by the detergents impact on the environment?
2) Is your dishwashing machine detergent buying choice influenced by the detergents impact on the environment?
3) Has your PSS failed to work properly at some point (i.e. blocked, overflowed or produced a bad smell)?
4) Does your PSS receive runoff?
5) Do you feel there is adequate information available on how to correctly maintain your PSS and change your domestic habits to improve the performance of your PSS? (Although these were delivered as two separate questions in the questionnaire, the responses were identical and have therefore been combined).
6) Do you feel there is adequate information available to help you reduce pollution from your PSS?

6.3 Results

6.3.1 Variation in Phosphorus Composition of PSS Effluent

In all NMR spectra orthophosphate (ortho-P) was the dominant P compound, and was observed at a median percentage composition of 93.57% (range 6.35-15.64 mg P l^{-1}, SD = 3.2 mg P l^{-1}, n = 10). Orthophosphate monoester (mono-P) was present at a median percentage composition of 6.09% (range 0.00-4.05 mg P l^{-1}, SD = 1.2 mg P l^{-1}, n = 10). Trace amounts of phosphonate (phospho-P) were observed in the effluents from PSS 5 and 9, pyrophosphate (pyro-P) in effluents from PSS 4 and 6, deoxyribonucleic acid P (DNA-P) in PSS 6 and phospholipid P (PL-P) in the effluents of PSS 5. All spectra are shown in Figure 6.2 and Figure 6.3 and the composition of P forms and compounds in each PSS is summarised in Table 6.1.

The median TP, TSP and SRP concentrations of PSS effluents sampled were 10.35 mg P l^{-1} (range 6.62-19.36 mg P l^{-1}, SD = 4.3 mg P l^{-1}), 7.97 mg P l^{-1} (range 3.99-15.81 mg P l^{-1}, SD = mg P l^{-1}) and 7.61 mg P l^{-1} (range 3.68-14.24 mg P l^{-1}, SD = 3.74 mg P l^{-1}), respectively (summarised in Table 6.1).

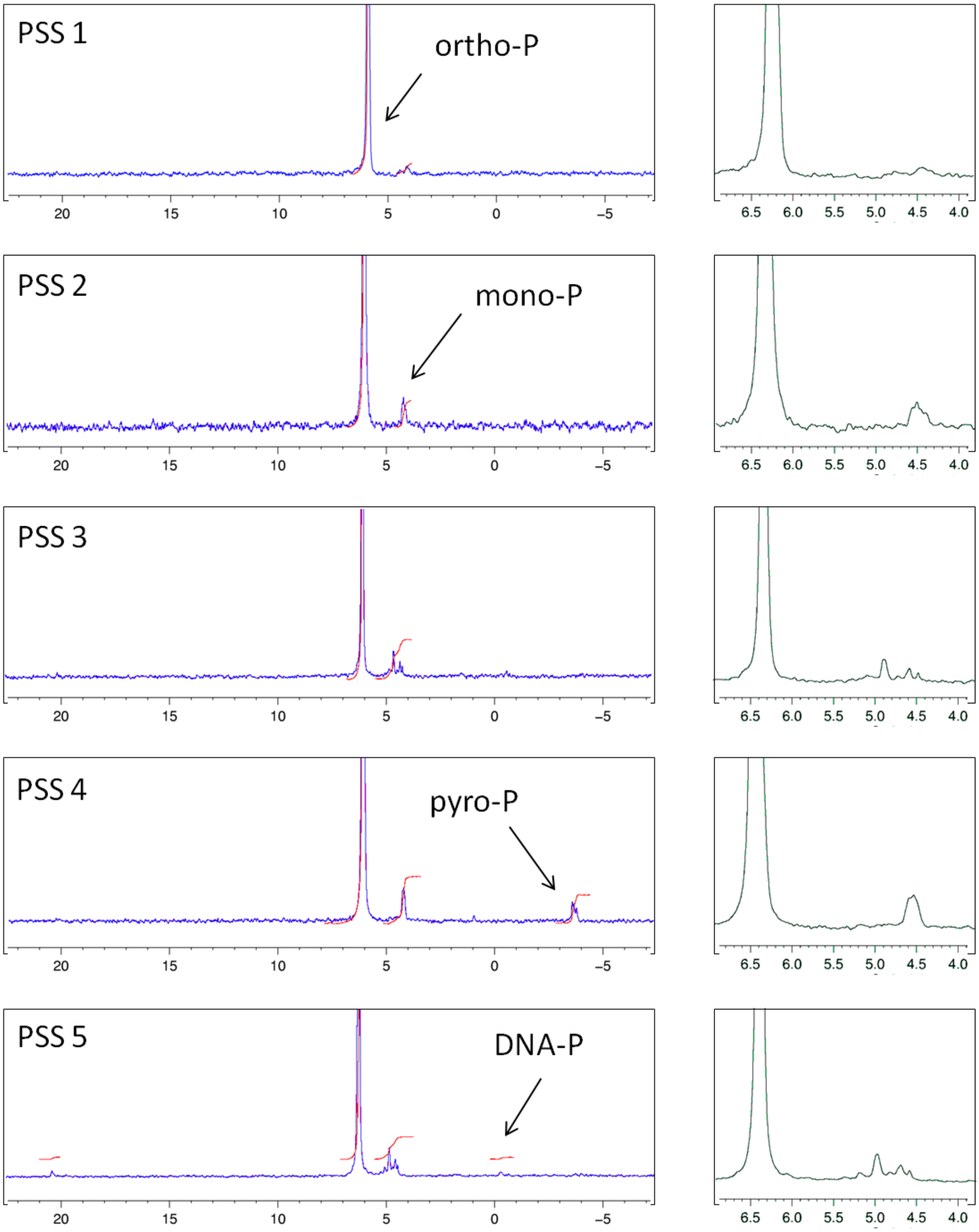


Figure 6.2 The NMR spectra of effluent from private sewage systems (PSS) 1-5; the orthophosphate (ortho-P) peak is cropped in all spectra. Expansion of the orthophosphate monoester (mono-P) region for each spectra is inset to the right. Peaks for deoxyribonucleic acid P (DNA-P) and pyrophosphate (pyro-P) are indicated. Red lines indicate axis length used to calculate peak area.

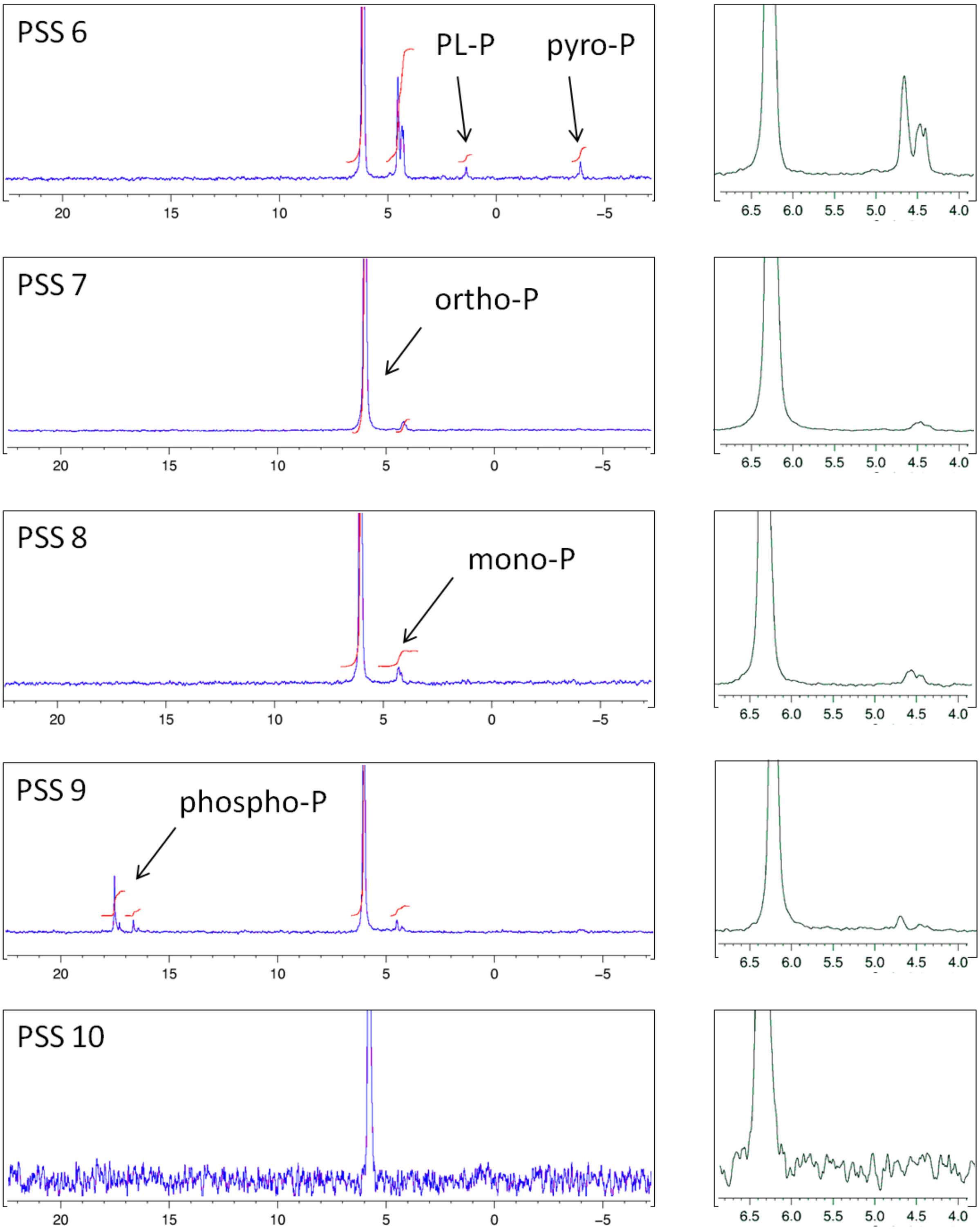


Figure 6.3 The NMR spectra of effluent from PSS 6-10; the ortho-P peak is cropped in all spectra. Expansion of the mono-P region for each spectra is inset to the right. Peaks for phosphonate (phospho-P); phospholipid P (PL-P) and pyrophosphate (pyro-P) are indicated. Red lines indicate axis length used to calculate peak area.

