Evaluation of the impact of treated wastewaters discharges on river water phosphorus and metal concentrations

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To

Mum, Dad, my daughter Lauren and the memory of my Grandfather, Raymond Millier

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ABSTRACT

Evaluation of the impact of treated wastewaters discharges on river water phosphorus and metal concentrations

It is standard practice for sewage treatment plants to discharge treated wastewaters to water-bodies and, in the UK, this has been the custom since the first sewerage system was completed in London around 1865. Before sewerage networks untreated sewage waste was discharged to rivers (wet carriage) or removed from domestic dwellings by "honey wagons" (dry carriage) and taken to rural areas to be used as fertiliser (Adams & Papa, 2000).

Wastewater inputs to rivers are governed by discharge consents issued by the Environment Agency in accordance with existing legislation, taking into account the physical and ecological characteristics of the receiving river. However, it has become apparent in recent years that wastewaters may have a detrimental effect on receiving rivers, particularly in terms of nutrients as they frequently discharge phosphorus (P) in concentrations > 1.0 mg P l^{-1}. Metals are not specifically removed by the wastewater treatment process and, although their affinity for particulates results in some removal during processing, it is suspected that dissolved metals may be present in treated wastewaters.

In 2000, the E.C. introduced the Water Framework Directive, which requires water bodies within member countries to attain "good ecological status" by 2015 in terms of biological and physico-chemical water quality. An umbrella Directive, it combines existing legislation on a range of contaminants including nutrients and metals with additional environmental standards to improve the quality of European waters. The purpose of this study was to consider whether the discharge of treated sewage wastewaters is likely to prevent rivers from achieving the standards required by this legislation.

During an eighteen month period, water samples were collected from two second order rivers, the Bourne and Hogsmill, up and downstream of sewage treatment works. Samples were analysed for a range of P species and metals in filtered and

unfiltered river water. Ultra-filtration was carried out on a selection of samples, as finer fractions are likely to be more bioavailable. River flow data was used to calculate potential contaminant loads downstream of the input source; this data was compared against published concentrations of agricultural derived P, historically considered the major contributor of P to UK riverine waters.

Until the introduction of P removal processing at the Hogsmill, downstream concentrations of all P species in both rivers, were greater than upstream by an order of magnitude. P removal reduced P concentrations in the Hogsmill by more than 60% although they remain significantly greater than upstream. The majority of P occurred as soluble reactive P (SRP), the most bioavailable species, and the continuous nature of wastewaters discharge meant concentrations were high during the growth season. Current P-removal processes may not remove sufficient P to meet quality targets recommended by the U.K. Technical Advisory Group on the Water Framework Directive. Estimated P loads upstream of the wastewaters outflow are < 8 kg SRP day^{-1} for both rivers, the combination of increased P concentrations and greater river water volume downstream of the outflow result in estimated P loads of > 45 kg SRP day^{-1} in the Bourne and > 80 kg SRP day^{-1} for the Hogsmill (after P-stripping). Comparison of P export figures from treated sewage wastewaters, calculated using daily load figures, with those from agriculture indicate that in all but the most rural catchments, sewage wastewaters are a greater source of P.

Downstream, dissolved metals concentrations were not significantly different from upstream except for As in the Bourne and Pb in the Hogsmill; neither metal exceeded regulatory limits.

River sediment from the Hogsmill and Bourne, and two additional rivers receiving sewage wastewaters, the Mole and Blackwater, were analysed for total metals and P. The ability of sediments to release (SRP) was investigated using kinetic release analysis. In the absence of U.K. standards, metals concentrations in sediments were assessed using the US EPA sediment quality guidelines (SQG). A range of metals in sediments from both the Hogsmill and Mole exceeded SQG to the extent that biota was likely to be affected. Although the greatest

concentrations of total phosphorus in sediment were found in the Bourne, it is the Hogsmill which exhibits most potential for the release of SRP from sediment to the water column.

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ABBREVIATIONS

BAT: best available techniques

BOD: biological oxygen demand

BMWP: Biological Monitoring Working Party

CSO: combined sewer outflow

DEFRA: Department for Environment, Food and Rural Affairs

DET: diffusive equilibrium in thin films

DO: dissolved oxygen

DOC: dissolved organic carbon

DOM: dissolved organic matter

DOP: dissolved organic phosphorus

D/S: downstream

E.A.: Environment Agency

E.C.: (also known as E.E.C. or E.U.) European Community

EDTA: ethylenediaminetetraacetic acid

ERL: effects range low

EPC: equilibrium phosphate concentration

EPC_0: equilibrium phosphate concentration co-efficient

EQS: environmental quality standard

ERM: effects range median

ICP-AES: inductively coupled atomic emission spectrometry

ICP-MS: inductively couple mass spectrometry

IPPC: Integrated Pollution Prevention and Control Directive (2008/1/EC)

IUPAC: International Union of Pure and Applied Chemistry

Kd: partition coefficient

LTA: long term average

LC: lethal concentrations

LOD: limit of detection

LOIS: Land Ocean Interaction Study

MW: molecular weight

NAW: National Assembly for Wales

NERC: Natural Environment Research Council

OFWAT: The U.K. Water Services Regulation Authority

PP: particulate phosphorus

PSYCIC: Phosphorus and Sediment Yield Characterisation in Catchments

R^2: Regression co-efficient

REE: rare earth elements

RSD: Relative standard deviation

SD: standard deviation

SME: small to medium enterprises

SQG: sediment quality guidelines (US.E.P.A.)

SRP: soluble reactive phosphorus (also known as ortho-phosphate), monomeric, inorganic phosphorus

SPM: suspended particulate matter

TDP: total dissolved phosphorus (SRP plus dissolved polymeric and inorganic phosphorus)

TEL: threshold effect levels

TP: total phosphorus (TDP plus PP)

TSS: total suspended solids

SNP: soluble non-reactive phosphorus

STW: sewage treatment works

SUP: soluble unreactive phosphorus

UKTAG: U.K. Technical Advisory Group (for the Water Framework Directive)

UWWTD: Urban Wastewater Treatment Directive (91/271/EEC)

WFD: The Water Framework Directive (2000/60/EC)

WHO: World Health Organisation

U.K.: United Kingdom

U.S. United States of America

U/S: upstream

U.S.E.P.A: United States Environmental Protection Agency

1. Phosphorus and metals in rivers: an overview

1.1. Introduction

Phosphorus (P) is a nutrient necessary for the growth and function of all life forms but, as it is not abundant geogenically, water bodies naturally contain < 10 μg P l^{-1} (Mainstone & Parr, 2002). Many anthropogenic sources of P exist, agricultural fertiliser, industrial processes and domestic detergents and it is also present in human and animal excrement so, inevitably, rivers and other water bodies receive P inputs above naturally occurring levels unless such sources are controlled. Depending on the chemical species and receiving water conditions P may be in soluble or suspended particulate form and may become adsorbed to sediment on the channel bed. In water bodies, excess P can lead to eutrophication, where nutrient enrichment results in unnaturally fast phytoplankton and macrophyte growth (The Urban Waste Water Treatment Directive, 2002).

Many rivers end in estuarine or transitional waters with reduced flow and depths which act as sediments traps, removing some P before it reaches the ocean (Jickells, 2005). However, rivers remain the major source of P to oceans, Galloway *et al.* (1996) estimates 3720 x 10^6 kg P is lost from inland water courses to the estuary and continental shelf of the North Atlantic Ocean, with approximately 25% reaching the open ocean where it has the potential to increase primary production.

Composition of underlying bedrock is a major influence on the type and quantity of metals in rivers as they dissolve naturally into water courses through weathering, but anthropogenic activities such as excavation may raise concentrations to harmful levels. Like P, many trace elements are essential for biota and occur naturally in concentrations appropriate to the surrounding ecosystem (Neal *et al.*, 2006). Metals are persistent in the environment; they bioaccumulate, working their way up the food chain. Whilst certain metals such as Fe, Cu and Zn are necessary in small amounts, excess supply may be harmful, and metals such as As, Hg, Pb and Cd are inherently toxic (Järup, 2003; Fraga, 2005). Anthropogenic sources of metals to water bodies also include agricultural fertilisers, animal and human excrement and industrial processing as well as mining, urban run-off and atmospheric deposition (Milovanovic, 2007). Metals have a propensity to adsorb to sediments which can, in favourable conditions, remove them from the water column and make them unavailable to

waterborne biota but this process is reversible due to the evolving nature of river systems (Förstner, 2004). Macrophytes, sediment bacteria and bottom-feeding biota are able to accumulate metals from sediment, potentially releasing them to their consumers. As sediments are generally transported through river systems and deposited in estuarial waters, anthropogenically derived metals may accumulate here (Tsai *et al.*, 2007).

1.2. Sources of phosphorus to rivers

Latest DEFRA figures, published in 2007, estimate 22 – 28% of total P entering British waters is agricultural in origin (Mainstone *et al.*, 2008). Research into the sources of P in waterbodies focused initially on agriculture and a number of authors have traced contamination pathways from fields and field drains to groundwater or watercourses following the application of fertilisers, manures and slurries (Edwards & Hooda, 2008; Hooda *et al.*, 1997; Hooda *et al.*, 1999; Hooda *et al.*, 2000; McGechan *et al.*, 2005; Withers & Lord, 2002). These studies recommend best management practices to mitigate P loss in agricultural runoff e.g. applying fertilisers and slurries during dry weather periods, testing soils for nutrient levels before adding additional P and introducing buffer strips between agricultural land and watercourses (Hooda *et al.*, 2000; Mainstone *et al.*, 2008). However, P concentrations in watercourses have not diminished as expected e.g. the Environment Agency (E.A.) states that in 1995, 50% of English rivers had P levels > 0.1 mg P l^{-1} and this situation was unchanged in 2007 (E.A., 2009a). Accumulation of excess P in soils over many years may mask recent improvements in fertiliser management (Mainstone *et al.*, 2008).

This lack of reduction to P levels in rivers, despite U.K. Government initiatives to reduce rural sources of P, coupled with increased understanding of the episodic, seasonal nature of agricultural P losses has persuaded authors to investigate alternative sources which may contribute significant concentrations of P to water bodies (Jarvie *et al.*, 2006). These include aquaculture where, in a review of current literature, Sarà (2007) concluded that fish farming was significant source of P to freshwater systems. Although Boaventura *et al.*, (1997) measured P concentrations in a river downstream of trout farms in Portugal which did not receive P from other sources and concluded that aquaculture did not represent a risk to the receiving river, their project farms discharged significantly less P than many in Europe.

Information on industrial sourced P has proved difficult to find, Lui *et al.*, (2007), comments on the world-wide issue of phospho-gypsum, a waste product from P fertiliser production, assessed as being responsible for 84% of industry derived P waste in China but admits lack of data prevents quantification of the issue.

The food industry, particularly dairy processing, is another significant source of P; a pilot study for the Irish Dairy Industry found more than 12 mg P l^{-1} in treated dairy effluent (Mulkerrins *et al.*, 2004). However, food processing as a source of P to waterbodies is not widely reported in literature, possibly because emissions are controlled by legislation under the IPCC Directive (O'Malley, 1999).

1.3. The impact of sewage wastewaters on phosphorus levels in rivers

Source	Influent concentrations mg P l^{-1}	Effluent concentrations mg P l^{-1}	% Removal
*STW E. Norway A	3.0 – 4.33	0.10 – 0.18	94 – 97
STW E. Norway B	5.0	0.10	98
STW W. Norway C	3.13 – 3.5	0.21 – 0.25	92 – 94
STW S. Norway D	1.63 – 3.5	0.41 – 0.44	73 – 94
STW N. Norway E	1.20 – 2.74	1.60 – 2.44	-33 – 11
Mean of 29 STW in Austria	not provided	0.75	85
STW Limbe, Malawi	0.79 ± 0.93	0.63 ± 0.23	variable
STW Soche, Malawi	5.39 ± 0.66	3.86 ± 0.76	variable
Dairy processing, Ireland	49.0	12.74	74

Table 1.1: Total phosphorus in wastewaters (Mulkerrins *et al.*, 2004; Sajidu *et al.*, 2007; Vogelsang *et al.*, 2006; Zessner & Lindtner, 2005) (*STW : sewage treatment works)

Table 1.1 provides an indication of the P inputs to and removal efficiencies of STW worldwide compared to an alternative wastewater source, the dairy industry. STW with P stripping technology can remove up 98% of P whilst those with basic treatment may discharge P concentrations which can exceed influent concentrations as a result of water evaporation during the treatment process.

The most recent DEFRA estimate for STW contribution to the total P load in U.K. waters is ≈ 61%, so it is hardly surprising that resources are now targeted towards better understanding this source (White & Hammond, 2007). Only recently acknowledged as a major source of P to rivers, treated sewage treatment wastewaters have been the focus of recent studies, particularly in the U.K. by researchers at the Centre for Ecology and Hydrology, and

frequently funded by NERC and the E.A. (Jarvie, Neal & Withers, 2006; Jarvie *et al.*, 2002a; Jarvie *et al.*, 2005; Neal *et al.*, 2005).

To date, there are no studies comparing P concentrations up and downstream of a single STW discharge point, in both the water column and river bed sediments, in situations where underlying receiving water conditions are greatly influenced by the volume of wastewater. These second or third order rivers are at risk of ecological imbalance, particularly during periods of low rainfall, when up to 80% of the downstream river water volume may be "treated" wastewater (Jarvie *et al.*, 2006). As it is suggested that the cumulative P load from third and second order rivers flowing into first order rivers is responsible for the consistently high P concentrations in them, despite the introduction of P stripping processes at larger STW, it is vital that inputs and their potential effect are quantified (Jarvie *et al.*, 2006; Mainstone & Parr, 2002).

1.4. The sources and impact of metals to rivers

A plethora of literature on dissolved, particulate and sediment-bound metals concentrations in rivers, estuaries and oceans exists. Bioassay analysis is frequently used to quantify accumulation up the food chain from phytoplankton and daphnia to fish and aquatic mammals, as the persistent nature of trace metals facilitates this investigative method (Borgmann, 2000; Roig *et al.*, 2007; Wong *et al.*, 1995). Metals speciation and partitioning in water and sediments are often researched to gain greater understanding of their behaviour in aquatic environments and to identify effective ways of removing them (Guéguen & Dominik, 2003; Meyer, 2002; Benoit & Rozan, 1999; Peakall & Burger, 2003; Turner & Mawji, 2005). The detrimental impact of mineral-rich mine-waters, seeping into rivers when aquifers recharge after decommissioning or as a result of dam-burst is another popular topic for researchers (Jarvis & Younger, 2000; Jeong *et al.*, 1999; Levings *et al.*, 2005; McGinness, S., 1999; Camm *et al.*, 2004; Tipping *et al.*, 2002; Younger, 2001).

Industrial emissions have been evaluated in terms of individual pollution events such as the accidental release of smelting wastes into the Lot River, France in 1987 or as continual discharges e.g. the flow of methyl mercury into Minamata Bay, Japan, over a thirty year period or unregulated discharges of tannery effluents in Albania (Audry *et al.*, 2004; Gbem *et al.*, 2001; Haraguchi *et al.*, 2000). Regulated discharges from industry as a source of

metals to rivers is also recognised by authors e.g. smelting, electroplating, pharmaceutical and agrochemical manufacture, power generation and used oil reprocessing plants (Achoka, 2002; Cave *et al.*, 2005; Cotman *et al.*, 2001; Fatta *et al.*, 2007; Floqi *et al.*, 2007). Settlement represents another source of metals to rivers, home building may cause bank erosion or landslide, increasing the quantity of mineral bearing soils in the river (Stumm *et al.*, 1992).

Lester (1983) recognised that sewage treatment processing at U.K. plants was inconsistent and sometimes ineffective at metals removal, with discharged wastewaters having concentrations up to 10 times greater than the receiving river water. Pollutants discharged to receiving rivers affect the river immediately downstream of the contaminant source but they may be transported into large river systems and, eventually, the marine environment. Elevated levels of trace metals and P estuarine sediments have been traced back to discharge points in rivers a considerable distance upstream as contaminants may remain suspended until river flow reduces as a result of physical changes to the river, e.g. widening of the river bed, reduced water column depth, etc (Vincent *et al.*, 2009).

However, until recently, this potential source of metals to waterbodies was generally disregarded, possibly in favour of the more obvious sources mentioned above, despite the fact that STW often receive metal-rich industrial waste as well as that from domestic sewers (Gagnon & Saulnier, 2003; Sajidu *et al.*, 2007; Upadhyay *et al.*, 2007). Gagnon & Saulnier (2003) studied wastewaters from the Montreal SWT discharging into the St Lawrence River, Canada and found highest dissolved trace metals concentrations 1 km downstream of the outfall, highest particulate concentrations 5 km downstream and evidence of increased metals concentrations as far as 40 km downstream.