Table 6.1 Concentrations (mg P l^{-1}) of total phosphorus (TP), total soluble phosphorus (TSP) soluble reactive phosphorus (SRP) soluble unreactive phosphorus (SURP); and the concentration (mg P l^{-1}) and percentage composition of TP (followed in parenthesis) of phosphonate (phospho-P); orthophosphate (ortho-P); orthophosphate monoesters (mono-P); phospholipid P (PL-P); deoxyribonucleic acid P (DNA-P) and pyrophosphate (pyro-P), in effluent from 10 private sewage systems (PSS). The median (mg P l^{-1}) and standard deviation (SD) (mg P l^{-1}) is also provided.

PSS	**TP (mg P l^{-1})**	**TSP (mg P l^{-1})**	**SRP (mg P l^{-1})**	**SURP (mg P l^{-1})**	**phospho-P (mg P l^{-1}) (% of TP)**	**ortho-P (mg P l^{-1}) (% of TP)**	**mono-P (mg P l^{-1}) (% of TP)**	**PL-P (mg P l^{-1}) (% of TP)**	**DNA-P (mg P l^{-1}) (% of TP)**	**Pyro-P (mg P l^{-1}) (% of TP)**
1	8.99	7.67	7.25	0.42	-	8.75 (97.33%)	0.24 (2.76%)	-	-	-
2	12.99	9.05	8.78	0.27	-	12.36 (95.19%)	0.62 (4.81%)	-	-	-
3	8.64	8.27	7.97	0.30	-	7.94 (91.95%)	0.70 (8.05%)	-	-	-
4	17.42	14.02	13.70	0.32	-	15.64 (89.76%)	1.11 (6.38%)	-	-	0.67 (3.86%)
5	13.17	6.69	6.61	0.08	0.12 (0.88%)	11.77 (89.36%)	1.19 (9.07%)	-	0.09 (0.69%)	-
6	19.36	15.81	14.24	1.57	-	14.52 (75.01%)	4.05 (20.91%)	0.26 (1.33%)	-	0.53 (2.74%)
7	11.71	9.74	9.261	0.48	-	11.49 (98.10%)	0.22 (1.90%)	-	-	-
8	6.62	4.60	3.92	0.68	-	6.35 (95.86%)	0.27 (4.14%)	-	-	-
9	8.87	4.21	4.21	0.00	0.85 (9.58%)	7.76 (87.45%)	0.26 (2.96%)	-	-	-
10	7.02	3.99	3.68	0.31	-	7.02 (100.00%)	-	-	-	-
median (mg P l^{-1}) (% of TP) / (SD (mg P l^{-1}))	10.35 (4.30)	7.97 (3.99)	7.61 (3.74)	0.31 (0.44)	0.00 (0.00%)	10.12 (93.57%) / (3.25)	0.45 (4.48%) / (1.19)	0.00 (0.00%)	0.00 (0.00%)	0.00 (0.00%)

One-way ANOVA revealed a significant difference in the P compounds concentrations (identified using NMR) within the PSS effluent samples ($F_{5,54}$ = 85.54, P = 0.001, n = 60). Using an tukeys test, three significantly different groups were identified: ortho-P, mono-P and other P compounds. The mean concentrations of ortho-P and mono-P were shown to differ significantly from the mean concentrations of each other, and all other P groups identified across the ten PSS (i.e. phospho-P, DNA-P, PL-P, pyro-P). The mean concentrations of phospho-P, DNA-P, PL-P and pyro-P were not significantly different (summarised in Figure 6.4).

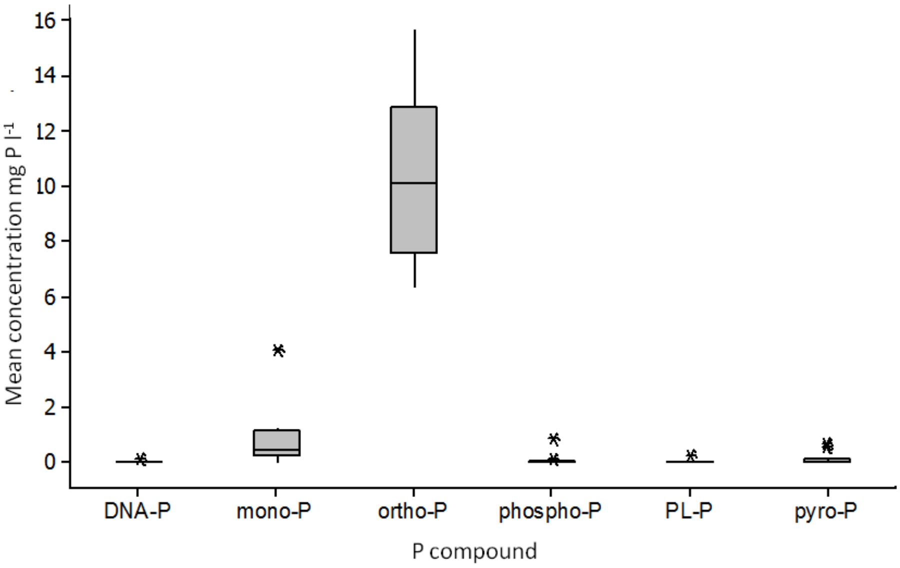


Figure 6.4 Boxplot showing mean (n = 10) concentration of deoxyribonucleic acid P (DNA-P) orthophosphate monoesters (mono-P), orthophosphate (ortho-P), phosphonate (phospho-P), phospholipid P (PL-P) and pyrophosphate (pyro-P), measured in the 10 PSS sampled. Asterisks indicate outliers. ANOVA indicated statistical difference between the mean concentrations of P compounds ($F_{5,54}$ = 85.54, P = 0.00, n = 60). The mean concentrations of ortho-P and mono-P differed significantly from the mean concentrations of each other and all other P groups identified.

6.3.2 Variation in Domestic and PSS Maintenance Behaviour

The median number of residents per household was 2.00 (range 2-4, SD = 0.70), with one PSS (PSS 6) connected to a shop/cafe that had no permanent residents, but had between 8000-10,000 visitors per month with access to public toilets. The median number of dishwasher cycles, washing machine cycles, baths and uses of a domestic waste disposal unit per week per household was 5.00 (range of 0-70, SD = 21.07), 4.00 (range 0-10, SD = 2.60), 1.00 (range 0-7, SD = 2.12) and 0.00 (range 0-15, SD = 4.74), respectively (Table 6.2). The median time since respondents had last desludged their PSS was 9.50 months (range 1-24, SD = 9.50) (Table 6.2).

Respondents were also asked a number of questions with binomial (i.e. yes or no) responses. Of those sampled, 90% felt the owner was responsible for correct maintenance of PSS, 70% had desludged their PSS within the last 12 months and the remaining 30% had desludged their PSS within the last 24 months. The ‘impact to the environment’ of dishwasher or washing machine detergents influenced the purchasing choice of 60% and 50% of users, respectively. An 80% majority did not feel adequate information was available for maintaining PSS correctly and 80% felt there was not adequate information available to help them change domestic habits to improve their PSS performance.

Table 6.2 Behavioural domestic and maintenance data of the residents of 10 properties connected to private sewage systems (PSS) in the Loch Leven catchment. The median followed by the standard deviation (SD) is also provided (* excluded from calculation of median and SD as not considered permanent residents).

PSS	treatment level	system description	residents	dishwasher cycles per (week^{-1})	washing machine cycles (week^{-1})	showers (week^{-1})	baths (week^{-1})	domestic waste disposal uses (week^{-1})	PSS age (years)	desludging frequency (i.e. time since PSS was last desludged) (months)
1	2^{o}	fibre glass tank with mechanical aeration	2	0	3	16	0	0	1	12
2	1^{o}	concrete septic tank	3	3	4	20	0	0	60	8
3	1^{o}	concrete septic tank	2	7	3	10	0	0	60	24
4	1^{o}	fibre glass septic tank	2	5	5	2	1	0	30	24
5	1^{o}	fibre glass septic tank	4	5	5	28	2	0	22	7
6	3^{o}	mechanical aeration and chemical treatment	8000-10,000*	70	10	30	0	0	2	11
7	1^{o}	fibre glass septic tank	2	2	2	4	2	0	25	24
8	1^{o}	fibre glass septic tank	2	7	9	7	7	0	19	1
9	1^{o}	concrete septic tank	2	0	4	12	1	0	27	2
10	1^{o}	fibre glass septic tank	2	6	4	14	2	15	20	1
median (SD)	-	-	2.00 (0.70)	5.00 (21.07)	4.00 (2.60)	13.00 (9.45)	1.00 (2.12)	0.00 (4.74)	23.50 (20.08)	9.50 (9.50)

6.3.3 Assessing the Interaction between Domestic and PSS Maintenance Behaviour and the Phosphorus Composition of PSS Effluent

Principal component analysis indicated TSP, ortho-P and SRP varied positively with desludging frequency (time since the PSS was last desludged), and negatively with the number of baths taken per household per week. Age of the PSS showed negative variation with dishwasher, washing machine use and shower use per week.