$\mu g\ l^{-1}$	Expected geogenic levels in rivers	Thessaloniki, Greece STW Untreated sewage wastewaters	Thessaloniki, Greece STW Treated sewage wastewaters	Kenya Treated pulp & paper mill discharges	Albania Tanneries (mean range of 13 plants)
Cd	< 1	3.3 ± 1.1	1.5 ± 0.74	5.0	
Cr	1.0	40 ± 12	20 ± 3.5	27.0	4750 – 49500
Cu	6.0	79 ± 35	33 ± 5.8	8.0	
Fe	670	480 ± 87	380 ± 47		
Mn	5.0	67 ± 12	19 ± 2.4		
Ni	0.3	770 ± 200	430 ± 97	208	
Pb	1 - 10	39 ± 9.4	27 ± 3.6	527	
Zn	10	470 ± 140	270 ± 53	110	

Table 1.2: Trace metals in rivers, sewage and industrial wastewaters (Achoka, 2002; Floqi *et al.*, 2007; Huheey *et al.*, 1993; Ntengwe, 2006; Karvelas *et al.*, 2003; Mandal & Suzuki, 2002)

Chipasa (2003) found concentrations of heavy metals in effluent discharged by a STW in Gdansk, Poland, were directly proportionate to the quantity of metals in the influent and that compliance limits in Poland for the release of metals to receiving waters were met. Karvelas *et al.* (2003) studied the passage of trace metals through the sewage treatment process and found dissolved metals in the final effluent but did not consider their fate in the receiving water body. Neal *et al.* (2000a & b and 2006) acknowledges STW discharges as a potential source of trace metals to all U.K. rivers receiving treated wastewaters. However, their impact is generally unquantified. Sewage sludge is widely recognised as a source of trace metals, hence legislative restrictions on its use as fertiliser on agricultural land (Fuentes *et al.*, 2006). In comparison, minute concentrations of trace metals from sewage wastewaters could be perceived as inconsequential, especially when compared to the metals content of some industrial discharges, e.g. Cr and Pb, (Table 1.2). However, as there is no doubt that sewage wastewaters continually discharge metals to receiving rivers, it is appropriate to investigate their impact (Achoka 2002; Floqi *et al.*, 2007; Karvelas *et al.*, 2003).

1.5. Aims and objectives of the research project

The aim of this research is to assess the impact of P and trace metals from treated wastewaters on receiving river water quality and sediments to ascertain whether such discharges are likely to prevent the U.K. from achieving "good ecological status" by 2015 as required by the Water Framework Directive (E.C., 2000).

To achieve this, the objectives of this project are:

- to analyse water from two rivers receiving substantial inputs of STW wastewaters for P species and metals in a range of fraction sizes over an eighteen month time frame;
- to ascertain river flows up and downstream of the input sources in order to calculate potential contaminant loads with the river system;
- to evaluate the function of channel bed sediments from four rivers receiving STW inputs in terms of P and trace metals storage and mobilisation; and
- to use data from these activities to assess the likely effect of treated wastewater inputs on water quality.

2. The impact of treated wastewaters discharges on phosphorus and metals in river water: a literature review

2.1. Introduction

According to Water Aid (2006), an estimated 1.1 billion people in the world still lack access to safe water, 2.6 billion lack adequate sanitation and 1.8 million children per annum die from causes related to unclean drinking water and poor sanitation. This situation prevails despite the fact that the right to supplies of clean water sufficient to prevent dehydration and disease was declared a "human right" by the United Nations Committee on Economic, Social and Cultural Rights in 2002 (WHO, 2007).

Lack of potable water is a widely publicised problem in developing countries (WHO, 2007). Charity advertising campaigns cite climatic conditions and inadequate infrastructure for the problem e.g. floods in Pakistan, July 2007, Sudanese conflict, November 2006, (Oxfam International, 2007). However, the deteriorating state of established water courses is an increasing source of concern in both developing and developed countries due to poor supervision, inadequate resourcing and disagreements over cross-border responsibilities (Biswas, 1999).

All water courses, whether above or underground, are at risk of contamination from a variety of anthropogenic pollutants. Underground aquifers located close to mining activities may become contaminated with metal sulphates leaching from mine dumps or when water tables rebound following mine closure (Sainz, *et al.* 2003). Water courses located in agricultural catchments receive run-off containing nutrients, pathogens and veterinary drugs during precipitation events (Diaz-Cruz *et al.*, 2003; Hooda *et al.*, 2000; Mawdsley *et al.*, 1995). Urban rivers and streams are polluted by metals and hydro-carbons from road drainage culverts (Robson *et al.*, 2006) and by accidental or deliberate discharge of industrial wastes (Altmann, *et al.*, 2001; Rule *et al.*, 2006). Water courses receiving domestic wastewaters may contain human pharmaceutical drugs e.g. contraceptives, analgesics and antibiotics and residue from personal care products e.g. fragrances and detergents (Breton & Boxall, 2003; Fernandes *et al.*, 2002). Clearly water can become polluted with a variety of contaminants

from a wide range of sources. The most common causes of water pollution and their effects are summarised in Table 2.1.

Pollutant	Primary Source	Effect
Organic matter	Industrial wastewater, domestic sewage and livestock farming operations	Depletion of O_2 from the water column, stressing or suffocating biota.
Excess nutrients	Agricultural & urban run-off	Over stimulates growth of algae and aquatic plants
Heavy metals	Runoff and leaching from industrial, mining and other contaminated sites	Persistent in the environment, toxic in excess quantities, bioaccummulate in muscle tissue, travel up the food chain.
Microbial contaminants	Domestic sewage, livestock, naturally occurring pathogens	Infectious diseases and parasites spread through water courses. May cause illness/death if untreated water is ingested by animals or vulnerable humans.
Toxic organic compounds	Many sources; industrial, agricultural, domestic	Range of toxic affects; immune suppression, sterility, poisoning.
Silt & suspended particles	Soil erosion, construction in watersheds	Degrades water quality. May interrupt riverine life by restricting U.V. light penetration.
Thermal pollution	Rivers are dammed for hydro-power, leading to slower water flow & increased temperatures. Recycling of water extracted for industrial water cooling	Alters riverine environment, may change species composition. Sensitive species failing to adapt to changes may die out.

Table 2.1: Common world-wide water pollutants and their effects (World Resources Institute, 2007)

Although water pollution emanates from a wide range of sources, this review considers just two specific groups of pollutants, phosphorus (P) and heavy metals, how they find their way into water courses, their dynamics within aquatic systems, the likely impact on biota and the efficacy of methods employed during sewage treatment to remove them.

2.2. An over view of nutrients and water quality

2.2.1. Phosphorus

Phosphorus as a macro-mineral essential for growth, bone mineralization, reproduction and energy metabolism in all species it is naturally present in the environment but it can be detrimental, particularly to water bodies, in excess quantities (Roy, 2004).

Geologically, P is not abundant, so upland water bodies which do not receive P inputs from diffuse or point discharge sources generally contain < 10 $\mu g\ P\ l^{-1}$ as soluble reactive P, (SRP)

(Mainstone & Parr 2002). Mainstone & Parr (2002) state that unpolluted lowland water bodies are likely to contain greater concentrations of P as it accumulates naturally, being taken up and then released by aquatic biota. They assessed lowland concentration levels at <30 μg SRP l^{-1}(Mainstone & Parr 2002). However, as bio-geo-chemical cycling occurs in upland water bodies too, the differences in concentration levels may not be so great.

Phosphorus is an essential nutrient; its availability governs the growth rate of many living organisms. Where P is in short supply, riverine plant life may be restricted, although contributing factors such as light availability, river flow and abundance of other nutrients are also relevant (Mainstone & Parr 2002). An oversupply of P in water bodies may result in eutrophication; the enrichment of water by nutrients, causing accelerated growth of algae and higher forms of plant life to produce an undesirable disturbance to the balance of organisms and the quality of the water (OFWAT, 2002). For example, phytoplankton multiply excessively when P levels are high, increasing the quantity of biomass in the river. This reduces the amount of dissolved oxygen (DO) available for other riverine life and also increases water turbidity (Painting *et al.*, 2007). In circumstances where excess P results in greater biomass, rivers may become hypoxic as plants die off and decompose, particularly in the region of the river bed (Painting *et al.*, 2007).

The impact of excess P in rivers varies according to underlying conditions such as water chemistry, sediment composition, velocity, depth and species of biota present (Hilton *et al.*, 2006).

2.2.2. Nitrates

Nitrate (N) is a naturally occurring chemical formed during the decomposition of animal or human waste, it is added to fertilisers to improve crop yield. About 60 per cent of the nitrate in surface and groundwater comes from agriculture; the other significant sources of nitrate are sewage effluent and atmospheric deposition (E.A., 2009b).

Like P, N is a "limiting nutrient" in aquatic systems, that is, if there is insufficient nutrient concentration to enable algal cells to divide in two and increase their biomass the algal growth rate becomes restricted (Hilton *et al.*, 2006). There is no consensus amongst researchers as to which nutrient limits plant growth, in their review of previous studies, Hilton *et al* (2006) concluded that the type of plant (macrophyte, epiphyte, benthic algae, attached filamentous algae, etc.) and the trophic state of the river determined whether P, N or both were limiting nutrients.

2.3. An overview of metals and water quality

As metals occur geologically, they are naturally present in rivers; their type, species and concentration depend upon the nature of bedrock through which the river flows (Neal *et al.*, 2006). Many trace metals are essential nutrients for biota, however, anthropogenic inputs from industrial and STW wastewaters may increase metal concentrations to levels which can be toxic to both biota and humans (Lester, 1983).

Metals are found in rivers and streams in solution, as suspended particulate matter (SPM) or adsorbed to sediments (Faulkner *et al.*, 2000). As metals have an affinity for particulates, metals which enter a water course in soluble form tend to adsorb to particulate matter and eventually settle out as sediment (Stead-Dexter & Ward, 2004). When adsorbed to sediment, metals are unavailable to species of riverine biota which feed from the water column. However, metals may re-mobilise when bottom feeding biota and macrophytes ingest them, or when the water chemistry changes e.g. pH levels, $CaCO_3$ or sulphide concentrations (Stead-Dexter and Ward, 2004).

Metals may bioaccumulate in tissue and major organs along the food chain. For example in rivers, *Penaeus aztecus* (brown shrimp) inadvertently ingests heavy metals and is eaten by predators such as fish which retain these metals in greater amounts (Carvalho *et al.*, 1999).
So far as the risk to human health is concerned, Pb (lead), Cd (cadmium), Hg (mercury) and As (arsenic) have been identified as those most likely to adversely affect human health (Järup, 2003). In appropriate amounts, metals such as Mn (manganese), Fe (iron), Cu (copper) and Zn (zinc) are essential for healthy functioning of humans and other living organisms, but they too may be harmful in excess quantities (Fraga, 2005).

The simplest method of establishing quality indicators for metals in river water is to establish maximum concentration limits, but this is not a reliable indicator of their toxicity to biota (Gueguen *et al.*, 2004). Analysis of individual metal concentrations in water overlooks the potential toxicity of a mixture of metals or metals and organic pollutants (Gueguen *et al.*, 2004). The unending range of potentially toxic combinations of pollutants in river water makes it difficult to assess their likely effect. Bioassays, i.e. using algae, larvae or fish to assess the effect of a selected combination of contaminants provide an overview of the likely outcome for the selected species but does not necessarily transpose across the entire range of organisms which differ in pollution tolerance and means of exposure. Bervoets *et al.* (1997) and Wong *et al.* (1995) favour analysis of water samples using a reference curve based on

the relationship between metal concentration and percentage algal growth. This is a species specific method and many reference curves would be needed to cover all possible combinations of metals and organic pollutants. As the chemical characteristics of individual water bodies, pH, Ca and organic content also influences the availability of pollutants the number of reference curves required makes this procedure impractical. It would seem that the simplest solution is to prevent these substances from entering the environment in the first place.

2.4. River water quality and legislation

Directive	Pollutant	Quality Target	Implementation Dates
Detergents Regulations 2005 (648/2004).	Total P (TP)	All domestic detergents must be ultimately biodegradable. Industrial or institutional detergents may be primarily biodegradable (lesser standard) if granted derogation by E.C.	8 October 2005
Water Framework Directive (2000/60/EC)	TP	*To achieve "Good ecological status"* nutrient concentrations must not exceed levels established to ensure the functioning of the ecosystem	Directive entered into force 22nd December 2000
	Metals and arsenic	Member states establish environmental quality standards for the protection of aquatic biota. Maximum annual average concentrations of metals and arsenic (and their compounds) to be established by member states for water, sediment & biota	*"Good ecological status"* to be achieved for all E.C waters by 22nd December 2015
Urban Wastewater Treatment Directive (91/271/EEC)	Sewage (SRP)	p.e.* 10k – 100k : 2 mg P l^{-1} p.e. > 100k : 1 mg P l^{-1}	1998 – 2005
Integrated pollution prevention and control Directive (96/61/EC) (IPPC)	Metals, Arsenic and TP	Use of best available techniques (BAT) to control release of pollutants to land, air and water from industrial and agricultural processes and large scale STW.	October 1996 (replaced the 1990 Environmental Protection Act)
The Mercury Directive (84/156/EEC) sectors other than the chlor-alkali electrolysis industry)	Mercury	Maximum 0.05 mg Hg l^{-1} effluent discharges	1st July 1986; current limits imposed 1st July 1989
The Cadmium Discharges Directive (83/513/EEC)	Cadmium	Total concentration in inland surface waters affected by cadmium discharges ≤ 5 µg Cd l^{-1}	From September 1985
The Mercury Discharges Directive (82/176/EEC) and 91/692/EEC (chlor-alkali electrolysis industry)	Mercury	Concentration of mercury in fish flesh 0·3 mg Hg kg^{-1} wet flesh. Total concentration of mercury in inland surface waters affected by discharges must not exceed 1 µg l^{-1} as the maximum annual average	1st July 1983 updated 1st January 1993
Freshwater fish Directive (78/659/EEC) and (2006/44/EC).	TP	Limit values of 0.2 mg l^{-1} for salmonid and of 0.4 mg l^{-1} for cyprinid waters, expressed as PO_4.	18th July 1980 updated 2006
	Total zinc	Salmonid waters : 0.003 – 0.5 mg Zn l^{-1} Cyprinid waters : 0.3 – 2.0 mg Zn l^{-1} depending on $CaCO_3$ levels	
	Dissolved copper	0.005 – 0.112 mg Cu l^{-1} depending on $CaCO_3$ levels	

Table 2.2: Summary of E.U. Legislation containing emission limits or quality standards to control metal or phosphorus pollution in water bodies (E.U., 2007). (*p.e. – population equivalent)

In Europe, the E.C. sets water quality targets within Directives which member countries ratify and turn into locally enforceable legislation. The resultant harmonised standards are

advantageous for cross-border water bodies as similar water quality targets apply, irrespective of boundary e.g. the River Rhine (E.C., 2006). Member countries report progress and compliance to the E.C. who may impose financial penalties for failure to achieve required standards (E.C., 2006).

In the U.K., responsibility for taking action to improve or maintain waters to meet E.C. standards resides with the Environment Agency, a non-governmental organisation sponsored by the Department for Environment, Food and Rural Affairs (DEFRA) and the National Assembly for Wales (NAW) (E.A, 2007).

Legislation to control pollution in water bodies by P or heavy metals is found in a number of statutes (Table 2.2). More stringent standards apply to water bodies used for drinking water abstraction; they are not covered in this review.

The Urban Wastewater Treatment Directive (UWWTD) has been a major influence in reducing P inputs to water bodies (Zabel *et al.*, 2001). In implementing the UWWTD, STW treating sewage from "population equivalents" (p.e.) greater than 2,000 are required to use a two stage sewage treatment to reduce overall biological oxygen demand (BOD) by at least70% and total suspended solids (TSS) by 90% or more in wastewaters by 1st January 2006 (E.C., 1991). If water bodies receiving treated wastewaters are identified as being at risk of eutrophication additional processing is required to reduce P concentrations of wastewater discharges to 2 mg P l^{-1} and if the p.e. is greater than 100,000 P concentration must be reduced to 1 mg P l^{-1} (OFWAT, 2002).

Industrial discharges to water bodies, frequently containing metals and P, are governed by the Integrated Pollution Control and Prevention Directive (IPPC). It was introduced to reduce toxic inputs from industries such as metals, energy, mining, chemicals, intensive farming and waste management. The legislation does not specify targets in terms of maximum discharge concentrations for pollutants, instead industries are encouraged to develop "best available techniques" (BAT) to control pollution within acceptable levels, whilst considering the expense of so doing (DEFRA, 2005). BAT is intended to stimulate innovative pollution prevention solutions within industrial processes although there is concern that it may become just another means of controlling emissions (Cunningham, 2000). It may be argued that reference within IPCC guidance notes to emission limits and acceptable pollution abatement systems fails to encourage innovation by ratifying existing solutions. However, as the IPCC also requires improved energy efficiency, waste reduction

and substitution of harmful chemicals, which are more likely to be addressed during the industrial process, this legislation appears at least to be encouraging more environmentally aware production systems and moving the emphasis away from discharge criteria (Honkasalo *et al.*, 2005). As the IPCC deadlines are recent, its' effect has not been fully evaluated; e.g. DEFRA's mid-term review declines to comment on possible reduction in water pollution stating that reductions may be due to legislation other than IPPC (DEFRA, 2007).

Discharges of Cd and Hg, two specific metals whose toxic effect on humans and biota are well documented, are covered by longstanding legislation which sets specific emission limits and quality targets (Table 2.2). However, even thirty years since these controls were introduced in Europe these metals are present above target concentration limits in many rivers (Audry *et al.*, 2004; Rémy *et al.*, 2003; Scerbo *et al.*, 2005). This is not necessarily due to specific pollution incidents; it may also be an indication of long term persistence of metals in the environment.

The Freshwater Fish Directive targets water bodies which contain or should contain indigenous fish and have been identified as requiring protection to ensure that pollution levels are sufficiently low to support fish life (E.C., 1978). In targeting specific biological species, the Freshwater Fish Directive differs from the UWWTD, IPPC, Mercury and Cadmium Directives, which control discharges from specific industries, by imposing maximum concentration limits in water bodies for a variety of contaminants including P, Zn and Cu (E.C., 1978).