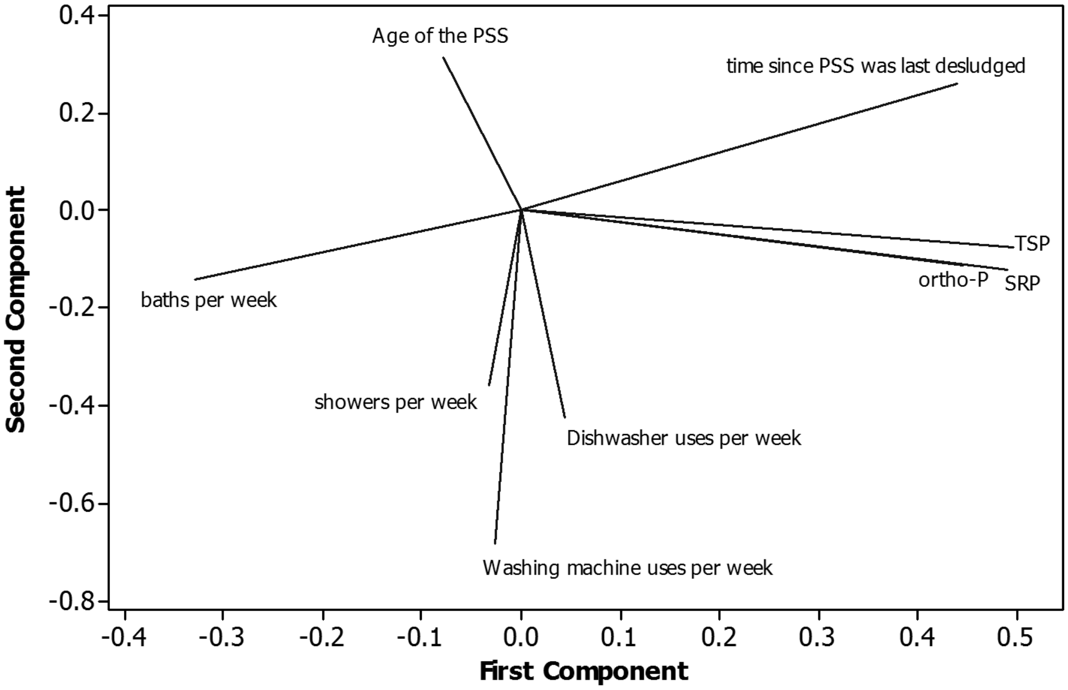


Figure 6.5 Results of principal component analysis for the assessment of 10 private sewage systems (PSS) and their users, within the Loch Leven catchment, showing the weighting and ordination of variables measured along both principal components. Variables were concentration of total soluble phosphorus (TSP), soluble reactive phosphorus (SRP) and orthophosphate (ortho-P), time since the PSS was last desludged, dishwasher and washing machine uses per week, showers and bathes per week and the age of the PSS. Principal component (PC), eigenvalue (EV) and cumulative variance (CV) were as follows: PC1, EV = 3.94, CV = 0.44 and for PC 2, EV = 1.87 and CV = 0.65.

Using the Pearson product moment correlation coefficient, correlations identified using PCA were tested for significance ($p = \leq 0.05$) (Table 6.3). A significant and positive linear correlation exists between the time since the PSS was last desludged and the concentration of TSP ($r = 0.80$, $p = 0.00$), SRP ($r = 0.83$, $p = 0.00$) and ortho-P ($r = 0.64$, $p = 0.05$) in PSS effluent. A positive significant positive correlation was also observed between TP concentrations and TSP (r = 0.88, p = 0.00), SRP (r = 0.90, p = 0.00), ortho-P (r = 0.98, p = 0.00) and pyro-P (r = 0.77, p = 0.00) concentration.

Table 6.3 Summary of significant ($p = \leq 0.05$) correlations between variables showing the Pearson product moment correlation coefficient (r) and p value for each set of variables assessed (n = 10).

	Time since PSS was last desludged (months)	TP concentration (mg P l^{-1})	TSP concentration (mg P l^{-1})	SRP concentration (mg P l^{-1})	ortho-P concentration (mg P l^{-1})
TSP concentration (mg P l^{-1})	r = 0.80 (p = 0.00)	r = 0.88 (p = 0.00)			
SRP concentration (mg P l^{-1})	r = 0.83 (p = 0.00)	r = 0.90 (p = 0.00)	r = 0.99 (p = 0.00)		
ortho-P concentration (mg P l^{-1})	r = 0.64 (p = 0.05)	r = 0.98 (p = 0.00)	r = 0.88 (p = 0.00)	r = 0.90 (p = 0.00)	
Pyro-P concentration (mg P l^{-1})		r = 0.77 (p = 0.00)	r = 0.76 (p = 0.01)	r = 0.75 (p = 0.01)	r = 0.71 (p = 0.02)

Stepwise multiple linear regression analyses indicated that 84.5% of the variation observed in SRP concentration, 85.4% of the variation in TSP concentration and 44.4% of the variation in ortho-P concentration was explained by the time since the PSS was last desludged and the number of washing machine cycles used per week in the property connected to that PSS (summarised in Table 6.4).

Table 6.4 Summary of significant relationships between dependent and independent variables, the regression equation describing the relationship, R2 (adj) value and P-value are provided.

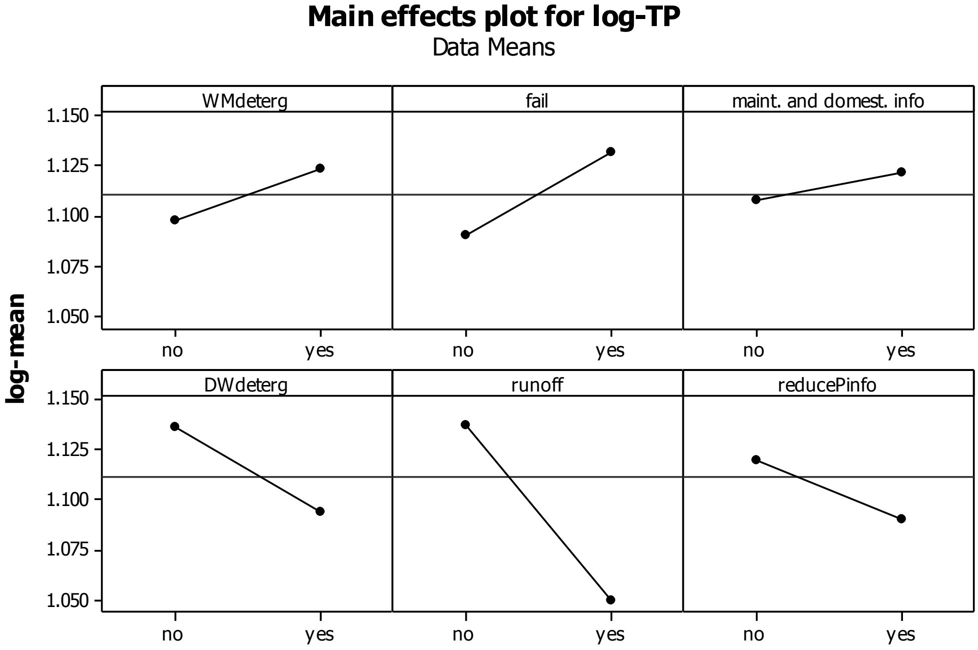
Relations	Equation of line y = ….	*P-value*	R^2 (adj)
SRP	*0.105 + 0.519 (weekly washing machine cycles)* *+ 0.442 (time since desludged)*	0.001	84.5%
TSP	*0.071 + 0.584 (weekly washing machine cycles)* *+ 0.442 (time since desludged)*	0.000	85.4%
Ortho-P	*0.564 + 0.329 (weekly washing machine cycles)* *+ 0.247 (time since desludged)*	0.020	44.4%

6.3.4 The Relationship between Qualitative PSS User Opinion Based Data and the Phosphorus Composition of PSS Effluent

Main effects plots were used to visualise the magnitude of the effect each predictor variable (summarised in Section 6.2.8) had on the mean of the response variables (TP, SRP, ortho-P, desludging frequency). Main effect factorial plots indicated that the response variables were strongly affected by whether or not the PSS received roof runoff or not. A lower mean concentration of TP, ortho-P and SRP and a shorter time since the PSS was desludged was observed in those PSS that received runoff (Figure 6.6 and Figure 6.7). PSS with a history of failure had a higher mean effluent TP and ortho-P concentration and a higher desludging frequency. Furthermore, respondents who stated their washing machine and dishwashing detergent buying choice was influenced by its impact on the environment, had desludged their PSS more recently, than those that stated impact to the environment did not influence which detergent they purchased (Figure 6.7)

Whether respondents felt there was adequate information available on how they should maintain their PSS correctly, or how to change their domestic habits to improve the performance of their PSS, had little effect on the mean concentration of SRP, TP or the time since their PSS was last emptied (Figure 6.6 and Figure 6.7). The group of respondents who stated they felt there was not adequate information available on how to reduce pollution from their PSS showed a lower mean concentration of TP, ortho-P and a marginally lower concentration of SRP in the effluent from their PSS, as well as a shorter time since the PSS was last desludged (Figure 6.6 and Figure 6.7).

GLMs were used to perform one-way ANOVA on those predictor variables (binomial response data from questions listed in 6.2.8) that displayed an effect on TP, SRP, ortho-P and the time since desludging. Analysis showed variation in SRP, TP, ortho-P or desludging frequency could not be explained by any of the predictor variables; demonstrating that none of the interactions observed in the factorial main effect plots (Figure 6.6 and Figure 6.7), were statistically significant.