The Water Framework Directive (WFD) has been described by DEFRA as the most substantial piece of E.C. water legislation to date (DEFRA, 2003). Like the Freshwater Fish Directive, it employs quality objectives; these take the form of descriptive parameters for the biological, hydromorphological and physico-chemical elements of defined water bodies, i.e. groundwater, lakes, transitional waters, rivers and streams (Borja, 2005). The WFD is an umbrella directive which combines existing legislation and new requirements in order to contribute to the Directive's overall goal that all European water bodies attain "good ecological status" by 2015 (E.C., 2000). One criticism levied at the WFD is its failure to include fish as a biological indicator for water quality except in transitional waters (Borja, 2005). Including the Freshwater Fish Directive under the "umbrella" would remedy this.

The WFD timetable sets a series of targets from 2000 through to 2015 to help member countries achieve compliance e.g. compartmentalising areas of water within their jurisdiction into river basin districts by December 2004, identifying problem areas and upward trends in pollution by December 2005 and implementing plans to manage improvements to achieve the 2015 deadline by December 2006 (DEFRA, 2003). However, member countries are beginning to voice doubts about their ability to reach prescribed targets by 2015 for a variety of reasons including lack of resources, insufficient knowledge and the effects of external factors such as climate change and pollution sources from outside the E.C. (László *et al.*, 2007; Wilby *et al.*, 2006; Wilkinson *et al.*, 2007). In the U.K., researchers such as Mainstone *et al* (2007) suggest that current initiatives such as P stripping at STW, aimed at reducing specific sources of contaminants are insufficient on their own. They recommend an integrated catchment management approach, looking at existing stores of pollutants in sediments and soils close to waterbodies, in addition to controlling direct input sources as the most appropriate method of combating excess contaminant concentrations and meeting the requirements of the WFD (Mainstone *et al.*, 2007). Most recent information from the E.A. indicates that only 26% of rivers in England and Wales are of good ecological quality, and as the deadline for compliance with the WFD draws closer, it looks increasing unlikely that the U.K. will meet the requirements of this legislation (E.A., 2009c).

2.5. Origin and inputs of phosphorus and metals

2.5.1. Geogenic sources

In locations where the environment is unaffected by anthropogenic activity, soils are the main source of metal and P inputs to water bodies (Gasparon & Matschullat, 2006). The quantity of geogenic P is small, so unpolluted rivers generally contain <10 μg SRP l^{-1}, which is generated by the natural bio-cycling of P through riverine plants and biota (Mainstone & Parr, 2002; Skoulikidis *et al.*, 2006).

	Al	As	B	Cd	Cr	Cu	Fe	Mn	Pb	Zn
Dissolved metal concentrations										
Teviot	46.13	0.61	23.10	0.021	1.39	2.57	56.2	7.40	0.20	4.93
Tweed, Boleside	20.72	0.65	14.80	0.03	0.41	3.79	52.8	3.70	0.34	7.43
Tweed, Norham	31.24	0.66	20.60	0.02	0.45	3.68	62.8	8.80	0.32	4.96
Particulate metals concentrations										
Teviot	36.60	0.09	n/a	0.01	0.15	1.43	75.10	18.33	1.22	12.21
Tweed, Boleside	27.40	0.10	n/a	0.01	0.21	1.54	78.50	11.08	0.95	25.72
Tweed, Norham	41.30	0.12	n/a	0.01	0.19	1.42	96.60	17.95	0.85	18.19

Table 2.3: Metal concentrations for two relatively unpolluted U.K. rivers (μg l^{-1}) (Neal & Robson, 2000)

Geogenic metal concentration figures for pristine rivers similar to those found in the U.K. are not readily available as few accessible rivers remain unaffected by anthropogenic activity. Table 2.3, is extracted from the Land-Ocean Interaction Study for the Tweed and one of its tributaries, the Teviot, these are rural rivers in south-eastern Scotland, which may be indicative of the level of heavy metal concentrations found in relatively unpolluted waters (Neal & Robson, 2000).

2.5.2. Anthropogenic sources

Non-natural concentrations of metals and P in rivers from anthropogenic sources may be industrial, agricultural or urban in origin. Despite the introduction of the E.C. Directives described in section 2.4, accidental and deliberate discharges to water bodies still occur. In the U.K. the trend is down; an 8% reduction between 2005 and 2006 meant that the 2006 figure of 605 incidents with a "serious impact on water quality" was the lowest annual total on record (i.e. in the last 14 years) (E.A., 2007). The E.A. is unable to identify the source of 46% of these incidents, which may indicate insufficient resources for monitoring and investigative activities.

2.5.3. Industrial sources

Mining, smelting and metal alloy plants are common industrial sources of metals into rivers (Milovanovic, 2007; Sainz *et al.*, 2003). Pollution does not necessarily result from direct discharge into water bodies; contaminants in unbunded waste heaps or from abandoned mines may run-off into rivers or leach into groundwater and recycling of river water for plant cooling may also deposit pollutants (Milovanovic, 2007). In the U.K. it is estimated that 700 km of rivers and streams are polluted by Fe from abandoned mining activities (Jarvis & Younger, 2000). For example, geogenic Fe concentrations in the River Ore, Scotland, of less than 0.1 mg l^{-1} increase to around 15 mg l^{-1} downstream of abandoned mines and spoil heaps, with daily loads during the peak flows of January and February being as high as 0.5 t^{-1} day^{-1} (Younger, 2001). Mine drainage inputs to this river make it unusable as a source of potable water. Species diversity is affected, the biological monitoring working party (BMWP) taxa score of 75 (healthy) upstream of mining activities drops to the mid-20's for sample points close to mine water inputs, indicating a substantial loss of biodiversity (Younger, 2001).

Published research on industrial sources of P are not common in literature except where large scale STW's and intensive farming operations fall within the IPPC Directive (O'Malley, 1999).

2.5.4. Agricultural

Run-off from manure and slurry stores and direct defecation by cattle provide inputs of agricultural P but it is farmland soil, rich with accumulated P from excess applications of fertilisers and manures from years of cultivation, which is the main source of agricultural P to water bodies (Hooda *et al.*, 1997; McGechan *et al.*, 2005). In the U.K., DEFRA estimates 25% of P in water bodies is agricultural in origin (White & Hammond, 2007). Increased understanding of the factors affecting agricultural pollution from P, e.g. type of soil, season and rate of fertiliser and slurry applications, land use etc. prompted DEFRA to run educational campaigns aimed at farmers in order to reduce pollution from this source (White & Hammond, 2007; Hooda *et al.*, 1997). As P adsorbs to soils and remobilises slowly in response to underlying chemical changes, overall reductions in P discharges to water from agricultural land are a long-term goal (Withers & Lord, 2002).

Intensive fish rearing, aquaculture, supplies excess P to water bodies via fish wastes and uneaten fish food (Coloso *et al.*, 2003). The extent to which nutrient contamination is caused by this relatively new form of farming is still the subject of investigation; a recent literature review by Sarà (2007) concluded that excess P was most problematic in rivers and lakes and that fish farming had greater impact than shrimp or mollusc farming due to its more intensive nature and the relatively greater quantity of excreta.

Sources of metal	Quantity	mg kg^{-1} dry solids						
	Applied (Mtds)	Zn	Cu	Ni	Pb	Cd	Cr	As
Sewage sludge	0.44	802	565	59	221	3.4	163	6
Cattle manure	8.45	68.0	16.0	2.8	2.4	0.2	2.0	1.2
Pig manure	1.37	240	168	5.2	3.2	0.2	2.4	0.8
Layer (poultry) manure	0.30	583	90	10.0	9.0	1.3	5.7	0.3
Cattle slurry	1.74	170	45	6.0	7.0	0.3	6.0	2.0
Pig slurry	0.27	650	470	14.0	8.0	0.4	7.0	2.0
Inorganic P fertiliser	0.33	654	94.0	63.0	10.5	30.6	319	2.2

Table 2.4: Estimated annual quantities of metals accumulated by agricultural land in England & Wales (Nicholson *et al.*, 2003) (Mtds: metric tonne dry solid)

The main agricultural sources of heavy metals to soils, which may eventually seep into water courses, are shown in Table 2.4. Like P, the extent to which these inputs leach into water courses is dependent upon soil type, season and application rate. Although the major source

of metals to soils is manures, because of the quantities applied to agricultural land, the highest concentrations are found in sewage sludge (Nicholson *et al.*, 2003). Sludge use is controlled by the Sludge Use in Agriculture Regulations 1989; where usage within regulatory limits is permitted, however, the potential for contamination of water bodies still exists (Nicholson *et al.*, 2003).

2.5.5. Urban

Light industry, transportation, waste management and domestic activities generate P and heavy metals within urban environments. Trade waste from small to medium enterprises (SME's), operating from light industrial estates in residential locations, is less strictly controlled than heavy industry (Hillary, 2004). As Hillary (2004) estimates that up to 70% of all industrial pollution in the U.K. emanates from SME's it is probable that a proportion comprises heavy metals from vehicle cleaning and small scale engineering activities. Rule *et al.* (2006) concluded that heavy metal concentration in foul water samples from light industrial estates was higher than domestic samples because of equipment and vehicle washing activities.

Road transportation is a major contributor of heavy metals from a variety of sources associated with vehicle propulsion which settle as dusts on roads and buildings, running into storm outflows during rain events (Hares & Ward, 2004; Rule *et al.*, 2006). Railway activities also produce heavy metals, for example Imperato *et al.* (2003) found Cu accumulated in soils close to train and tram lines around Naples. In the U.K., storm outflows from roads are routed into nearby rivers and streams. Run-off from major, recently constructed or upgraded roads e.g. Newbury Bypass A34, discharge into detention ponds with reed beds, which can remove over 85% of heavy metals, but more usually run-off flows directly into nearby water bodies (Hares & Ward 2004; Stead-Dexter & Ward 2004). Reed beds can be highly effective in removing metals and nutrients from rivers, Headley *et al.* (2003) found up to 96% of TP removed from reed beds in a test environment and Begg *et al.* (2001) 80% of P and 87% of trace metals from municipal sewage sludge were removed by reed beds. Whilst reed beds may be effective in small rural catchments, for example to treat septic tank discharges before release to rivers, it is impractical to construct sufficient area of reed bed to treat urban wastewater volumes which may exceed 30,000 m^3 per day (A. Wallis, Thames Water plc. pers. comm., 2008).

Landfill is frequently cited as a potential source of heavy metals to the environment, leachate may enter rivers directly or via groundwater. Xiaoli *et al.* (2007) established that metals in landfill were stabilised by other waste matter and, apart from Zn which became mobile under water, generally leached less than 1% in neutral pH conditions. Baumann *et al.* (2006) also found that unsealed landfill sites in Germany leached less heavy metal into groundwater than expected as metals were retained by particulate matter acting as a buffer between the landfill site and the water, but concluded that this sink had pollution potential in the event of over-saturation of soils or changes to water chemistry.

P is also found in landfill e.g. the annual mean of TP in leachate in an active landfill in Italy over a ten year period ranged between 10 – 25 mg l^{-1} (Frascari *et al.*, 2004). In this study, leachate was analysed prior to biological treatment in situ, but it implies the potential for P from this source to enter groundwater.

Although atmospheric deposition is a source of P and metals, in isolation, it is not usually a major contributor of pollutants to second order rivers as they have a relatively small surface area for deposits to settle. Their impact is greatest in circumstances where atmospheric dusts settle on hard surfaces, becoming incorporated in rainwater run-off during precipitation events, especially in dessert countries where rain is infrequent (Taebi & Droste 2004). Jickells (2005) states that atmospheric P deposits to rivers are minor in comparison to other sources, estimating ~ 5% of TP in the Mississippi plume, U.S. was derived from atmospheric deposits whilst Manny & Owens (1983) attribute 10% of TP in Lake Huron, U.S. to atmospheric inputs. Radakovitch *et al.* (2007) estimate atmospheric metals inputs to rivers in the Gulf of Lion area, France, at less than 5% although they comment that fluxes may vary in individual locations where sources of localised airborne contamination exist.

Foul domestic and trade waste flushed into the sewage network is piped to a local STW for treatment before wastewaters are discharged into nearby water bodies (Marsden & Mackay, 2001). However, sewage misconnections are common, and Thames Water estimates 10% of properties within their catchment discharge foul waste into the surface water drainage system (Thames Water, 2007).

Gruau *et al.* (2005) estimate that 30 – 50% of P in untreated wastewater is derived from human body and food wastes, the remainder from phosphate based detergents. Not all P is removed during the sewage treatment process and, depending on the extent of treatment,

capacity of the water body receiving treated effluent and season; treated wastewater may be a significant source of P (Jarvie *et al.*, 2006; Neal *et al.*, 2005; Neal *et al.*, 2002b).

Although a proportion of the heavy metals in raw sewage waste settle into sludge during treatment, dissolved metals are present in treated wastewaters, as shown in Tables 2.5 – 2.8, in the following section. These metals may have a detrimental effect on the receiving water body (Buzier *et al.*, 2006; Lester, 1983).

2.6. Inputs and impacts of treated waste water discharges

2.6.1. Treated Wastewater Outfall

The chemistry of treated wastewaters entering water bodies from STW outfalls is dependent upon factors such as catchment type, physical condition of the sewage infrastructure, technologies used to treat sewage waste, standards defined in local legislation and budgets (Lester, 1983; Chipasa, 2003; Gagnon & Saulnier, 2003). Scant published information on discharges may be due to reluctance by water treatment companies to release information that might generate adverse publicity.

Studies on the quantities of P and metals in treated wastewaters released to receiving water bodies are scarce in literature; the impacts downstream of the source are covered in the next section. Here, impacts are considered in terms of STW size and removal efficiencies.

2.6.2. Efficacy of metals removal

Stevenson & Ng (1991) estimate mean loads to the Thames estuary from 11 STW discharging to the tidal Thames downstream of Teddington Weir at 28 kg Cu day^{-1}, 33 kg Ni day^{-1} and 188 kg Zn day^{-1}, representing between 39 – 54% of the total daily metals load. Within their project catchment nine second order rivers flow into the Thames, including Beverley Brook which receives around 20% of wastewaters from the Hogsmill STW and the River Wandle, recipient of Beddington SWT wastewaters. The overall contribution from STW's may be greater than their estimates suggest as these rivers are likely to transport wastewater derived metals to the Thames.

Sewage Treatment Plant	Thessaloniki (Greece)	Seine-Aval (Paris, France)	Limbe (Blantyre, Malawi)	Soche (Blantyre, Malawi)	Dinapur, (Varanasi, India)
Cd	1.5	< 0.2	10	< LOD	90
Cr	20	2.54	48	35	1200
Cu	33	8.92	11	18	110
Fe	380	1234.57	837	761	1800
Mn	19	n/a	45	60	n/a
Ni	430	10.95	234	183	75
Pb	27	< 1.0	90	104	n/a
Zn	270	n/a	236	324	920
Process	secondary	FeCl3 tertiary treatment	secondary		secondary
Source	Karvelas *et al.* (2003)	Buzier *et al.* (2006)	Sajidu *et al.* (2007)		Upadhyay *et al.* (2007)

Table 2.5: Mean metal concentrations in treated effluent from STW (μg l^{-1}) (n/a : not analysed, LOD : limit of detection)

Table 2.5 shows recently published data for STW in Europe, Africa and India, but the variety of influent sources and technologies employed during treatment mean that direct comparisons are not necessarily useful. In Dinapur, industrial effluents are fed into the SWT which treats to secondary level only, hence the high metal concentrations discharged into the Ganga River (Upadhyay *et al.*, 2007).

Tertiary sewage treatments may increase metal concentrations, for example where $FeCl_3$ or Ni are used during processing (Sörme & Lagerkvist, 2002; Buzier *et al.*, 2006). As regulations applying to dissolved Fe compounds in water are generally an order of magnitude greater than other metals, the elevated Fe discharge levels at Seine-Aval do not breach water quality legislation (Ciesla *et al.*, 2004; E.C., 2000). In Stockholm, a Ni rich antibacterial processing treatment increases overall Ni concentrations in the final effluent by up to 30% (Sörme & Lagerkvist, 2002). Discharge concentrations are not quoted, but in 1999 the annual Ni input at the plant was 310 kg and the flow was 256 000 m^3 day^{-1} which suggests the STW contributes approximately 3.2 μg l^{-1} within a total discharge concentration of around10 μg l^{-1}, comparable to Ni levels in discharged wastewater at the Seine-Aval plant.

Metal	Raw wastewater µg l^{-1}	Treated wastewater µg l^{-1}	Removal Efficiency
Cd	0.66	< 0.2 (LOD)	within LOD
Co	1.60	1.17	27%
Cr	10.12	2.54	75%
Cu	65.70	8.92	86%
Fe	702.23	1234.57	76%
Ni	11.49	10.95	5%
Pb	17.98	< 1.0 (LOD)	within LOD

Table 2.6: Metals removal from tertiary treated sewage wastewaters at Seine-Aval, Paris (Buzier *et al.*, 2006) (LOD: limit of detection)

The STW at Seine-Aval provides insight into the likely efficiencies of modern urban sewage treatment in developed countries. It has a p.e. capacity of 6.5m and processes 80% of the effluents generated in Paris to a tertiary treatment stage before discharge (Buzier *et al.*, 2006). Table 2.6 shows metals concentration after screening/solids removal and pre-treatment of sewage (raw wastewater) and at the discharge stage (treated wastewater).

Metal	Raw wastewater µg l^{-1}	Primary sedimentation effluent µg l^{-1}	Treated wastewater µg l^{-1}	Overall removal efficiency
Cd	3.3	2.3	1.7	48.5%
Cr	40	25	20	50%
Cu	79	58	33	58.2%
Fe	480	450	380	20.8%
Mn	67	26	19	71.6%
Ni	770	600	430	44.2%
Pb	39	31	27	30.8%
Zn	470	380	270	42.6%

Table 2.7: Metals removal from sewage wastewaters at Thessanloniki, Greece (Karvelas *et al.*, 2003).

Metal	Raw wastewater µg l^{-1}	Overall removal efficiency
Cd	< 20	15%
Pb	< 50	30%
Cu	< 150	55%
Zn	< 470	90%

Table 2.8: Metals removal from sewage wastewaters at Gdansk, Poland (Chipasa, 2003)

In contrast, Tables 2.7 and 2.8 describe metal removal efficiencies at smaller, less advanced SWT in Thessaloniki, Greece and Gdansk, Poland. Here the p.e. capacities are 1 and 0.47

million respectively and sewage is treated by primary and secondary sedimentation only, without the use of chemical coagulants (Karvelas *et al.*, 2003; Chipasa, 2003).

These examples of STW's removal efficiencies highlight the problem of inconsistent processing across the range of metals (Tables 2.6 – 2.8). Influent entering the Gdansk plant is particularly high in Cd and removal efficiency is poor in comparison to the other SWT cited here, suggesting greater industrial inputs and less advanced processing facilities. The Gdansk STW has received major investment and is considered amongst the most effective in Poland, other plants use even older, less efficient technology and E.C. investment is being sought to meet WFD standards (Motte, 2007). Targeting improvements in metals removals towards those with the most stringent discharge standards such as As, Cd and Cr may overlook the potential toxicity or persistence of other metals individually or in conjunction with other compounds prevalent in wastewaters such as chelating agents (Ridge & Sedlak, 2004).

Lester (1983) and Chipasa (2002) agree that individual metal removal efficiencies vary between STW and on different sampling occasions within the same works. Discounting changes in operating parameters within the same works, Lester (1983) attributed removal efficiency variations within the same plant to metal speciation but commented that high influent metal concentrations which increased removal efficiencies as a contributory cause. Chipasa (2003) additionally cites factors such as the reactivity and available surface area of biopolymers or biomass which remove dissolved metals from wastewaters through adsorption.

Evolving research has identified the potential for synthetic chemical compounds such as the chelating agent EDTA, found in many industrial and chemical applications. It is not removed during sewage treatment and has been found to prevent metals from adsorbing to particulates, thereby decreasing the efficiency of dissolved metals removal (Ridge & Sedlak, 2004).

2.6.3. Impact of metals on receiving rivers at point of discharge

Many sources of metals enter water bodies, they may originate from industrial wastewaters and in urban areas road run-off is a significant contributor. Industrial waste from disparate activities within catchments may flow directly to the sewage system, making it difficult to distinguish individual sources (Sörme & Lagerkvist, 2002; Upadhyay *et al.*, 2007). Mine

drainage is another common source of metals but, as the subject is complex, it is not discussed in this review.

Cotman *et al.* (2001) found significantly higher mean Zn concentrations in pharmaceutical wastewaters entering the River Krka, Slovenia, than from the STW nearby, 2.89 mg l^{-1} compared to 0.18 mg l^{-1}. However, in analyses of river water up and downstream from the two discharge points, Zn concentrations were 0.02 mg l^{-1} and 0.03 mg l^{-1} respectively owing to the dilution effect of the receiving river (Cotman *et al.*, 2001). Although both wastewaters exceed Slovenian regulatory limits, river concentrations in the River Krka fall within E.C. limits (E.C., 1978).

A study of 10 tanneries in Albania, many of them unregulated, found 5 – 45 mg Cr l^{-1} in wastewaters, discharging up to 500 m^3 day^{-1} to receiving water bodies (Floqi *et al,* 2007). This concentration is much higher than that in STW effluents illustrated in Tables 2.6 – 2.8; it equates to an annual load of up to 8.2 kg Cr yr^{-1} per tannery. Some of the rivers into which these tanneries discharge are used for potable water; the current WHO limit for Cr in drinking water is 0.05 mg l^{-1} (Floqi *et al,* 2007).

Metal	Process wastewaters mg l^{-1}	Discharged wastewaters mg l^{-1}	Removal Efficiency %
Cd	0.072	0.081	+ 12.5
Cr	0.042	0.027	- 35.7
Cu	0.012	0.008	-33.3
Ni	0.246	0.208	-15.4
Pb	0.497	0.527	+6.0
Zn	0.112	0.110	-1.8
Mg	1.560	2.130	+36.5

Table 2.9: Estimated metal concentrations in wastewaters from the Webuye mill (Achoka, 2002)

In Table 2.9, percentage figures for metals removal from wastewaters discharged by the Webuye paper and pulp mill in Kenya were calculated using the author's influent and effluent figures. Cd, Mg and Pb concentrations increase in the oxidation ponds because of water evaporation; this is the only treatment process for wastewaters prior to discharge to the receiving river (Achoka, 2002). Neither the river flow nor concentrations downstream of the discharge point are supplied, so the overall impact cannot be evaluated. However, Cd, Mg and Ni metal concentrations in wastewaters are the greatest of all studies discussed in this review exceeding E.C. drinking water limits (Achoka, 2002).

Unlike STW and industrial wastewaters which may discharge continually, pollution from urban run-off only occurs during precipitation events when dusts are carried into rivers by rainstorms and snowmelts. In a study of urban run-off in Iran, Taebi & Droste (2004) found mean concentrations of 453 μg Zn l^{-1} and 314 μg Pb l^{-1} in run-off during 10 rain events over a two year period where average rain intensities were between 0.80 – 1.25 mm rain per hour. As Iran has low precipitation rates, the build up of dusts between rain events may be higher than normal, explaining the differences between this study and data from the U.S. urban run-off database which cites mean concentrations of 67 μg Pb l^{-1} and 162 μg Zn l^{-1} (Taebi & Droste 2004). These concentrations are high in comparison to those of treated sewage wastewaters but their impact could be considerably less as the discharge events are intermittent.

2.6.4. Transportation of metals from wastewaters to receiving rivers

In this section, the metals under discussion are those suspended in the water column as either dissolved, less than 0.45 μm fraction, particulate; greater than 0.45 μm fraction or total (unfiltered) unless stated otherwise (Neal *et al.*, 2000c). Published studies of anthropogenic inputs to receiving waters often fail to track metals inputs downstream of their source and so quantify the distance over which discharges influence river chemistry, when they do, distances between sampling points are often so great that additional input sources are likely to influence findings. Markich & Brown (1998) found peaks in total concentrations of Al, Cd, Co, Cu, Fe, Mn, Ni and Pb at points downstream of four STWs on the Hawkesbury-Nepean River in Australia. Metals concentrations immediately downstream of the STW wastewater outfalls were up to 10 times greater than those in upstream water samples, concentrations at sample points further downstream were no more than 2.4 times greater (Markich & Brown, 1998). As sampling points downstream from the outfalls were greater than 10 km and sampling took place along a 186 km stretch of river into which a major dam and two large tributaries flow, it is probable that the metals concentrations were affected by other anthropogenic inputs.

Possible contamination of results by metals inputs from sources other than the STW under consideration also features in the study by Cotman *et al.* (2001) who identified total Zn concentrations of 0.18 mg l^{-1} in discharged wastewaters diluting to 0.03 mg Zn l^{-1} in the downstream River Krka which has a estimated dilution factor of 1:1580; the upstream concentration was 0.02 mg Zn l^{-1}. The location of a pharmaceutical plant 50 m upstream of the STW prevents apportionment of the metals load between sources

Unsurprisingly, Robson & Neal (1997) found increased concentrations of metals in rivers downstream of STWs varied according to the type of industry discharging into the sewer network. Their study describes sewage wastewaters in terms of total metals concentrations and river water in terms of dissolved metals concentrations. They found that mean metals concentrations in river water complied with environmental quality standards, but their data may understate the situation downstream of SWT as i) mean river water concentrations included upstream samples and ii) particulate metals in the water column were not evaluated. Although the authors state SWT receiving industrial inputs affect Cu, Ni, Cr and Pb results at downstream sample points for some distance, but these are not individually quantified and their use of combined up and downstream figures may mask potential input sources.

In a study investigating the spatial distribution of metals, Gagnon & Saunier (2003) found dissolved metal concentrations from STW wastewaters in Montreal, Canada, were significantly increased 0.5 km downstream from the discharge point and at their maximum level 1 km from the discharge point, decreasing to minimum concentrations at 5 km. The only exception was dissolved Pb, which increased over the distance sampled, indicating additional input sources (Gagnon & Saunier, 2003). Concentrations for particulate metals decreased slightly between 0.5 km and 1 km then increased to maximum values at 5 km (Gagnon & Saunier, 2003). Variations in the concentration patterns of particulate metals over distance were attributed to geochemical influences on individual metals. The Canadian study suggests that there is merit in spatial analysis of river water downstream from known discharge points as concentrations may be more than 50% greater at locations between 0.5 – 5 km downstream than those at the discharge source. It should be noted, as the study site was sampled only once, that results may not truly represent the situation.

2.6.5. Changes to metals concentrations in receiving river waters

Difficulty in obtaining accurate results when analysing minute concentrations of dissolved trace metals in river waters may explain why information on changes to metals concentrations downstream of wastewater discharge points is scarce (Elbaz-Poulichet *et al.*, 2006). Alternatively, as individual dissolved metal concentrations in rivers downstream of STW rarely exceed local environmental standards researchers may have overlooked them in favour of more obvious pollutants such as pesticides and pharmaceuticals (Kümmerer, 2001). So far as the effect on biota are concerned, laboratory research into the effect of synthetic wastewaters of varying concentrations on small organisms such as *Daphnia* Sp. are common, but these studies tend to have a short time span, i.e. weeks and concentrate on an

individual metal, or perhaps several associated metals under artificial conditions at high concentrations (Hewitt & Marvin, 2005). Therefore, they are not a realistic representation of ecological conditions in receiving waters. Some toxicological assays use bioluminescent bacteria to detect trace metal concentrations in river water samples but these are artificially introduced organisms designed to detect the presence of metals not to ascertain the impact on local biota (Roig *et al.*, 2007). Although useful, such laboratory studies are unable to quantify the effect of anthropogenic source metals on the riverine environment, to do so requires greater species diversity as well as spatial and temporal measurements to ascertain the likely impact of wastewaters.

It is difficult to predict how metals react in river water; individual metals exhibit different behaviours not just between types of metals but also between metal species e.g. Cr (VI) is harmful to biota in even minute quantities whilst Cr (III) is toxic to only the most sensitive biota and is less mobile in the environment (Gueguen & Dominik, 2003; Xu *et al.*, 2004). Under laboratory conditions, Cr (VI) reduces to Cr (III) in the presence of ascorbic acid or through microbial activity but its behaviour in the environment cannot be guaranteed (Xu *et al.*, 2004). Metals concentrations in receiving rivers vary seasonally, for example, partition coefficients and metals mobility changes as water temperature, pH and bacterial activity increase and river volume and flow rates fall (Hatje *et al.*, 2003; Bibby & Webster-Brown, 2006). Hatje *et al.* (2003) found dissolved Mn and Ni concentrations were significantly lower in the Port Jackson estuary during the summer months, correlated to temperature and influenced by redox conditions. Conversely, Cu concentrations increased during summer, possibly due to increased quantities of organic matter in the water body which may inhibit biological removal processes (Hatje, *et al.*, 2003).

There is no argument that trace metals are likely to affect the quality of receiving water bodies, but the overall impact is difficult to quantify because metals and metal species react uniquely to constant physical and chemical changes within the receiving water column (Cotman *et al.*, 2001).

2.6.6. Efficacy of P removal

Phosphorous removal from influent is dependent upon the treatment process, plant capacity, speciation and sources of influent. Dueñas *et al.* (2003) found particulate phosphorous to be the most completely removed species during processing. In his study of two STW near Barcelona, described as typical of treatment works in Spain, sewage is processed to

secondary level, without chemicals. The larger SWT at La Llogosta which treats 43000 m^3 day^{-1} and uses anaerobic digestion at the secondary stage was less effective at overall P removal than the smaller plant at Vilanova which uses a biological reactor and treats 3000 m^3 day^{-1} (Dueñas *et al.*, 2003). Vilanova removed around 70% TP, as particulate species, but failed to remove any SRP whilst La Llogosta removed 60% TP, 20% of which was SRP (Dueñas *et al.*, 2003). Several reasons are suggested for the poor removal rate of SRP at both plants, including recirculation of supernatant during secondary processing and, in the case of Vilanova, continually operating the system at full capacity (Dueñas *et al.*, 2003).

P concentrations in processed wastewaters from two STWs in Blantyre, Malawi were not the main areas of concern for researchers, given the high metal concentrations (Table 2.5). At Soche STW only 28% of P from concentrations in the region of 5.39 mg TP l^{-1} was removed. Limbe was less efficient, removing around 20%, but mean influent levels of 0.79 mg TP l^{-1} meant that discharged concentrations were lower (Sajidu *et al.*, 2007). Septic tank and latrine emptying vehicles were major contributors of influent to the Soche STW and, as P removal processes are not used, discharged wastewaters carry excessive quantities of P (Sajidu *et al.*, 2007).

	Treatment process	TP concentration in final effluent (mg l^{-1})	% removal efficiency
A	Mechanical pre-treatment, biological treatment & chemical precipitation	0.10 – 0.18	94 – 97
B	Mechanical pre-treatment & chemical treatment	0.10	98
C	Mechanical pre-treatment & chemical treatment	0.21 – 0.25	92 – 94
D	Mechanical pre-treatment & chemical treatment	0.21 – 0.44	73 – 94
E	Mechanical treatment	1.60 – 2.44	-33 – 11

Table 2.10: P removal at five STW in Norway (Vogelsang *et al.*, 2006)

In contrast to Malawi where sewage receives only primary processing, Norwegian sewage is usually processed to at least secondary level, frequently including chemical precipitation, which is effective at reducing TP concentrations in final effluent (Table 2.10). However, chemical precipitation is not without disadvantages, often resulting in increased levels of dissolved metals in the final effluent (Section 2.6.2). No explanation is offered for the range of removal efficiencies, particularly at the chemical treatment plant D, but discharges meet UWWTD parameters.

Of the different processes shown in Table 2.10 that used in Plant E is probably most similar to those in the examples from Spain or Malawi. The capacity of Plant E, 15,000 p.e., is 20 times less than that of Plant A, and P concentration levels currently meet the E.U. WFD providing the receiving water body is not designated "sensitive" under this legislation (Vogelsang *et al.*, 2006; E.C., 2000).

Specific literature on U.K. STW wastewaters at the point of discharge was not located. Studies into the impact of U.K. STW discharges on receiving waters indicate that the introduction of P removal processes, usually at plants where p.e. is greater than 10,000, reduces P discharges to within the E.C. limits for rivers. However, continued discharge of wastewaters containing elevated P concentrations from smaller, rural STWs, which currently lack P removal infrastructure, may mean that rivers continue to transport high P loads despite overall compliance with the WFD (Jarvie *et al*, 2006).

2.6.7. Impact of alternative sources of P close to discharge point

Like metals, industrial wastewaters e.g. from paper manufacture and food processing may discharge P to water bodies, but run-off from agricultural activities, particularly intensive livestock husbandry is the major contributor (Bowes *et al.*, 2005; Hooda *et al.*, 2000; McGechan *et al.*, 2005; Drolc & Zagorc Koncan, 2002).

Industrial discharges may be constant throughout the year or, in the case of industries such as food processing, seasonal (Jarvie *et al.*, 2008a). Unlike non-point source, agricultural inputs, it is possible to monitor wastewater at the discharge point and accurately establish P contributions to the receiving water body although individual examples are not often reported in literature. As with metals, where industrial discharges flow directly to STW, identification of P at source is not usually feasible (Antikainen *et al.*, 2005).

The agricultural impact of P to water bodies is usually seasonal, it originates from both arable and livestock farming and occurs as run-off from top soils during precipitation events or macropore flow through soils into field drains (Hooda *et al.*, 1997; McGechan, *et al.*, 2005). The contribution of agricultural source P to receiving waters has been extensively studied at field scale and the control of P within specific field sites is understood (Hooda *et al.*, 1999). It is also likely that agricultural P seeps into groundwater, ultimately flowing into rivers, although studies modelling this scenario were not identified.

As fields differ in topography, history, use etc. even within the same farmstead it can be difficult to predict the behaviour and fate of P at one location using information from another field in the same catchment. McGechan *et al.* (2005) use weather driven field scale simulations to model the transport of P deposited either in cattle faeces during summer grazing or from winter slurry applications to field drains. The authors accept that their model did not fit exactly with measured P losses during the trial but considered it a useful tool in understanding that P enters receiving rivers in a catchment not just as run-off but also through macropore flow (McGechan *et al.*, 2005). Authors frequently quantify agricultural P losses in kg ha^{-1} $year^{-1}$, making it difficult to equate with STW discharges expressed as mg P l^{-1}. Comparison is easier when sources are expressed as a percentage of the total P load; e.g. Drolc & Zagorc Koncan (2002) suggest 33.3% of P in the River Krka is from diffuse agricultural sources, 7.8% is from the direct discharge of manure and 52.2% is attributed to STW. Comparisons are simpler when inputs are expressed in the same scale as STW inputs, e.g. McGechan *et al.* (2005) found P inputs of 0.05 – 0.167 mg P l^{-1} in field drains flowing to a nearby stream.