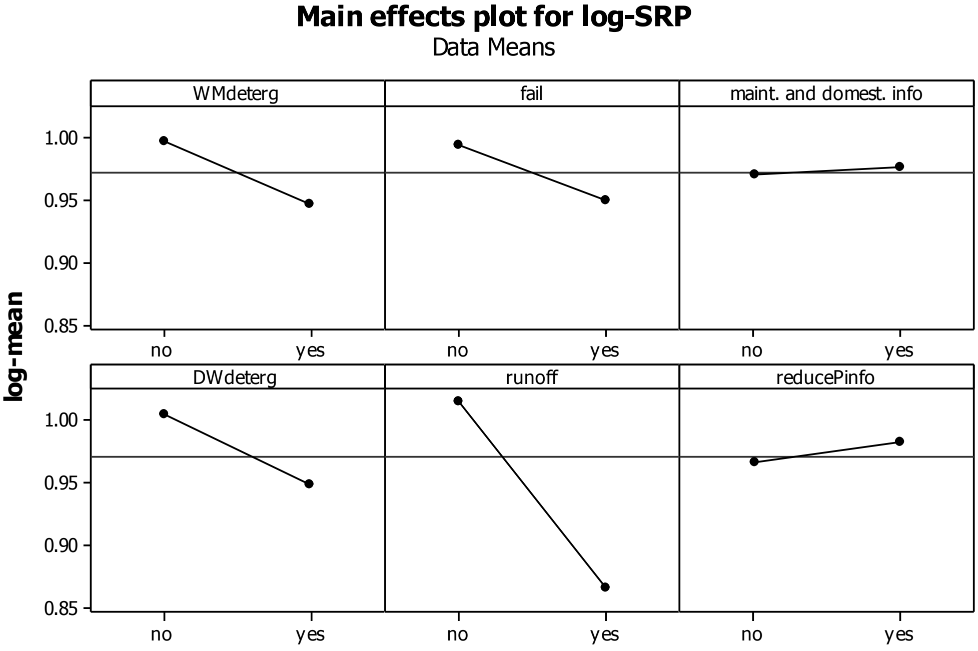
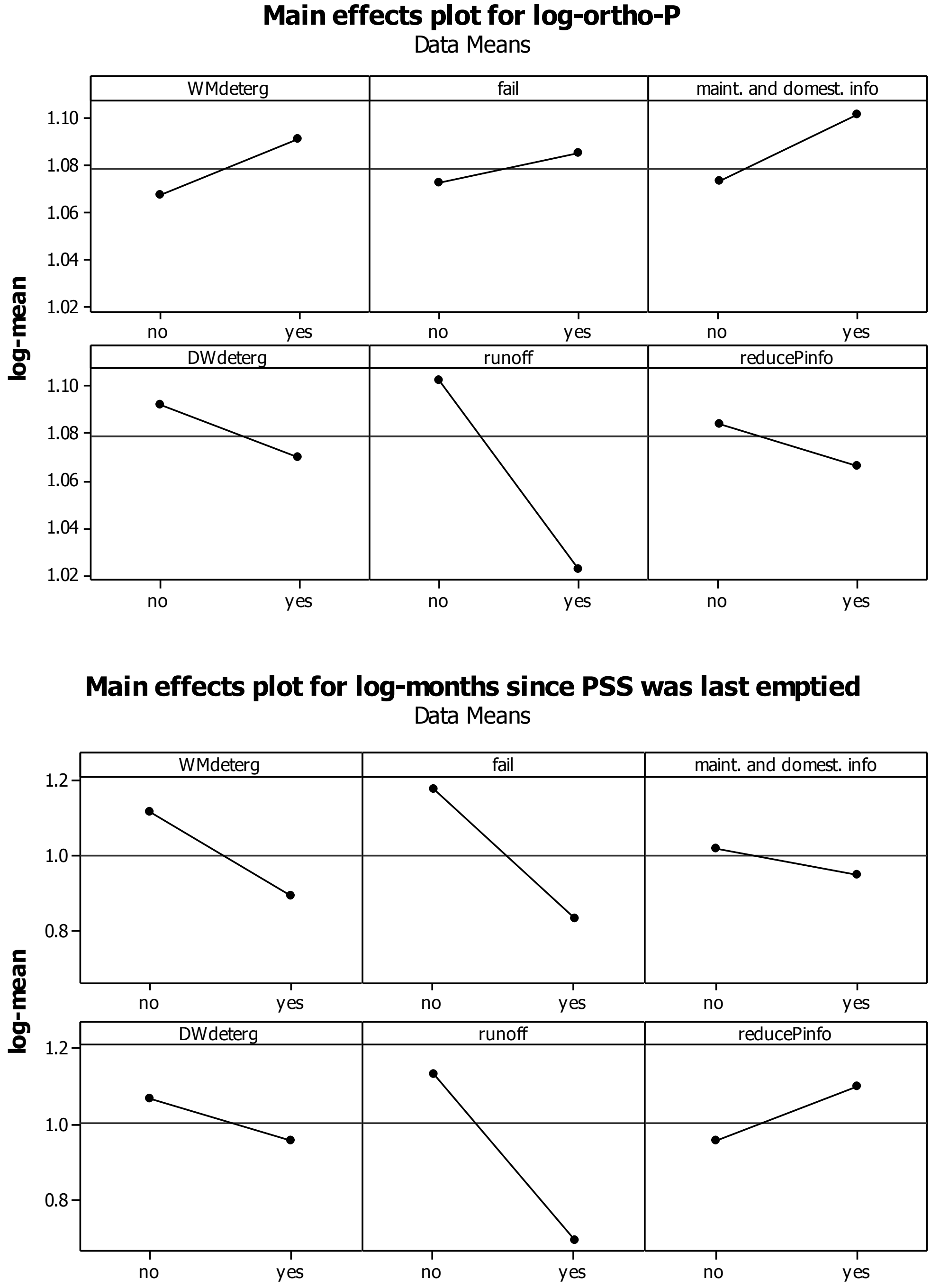


Figure 6.6 Factorial plots showing the main effects on the log-mean concentration (mg P l^{-1}) of total phosphorus (TP) and soluble reactive phosphorus (SRP), of whether respondents who 1) stated that their washing machine detergent buying choice was influenced by the detergents impact on the environment (WMdeterg); 2) stated that their dishwashing machine detergent buying choice was influenced by the detergents impact on the environment (DWdeterg); 3) stated their private sewage system (PSS) had at some point failed to work properly (fail); 4) stated that their PSS received runoff (runoff); 5) stated that they felt there was adequate information available on how to correctly maintain their PSS and change their domestic habits to improve the performance of their PSS performance (maint. and domest. info); and 6) stated they felt there was adequate information available to help them reduce pollution from their PSS (reducePinfo).



6.7 Factorial plots showing the main effects on the log-mean concentration (mg P l^{-1}) of orthophosphorus (ortho-P) and time since the PSS was last emptied/desludged (months), of whether respondents who 1) stated that their washing machine detergent buying choice was influenced by the detergents impact on the environment (WMdeterg); 2) stated that their dishwashing machine detergent buying choice was influenced by the detergents impact on the environment (DWdeterg); 3) stated PSS had at some point failed to work properly (fail); 4) stated that their PSS received runoff (runoff); 5) stated that they felt there was adequate information available on how to correctly maintain their PSS and change their domestic habits to improve the performance of their PSS performance (maint. and domest. info); and 6) stated they felt there was adequate information available to help them reduce pollution from their PSS (reducePinfo).

6.4 Discussion

6.4.1 Assessing Variation in Phosphorus Composition of PSS Effluent and User Behaviours

The majority of P in effluent from the ten PSS included in this study was ortho-P; the median percentage composition of TP present as ortho-P was 93.57% across the sampled tanks. The percentage composition of TP present as ortho-P and the SRP concentration, determined through reaction of orthophosphate-P, of effluent samples were assessed using different analytical methods, NMR spectrophotometry and colorimetric spectrophotometry, respectively. The highly significant positive correlation observed between ortho-P and SRP concentrations in all samples demonstrates the NMR method is sensitive enough to give comparable data with SRP concentrations identified using colorimetric spectrophotometry. However ortho-P concentrations were shown to be higher than SRP concentrations in nine of the ten samples, suggesting that the sample preparation method may convert some PP or SURP into ortho-P, or that there is an analytical error causing such discrepancy. The high ortho-P composition of P in PSS effluent is in agreement with Bouma (1979) who reported studies finding PSS effluent to be > 85% SRP, whilst Whelan and Titamnis (1982) observed PSS effluent to be 93 to 100% SRP. Although delivery from PSS to water bodies within many catchments may be relatively small in comparison to other sources (i.e. agricultural runoff, industrial point sources and municipal sewage treatment works), PSS have the potential to cause persistent inputs (Arnscheidt et al. 2007). This is of concern during low flow summer months when the dilution capacity of receiving waters is reduced and ecological sensitivity is greatest (Macintosh et al. 2011).

The second largest group of P compounds found in the effluent samples were mono-P; the median percentage of TP present as mono-P was 4.48%. This group of organic P compounds includes sugar phosphates (intermediaries in glycolysis and the Krebs cycle), phosphoproteins (most enzymes are phosphoproteins (Corbridge 2000)), mononucelotides (commonly formed from the breakdown of nucleic acids (Condron et al. 2005)) and inositol phosphates (phytic acid) in varying degrees of phosphorylation. Inositol P is the dominant organic P type in soils (Turner et al. 2002) and can account for up to 100% of organic soil P content (Condron et al. 2005). Inositol-P is also present in seeds, rice, breads, legumes and other grains, and is used as food preservative

E391. Monogastric animals (most animals (including humans)) cannot produce endogenous phytase, and therefore cannot digest phytic acid (Pallauf and Rimbach 1997). Phytase dietary supplements have been added to poultry and swine feed to increase P uptake and reduce the inositol-P content of their waste, thereby reducing P leaching from their waste to aquatic systems (Childers et al. 2011; Silkeborg 2007; Klopfenstein et al. 2002). It is suggested that the mono-P compounds detected in PSS effluent are largely inositol-P and originate from human dietary intake. Without further information on the diets of respondents it is difficult to explain variation in mono-P concentration.

Concentration of mono-P ranged from 0-1.19 mg P $^{-1}$. Turner et al. (2002) states the relatively low concentrations of inositol-P in lake waters, and the difficulties associated with detecting such low concentrations of organic P species, has resulted in a lack of information regarding the transfer of inositol-P from terrestrial systems (e.g. PSS and soakaways) to water bodies. Inositol-P accumulation in lake sediments suggests they are relatively biologically unavailable (Turner et al. 2002); e.g. Ahlgren et al. (2006) measured between 32%-39% of the TP in the sediments of three separate lakes to be mono-P compounds. This would suggest mono-P does not play an important role in eutrophication. Turner et al. (2002) suggest the role of mono-P in the promotion of eutrophication is contradictory, as there is also evidence that 35 different types of cyanobacteria can utilise mono-P as a sole P source (Whitton et al. 1991).

Phospholipid-P was present only in the effluent collected from PSS 6, the only PSS with tertiary treatment (the treatment system which uses a second chamber where effluent is periodically mixed and aerated to aid aerobic bacterial digestion of wastes). The presence of PL-P may be explained by microbial functioning specific to this tank. Aerobic digestion may have caused increased bacterial growth within the tank (phospholipids are a key component of the bacterial cell wall) and aeration may have mixed bacteria (settled in the sludge) into the water column, providing higher concentrations of bacterial derived PL-P in samples collected. Miron et al. (2000) report hydrolysis of lipids is higher in sewage treatment systems that have undisturbed anaerobic sludge beds (as seen in PSS with primary treatment) that support acidogenic conditions, in comparison to 'completely stirred tank reactor' systems (comparable to the mechanical stirring treatment system in PSS 6), that favour methanogenic conditions. This may have also contributed to higher PL-P concentrations.

Poly-P was not detected in any of the PSS effluents sampled. Poly-P, such as sodium triphoshate (STP) and pyro-P is present in many dishwasher and washing machine detergents (Lusk et al. 2011). Detergent-P makes up between 9% and 50% of P in wastewater (Morse et al., 1993). In the UK reduction of P from detergents could potentially offer a < 28% reduction of wastewater P (Comber et al. 2012). In water, STP is highly unstable and will easily hydrolyse to orthophosphate (Lusk et al. 2011); it is likely that hydrolysis of P compounds used in detergents may have contributed to the ortho-P signal observed in all PSS.