According to literature, cumulatively rivers receive greater quantities of P from STW wastewaters than from agriculture, particularly during seasonally dry periods when agricultural run-off is negligible (Jarvie *et al.*, 2006). However, the surface area from which agricultural inputs emanate means that the quantity of agricultural source-P may be greater by many orders of magnitude during individual run-off events.

2.6.8. P in receiving River Waters

More studies have been undertaken on river water quality downstream of STW than at the treated wastewaters outfall, possibly because permission to access to sampling points is more easily obtained and the resultant data has wider research applications (Perez *et al.*, 2005; Thévenot *et al.*, 2007; Kelly & Wilson, 2004; Neal, 2002b; Jarvie *et al.*, 2006). However, once wastewater discharges merge with receiving water bodies, downstream physical and chemical characteristics are less easily attributable to one specific discharge source as other determinants become involved e.g. underlying water chemistry and sediment composition as well as inputs from industry, agriculture and road run-off. The volume and flow of receiving waters and, particularly for metals, the underlying geology, may render anthropogenic inputs of P and metals unquantifiable in the water column unless upstream data is available for comparison (Markich & Brown, 1998).

2.6.9. Phosphorous inputs to rivers

A number of authors have quantified the amount of STW derived P entering receiving rivers in recent years (Dueñas *et al.*, 2003; Neal *et al.*, 2002b; Neal *et al.*, 2005; Neal *et al.*, 2006; Jarvie *et al.*, 2006; Jarvie *et al.*, 2002b; Filella *et al.*, 2006; Bowes *et al.*, 2003; Bowes *et al.*, 2005). Within the E.C., funding for studies has been forthcoming because, unlike trace metals, many member countries are at risk of failing to comply with the WFD parameters for nutrient concentrations in some of their water bodies (Cave *et al,* 2003). As reductions in diffuse, agricultural sourced P inputs take effect, inputs from STWs, especially during periods of low flow are becoming the major source of P to rivers (Jarvie *et al.*, 2008a; Jarvie *et al.*, 2006).

Recent studies report increased levels of P, particularly SRP, downstream of STW (Bowes *et al.*, 2005; Neal *et al.*, 2006; Neal *et al.*, 2005). With the introduction of tertiary (P stripping) at some STW's with p.e. greater than 10,000 and access to E.A. data, authors have been able to compare P concentrations in the same river before and after the process commenced. For example, pre-stripping mean concentrations of 1.067 mg P l^{-1} in the River Thames reduced to 0.406 mg P l^{-1} and mean concentrations of 0.456 mg P l^{-1} in the River Kennet fell to 0.096 mg P l^{-1} (Neal *et al.*, 2005). Although these are noticeable reductions in SRP, concentrations remain higher than upstream as the quantity of P removed by stripping is variable and sewage derived SRP, previously adsorbed to river sediments, may remobilise (Jarvie *et al.*, 2006). In the Thames study, SRP concentrations reduced by more than 60% but still exceed E.A. designated threshold limit of 0.1 mg P l^{-1} for calcareous rivers implying that it remains at risk of eutrophication (E.A., 2005). Often, published research provides only annual mean concentration figures and, although they may be based on more complete datasets, grouping data in this way may overlook seasonal variations which are known to play an important role in P fluxes (Hillton *et al.*, 2006).

Spatial study of P transportation through the river system is often overlooked, possibly because many potential contributors of P along a river course make it difficult to isolate one specific source and because considerable distances of river must be monitored (Bowes *et al.*, 2003). Neal *et al.* (2005) and Jarvie *et al.* (2006) use Boron (B) as a marker of sewage derived P in rivers as it is chemically conservative and displays a strong positive correlation with sewage derived P due to its presence in washing powders . This method is not suitable in locations where weathering of igneous rocks or leaching of salt deposits occur as these

may produce geogenic B in concentrations greater than 1 mg B l^{-1} which can mask sewage derived B levels (Neal *et al.*, 1998). Also, in heavily populated urban catchments, it is often difficult to track the effect of one discrete STW for any distance because of the cumulative effect of additional STW discharges feeding into the river; for example, the River Blackwater in this project receives inputs from seven STW (Section 3.2.3). Tolson & Shoemaker (2007) obtained good results from modelling P transportation in rivers feeding the Cannonsville Reservoir and the reservoir itself, in New York City (U.S.), although during peak flow periods, modelled TP concentrations were understated in comparison to actual concentrations.

The effect of STW on receiving rivers is illustrated by a study of the River Swale, U.K. where less than 5% of the annual TP load can be attributed to the upland, rural section of the river (approximately 30% of the 110 km river course) (Bowes *et al.*, 2003). At a sample point downstream of the first STW (15,400 p.e.), concentrations of all P species increased by 200 – 400% and at a subsequent sample point downstream of two additional STW (25,500 & 17,500 p.e.) SRP and total dissolved P (TDP) concentrations increase again, although at a lower rate (less than 25% of the first downstream sampling point) (Bowes *et al.*, 2003). It is likely that a substantial proportion of P in the river Swale is attributable to STW wastewaters but the impact of P from intensive agricultural activities in the lowland study area and changes in river bathometry along the river course means that accurate apportionment of P between STW and agricultural sources is not possible.

A more accurate illustration of how P inputs affect receiving rivers may be found in a study of the River Kennet at Marlborough, U.K. where only one STW releases treated wastewaters to the upper reaches of the river and spatial water quality data is provided before and after P-stripping processes were introduced (Neal *et al.*, 2002b). In terms of the E.A. classification, all downstream pre P-stripping concentrations are classified Grade 5, very high in P, whilst the upstream and post P-stripping figures are Grade 3, moderate, (E.A., 2007). In this example upstream concentrations are higher than expected, mean 0.074 mg P l^{-1}, maximum 0.444 mg P l^{-1}, and contribution from agricultural sources is surmised. The first downstream sample point was 1 km downstream of the STW, with subsequent points at 2 km intervals to a total distance of 9 km. Whilst all downstream sample locations had mean post-stripping SRP reductions of at least 65%, variations in the % reduction between sample sites indicate additional downstream P inputs . Therefore, whilst the first downstream sample point is most likely to provide an accurate assessment of STW derived P to the receiving river, data from sample points further downstream may not be so reliable.

2.6.10. The impact of phosphorus on receiving river waters

There is no shortage of literature on the impact of P in water bodies and authors generally agree on key features (Jarvie *et al.*, 2006; Bowes *et al.*, 2005; Garnier *et al.*, 2005; Neal *et al.*, 2005; Kelly & Wilson, 2004; Mainstone & Parr, 2002; Hilton *et al.*, 2006). Excessive P input to water bodies can lead to eutrophication where excessive plant growth increases biological oxygen demand (BOD) and restricts light penetration to the river depths, adversely affecting the ecological balance (Jarvie *et al.*, 2002b). In lakes and slow running streams, algae bloom is an obvious feature of eutrophication during the growing season (Hilton *et al.*, 2006). Rivers do not necessarily exhibit this sign of eutrophication as algal growth is usually limited by water flow but excessive plant growth is likely to occur where P levels are high (Hilton *et al.*, 2006).

The main consequences of excess P in rivers are linked to excessive plant growth, for example, faster growth rates and an increase in the numbers of macrophytes in comparison to smaller plant species, preventing light penetration of river depths (Mainstone & Parr, 2002). Excess P may cause shallow rooting of macrophytes as they no longer require anchoring roots to obtain nutrients, making plants vulnerable to uprooting during high flows (Mainstone & Parr, 2002). Other potential effects include increased pH levels, nocturnal dissolved oxygen (DO) reductions leading to hypoxic, less than 3 mg O_2 l^{-1}, or anoxic, 0 mg O_2 l^{-1} conditions and the silting up of slow flowing rivers as suspended particulate matter becomes trapped in plant material (Mainstone & Parr, 2002).

Seasonality is a key feature of eutrophication, irrespective of the type of water body, for example, in Northern temperate regions plant growth occurs from March to the end of September (Hilton *et al.*, 2006). The relevance of STW inputs in terms of P is twofold; it is generally the dominant source of P to receiving rivers during the growth period and it is the most bio-available form of P for both phyto-plankton and macrophytes (Hilton *et al.*, 2006; Jarvie *et al.*, 2006). Whilst P-stripping is widely promoted as a panacea for improving water quality in rivers, particularly during the growing season, Kelly & Wilson (2004) found little difference in the amount and type of nuisance algae before and after P-stripping in the River Stour, underlining the fact that P alone does not control plant reproduction rates and that P stored in sediments may remobilise as concentration levels in the overlying water column reduce.

River flow and water depth influence the fate of STW derived P inputs in receiving waters, often in conjunction with seasonal changes (Hilton *et al.*, 2006). Mainstone & Parr (2002) comment that fast flowing rivers carry P downstream before plant biota are able to utilise it in the water column but presumably, as rivers usually decelerate and broaden towards their confluence or estuary the impact of this P load remains, albeit further downstream from its source. Certainly Hilton *et al.* (2006) found plant bio-mass was most likely to reach nuisance proportions in middle and lower downstream reaches where retention times for P increased as rivers deepened and slowed.

Overall, there are a number of factors to be considered when assessing the impact of P on receiving rivers which makes them less predictable than lakes and other still waters; hence the prevalence of monitoring programmes such as PSYCIC (Phosphorus and Sediment Yield Characterisation in Catchments) and LOIS (Land Ocean Interaction Study) in the U.K. which aim to advance understanding as the U.K. prepares to comply with E.C. Water Framework Directive (Jarvie *et al.*, 2002b; Jarvie *et al.*, 2006).

2.7. Size Fractionation

So far, within this review, discussion of dissolved P and metals in wastewaters and river water assumes a size fraction less than 0.45 μm where analysed samples are filtered. This has been a reported differentiator between dissolved and particulate fractions for many years, being a U.S. Environmental Protection Agency standard (Long, *et al.*, 1990; Jarvie *et al.*, 2002a; Buzier *et al.*, 2006; Jarvie, *et al.*, 2008b). Suspended particulate matter (SPM) analysts often use 0.70 μm filters, but it is the residue on the filter, not the filtered liquid that is of interest (Coynel *et al.*, 2007; Lead & Wilkinson, 2007). As technological improvements make finer filtration viable, recent studies may use membrane filters less than 0.45 μm e.g. 0.2, 0.1 μm or 0.01 um whilst some scientists employ centrifuge and ultrafiltration techniques to obtain fractions in the region of 5 kD (0.0015 μm) (Allard *et al.*, 2004; Pourret *et al.*, 2007).

Consensus on descriptive parameters may vary in literature, but in this review particulates or particulate matter is materials greater than 1 μm, and colloids are within the range 1 nm – 1 μm, as defined by the International Union of Pure and Applied Chemistry (IUPAC) (Lead & Wilkinson, 2007). As nanoparticles seem to fall within the range 0.1 – 100 nm, roughly equivalent to < 5kD – 1,000 kD or < 0.0015 μm – 0.1 μm there may be an overlap with

colloids. The smallest nanoparticles are able to enter organisms by endocytosis as well as conventional pathways such as ingestion, generating concern that even at minute concentrations contaminants this small may present a proportionately greater environmental hazard (Moore, 2006). Scientific research may focus on chemical species and complexation behaviours at micro and nanoparticle scales or on the environmental implications of minute fractions of contaminants and their potential to harm organisms (Baalousha & Lead, 2007).

2.7.1. Phosphorus

Aquatic studies of colloidal particles are generally confined to metals and synthetic compounds rather than P, possibly because P is not toxic. An agricultural study of P colloidal fractions between 0.45 – 0.22 μm in soil solution found particles that should have passed through filter pores were often retained on the filter highlighting a potential weakness in the process (Shand *et al.*, 2003). Hens & Merckx (2002) suggest that as SRP was the only P species they found in soil solution filtrate passed through 0.025 μm filter; this was a more appropriate measure of bioavailability than the U.S.E.P.A prescribed 0.45 μm. However, by using such a small filter, the contribution of SRP from PP fractions that occur naturally in the riverine environment is overlooked.

The use of 0.45 μm filters by environmental organisations worldwide allows for comparison of water bodies spatially, temporally and against legally defined criteria. Whilst authors often promote smaller size fractions as being a more representative assessment of bioavailability, it is generally more appropriate to look at fraction sizes in which the majority of P concentration is found and consider the transformation between larger and smaller fractions which may affect bioavailability.

2.7.2. Metals

Minute fractions of dissolved metals are frequently quantified in order to study bioavailability, bioavailable fractions and mobility with the aim of calculating relative toxicity indices according to filtered particle size, alone or in conjunction with secondary processes such as acid digestion (de Vives *et al.*, 2007). There does not seem to be consensus between the terms bioavailable and bioavailable fraction, for example, Meyer (2002) advocates the use of bioavailabile as a qualitative descriptor to show that some metals in the water column may be acutely toxic whilst others will be adsorbed to ligands and practically inert he argues that the term "bioavailable fraction", which suggests a more scientific

approach to particle size, is inappropriate unless the individual metal species, the underlying water chemistry and the type of organism are considered.

Ultrafiltration techniques are frequently encountered in studies of marine systems where they have been in use for more than ten years (H. Zang, Lancaster University, pers. comm. 2009). They are less common in river studies where research is at an early stage of development and their significance in terms of environmental understanding is in its infancy. It would be convenient to establish parameters for toxicity based on particle size alone but this simplistic approach excludes other important determinants.

2.8. Sediments

Sediments, particulate matter in the water column which settles in layers on the river bed, are a reservoir of contaminants in the river system acting either as sink or source, depending on physical, geological and chemical conditions in the overlying water course (Jarvie *et al.*, 2008b; Taylor & Boult, 2007). Porewater, between sediment particles, frequently differs chemically from that in the overlying water column and, when analysed in conjunction with sediments, may indicate whether sediments are leaching contaminants into the water body (Jarvie *et al.*, 2008b).

A number of studies have established that the highest concentrations of contaminants in freshwater aquatic systems are found in channel bed sediments (Taylor & Boult, 2007; Cotman *et al.*, 2001; Cave *et al.*, 2005; Jarvie *et al.*, 2005). Thus, it is important to examine sediments in conjunction with river water to gain a more complete understanding of the impact of pollutants on the aquatic system (Cotman *et al.*, 2001; Owens *et al.*, 2001). River sediments are an important habitat and food source for aquatic plants and organisms, so there is potential for contaminants from this source to enter the food chain (Förstner, 2004; Cave *et al.*, 2005).

The rate at which particulate matter settles as sediment is affected by many factors including rate of river flow, morphology, seasonality, underlying geological composition of particulates and particulate grain size (Gurnell & Petts, 1995). The likelihood that chemicals from treated wastewater discharges settle as sediment in the river system is also determined by its fraction size in wastewaters (dissolved or particulate), propensity to adsorb to other particulates, the quantity of SPM in the receiving river and chemistry of the water column (Golterman *et al.*, 1983).

Although settled, river bed sediments are not immobile and particles are frequently transported downstream during floodwater scouring of the channel bed or following re-suspension in the water column after anthropogenic activity (Golterman *et al.*, 1983). Changes in water chemistry, particularly reduced levels of D.O. resulting in anoxic conditions may result in remobilisation of metals and P sorbed to sediments (Förstner, 2004).

2.8.1. Phosphorus in sediments

Dueñas *et al.* (2003) found the sewage treatment process to be effective at removing particulate P, i.e. P which does not pass through a 0.45 μm filter. In the primary, screening, and secondary, clarification, stages of sewage treatment they found particulate P completely removed. However, Teihm *et al.* (1999) found between 54 – 81% of TP as particulate P in final effluents from four STW in Germany. Although the lower threshold for particulate P used by Teihm *et al.* (1999) was finer at < 0.1 μm; the upper limit was 8.0 μm and they found particulate P randomly distributed throughout the size range. It seems likely that the ratio of particulate to dissolved P within cleaned wastewater discharges varies between STW depending on process type, influent sources and plant efficiency, so it may be inappropriate to generalise about the affinity of wastewater derived P to adsorb to sediments because of the variation in discharges. Instead, this section of the review will look at the behaviour of P in sediments, its storage and transportation.

2.8.2. Behaviours of P in sediment

In literature, researchers favour two main techniques to evaluate the quantity and behaviour of P in sediments; i). fractionation of sediment into preferred size range(s) followed by sequential or total chemical digestion, and ii). equilibrium phosphate concentration (EPC), the concentration of SRP from sediment released into water over a 24 hour period (Walling *et al.*, 2003; House & Denison, 2000). As authors frequently adapt previously published methods and often combine methods e.g. size fractionation and sequential extractions with differing chemical strengths it can be difficult to compare research projects.

Three recent studies, Kim *et al.* (2004), Avilés *et al.* (2006) and Katsaounos *et al.* (2007), use sequential chemical extractions to analyse P species from river sediments in South Korea, Spain and Greece respectively. Using descriptors ranging from plant available and water extractible to residual and non-extractible they partition total P and use statistical models to predict likely behaviours under variable river conditions. Within these studies the type and

strength of chemical extractor, the number of extractions, sample depth and the description of the P analyte varies, thus it is difficult to compare laboratory results. For example, Katsaounos *et al.* (2007) found mean concentrations in sediments from 6 sampling points on the River Louros ranged between 440 – 620 mg TP kg^{-1} in the top 5 cm layer of sediment and that 43% of it was non-bioavailable apatitie P, extracted sequentially with 30 ml de-ionised water, followed by 0.5M $NaHCO_3$ then 0.1M NaOH and finally 1.0M HCl. Avilés *et al.* (2006) found between 240 – 634 mg TP kg^{-1} in the top 5cm layer of sediment from the River Guadalfeo of which more than 68% was classed as apatite inorganic P, which is considered as available for plant production. Kim *et al.* (2004) found mean concentrations of between 580 – 1150 mg TP kg^{-1} in the top 15cm layer of the Han River and that more than 65% of it was either in apatite or residual P form. Whilst Katsaounos *et al.* (2007) consider HCl extractible apatite P non-bioavailable, Kim *et al.* (2004) consider it potentially bioavailable and class residual P as non-bioavaible, but then Katsaounos *et al.* (2007) used higher strength HCl. As it would be difficult to find naturally occurring riverine conditions with an acidity equivalent to the 0.5M HCl solution used in Han River extraction, non-bioavailable or least bio-available descriptors might be more appropriate.

As a guide to acceptable levels of P in sediment, the Province of Ontario Guidelines suggest 600 mg TP kg^{-1} represents clean to marginally polluted sediment (Persaud *et al.*, 1993). However, reliance on TP concentrations in sediments as a potential indicator of pollution in isolation can be misleading as the physical and chemical properties of the sediment and overlying water conditions influence the likelihood of release.

Oxygen levels in the water column affect the release of P from sediment to the water column; generally greater quantities of P remobilise under anaerobic conditions at the sediment–water interface (Wang et al., 2003). Using a model based on Chesapeake Bay, U.S., Wang *et al.* (2003) found 20 to 70 mg SRP m^2 day^{-1} under anaerobic conditions and 0.5 to 15 mg SRP m^2 day^{-1} under aerobic conditions. However, if high concentrations of P in sediment are found in conjunction with Fe and anaerobic conditions, P may co-precipitate to form vivianite, making it less likely to mobilise (House & Denison, 2002). House & Denison (2002) found vivianite in the River Blackwater, one of the rivers in this project, downstream of the STW. It is possible, during periods of seasonal low flow that the study rivers upstream of STW outflows may become anaerobic as oxygen levels fall due to a lack of turbulence in the water column, increasing the quantities of P released from sediments.

Hydrological factors also influence the behaviour of P in sediments, when river water flows decrease seasonally, e.g. during dry summer conditions, stronger interaction between water and sediments occurs as water residence time increases, the ratio of sediment surface area to water increases and water temperature rises (Avilés *et al.*, 2006). In $CaCO_3$ rich waters when higher temperatures increase primary production, greater quantities of P are consumed by biota and overall concentrations may reduce (Neal, 2002b). Water borne P may co-precipitate to calcite, removing it from the water column, but the resultant increase in sediment-bound P concentrations means that the process may be incorrectly interpreted as indicator of increased pollution in the water-body unless additional river quality criteria such as those discussed in the following paragraph are considered (Avilés *et al.*, 2006).

The equilibrium phosphorus concentration co-efficient (EPC_0) of channel bed sediment is defined as the concentration of SRP which, when placed in contact with sediment produces no change in the SRP in solution over a relatively short period of time e.g. 24 hours (House & Denison, 2000). Using this method, the potential flux of SRP between channel bed sediments and the overlying water column (exchangeable P) and so the likelihood of sediment in a specific location being sink or source of P can be determined (Jarvie *et al.*, 2005). This technique can be used to monitor the behaviour of P in sediments following the introduction of P-stripping at STW where there is a possibility that river water quality may not improve as expected because lower SRP inputs from discharged wastewaters are replaced by desorbed P from sediments (House & Denison, 2000).

EPC_0 may be a more useful measure of P than chemical extraction tests because it describes the behaviour of P in a specific riverine environment. However, as a modelling tool rather than to analyse channel sediment from a specific river EPC_0 was found to incorrectly estimate the quantity of adsorbed P for reasons such as shorter residence time of river water in sediment, lesser volume of water in contact with the defined 0.1 m sediment depth and more limited interaction between river water and sediment than the model (where thorough mixing occurs) (House & Denison, 2000; Jarvie *et al.*, 2005). On occasion, House & Denison (2000) found the EPC_0 of specific river sediment was up to twice the calculated, modelled value. These differences were attributed to pH, DOC, Ca, Mn and Fe levels which influence the precipitation and dissolution of P in sediments (House & Denison, 2000). They recommend measuring these factors before and after EPC_0 analysis and using the results to model additional chemical reactions in the river water /sediment interface, highlighting the weakness in using EPC_0 modelling in isolation to classify the impact of P in river sediment.

Linked to sediment analysis is the study of porewater, using diffusive equilibrium in thin films (DET) gel probes which may provide further insight about sediment interactions with river water. Currently the only publication examining P concentrations in porewater from riverbed sediments using this technique is Jarvie *et al* (2008b). They found SRP concentrations in pore water from a stream subject to intensive arable and sewage inputs contained between 850 – 3419 μg SRP l^{-1} whilst pore water from two comparative streams, one with arable inputs and the other described as pristine each contained less than 40 μg SRP l^{-1}. The fine sediment layer at the water/sediment interface of these three rivers had potential as a cleansing mechanism for river water but the authors deduced that it was removing less than 1% of SRP. However, as SRP concentrations in the pore-water were greater than in the river water column the authors concluded that the main role of this fine sediment layer was to prevent upwards diffusion of SRP from lower sediment layers into the river. At the only sample site which contained no fine sediment, just a coarse, armoured, gravel layer, the topmost sediment layer had a significantly lower SRP sorption capacity and SRP concentrations in the sediment porewater were less than those in the river (Jarvie *et al.*, 2008b). Porewater analysis using DET gel probes may become a useful tool in understanding the behaviour of P in sediments, but it seems resource intensive and a lack of comparative studies make it difficult to assess its value at the present time.

2.8.3. Phosphorus transportation in sediment

Owens *et al.* (2001) found little previous data on the spatial transportation of contaminated sediments in rivers when they sampled rivers in Yorkshire, U.K. Unfortunately, the limited number of channel bed sample sites (two) in their study, taken from the least anthropogenically influenced river, the Swale, restricts the usefulness of their results in relation of the study of channel bed sediments (Owens *et al.*, 2001). However, their widespread sampling of floodplain sediments in the River Aire, running through major urban areas of Bradford and Leeds and receiving SWT and industrial inputs showed increases from 1035 mg TP kg^{-1} in the most upstream site to 4001 mg TP kg^{-1} in the furthest downstream site. They found a similar trend in suspended sediment samples from the same river, although the suspended sediment concentrations tended to be greater, this was attributed to the smaller particle and larger surface area of the suspended matter (Owens *et al.*, 2001; Horowitz & Elrick, 1987). Cook (2007) suggests that P in floodplain soils may reduce when floods occur frequently and soils containing P are removed to the river in the receding waters, conversely he suggest that floodwaters rich with sediment bound P may be retained by floodplain soils, increasing the P content of top soils.

In a related paper, Walling *et al.* (2003) found downstream TP values in river bed sediment increased to from 1600 to 5870 mg TP kg^{-1} along the course of the River Aire which, with its' main tributary, the River Calder, has 69 STW outflow points and a further 1734 consented discharges from other sources. Bed sediments from the neighbouring and relatively unpolluted River Swale ranged between 941 – 1237 mg TP kg^{-1} and, although it receives a number of STW inputs, the catchment is predominantly rural (Walling *et al.*, 2003). In considering the relationship between the channel bed sediments, flood plain sediments and the extent to which P is transported to the river, the authors concluded that sediments contributed less than 3% of contaminants to the catchment but, depending on hydro-morphological factors, up to 50% of contaminants could be removed from the channel bed and deposited on the surrounding floodplain (Walling *et al.*, 2003). Thus floodplains represent an additional source of P when flood events occur and sediments are remobilised into the river system (House, 2003).

TP in sediments from the River Blackwater, where up to 85% summer flow emanates from STW wastewater inputs, were 589 mg TP kg^{-1} upstream and 4061 mg TP kg^{-1} downstream of the main SWT at Aldershot (House & Denison, 2002). Overall, it has proved difficult to find studies whose main interest is the transportation of P downstream of an STW source as researchers are more interested in in-stream relationships with elements such as Fe, Ca and organic carbon at a single downstream sample point rather than spatial variation. Similarly, studies of agricultural source P tend to concentration on the effect of P inputs on water or suspended sediment rather than channel bed concentrations (Bowes *et al.*, 2003; Edwards & Withers, 2008).

2.8.4. Metals

Studies into the impact of STWs on river sediments are not common. This review has already discussed the release of trace metals into receiving waters and, although the following studies do not refer specifically to STWs, it may be assumed that the characteristics described for trace metals from other pollution sources may apply similarly.

2.8.5. Behaviour of trace metals in sediments

Metal concentrations in river bed sediments may be quantified using extraction methods similar to those described for P (section 2.8.2). As with dissolved metals, authors may

separate species within metals (partitioning) or identify theoretically labile fractions using extraction chemicals of differing strengths (Desrosiers *et al.*, 2008).

Heavy metals preferentially adsorb to finer sediment fractions and their mobility following adsorbtion is influenced by underlying riverine chemistry such as pH, oxidation potential (Eh), salinity, DO, conductivity etc. (Foster *et al.*, 1995; Förstner, 2004). Where in-stream chemical processes involve the precipitation of Fe or Mn which form a coating on larger sized sediment grains e.g. in water bodies receiving mining effluents; other metals may be retained on this coating (Foster *et al.*, 1995). These processes of adsorption or co-precipitation with Fe or Mn sulphides in reducing river conditions may render trace metals, particularly Zn, Cu, Cd, Ni and Pb; less mobile and hence potentially less bioavailable (van Griethuysen *et al.*, 2002).

Metals frequently reside in sediments for a long time and sediment cores can be used in impact assessments of historic pollution events such as mining dam breaches, particularly where the presence of specific metals is anticipated (Osán *et al.*, 2007). When investigating the effect of continuous anthropogenic activities, metals found in underlying geology can be used to establish background loads against which elevated levels can be measured (Cave *et al.*, 2005). For example, Cave *et al.* (2005), assessed pre-industrial background concentrations in Humber estuary sediments at 17 mg Cu kg^{-1}, 22 mg kg^{-1} for As and Pb and 84 mg Zn kg^{-1} whilst levels during 1996 – 7 were 17 – 55 mg Cu kg^{-1}, 11 – 37 mg As kg^{-1}, 35 – 129 mg Pb kg^{-1} and 86 – 231 mg Zn kg^{-1}. Whilst these figures can be used to assess the quantities of metals entering the North Sea, the authors have not considered individual emissions, so comparison between sewage and industrial sourced metals is not possible.

2.8.6. Trace metals transportation in sediment

Tracking transportation of metals in channel bed sediments to establish the pollution catchment of a specific source has proved challenging to authors for reasons such as unpredictable seasonal channel bed alteration e.g. scouring during high flows, changes in geology along the river course, landslides and inputs from additional sources downstream of the source under investigation (Foster *et al.*, 1995). Metals concentrations within sediment strata may be used in conjunction with spatial distribution of sediments to investigate historic changes as lower sediment layers may be undisturbed and able to contribute information on long term trends (Miller *et al.*, 2000). Where ongoing contamination is suspected, surface sediments are likely to provide the most relevant information but their transience,

particularly following seasonal high flow events means that samples provide a view of the river bed at a specific time; temporal sampling over a significant period is required to obtain a more accurate overview (Stutter *et al.*, 2007; Smith *et al.*, 2003). For example, one storm event in February 1995, with river discharge of more than 200 $m^3 s^{-1}$ is estimated to have removed the equivalent of 19 mm of bed sediment along a 55 km reach of the River Swale (Smith *et al.*, 2003).

The benefit of top layer sampling to assess the immediate pollution scenario may be seen in Ouyang *et al.* (2002) who found the highest levels of Pb, Cd, Zn and Cu in the upper 0.56 m layers of sediments from the Cedar and Ortega Rivers in Florida, U.S. Between 74 – 87% of samples taken from the top 0.1 m sediment layer exceeded threshold effect levels (TEL) for Florida coastal waters above which aquatic organisms may be adversely affected. The mean values of 84 mg Pb kg^{-1}, 38 mg Cu kg^{-1} and 272 mg Zn kg^{-1} in this upper 0.1 m sediment layer were more than twice as great as the TEL values whilst Cd, at 1.26 mg kg^{-1}, was 75% higher than its TEL limit (Ouyang *et al.*, 2002). An issue highlighted by this study is the lack of homogenous results across sampling sites e.g. for Zn, the range was 47 – 2050 mg

kg^{-1}, standard deviation (SD) 325 mg Zn kg^{-1} and for Pb the range was 10 – 315 mg kg^{-1}, SD 67 mg Pb kg^{-1} from 43 samples; differences attributed to variations in depositional timeframes and biogeochemical cycles for individual metal species along the river reaches (Ouyang *et al.*, 2002).

In a recent Taiwanese study, the transient features of sediment in flowing rivers was exploited by selecting downstream sites within 12 km of the river estuaries where wider, slower flows cause sediment deposition, particularly following seasonal heavy rains, to investigate the relationship between anthropogenically derived metals (Tsai *et al.*, 2007). However, as vertical distribution of metals in sediment layers was inconsistent, the authors could not identify changes to metal concentrations in sediments as a result of stricter industrial and domestic discharge consents. In conjunction with government water quality data they were able to confirm that highest metals concentrations in the water column over a 16 year study period corresponded to those with the highest metal concentrations in sediments (Tsai *et al.*, 2007).

Inconsistencies in sediment deposition make it difficult to extrapolate data from a limited number of sample sites to explain an entire river system whilst resource constraints frequently restrict sampling and testing. So statistical modelling is often employed to

describe possible metal contamination scenarios from limited information. Ouyang *et al.* (2002) uses kriging estimates to quantify sediment distribution along two rivers, but this requires intensive sampling to get accurate results, and Terrado *et al.* (2006) use chemometrics modelling to investigate correlation between data sets, identify contaminant sources and define geographical distribution. Uncertainty of modelled results from errors in parameter settings, data integrity and model structure necessitates caution when models are used and findings may be subject to so many provisos as to discredit the final conclusion (Lindenschmidt *et al.*, 2007). In the paper by Terrado *et al.* (2006), the source and extent of metals contamination in sediments from the Ebro river basin were not satisfactorily identified and the project might have been more useful if tabulated data for individual sampling sites had been supplied.

2.9. Conclusion

The E.C. Water Framework Directive and preceding water quality legislation has generated a substantial body of research into the impact of P and metals in river water and sediments. Researchers have identified a variety of contaminant sources discharging to water bodies, including STW, quantifying downstream concentrations and assessing the potential effects to biota from multi-origin pollutants. As U.K. Government initiatives to reduce diffuse inputs from agriculture take effect, the impact of pollutants from urban sources is likely to become more apparent.

Recently, considerable research has been undertaken by the U.K. based Centre for Ecology and Hydrology into discharged SWT wastewaters, particularly focussing on geological and chemical influences affecting the behaviours of sewage derived P in river systems. Elsewhere, researchers in Paris have examined dissolved and particulate metals species in effluents from the main Paris STW at Seine-Aval and a project in Canada traced the transportation of dissolved metals from STW along the St Lawrence River. There is a large body of research from Eastern European on water courses which have deteriorated through lack of discharge regulation and infrastructure maintenance and projects from developing countries into the impact of insufficiently treated wastewaters on rivers downstream of inputs.

Whilst these studies provide essential background information on potential pollution scenarios applicable to discharged effluents, they do not specifically evaluate the impact

STW derived phosphorus and metals on receiving rivers where wastewaters comprise a greater proportion of downstream flow than the underlying river.

3. Site description and methodology

Figure 3.1: Study area

3.1. Introduction

When selecting study sites for this project the primary concern was regular inputs of STW wastewaters, other considerations included a discernable impact on the receiving river and regular access to sites up and downstream of the outflow. This chapter describes the study sites selected for this project (Figure 3.1) and the reasons for their inclusion, sampling procedures, laboratory processes and quality control protocols.

3.2. Study sites descriptions

3.2.1. Hogsmill River

The Hogsmill River is a tributary of the River Thames. Its source is a chalk spring at Bourne Hall Lake, Ewell, Surrey, grid reference TQ219627. From there it runs for 9.9 km through an increasingly urbanised environment before flowing into the Thames at Kingston, grid reference TQ177691. A number of tributaries flow into the Hogsmill, of which the Bonesgate Stream (5 km) is the principal. The Hogsmill is not pristine upstream of the STW, continuous discharge consents exist for sports fields and a mobile home park approximately 3.5 km of the STW and storm sewer overflows discharge intermittently along the entire upstream reach (J. Smith, E.A., pers. comm., 2009).

3.2.1.1. Hogsmill Valley Sewage Treatment Works

The Hogsmill Valley Sewage Treatment Works (STW) serves 350,000 Thames Water customers in the Kingston area of South West London, treating up to 205 m litres of wastewater per day (Anon, 2009). It is adjacent to the Hogsmill River, downstream of Berrylands railway station and 2 km upstream of the Hogmill/Thames confluence. Hogsmill Valley STW is the only sewage treatment works discharging into the Hogsmill River or its tributaries. The outfall, discharging approximately 80% of wastewaters from the STW, is located at grid reference TQ192686. The remaining 20% of wastewaters are discharged into the Beverley Brook, a river independent of the Hogsmill which flows into the Thames near Putney Common.

Sewage processing comprises primary treatment, secondary treatment using activated sludge, and tertiary treatment using sand filtration (A. Wallis, Thames Water plc. pers. comm., 2007). The average flow through for treatment was 82,554 m^3 day^{-1} (2007) and 74,537 m^3 day^{-1} (2008) (A. Wallis, Thames Water plc. pers. comm., 2008; T. Ghilespy, Thames Water plc. pers. comm., 2009). From 1st April 2008, a P-stripping process using Al salts was introduced to comply with a revised discharge consent from the E.A. reducing the average annual P concentration in wastewaters to 1 mg P l^{-1} (A. Wallis, Thames Water plc. pers. comm., 2008).