Pyro-P detected in PSS 4 and PSS 6 may have partially originated from the hydrolysis of poly-P contained in detergent inputs, although pyro-P is also found in some detergents (Yeoman et al. 1988; Lusk et al. 2011). The property connected to PSS 6 had the highest weekly dishwasher use (70 cycles week^{-1}) and washing machine use (10 cycles week^{-1}), and thus PSS 6 would be expected to receive higher detergent inputs. The property connected to PSS 4 has the lowest bath (1 bath week^{-1}) and shower use (shower week^{-1}) which could potentially result in lower dilution of their detergent inputs, although their pyro-P detection may not be related to detergent use. Pyro-P is commonly used as a food additive (Uribarri and Calvo 2003) and maybe, therefore associated with dietary choices.

Sale of detergents with more than 0.5% P is banned in sixteen states in the US due to the risks they pose to freshwaters (Lusk et al. 2011), resulting in a reduction of P in wastewaters by 40%-50% (US EPA 2002b). From June 2013, similar bans in the E.U. now prohibit sale of consumer laundry detergents that provide ≥ 0.5 g P per standard dosage, with future bans on sale of dishwasher detergents with ≥ 0.3 g P per standard dosage planned for 2017 (EC 2011). A common replacement for P in detergents is xeolite in combination with polycarboxylates (Nowosielski 2009), both of which have been found to be non-harmful to humans or the environment as reported in HERA (2005) and HERA (2007), respectively.

6.4.2 Assessing the Interaction between Domestic and PSS Maintenance Behaviour and the Phosphorus Composition of PSS Effluent

A positive linear relationship was observed between SRP, TSP and ortho-P effluent concentration and time since last desludging. It was shown that 85% of the variation in SRP and TSP could be explained by a combination of the time since last desludging and the household's weekly number of washing machine cycles. An array of P compounds are present in detergents, cleaning products, toothpastes and other personal products, food preservatives and indigestible orthophosphate monoesters in human waste. Within a PSS, over time many of these compounds will be hydrolysed to orthophosphate. Our results indicate that the longer the time a PSS is left without desludging the greater the potential concentration of orthophosphate within its effluent. Similarly the greater the number of washing machine cycles used by a household, the greater the detergent P input to the PSS, causing potential increase in the P concentration of PSS effluent.

A common misconception exists in many parts of the UK that if a PSS is working correctly then it does not need emptying (May et al. 2010). Regular septic tank desludging is recommended as good PSS maintenance practice (University of Minnesota 1998; SEPA et al. 2006; US EPA 2002b). A variety of different information sources advise a variety of different frequencies of desludging, ranging from 1 to 6 years (SEPA 2006; Angus Council 2012; Aberdeenshire Council 2012; US EPA 1999), whilst other sources of information state PSS should be emptied in accordance with the manufacturer's specifications, although the manufacturer's details may not be known by many PSS owners (HM Government 2010a). This makes it challenging for PSS users to know what the correct maintenance procedure is for their PSS. Although all surveyed in this study had desludged their tank within 24 months, in an earlier study of 156 PSS users within the Loch Leven catchment (detailed in Chapter 3), 23% had never desludged their PSS and 56% of respondents desludged their PSS in the last 24 months.

The required frequency of desludging of a PSS depends on the capacity of the tank and the volume and type of waste it receives, and may, therefore, be considered PSS specific (Withers et al. 2012). Moore (2000) provides a matrix in which household size and tank capacity can be used to estimate desludging frequency (i.e. a family of two with a 500 gallon (2273 l) tank should empty their tank every 2.6 years). In the UK, a lack of data on PSS (Withers et al. 2012) could make such calculations difficult. It is, therefore, challenging for users to determine the correct maintenance practices for their PSS using this approach.

The lowest TP concentration was observed in the property with the highest bath use per week (n = 7). Baths and high (low P concentration) water producing behaviours may dilute concentrations of P in PSS. Using only effluent P concentration to substantiate the risk of P pollution from a specific PSS, or its ability to process the P is potentially misleading. Water usage must also be considered. A PSS with low P effluent concentrations may simply have effluent highly diluted with low P concentration wastewaters (i.e. grey waters from baths and showers). Emptying vast amounts of water, such as ‘hot tubs’, into PSS is not advised due to the potential hydraulic failure it may cause to the soakaway (NSFC 2004; US EPA 2002a). As PSS are designed not to leak; every litre of water poured down a sink will result in a litre of PSS effluent leaving the PSS into the soakaway, drainage ditch or in some cases straight to a river or stream. P load as well as effluent P concentration may also need to be considered when estimating the eutrophication risk posed by a PSS.

6.4.3 The Relationship between Qualitative PSS User Opinion Based Data and the Phosphorus Composition of PSS Effluent

No statistically significant relationships were reported between the opinion based data, collected from respondents and the P chemistry of their PSS effluent or their desludging frequency. This is not to say relationships do not exist, but more that sample size was potentially too small to draw out any relationships that may exist. Collection of qualitative and quantitative data simultaneously, of large enough sample size to be used in statistical analysis, is a particularly challenging part of this work and highlights the difficulties in attempting to explain quantitative data using qualitative data.

6.4.4 Combining Natural Sciences with Social Sciences

Phosphorus pollution from PSS is a multi-dimensional problem and therefore requires a multidimensional solution. Integration of the social science with natural science was acknowledged as a one of the six key and necessary requirements in tackling sustainable use of P by the European Sustainable Phosphorus Platform (ESPP, www.phosphorusplatfrom.eu) (set up at the European Sustainable Phosphorus Conference in 2013 (www.espc2013.org)) (Ulrich 2010; Ulrich et al. 2013).

Ulrich et al. (2013) highlights that there is often a reticence in the integration of multi and interdisciplinary research and, whilst Stewart et al. (2002) point out that dialogue between disciplines is vital if environmental quality is to be preserved, in reality the complexities in interpreting the relationship between qualitative and quantitative data should not be underestimated.

6.5 Conclusions

In this chapter, the methods developed within this thesis have been combined to assess the impact human behaviour has on the quality and quantity of domestic P emissions into the ecosphere. A statistical procedure has been followed to analyse the data to better understand the relationships that exist between variables. From this the following conclusions have been made:

- Variation in P quality and quantity was observed in PSS. Samples contained a median of 93.57% orthophosphate and 4.48% orthophosphate monoesters, with trace phosphonates, orthophosphate diesters (phospholipid-P and DNA-P) and pyrophosphonates.
- The frequency of desludging plays a key role in the P composition of PSS, with higher concentrations of ortho-P in effluents taken from tanks that had not been recently desludged (possibly due to microbial conversion of organic P compounds to orthophosphate).
- 85.4 % and 84.5% of the variation in SRP and TSP, respectively, could be explained by time since desludging and frequency of washing machine use.
- Increase in low P concentration water usage (such as showers and baths) appears to have a diluting effect on TP concentration of PSS effluent; P load must be considered as well as effluent concentration when assessing the eutrophication risk posed by a PSS.
- To comprehensively understand relationships between the qualitative social science based data and the quantitative P chemistry data collected in this study, assessment using a larger sample size is required. Although some relationships have been indicated, it is difficult to draw firm conclusions due to a lack of statistical power.

In chapters 3 to 6, the specific hypotheses (outlined in Figure 1.10) were tested through experimentation and the statistical analysis of collected data. In the last chapter of this thesis, these findings are viewed as a whole, and used to answer the overall Aims of the thesis, as outlined in Section 1.13, in the context of wider research. Key findings are summarised. Methodological advancements that have been achieved by this work are outlined and the challenges encountered by the experimental design discussed. The implications of this work on policy, the P human footprint and the sustainable use of P are discussed, and considerations for future research that have been highlighted, are proposed.

Chapter 7 Discussion

7.1 Final Summary and Discussion of Findings

The initial finding of this thesis shows that the treatment type of a private sewage system (PSS) does not have a significant impact on the phosphorus (P) concentration of its effluent (Brownlie et al. 2014) (Chapter 3). This challenges the efficacy of policies aiming to reduce P pollution from PSS that rely on commonly available technological solutions associated with in tank treatment. Following this, an assessment of domestic and PSS maintenance behaviours of 156 users within the Loch Leven catchment (Chapter 4) indicated that potential reductions in P emissions can be achieved through behavioural change. To understand the impact of human behaviour on domestic P emissions to the ecosphere, a method to identify specific P compounds in PSS effluent was developed and optimised (Chapter 5). This method enabled the analysis of PSS effluent using ^{31}P nuclear magnetic resonance (NMR) spectroscopy, and was used to successfully identify the composition of P compounds within ten PSS effluent samples. By integrating social science with natural science within a single study, an assessment of the impact of specific behaviours on the quality and quantity of P compounds in the human P footprint of ten individual households was conducted (Chapter 6).

From this assessment it was concluded that frequency of desludging plays a key role in the P composition of PSS effluent, with higher concentrations of orthophosphate (ortho-P) in effluents taken from tanks that had not been recently desludged (possibly due to microbial conversion of organic P compounds to orthophosphate). It was shown that 85% of the variation in soluble reactive P (SRP) and total soluble P (TSP) in the effluent of sampled PSS could be explained by a combination of ‘time since PSS was last desludged’ and ‘frequency of washing machine use’. Although a large proportion of PSS users feel responsible for correctly maintaining their PSS, they are potentially not maintaining them effectively (i.e. lack of regular annual desludging) or have poorly installed or inadequate systems (i.e. unaddressed cracks in PSS with PSS receiving roof runoff). There is a need for better education and information on PSS maintenance and how the public can reduce their domestic P emissions. Although, in order to change target behaviours, situational barriers such as the provision of cheap, accessible behavioural alternatives that are considered the social norm, must first be provided before attempts are made to change underlying motivational factors through education. Increase in low P concentration water usage, such as showers and baths, may have a diluting effect on TP concentration of PSS effluent. Hence P load must be considered as well as effluent concentration, when assessing the eutrophication risk posed by a PSS.

A major challenge of this study was enlisting enough participants to provide a sufficient sample size. Although links between domestic and PSS maintenance behaviours and domestic P emissions have been indicated, it was difficult to draw firm conclusions due to a lack of statistical power. This work highlights that, although there is a critical need to integrate the social sciences with natural sciences to tackle the challenges of the sustainable use of P (Ulrich 2010), the complexities of interpreting the relationship between qualitative and quantitative data should not be underestimated.

7.2 Methodological Advancement Provided by this Work

A major methodological advancement provided by this work, is the development of a method to prepare effluent samples for analysis using ^{31}P NMR spectroscopy. Colorimetric spectrophotometry is a commonly used and standard method to analyse the P composition of environmental samples. A shortfall of this method is that specific P compounds cannot be identified directly. ^{31}P NMR spectroscopy is a non-destructive, non-invasive method that can be used to directly detect both inorganic and organic P compounds from samples simultaneously. As discussed in Section 5.1, the lack of a standardised method of sample preparation, and the cost and time required for analysis, are a challenging part of using ^{31}P NMR. The successful development of a simple and effective method to prepare effluent samples for analysis using NMR spectroscopy as a result of this work opens the door to more detailed study of PSS effluent composition. This advancement increases the analytical potential in understanding the relationships between human domestic behaviour and the quantity and quality of P compounds within the stages of the human P cycle (Figure 1.2).

In the preparation of effluent samples for analysis using NMR, poly-aluminium chloride (PAC) flocculation was shown to extract >99% of the TP from the solution, when at a pH between 6.5 and 7.0. It was therefore assumed the P composition displayed in spectra were representative of raw samples. A further and major advantage of the method developed here, is that PAC extraction effectively precipitates P compounds from iron, calcium or manganese complexes, which can cause line broadening of NMR spectra (Reitzel et al. 2009). Spectra produced were of high resolution and signal to noise ratio (S:N), and allowed successful identification of ortho-P, orthophosphate monoesters (mono-P), phosphonates (phospho-P), phospholipid-P (PL-P), deoxyribonucleic acid-P (DNA-P) and pyrophosphonates (pyro-P); as well as multiple P groups of myo-inositol hexakisphosphate. By using a combination of both NMR spectroscopy and colorimetric spectrophotometry it was also possible to identify the concentration of each specific P compound within the effluent sample. This method was modified from the work of Reitzel et al. (2009), and highlights the potential to develop methods for the preparation of other types of environmental sample for analysis using NMR.

Although this method worked successfully, NMR spectra of PSS effluent were not easily used to identify relationships between specific P compounds and specific behaviours. This is not a criticism of the method developed in this work to prepare PSS effluent samples for NMR analysis. It is rather a criticism of:

a) the use of PSS effluent to quantify specific P compounds that contribute to P emissions from households, and
b) the difficulties in assessing human behaviour by a single mail delivered questionnaire.

Both are discussed in further detail in the following passages.

In further explanation of a) and the problems encountered using PSS effluent to quantify specific P compounds that contribute to P emissions from households, it is considered that many P compounds associated with specific domestic sources may be hydrolysed to ortho-P by the time they reach PSS effluent. Although significant variation in P quality and quantity was observed between PSS samples, the P content of samples was dominated by ortho-P. Samples contained a median of 93.57% ortho-P and 4.48% mono-P, with some samples containing trace concentrations of phospho-P, PL-P, DNA-P and pyro-P. Specific ‘signal’ P compounds associated with particular behaviours may have been lost, such as poly-P (i.e. sodium triphoshate (STP)) and pyro-P, both of which are present in some dishwasher and washing machine detergents, and are both highly unstable, and easily hydrolysed to ortho-P in water (Lusk et al. 2011)). This makes detecting the impact detergents have on the overall P concentration of PSS effluent difficult to quantify directly; it is likely that hydrolysis of P compounds used in detergents contributed to the concentration of ortho-P. Results of spectra do however highlight that PSS effluent is highly bioavailable (> 85%), although this can, and was also demonstrated using colorimetric spectrophotometry.

It is necessary to raise the issue of how usable NMR spectroscopy is as a tool to be used by regulating authorities in policy auditing. There is a documented lack of data regarding P discharges from PSS (May et al. 2010; Withers et al. 2013), findings outlined in Chapter 3 suggest that high frequency monitoring of PSS effluent is required to improve the efficacy of policy aiming to reduce P pollution from PSS. NMR spectroscopy is a highly specialist tool and expensive to use, furthermore the achievable level of detail it provides may not be needed to assess the impact of a policy on the P flows in a catchment. This may be better achieved using colorimetric spectrophotometry. In terms of the future use of NMR in this field, academic studies may find NMR a valuable tool in understanding the conversion of P compounds from domestic sources through the stages of PSS treatment systems, and into the ecosphere, and this may well influence policy and decision makers.

In reference to b), and the difficulties in assessing human behaviours; the questionnaire used to assess relevant domestic behaviours (Table 2.2), maintenance behaviours and some of the known factors that control them (Table 2.3), was part of an exploratory study not designed to be used to fully describe or fully predict domestic behaviours. Such a study would require a much more in depth analysis of many other factors, such as environmental influences and the personality characteristics of respondents. The complexity of behavioural models (as outlined in section 2.6) highlight the amount of information required to predict behaviours (such as beliefs, attitudes, degree of personal behavioural control and behavioural intention). The acquisition of such information was beyond the scope of this questionnaire.

Despite these challenges, this work did reveal that a majority of PSS users in the Loch Leven catchment do feel responsible for maintaining their PSS properly, but feel there is not adequate information available to them, outlining how to maintain a PSS properly or how to change their behaviours to reduce P pollution from their PSS. Although caution should be emphasised in interpreting these results; this work does highlight a potential lack in access to information, but does not suggest how successful a program to educate PSS users would be at modifying behaviours. An education program may be a consideration of local authorities aiming to adopt a more holistic management approach in the reduction of P flows from the technosphere to the ecosphere. Although potentially the cheapest intervention in managing PSS pollution may be educating users to adopt better maintenance behaviours, Silverman (2005) showed that a door to door delivered education program did not modify behaviour. Individuals do not respond voluntarily to education programs about how to properly manage their PSS, even when value is both societal and personal (Silverman 2005). It is widely agreed in environmental psychology that increasing environmental concern does not result in pro-environmental behaviour (Kollmuss and Agyeman 2002; Barr 2004; Geller 2002; Bamberg 2003). This is not to say education programs do not work, more that they do not work in isolation (clearly if people do not have the correct information then they cannot manage their PSS successfully), and must be part of more invasive management measures that make the desired behavioural alternative easier than the existing behaviour. Alternatively, imposing regulations that legally require behavioural change impose substantial costs in terms of funding and, as shown in Chapter 3, policy based on incomplete or unclear data may not be effective.

7.3 Implications for Policy

A reliance on technological solutions (i.e. treatment level) to provide low P output from PSS has been recognised in development policy (Irish Government 2010; Loch Leven Special Protection Area and Ramsar Site 2011). The policies that make up the 125% rule in the Loch Leven Catchment (Loch Leven Special Protection Area and Ramsar Site, 2011) uses P offsetting to ensure new developments do not cause a net increase of P to the catchment. Developers must offset the calculated discharge of their P development by upgrading existing 3rd party PSS with primary treatment, to systems with secondary and tertiary treatment. The assumption at the core of this policy is that increased treatment level will cause a reduction in the P concentration of PSS effluent.

In the work we present here, we show there is no significant difference in TP, TSP and SRP concentration in the effluent from different PSS, no significant difference in the TP:SRP ratio in the effluent from different PSS, and that treatment type of PSS assessed in this project did not affect concentration of TP in PSS effluent (Brownlie et al. 2014) (Chapter 3). Albeit we are considering a small population of tanks, it raises serious concerns that such a policy is driving developers and homeowners to pay for expensive technological solutions that do not result in significant P reductions.

The 125% rule invokes ‘The Precautionary Principle’ (EU 2010; Commission of the European Communities 2000), which allows rapid preventative decision-taking in the face of a possible threat to the environment where scientific data does not allow full risk assessment, and carries a ‘polluter must pay’ principle. Furthermore, the use of a ‘125%’ reduction in P in this policy acknowledges there is uncertainty in the estimation of PSS P load, and is designed to offer a buffer against a net increase of P to the catchment from development where data are lacking. In the face of such a lack of certainty, an urgency to obtain sufficient data to validate whether such ‘rapid’ policy instruments achieve their aims must be a priority. In light of the findings presented here, an assessment using a larger sample size of PSS is absolutely necessary to ensure this policy is appropriate.

In the long term, to offset 125% of the P from the 3486 extra people predicted to be connected to PSS in the Loch Leven Catchment by 2100, developers would be required to mitigate 2.19 t TP yr^{-1}. This exceeds the current estimate of 0.99 t TP delivered annually to the catchment from PSS (based on the median P concentration of PSS effluent sampled in this work 9.28 mg P l^{-1}), and this caps development potential by placing a limit on the P available to offset.

Despite the reservations regarding the 125% rule outlined here, the policy is conceptually strong. The notion that development should be ‘P neutral’ and the use of P offsetting to achieve this, as well as making this a legal requirement for planning permission to be granted, is an example of the type of progressive thinking that is needed to improve the resilience and sustainability of societies. Although, the policy should make significant reductions in TP discharge from PSS, further work is required to improve PSS technologies, support better PSS management and increase reduction of domestic P emissions. In the short term alternative P offsetting options, such as change in land use (Abell et al. 2011) or removal of PSS systems into municipal waste water treatment works may be needed. Pioneering policies such as the 125% rule must be further developed using quantitative approaches to provide a means of supporting impending rural development, and take an approach that covers not only PSS outputs, but also the ‘upstream’ P that users input into their PSS from their homes as well as the method of ‘downstream’ P processing of the PSS (i.e. soakaway, drainage ditch, etc.).

The work here indicates that user inputs of washing machine detergent have an impact on the concentration of SRP and TSP in PSS effluent. Detergent P forms between 9% and 50% of P in wastewater (Morse et al., 1993). Although changes in domestic behaviour such as reduction in washing machine use, reduction in the amount of detergent used per cycle and choice of low P detergent may reduce this source; policy plays a large role in facilitating this reduction. In the US, sale of detergents with more than 0.5% P is banned in sixteen states due to the risks they pose to freshwaters (Lusk et al. 2011), resulting in a reduction of P in wastewaters by 40-50% (US EPA 2002b). In June 2013, similar bans in the EU now prohibit sale of consumer laundry detergents that provide ≥ 0.5 g P per standard dosage, and will ban sale of dishwasher detergents with ≥ 0.3 g P per standard dosage by 2017 (EC 2011). Use of low P detergents and reductions in the volume of detergents used will reduce P entering PSS. In the UK this could potentially offer a < 28% reduction of wastewater P (Comber et al. 2012) and is a positive step towards reducing our human P footprint. Such policies make it easy for individuals to reduce their individual P emissions.