The STW is licensed by the E.A. which has overall responsibility for the Hogsmill River. The E.A. monitors water discharge using an auto-sampler located downstream of the STW at the weir by Mill Place, Kingston, grid reference TQ182687 which captures data every 15

minutes (Anonymous, 2004). Discharge data from this source was utilised during the research project to calculate contaminant loads downstream of the STW.

3.2.1.2. Hogsmill sampling sites

Figure 3.2: Hogsmill river water sampling points

Figure 3.3: Hogsmill river sediment sampling points

The first sampling point (U/S 1) is located at the pedestrian footbridge leading to Green Lane recreation ground, approximately 350 m upstream of the STW outflow (Figure 3.2). The Hogsmill River immediately downstream of the STW was not accessible from either bank, because Thames Water plc has fenced them and restricted access to authorised personnel. Sampling point two (D/S 2) is at Fairfield Industrial Estate, Villiers Road. The other downstream points are approximately 20 m downstream of the weir and E.A. automated sampler (D/S 3) at Watersplash Close, and at Wadbrook Street Bridge leading to Charter Quay and the confluence with the River Thames (D/S 4). When sampling for sediments, the third downstream point (D/S 3) is located at Kingston University Knight's Park campus, as it was not possible to gain access to the river bed at Watersplash Close, and an additional sampling site at College roundabout was included (D/S 4) (Figure 3.3). The furthest downstream sediment sampling point (D/S 5) is adjacent the bridge on the High Street as it is not possible to access the river at Wadbrook Street.

3.2.2. River Bourne

The River Bourne (sometimes called the North or Chertsey Bourne) rises in Windsor Great Park and flows into Virginia Water Lake; it flows through the towns of Thorpe and Chertsey before joining the Thames at Weybridge. Its geology classification is siliceous and the catchment area is 34.07 km^2 (E.A., 2007). The most recently published chemical water quality (2005) describes the Bourne as category B, indicating that the ecosystem is at or close to natural (E.A., 2007). It is compliant to nutrient water quality target 3, (mean concentrations of 0.1 mg P l^{-1} and 20 mg NO_3 l^{-1} (E.A., 2007). However, the Bourne is also designated "at risk" from point source and diffuse pollution by the E.A. under the WFD risk assessment (E.A., 2007).

3.2.2.1. The Lyne Lane Sewage Treatment Works

The STW is located at Lyne Lane, between Thorpe Green and Lyne, under the south-west quadrant of the M25/M3 motorway junction. It is managed by Thames Water plc. The sewage process uses primary sedimentation followed by double filtration in percolating filters finishing with P removal to meet mean annual discharge criteria of 2 mg P l^{-1} (A. Wallis, Thames Water plc. pers. comm., 2007). At Lyne Lane, the average flow through treatment during the project period was 27,893 m^3 day^{-1} (2007) and 26,970 m^3 day^{-1} (2008) around a third that of the Hogsmill Valley STW (A. Wallis, Thames Water plc. pers. comm., 2007; T. Ghilespy, Thames Water plc. pers. comm., 2009). Discharged wastewaters flow approximately 150 m from the STW to the Bourne through private land; it was not possible

to gain access to the outfall stream. The E.A. monitors flow and water quality downstream of the STW at grid ref. TQ01676810. Data from this source was utilised during the research project to calculate contaminant loads downstream of the STW.

3.2.2.2. River Bourne sampling sites

Figure 3.4: River Bourne water and sediment sampling points

The first sampling point (U/S 1), upstream of the outflow is located under the road bridge on Lyne Lane (Figure 3.4). The second sampling point (D/S 2) is slightly downstream of the outfall confluence with the Bourne, the third (D/S 4) is by the E.A. stage height marker at the eastern side of the M3/M25 reinforced river bank and the fourth (D/S 5) is opposite the Mill House Lane/ Mill Lane road junction. An additional sampling site, on the western side of the M3/M25 bridges, was included during sediment collection (D/S 3*).

3.2.3. River Blackwater

The Blackwater rises from springs at Rowhill Nature Reserve, Aldershot (Anon, 2008). These are on the edge of the Tertiary Bagshot Beds (sandy clay), so the water is fairly acidic (Daniels, 2000). The river bed comprises valley gravels and alluvium. The river drains a heavily urbanised area; thus, although it is spring-fed, treated sewage effluent is its major

flow component (as much as 85% of summer flow) because it receives discharge from seven STW (Daniels, 2000; Anon, 2008).

3.2.3.1. Sandhurst Sewage Treatment Works

This STW is located at Swan Lane, Sandhurst (Grid ref. SU832609). Treatment is based on a percolating filter system with additional tertiary treatment using sand filters. Sewage is dosed with $Fe_2(SO_4)_3$ (ferric sulphate) in the primary settlement tanks (P. Packham, Thames Water plc. pers. comm., 2009). The plant treats up to 23,760 m^3 day^{-1} and average dry weather flow into the Blackwater is 6,000 m^3 day^{-1} (P. Packham, Thames Water plc. pers. comm., 2009). Annual mean discharge consents are 2 mg P l^{-1} and 4 mg Fe l^{-1} (P. Packham, Thames Water plc. pers. comm., 2009).

3.2.3.2. River Blackwater sampling sites

Figure 3.5: Blackwater river sediment sampling points

The first sampling point (U/S 1) is less than 100 m upstream of the STW outflow channel; the second (D/S 2) is opposite the outflow the discharge pipe, the third (D/S 3), fourth (D/S 4) and fifth (D/S 5) are approximately 150 m, 500 m and 1000 m downstream of the wastewater outflow (Figure 3.5).

3.2.4. River Mole

The River Mole rises in the North Sussex hills near Rusper and flows 80 km northward to join the River Thames at Molesey, near Hampton Court, the catchment is 487 km^2. The Mole headwaters are situated on weald clay, further downstream, the Mole crosses major aquifers

in Lower Greensand and North Downs belts before reaching clays, sand and gravels in the London Basin (Anon., 2008). Thames Water has discharge consents for 15 STW along the Mole (Hazelton, 1998). The STW at Crawley, less than 10 km upstream of the sediment sampling sites has an average dry weather discharge of 25,500 m^3 day^{-1} and supplies more than 75% of the dry-weather flow to the upper Mole (E.A., 2005; Hazelton, 1998; P. Packham, Thames Water plc. pers. comm., 2009). The Crawley STW has annual mean discharge consents of 1 mg P l^{-1}, 4 mg Fe l^{-1}, and 4 mg Al l^{-1} (P. Packham, Thames Water plc. pers. comm., 2009).

3.2.4.1. Horley Sewage Treatment Works

This is the second STW on the upper reach of the Mole and the plant closest to the sediment sampling sites. It is an activated sludge plant using diffused air aeration followed by tertiary treatment in lagoons; $FeCl_3$ is added to the aeration plant to encourage flocculation (P. Packham, Thames Water plc. pers. comm., 2009). The plant treats up to 23,760 m^3 day^{-1} and average dry weather flow into the Mole is 6,000 m^3 day^{-1} (P. Packham, Thames Water plc. pers. comm., 2009). Annual mean discharge consents are 2 mg P l^{-1}, 4 mg Fe l^{-1}, and 4 mg Al l^{-1} (P. Packham, Thames Water plc. pers. comm., 2009).

3.2.4.2. River Mole sampling sites

Figure 3.6: River Mole sediment sampling points

The first sampling point (U/S 1) is about 300 m upstream of the outflow pipe, access to the river being restricted by private ownership of land surrounding the STW. The second point (D/S 2) is less than 50 m downstream of the outflow pipe, the third (D/S 3) and fourth (D/S 4) are approximately 300 m and 600 m downstream of the outflow pipe (Figure 3.6). It was not possible to gain access further downstream for a fifth sampling point as the land beyond this point was private and the river was too deep to wade.

3.3. Sample collection

3.3.1. River water sampling

Water samples from the Bourne and Hogsmill were taken between February 2007 and August 2008, 49 (Hogsmill) and 47 (Bourne) sampling campaigns were undertaken. Samples were taken from the water column, the area of water above the channel bed. Samples were collected on weekdays, weekends, some public holidays, morning and afternoons to cover a range of conditions. Access to sampling points close to the STW is restricted by the operator, Thames Water, who fenced the river for some distance either side of the Hogsmill Valley STW and around the outflow stream from the Lyne lane STW to the Bourne. Safety considerations, such as the isolated nature of some sampling sites, precluded early morning/late evening or night sampling. More intensive or automated water sampling was not feasible due to resource constraints.

3.3.1.1. Water sampling procedure

Water samples were obtained from the river bank or from footbridges using a modified "grab sampler". This comprised a 500 ml laboratory grade wide mouth polyethylene bottle with a length of nylon twine secured to its neck, fitted with a central aluminium rod at the base for directional throwing and increased stability in the water. The base is drilled with 5 x 10 mm diameter holes through which water enters the bottle. A sheet plastic disk fitted to the inside of the bottle acts as a non-return valve, sealing the water entry holes as the bottle is pulled out of the water. The sampler was rinsed with river water twice before each water collection. Samples were collected from one depth of water, approximately 30 cm below the surface, in a flowing water stream and were transferred to 250 ml acid washed sample bottles.

3.3.2. River sediment sampling

The sediment sampling campaign was undertaken during September 2007, sediment was taken once from each of the four rivers. In line with the water sampling programme, sediments were collected from the Hogsmill and Bourne. Sediment from two additional rivers, the Blackwater and Mole, selected for their accessibility up and downstream of STW were included in the study to increase the sample population.

3.3.2.1. Sediment sampling procedure

Sample locations were selected to avoid obvious contamination from field drains and storm overflows. Samples were obtained by wading into the river and collecting the top 5 cm of sediment from four or five discrete points across the riverbed using a trowel which was covered as it was bought up through the water column (Stutter *et al.*, 2007). Sediment was mixed in a clean polythene bag to provide a homogeneous sample from each location, labelled and taken back to the laboratory for drying.

3.4. Flow measurements

The E.A. does not monitor water flow immediately above STW, so the following method was employed to obtain approximate upstream discharges for the Hogsmill and Bourne; using stage height measurements taken across the river beds at the upstream sampling sites graphs of both channel beds were constructed. The central stage height, measured on each sampling visit, was used to calculate the cross-sectional channel area under water from these graphs.

Flow was estimated by timing the passage of a float between two fixed points, in this case the upstream span of the bridges over each river (Point A) to the downstream span (Point B) as per Shaw (1994) and as used by other authors when river conditions or resources do not permit use of a flow meter (Dyer, 1970; Soldner *et al.*, 2004; Kra & Merkley, 2004). The most accurate method of flow measurement is likely to be a flow meter on a wading rod but practical constraints such as the requirement to carry all field survey equipment on a bicycle precluded its use (Shaw, 1994). However, E.A. personnel advised that the float method was probably as accurate the E.A. auto-samplers, given their propensity to accumulate debris around the measuring apparatus (M. Lowenthaal, E.A., pers. comm., 2007).

The "float" was thrown several metres upstream of Point A to allow it to settle in the centre of the river before it reached the bridge. Flow was timed using a stop watch (Timex T59761) and repeated 10 times at each visit. This measurement was accepted as representative of average river flow and a correction factor of 0.7 for streams with a depth of around 1 m was applied to the mean flow figure ($\overline{v}$) (A. Dykes, Kingston University, pers. comm., 2007; Shaw 1994). The float method is recommended by Shaw (1994) as an acceptable means of determining flow providing the appropriate correction factor is applied to the result.

This estimated mean flow together with cross sectional channel area was used to estimate discharge:

$Q = \overline{v}$ A, where Q is discharge, A is capacity and $\overline{v}$ is mean flow

Flow weighted mean concentration (FWMC) is calculated using the formula

$$\text{FWMC} = \frac{\sum C \, x \, Q}{\sum Q}$$

where C is mean concentration and Q is mean discharge during the sampling period

Upstream, where flow is measured using the timed float method, flow is measured only at the time of sampling. Downstream, flow is measured every fifteen minutes during each twenty-four period. Mean flow covers the sampling period for the individual element or species.

The relationship between upstream stage height and calculated discharge for the Hogsmill and Bourne is shown in Figures 3.7 and 3.8. Upstream flow patterns are similar to those plotted using E.A daily mean flow data from auto-samplers downstream of the STW (Figures 3.9 and 3.10). Although the E.A. monitors flow close to the source of the Hogsmill at Ewell, as shown in Figure 3.9, this upstream point is too far removed from the STW to calculate upstream discharge.

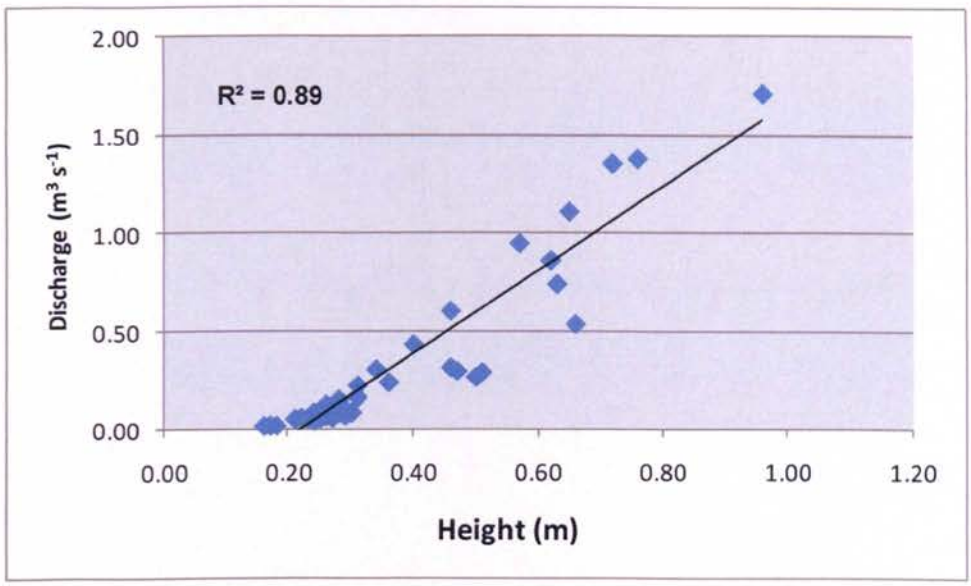

Figure 3.7: River Bourne measured stage height vs calculated discharge

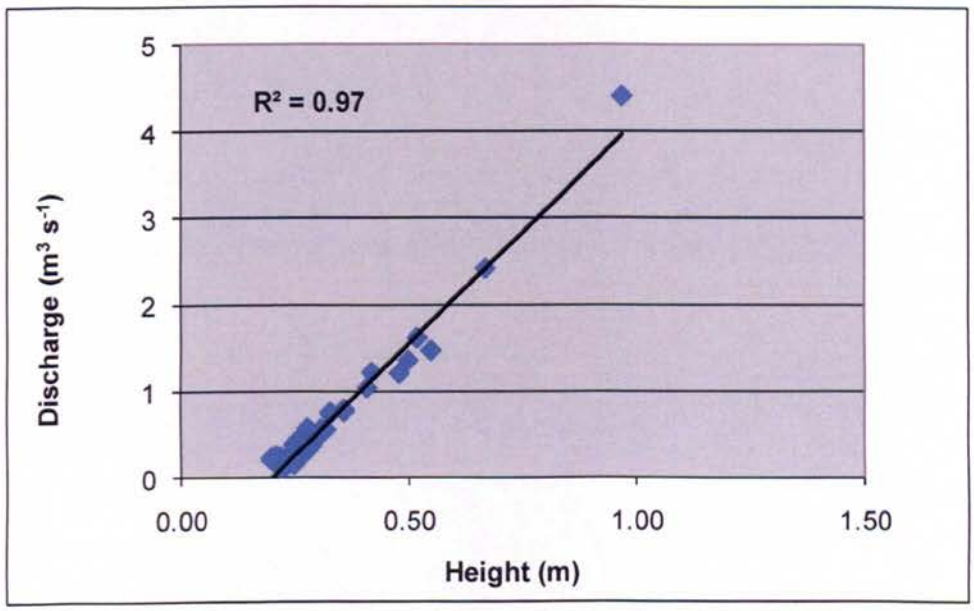

Figure 3.8: River Hogsmill measured stage height vs calculated discharge

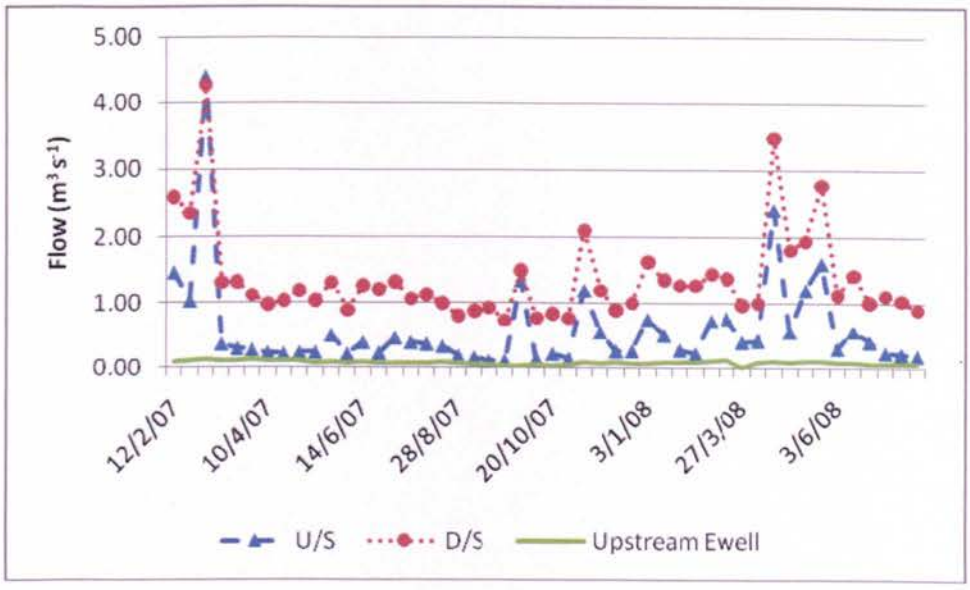

Figure 3.9: Comparison of Hogsmill River up and downstream flows. Upstream: downstream $R^2 = 0.89$, n = 49.