Policy that aims to reduce the amount of P used in food production is also needed to continue this progression. Lusk et al. (2011) suggests between 30-70% of P in wastewater can come from urine and faecal derived nucleic acids and tri-phosphates. Some diets will certainly contain higher P content due to the amount and type of food consumed. Vegetal protein contains on average twice as much P g^{-1} than animal (Jonsson et al. 2004), whilst animal protein has a much higher inherited P footprint associated with its production (Cordell et al. 2009). Modifying diets to reduce environmental impact can be complex and difficult to achieve (Vieux et al. 2012) and as such this behaviour was not assessed in this study.

Where policy may be most successful in reducing dietary P emissions, is by imposing a reduction in the use of food additives by the food industry. Comber et al. (2012) consider individual consumption of food additives provide up to 0.58 g P day^{-1} to wastewater. Similarly Uribarri & Calvo (2003) showed additives in processed foods, such as restructured meats and spreadable cheeses, and cola drinks, can add an extra 0.47-1.00 g P day^{-1} to diets. Such additives are mainly added to foods for aesthetic and preservative reasons (Comber et al. 2012). In the U.S.A., 44% of the bestselling grocery products contain P additives that contribute significantly to their P content. Moreover, foods with P additives were less expensive, further promoting their consumption (León et al. 2013). Policy imposed reductions in P additives to food by the food industry would decrease dietary P intake. Currently food labelling regulations do not enforce the declaration of a product’s P content (León et al. 2013). Food labelling that provides transparent information outlining the P content of foods would enable consumers to make informed decisions regarding the P content of their diets. This is important in regard to reduction of the human P footprint, as well as for human health. Increasing epidemiological evidence suggests serum P may be a predictor risk factor of mortality, cardiovascular morbidity and bone metabolism, especially in individuals suffering from kidney disease (Palmer et al. 2011; Foley et al. 2008; Onufrak et al. 2008).

The volume of food consumed by an individual is also driven by consumer choice, and in simple terms, the more food the larger the P footprint. Both in terms of P emissions from human waste, but also the amount of P needed to produce the food, a greater demand for food, requires a greater demand for fertilisers (Cordell et al. 2009). As obesity in the western world is increasing (Cameron et al. 2012), it is necessary to consider not only how this affects the health of the individual, but also how this affects the health of the environment (Sutton et al. 2013).

7.4 Phosphorus Sustainability; a Wasted Waste Product

Societal use of P is unsustainable (Cordell and White 2011; Smil 2000; Childers et al. 2011). Sustainable management of P is the responsibility of all involved in its use, from policy makers, to farmers and to the consuming public (Sharpley et al. 2005). Legacy P stores along the land-freshwater continuum slow recovery of waters from eutrophication. Even if P inputs were stopped immediately, deterioration of waters will continue for years to decades (Jarvie et al. 2013; Sharpley et al. 2013). The accumulation of P within the ecosphere is quite literally storing up future problems for the next generations (Sharpley et al. 2005), much in the same way as the impacts of carbon emissions in the last century are now the inherited responsibility of the current and future generation. P accumulation in the ecosphere is a global problem and the solution must be to reduce P flows within the human P cycle. Conceptualisation of the human P cycle (Figure 1.2) highlights the variation and uncertainty in estimates of P flows between stages within the cycle.

The work in this thesis has provided a better understanding of part of the human P cycle concerned with domestic P emissions and the domestic behaviours that impact this. Understanding the magnitude of P flows within the human P cycle will allow targeted improvement in P use efficiency. Furthermore closing the loop in the human P cycle by increasing reuse and recycling of P is a vital part of increasing societal sustainability and resilience. It is suggested that the following aims must be a primary focus in achieving these goals:

- P accumulation in the ecosphere should be used as the primary P source for use within the technosphere, and must be selected in favour of P stores within the lithosphere.
- P must be used more efficiently within the technosphere.

To achieve these aims, a paradigm shift in how we view P is required; P is not a waste product, it is a wasted product. Currently only an estimated 50% of the P excreted by humans (Childers et al. 2011) and livestock (Gilbert 2009) is recycled back into food production. A major barrier in the use of human waste as fertiliser is the psychological stigma attached to the consumption of food grown with human excreta as fertiliser (Childers et al. 2011). Urine is essentially sterile and can be applied directly to farm fields or in the form of precipitated struvite crystals, as a source of bioavailable P (Mihelcic et al. 2011). The Swedish government has set targets of reusing 60% of P in sewage treatment, and two Swedish cities now require urine diverting toilets to separate solid from liquid waste, aiding P reclamation (Childers et al. 2011).

To increase efficient use of P and reduce individual P emissions there must be a comprehensive understanding of how individual behaviour can impact individual P emissions. To design effective interventions to support behaviours that reduce personal P emissions, antecedents promoting the behaviours must be encouraged and those inhibiting the behaviours removed (Steg and Vlek 2009). An understanding of this type requires integration of both the natural sciences and the social sciences.

In this thesis, social science and natural science were integrated and data from each field combined to identify relationships between behaviour and quality and quantity of P emissions from domestic sources to the ecosphere. The value of integrating social science with the natural sciences is widely recognised, both in terms of understanding general environmental impacts, sustainability and natural resource use (Wilson 1998; Holm et al. 2013; Reboratti 1999), as well as specifically in understanding P sustainability (Ulrich 2010; Ulrich et al. 2013). Much of the data collected from PSS users was general and qualitative, whilst the data collected regarding the composition of P in PSS was specific and quantitative. A challenge of this work was how to effectively combine such datasets into a single predictive model that could be used to forecast behavioural impacts on domestic P emissions. The lack of models to combine qualitative social science data with quantitative natural science data is a recognised problem (Nyhus et al. 2002). Despite the clear importance of social sciences in understanding earth systems and human motivations for decision makers, it is often neglected or overlooked (Holm et al. 2013). Although good interdisciplinary research does exist, integration of data from different scientific fields such as social science with natural science is not common place, and not currently conducted on a scale that can facilitate the assessment of global change issues (Holm et al. 2013).

7.5 Future Research Considerations

The work presented in this thesis raises the following questions and topics to be considered in future research:

1) Repeating the work of this thesis at a larger scale.

To obtain a more comprehensive understanding of the relationships that exist between domestic behaviour and domestic P emissions, the methods described in this thesis should be used to assess a much larger number of PSS and users. Combining both qualitative, social science based data of PSS users in a more detailed analysis, and quantitative P chemistry data of PSS effluents would help to identify the best opportunities available to make significant reductions in domestic P emissions.

2) Identification of the transport and conversion process of P compounds from domestic sources, through PSS treatment, as well as P load to the aquatic environment.

Analysis of samples collected directly from the actual domestic sources (i.e. detergent, grey water directly from appliance, human waste), at numerous stages throughout treatment and within the soakaway, drainage ditch or river would give a greater understanding of the processes by which P compounds are converted from domestic sources to the aquatic environment, as well as the impact individual domestic sources have on the P content of domestic emissions. Furthermore, sampling the transport of P from soakaways to the aquatic environment, as well as an assessment of the efficiency of soakaways to capture P, would provide a fuller understanding of the risk posed to the aquatic environment from PSS P pollution.

3) Catchment scale sampling regime of PSS effluent concentrations to validate policy.

There is a need to validate the future use of policies that rely on the assumption that increasing PSS treatment level will reduce the P concentration of PSS effluent (such as the 125% rule in East Scotland). To achieve this sampling of effluent from PSS of different treatment levels at a much larger scale than conducted in this thesis is required, in number as well as temporally and spatially.

4) Research addressing how to better retain P in PSS sludge and reclaim P from PSS sludge.

To improve societal P sustainability a better understanding of ‘in tank’ processing of P compounds is required, with a view to improve treatment technology, better retain P compounds within the PSS sludge, and ultimately reclaim P from PSS sludge for use as fertiliser.

5) Assessing domestic P emissions using controlled changes in domestic behaviours.

A living experimental model such as a test village, where controls can be put in place and specific behaviours of residents can be changed and monitored, and the subsequent impacts on water use and P emissions closely examined, would provide a much greater understanding of these systems.

6) Assessment of the impact of dietary P intake on the human global P cycle and the redistribution of global P stores.

Further assessment of diet on the impact of P in wastewaters, with an assessment of the contribution diet makes to P emissions of individuals from different cultures, continents and global areas, and the implications this has for redistribution of P (i.e. import and export of P containing foods) within the global human P cycle is necessary to ensure P sustainability and food security for future generations.

7) The impact of flooding on PSS P pollution.

During the writing and completion of this thesis, we have had unprecedented flooding across southern England. The impact of flooding on agriculture and on property is clearly evident and may have long-term damage to both rural and urban communities. It will be important that some consideration is also given to the impact of flooding on PSS and the wide spread release of P into water-courses and underlying aquifers. Possibly some consideration of the security of PSS during flooding might be assessed as extreme weather conditions are predicted to increase in the future.

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Chapter 8 Appendix A

8.1 Appendix A: Reagents and Solutions used in Phosphorus Analysis

Detailed descriptions of the preparation of stock solutions and reagents used in phosphorus (P) analysis using colorimetric spectrophotometry (Figure 2.3) are provided in tables A1-A4. Reagents and solutions used in soluble reactive P (orthophosphate) analysis are given in Table A1. Reagents and solutions used in the preparation of total P and total soluble P (TSP) are provided in Table A2. For the determination of digested samples (TP and TSP), and SRP samples, 1.0 ml of mixed reagent was added to 5.0 ml of filtered sample (Figure 2.3). The composition of reagents and solutions used to prepare the mixed reagents for SRP is provided in Table A3, and for TP and TSP in Table A4. Using these tables, the required volume of mixed reagent was calculated for each batch of analysis.

The reagents and solutions used in P extraction in the preparation of samples for ^{31}P nuclear magnetic resonance (NMR) spectroscopy are provided in Table A5.

Table A1 Reagents and solutions used for soluble reactive phosphorus analysis.

Reagents or solution	Preparation	Storage and Use
2.5 M Sulphuric Acid (H_2SO_4)	A 25 ml volumetric pipette was used to transfer 135 ml of concentrated analysis grade sulphuric acid to 800 ml of distilled H_2O, within a fume cupboard. Further distilled water was added to make a final volume of 1.0 l.	H_2SO_4 The solution was stored in darkness at room temperature for up to two months.
Ammonium Molybdate Solution	No more than 30 ml was required for a single batch. To prepare this volume, 1.2 g of ammonium molybdate was dissolved in 30 ml of distilled water. Appropriate volumes could then be used in the mixed reagent (see Table A4 and A5).	Ammonium molybdate solution was prepared freshly for each set of analysis.
Ascorbic Acid	For the mixed reagent for filtered samples, the required weight of ammonium molybdate was dissolved in a known volume of distilled water and added to the mixed reagent (see Table A3). For mixed reagent for digested samples (TP and TSP) the required weight of ammonium molybdate was dissolved in a known volume of distilled water and added to the mixed reagent (see Table A4).	Ascorbic acid solution was prepared freshly for each set of analysis.
Potassium Antimonyl Tartrate (PAT)	A weight of 0.137 g of potassium antimonyl tartrate was dissolved in 50 ml of distilled water.	PAT was stored in darkness at room temperature for a maximum of two months.

Table A2 Reagents and solutions used for total phosphorus and total soluble phosphorus analysis

Reagents and solutions	Preparation	Storage and Use
Potassium Persulphate	No more than 100 ml was required for a single batch of analysis. To prepare this, 8.0 g of potassium persulphate was dissolved in 100 ml of distilled water.	Potassium persulphate was prepared freshly for each set of analysis
30% H_2SO_4	To prepare this reagent, 30 ml of concentrated analysis grade sulphuric acid was slowly added to 70 ml of distilled water.	Once cooled, the solution was stored in a glass bottle in darkness at room temperature for a maximum of two months.

Table A3 Composition of the mixed reagent used for filtered samples (SRP analysis)

Reagent Volume (ml)	2.5M Sulphuric Acid (H_2SO_4) (ml)	Ammonium Molybdate (ml)	Ascorbic Acid (g)	PAT (ml)	Distilled Water (ml)
100	50	15	0.6	5	30
150	75	22.5	0.9	7.5	45
200	100	30	1.2	10	60

Table A4 Composition of the mixed reagent used for digested samples (TP and TSP analysis)

Reagent Volume (ml)	2.5M Sulphuric Acid (H_2SO_4) (ml)	Ammonium Molybdate (ml)	Ascorbic Acid (g)	PAT (ml)	Distilled Water (ml)
100	27	15	0.6	5	53
150	7540.5	22.5	0.9	7.5	79.5
200	54	30	1.2	10	106

Table A3 Reagents and solutions used to prepare samples for analysis with ^{31}P NMR

Reagents and solutions	Preparation	Storage and Use
1.0 M Sodium Hydroxide (NaOH)	To prepare NaOH solution, 40.0 g of NaOH pellets were added to 1.0 l of distilled water and mixed using a magnetic stirrer.	Sodium hydroxide was prepared freshly for each batch of P extractions.
0.5 M ethylenediaminetetraacetic acid (EDTA)	EDTA was prepared by dissolving 18.61 grams of $EDTA.Na_2.2H_2O$ in 80 ml of water. To aid dissolution, the pH was maintained at pH 8.0 with the addition of c. 2 g of NaOH pellets and the solution mixed using a magnetic stirrer for up to 1 hour, until the EDTA had completely dissolved.	The solution was then stored in darkness at 4°C and used within 4 months.

Survey page 2

8.2 Appendix B: Questionnaire and Cover Letter used in the Assessment of Human Behaviour

The cover letter and questionnaire used to assess human behaviour is provided in the following section. Both documents were posted to all addresses in Loch Leven catchment considered to be connected to PSS, as outlined in Section 2.6.9.

Mr. William Brownlie
PhD student
School of the Built Environment
Heriot Watt University
Tel: 0131 451 4434/ 0131 445 4343
Email: wjb5@hw.ac.uk

Dear Sir or Madam,

I am contacting you because you live within the Loch Leven catchment; an area of international importance for biodiversity and in which many people have septic tanks. Septic tanks are not normally the topic of polite conversation, but they can play an important role in your area by reducing the inputs of waste water to Loch Leven. I would like to invite you to participate in an anonymous survey to help us understand more about how you perceive septic tanks in your area and whether they meet your needs for waste water management. No personal data will be recorded in this survey, unless provided by you voluntarily on page 4.

By participating in this survey you will be helping us to improve waste water management in your area. The survey will collate information in the following areas:

- the use of household products and domestic appliances (such as dishwashers and washing machines),
- septic tank operation and maintenance, and,
- other waste water management issues.

You may return the questionnaire before the **5th October 2012** using the enclosed stamped addressed envelope

Please feel free to contact me should you require further information on the questionnaire or if you would like to complete the questionnaire by telephone.

Sincerely,

Will Brownlie

SECTION 1 - Background

Many homes are connected to a mains sewerage system (pipes in the street that carry your waste water to a treatment works). Other homes, particularly ones in rural areas, have a 'septic tank' to deal with wastewater. These are often buried in your (or your neighbour's) garden. You may be able to see the manhole and inspection covers in your garden. The outflow from your septic tank may run into reed beds or be further connected to other tanks with mechanically powered pumps, making them 'private sewage works'.

---

1) Which of the following describes the type of sewerage system that your property is connected to?

Mains sewerage ☐ septic tank ☐ private sewage works ☐ not sure ☐

(If you did not answer septic tank or private sewage works please skip to question 15)

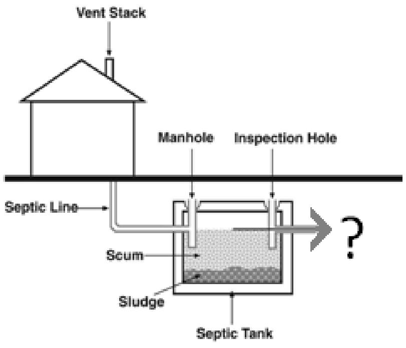
2) Roughly, how old is your property? ....years

3) How long have you lived there? ....years

4) How old is your septic tank/private sewage works? ....years

5) Do you know where the output from your septic tank/private sewage works drains to?

- ☐ **Direct to a river or stream**
- ☐ **Soakaway**
- ☐ **Open drainage ditch**
- ☐ **Reed bed**
- ☐ **Other**
- ☐ **Unsure**



6) Is your septic tank shared with neighbouring properties?

Yes ☐ (how many, if known?………….)

No ☐

7) Has your septic tank ever failed to work properly, for example, becoming blocked, over flowing or producing a bad smell?

Yes ☐ (If known, how many times during your residency?…………) No ☐

SECTION 2 - Background

Septic tank owners often have to pay for their tanks to be emptied, although the time period between emptying a septic tank can vary between properties.

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8) Have you ever emptied your septic tank, and if so how frequently do you empty your tank?

Yes ☐ **(date last emptied, if known and frequency) ....**

No ☐ **I have never emptied my septic tank**

9) Do you know if your septic tank has any cracks or leaks? **Yes** ☐ **No** ☐

10) Does your septic tank receive roof runoff (rainwater from your roof)? **Yes** ☐ **No** ☐

11) Who do you think should be responsible for maintaining your septic tank? (tick multiple boxes if required)

☐ **Private property owner**

☐ **Local council**

☐ **Scottish Water**

☐ **Scottish Environment Protection Agency (SEPA)**

☐ **Other** (please explain) ……………………………..

12) Who should be responsible for fixing a septic tank known to be operating incorrectly? (tick multiple boxes if required)

☐ **Septic tank owner**

☐ **Local Council**

☐ **Scottish Water**

☐ **Scottish Environment Protection Agency (SEPA)**

☐ **Other** (please explain) ……………………………..

13) How many septic tanks, as a percentage, are operating incorrectly in the Loch Leven catchment?

0-25% ☐ **26- 50%** ☐ **51-75%** ☐ **75-100%** ☐

SECTION 3 - Background

The performance of a septic tank is thought to be dependent upon the volumes and types of household products and wastes that enter it.

---

14) How many times per week do use your dishwasher? ....

15) How many times per week is your washing machine used? ....

16) How many times per week is the shower used? ....

17) How many baths are run per week? ....

18) If you have one, how many times per week do you use a 'plumbed-in' garbage/food disposal unit in your kitchen? ....

19) What of the following do you consider when purchasing dishwasher detergent? (tick multiple boxes if required)

☐ **Price**
☐ **Cleaning performance**
☐ **Allergies**
☐ **Impact on the environment**
☐ **Low phosphorus content**
☐ **Other (please explain) …………………………….**

20) Which of the following do you consider when purchasing detergent for your washing machine? (tick multiple boxes if required)

☐ **Price**
☐ **Cleaning performance**
☐ **Allergies**
☐ **Impact on the environment**
☐ **Low phosphorus content**
☐ **Other (please explain) …………………………….**

SECTION 4 - Background

At present, the need for septic tanks and private sewage works to be registered is under review. The current situation in Scotland is that septic tanks/private sewage works need only be registered with the Scottish Environment Protection Agency (SEPA) when connected properties are sold. New guidance (termed the '125% rule') is available within your area to assist anyone submitting a planning application that may affect Loch Leven, especially if a new septic tank is proposed as part of the application. Compliance with this guidance is now considered as part of the planning application process.

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21) Do you feel well informed about current legislation in relation to your septic tank/private sewage works? **Yes ☐ No ☐**

22) Do you feel adequate information is available on measures to reduce pollution from septic tanks/ private sewage works?

Yes ☐ No ☐

23) Do you feel adequate information is available on how to correctly maintain your PSS?

Yes ☐ No ☐

24) Do you feel adequate information is available on how to change your domestic habits to improve the performance of your PSS (i.e. change of household detergent)?

Yes ☐ No ☐

SECTION 5 - Background

Knowledge of waste water treatment may be related to cultural trends in Scotland, for example, rural populations may be better informed than urban populations. It is important to analyse survey results within a well defined demographic context. The following questions will help us gather this demographic information.

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25) What is your age? **……….**

26) Are you male or female? **Male ☐ Female ☐**

27) How many people live in your house? **……….**

SECTION 6 – Follow up contact

We plan to conduct a more detailed survey which will include a face-to face survey and an analysis of your septic tanks performance. Advice on how to improve the performance of your septic tank will also be given free of charge. Please provide your contact details below should you wish to be involved in this follow up survey.

Preferred contact details and other comments*:*