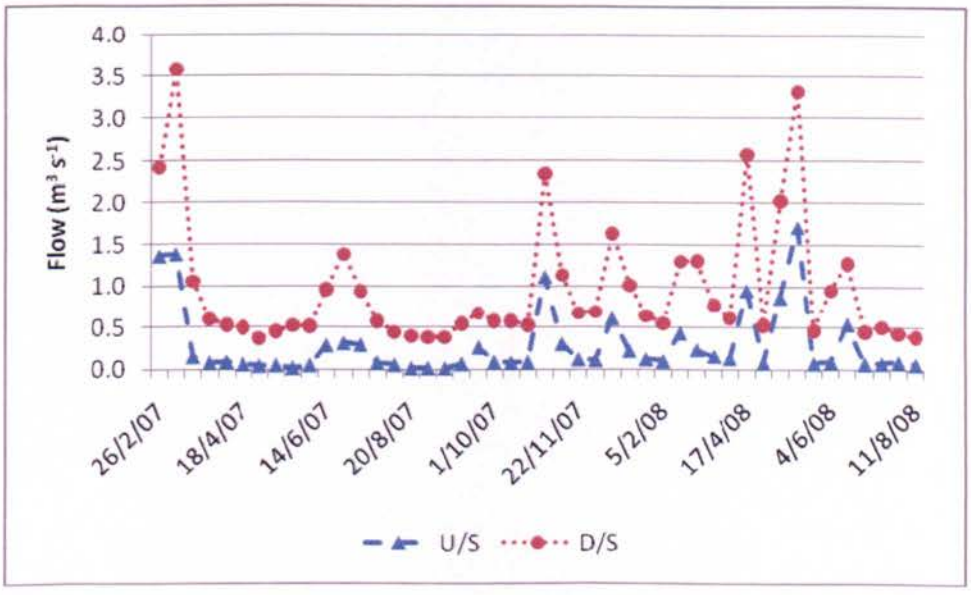

Figure 3.10: Comparison of River Bourne up and downstream flows. Upstream: downstream $R^2 = 0.94$, n = 47.

Monthly rainfall and downstream river flows during the sampling period were compared with the long term average rainfall pattern (Appendix VIII). Rainfall data, supplied by the Meteorological Office, is from the Heathrow sampling station, approximately 11 km from the Bourne and Hogsmill rivers in a direct line (www.metoffice.gov.uk).

3.5. Chemical analysis

3.5.1. Sample preparation and analysis

3.5.1.1. River water samples

Samples were prepared for analysis within 24 hours of collection. Approximately 100 ml of each sample was vacuum filtered through Whatman 0.45 μm cellulose nitrate membrane filter paper, on seven occasions these filtered samples were additionally filtered through 0.1 μm filters. A portion of filtrate was immediately analysed for SRP using the method described by Allen (1974) as modified by Rowland & Haygarth (1997):-

3.5.1.1.1. SRP Analysis

1. Preparation of P stock solution:
0.4390 g of Analar potassium dihydrogen phosphate (KH_2PO_4) was dried in an oven for for 1 hour at 105° and then diluted with deionised water to produce 1 litre of P stock solution of 100 mg P l^{-1}.

2. Preparation of working stock solution
For 100 ml working P solution of 2.5mg P l^{-1} dilute 2.5ml P stock solution (100mg P l^{-1}) with 100 ml deionised H_2O.

3. Preparation of Reagent A

Dissolve 12 g of ammonium paramolybdate in 25 ml distilled water and 0.2908 g potassium antimony tartrate in 100 ml distilled water. Add both solutions to 1,000 ml of 2.5M H_2SO_4 (sulphuric acid), dilute the solution to 2,000 ml with distilled water and mix well. Store the solution in a Pyrex bottle in a cool, dark area.

4. Preparation of Reagent B (Combined Colour Reagent)

On the day of testing, mix Ascorbic Acid with Reagent A in the proportions shown below. Combined colour reagent does not keep for more than 24 hours

No. of samples	Reagent A	Ascorbic acid
6	50ml	0.264g
12	100ml	0.528g
18	150ml	0.792g
24	200ml	1.056g
30	250ml	1.32g
36	300ml	1.584g
42	350ml	1.848g
48	400ml	2.112g
54	450ml	2.376g
60	500ml	2.64g

5. Calibration standards

Pipette working phosphorus solution (2.5 mg P l^{-1}) into 50ml volumetric flasks in the quantities shown below.

Volume of working solution (ml)	P equivalent (mg P l^{-1}) when diluted to 50 ml
0	blank
0.5	0.025
1	0.05
2	0.1
3	0.15
4	0.2
5	0.25
8	0.4
10	0.5
12	0.6
15	0.75
20	1.0

6. Pipette 10 ml river water sample into 50 ml volumetric flasks
7. Dilute all volumetric flasks (river water samples, standards and blank) with de-ionised water to approximately 30 ml
8. Add 8 ml combined colour reagent and swirl to mix
9. Dilute contents to 50 ml, shake well, leave for 30 minutes to develop colour
10. Measure absorbance at 880 nm
11. Prepare calibration curve using standards (x = absorbance / y = P concentration)
12. Take 4 readings of "blank" and average to give limit of detection (LOD)
13. Prepare 2 replicates of a random sample on every analysis occasion
14. Obtain P concentration readings using calibration curve/excel equation and multiply by 5 to allow for initial dilution of sample with de-ionised water.
15. Data and calculations for the LOD are shown in Appendices 1 & 2.

3.5.1.1.2. TP Analysis

1. A 25 ml sample of river water (or deionised water for the blank) was poured into a 50 ml Erlenmeyer flask
2. The contents of 1 packet potassium persulphate ($K_2S_2O_8$) powder was added to the flask and swirled to mix.
3. 2.0 ml of 5.25 N Sulphuric acid solution (H_2SO_4) was added to the flask.
4. The solution was simmered on a hot plate for 30 minutes or until the contents reduced to 20 ml.
5. The contents of the flask were cooled to room temperature
6. 2.0 ml sodium hydroxide (NaOH)was added to the flask and the contents swirled to mix
7. 10 ml of the sample solution (and blanks) were tested as per SRP (above)

3.5.1.1.3. ICP-MS Analysis

Approximately 25 ml of the remaining filtrate from each sample was acidified with 0.5 ml Aristar HNO_3 (2% HNO_3) to less than pH 2 and stored at below 5°C, alongside similarly treated quantities of unfiltered samples, for batch analysis of i).total dissolved P and dissolved metals, ii).total P and total metals by inductively couple mass spectrometry (VG PlasmaQuad ICP-MS). The range of metals tested were Al, As, Cd, Cr, Cu, Fe, Ni, Mn, Pb, Zn.

Quality control standards were prepared using a combination of four commercial multi-element reference solutions to cover the elements of interest, diluted to 1 μg l^{-1} with de-ionised water in the concentration range 0.1, 0.5, 1.0 and 2.0. Blanks were prepared with de-ionised water and 2% Aristar HNO_3.

After each sample test, a two minute wash cycle was carried out to reduce the risk as a signal drift monitor to check the constancy of the equipment (Jarvis *et al.*, 1994).

The limits of detection (LOD) for metals in river water are shown in Appendix III and for metals in sediments in Appendix V.

3.5.1.2. River sediment samples

3.5.1.2.1. Analysis of TP and total metals in sediment

Sediments were refrigerated at below 5°C until the sampling campaign was complete (less than three weeks), then transferred to acid washed open porcelain dishes and placed in a drying oven at 50°C for up to seven days until all moisture had evaporated. Samples were lightly crushed to break up sediment clumps, sieved to less than 2 mm fraction and stored in labelled polythene sample bags until analysis.

Triplicate sediment samples weighing ~1.5 g were prepared for total metals and total P analysis using Method 3050B, Acid digestion of sediments, sludges, and soils (USEPA, 2003). Certified reference materials and blanks were included in each batch. Analysis was undertaken twice, using the VG PlasmaQuad Inductively Coupled Plasma Mass Spectrometer (ICP-MS) and Inductively Coupled Atomic Emission Spectrometer ICP-AES. As the percentage recovery from certified reference materials was highest for ICP-MS, these results were used in this study (Chapter 7). The exceptions are Al and Fe which were only analysed using ICP-AES as they occur in concentrations too high for ICP-MS analysis at the solution strength necessary to detect the other elements.

3.5.1.2.2. Method 305B (USEPA)

N.B. This method is not a total digestion technique for most samples. It is a very strong acid digestion that will dissolve almost all elements that could become "environmentally available".

1. 3 x ~1.5 g samples from each river site were placed in 250 ml flasks, mixed with 10 ml of 1:1 HNO_3 and covered with a watch glass
2. The samples were heated to 95°C ± 5°C and allowed to reflux for 10 to 15 minutes without boiling.
3. The samples were cooled to room temperature then 5 ml of concentrated HNO_3 was added, the watch glass replaced and allowed to reflux for 30 minutes. If brown fumes

were generated, indicating oxidation of the sample by HNO_3, step 3 was repeated until no brown fumes were given off by the sample indicating the complete reaction with HNO_3.

4. With the watch glass on the flask, the solution was heated at 95°C ± 5°C without boiling for two hours, it was allowed to cool.
5. 2 ml of deionised water and 3 ml of 30% H_2O_2 was added. The flasks were covered with a watch glass and returned to the hot plate to warm and to start the peroxide reaction.
6. The flasks were heated until effervescence subsided and then removed from the hot plate to cool.
7. 30% H_2O_2 was added to the flasks in 1ml aliquots with warming until the effervescence was minimal. (Not add more than a total of 10 ml 30% H_2O_2 was added)
8. The samples were covered with a watch glass and returned to the hotplate. They were heated at 95°C ± 5°C without boiling for two hours.
9. After cooling, flasks were diluted to 100 ml with water and particulates were removed by filtration through Whatman No. 41 filter paper.
10. The samples were analysis by ICP-MS or ICP-AES.
11. Data and LOD are shown in Appendix V.

3.5.1.2.3. Analysis of P release in water

Using the method described by House *et al.* (1995) and Jarvie *et al.* (2005):

1. Triplicate river bed sediment samples weighing ~0.5 g were placed in 250 ml polypropylene bottles with 200 ml of 2 mmo l^{-1} $CaCl_2$ solution to mimic the hard-water conditions of the rivers studied.
2. Samples were agitated overnight at 150 rpm, the laboratory temperature was reduced to 10 °C and the samples covered to exclude light in order to limit microbial action.
3. A 25 ml subsample from each 250 ml bottle was centrifuged for 15 minutes.
4. The supernatant was analysed for SRP as described in 3.5.1.1. to ascertain whether P would release into water without the use of reagents.
5. Data and LOD are shown in Appendix V.

3.5.1.3. Analytical issues

3.5.1.3.1. Phosphorus

Filtered samples collected between February 2007 and February 2008 were analysed for TDP and dissolved metals using ICP-MS. TDP concentrations were frequently similar to or less than those for SRP, an unanticipated result as TDP contains dissolved hydrolysable (polymeric and organic) P in addition to SRP and concentrations were expected to be greater (Jarvie *et al.*, 2002a). A review of literature indicates that acid-persulphate digestion may not release all P adsorbed to oxides and hydrous-oxides, particularly where rivers are rich in particulate matter or carbon, so TP or TDP concentrations in this project may be understated (Jarvie *et al.*, 2002a).

Additionally, SRP and TDP concentrations in river water receiving STW wastewaters are frequently similar as the majority of P in wastewaters is in dissolved, inorganic form (Neal *et*

al., 2000b; May *et al.*, 2001). It may have been appropriate to have continued ICP-MS analysis for TDP beyond 12 months, however, an intervening factor was transfer of the NERC ICP-MS facility from Kingston University to Imperial College, Silwood Park Campus, Ascot in spring 2008, the equipment being unavailable for several months whilst it was moved and recommissioned and subject to increased demand for analysis before and after relocation from better resourced projects.

3.5.1.3.2. Metals

Concentrations of total metals in samples subjected to H_2SO_4 /$K_2S_2O_8$ digestion before analysis should exceed those of the dissolved metals in filtered (only) samples as metals absorbed to particulate matter mobilise during the digestion process. However, comparison of total and dissolved metals from five sampling campaigns showed dissolved metals concentrations frequently exceeded total metals concentrations. Before analysis, digested samples were diluted 1:99 with Millipore de-ionised water to overcome interference from sulphur (S) in the reagents, it is possible that dilution reduced metals concentrations to below the limit of detection (LOD) or that S interfered with analysis despite dilution. An alternative digestion process using HNO_3 did not provide more consistent results. This may be due to the fact that that HNO_3 does not usually extract all trace metals from samples (Van Loon, 1985).

Metals data from blanks of unfiltered de-ionised water and blanks of filtered de-ionised water indicated that cellulose nitrate filters contain variable concentrations of trace metals, most noticeably Zn, although Cr and Cu are implicated. Researchers at Lancaster University advised pre-soaking filters in 0.01M HNO_3 and rinsing thoroughly with de-ionised water before use (Zhang, 2008). For ICP-MS analysis undertaken on 24/1/08, all filters were soaked in 0.1M HNO_3 solution for 3 hours before use, but analysis of filtered blanks still contained high levels of trace metals. The solution was increased to 1.0M HNO_3 and soaking time reduced to 1 hour but the problem was not satisfactorily resolved (H. Zhang, Lancaster University, pers. Comm., 2008).

Anecdotal evidence indicates this issue is frequently encountered in liquids passed through cellulose nitrate filters although it is not widely report in literature, Van Loon (1985) advocates acid washing membrane filters before use to eliminate trace metals contamination but does not propose solution strengths or soaking times. Zn concentrations in this project are exceptionally high in comparison to major U.K. rivers analysed during the Land Ocean Interaction Study (LOIS) (Neal & Robson, 2000).

3.5.2. Quality control procedures

Glassware and sample bottles were soaked overnight in dilute HCl and rinsed three times in de-ionised water before use. The undernoted measures were implemented for specific procedures.

3.5.2.1. Soluble reactive phosphorus (SRP)

- Blanks of deionised water were used for each batch of analyses and the blank value subtracted from each sample to exclude background contamination from the results.
- One sample, per batch of samples, were analysed in triplicate. % co-efficient of variation between triplicate samples is acceptable at 2.35%.
- 10 ml of purchased phosphate standard solution (1 mg PO_4 l^{-1}) was subjected to the analytical procedure for SRP to ascertain the recovery of a known amount of P; % mean difference from expected recovery is acceptable at 4.48%.
- Two additional samples of known concentrations of 2.5 mg P l^{-1} "stock solution" were used to monitor equipment drift, absorbance being read by colorimeter every 10 samples; % relative standard deviation (RSD) is acceptable at 1.17%.
- Two additional samples of known concentrations of 2.5 mg P l^{-1} "stock solution" (as above) were included in each batch of analyses to check recovery of P; mean difference from expected recovery is 4.08%.
- HACH 2500 colorimeter was tested for accuracy using purchased phosphate standard solution (1 mg PO_4 l^{-1}) and P calibration standards.
- Regression co-efficient (r^2) of P standards calibration curve ranged from 0.97 – 1.0 during the period of analysis, indicating accurate sample preparation.

3.5.2.2. Total Phosphorus (TP)

In addition to the quality control procedure for SRP analysis, these additional checks were used when preparing samples for digestion:

- One sample per batch digested in triplicate, % co-efficient of variation between triplicate samples is acceptable at 2.79%.

- One digested blank of deionised water used for each batch of analyses and the blank absorbance value deducted from each sample absorbance reading.

3.5.2.3. P and metals in river water (ICP-MS analysis)

- One sample per batch prepared in triplicate.

- Blanks of deionised water used for each batch.

- Certified reference materials used for preparation of calibration standards.

- All samples analysed in triplicate.

- After each analysis, a two minute wash cycle was carried out to reduce the risk of cross contamination between samples.

- After every five sample tests the 10 $\mu g\ l^{-1}$ standard was run as a signal drift monitor to check equipment stability (Table 3.1) (Jarvis *et al.*, 1994).

Date of analysis	Al	P	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
5/3/07	2.38	1.82	n/a	2.38	1.47	2.49	2.65	2.93	1.99	2.79	2.63
1/5/07	1.70	1.72	n/a	1.64	1.39	1.70	2.06	1.94	2.01	2.02	2.29
26/6/07	2.11	1.49	n/a	1.54	1.47	1.80	1.51	2.15	1.76	1.58	1.28
19/9/07	1.35	1.22	1.59	1.53	1.49	1.86	2.11	1.85	1.65	2.21	2.06
31/10/07	1.39	1.13	1.82	1.54	1.25	1.82	1.91	2.09	1.83	1.97	1.97
31/12/07	1.85	2.06	2.08	2.06	2.09	2.12	2.24	2.23	2.25	2.91	2.47
21/1/08	1.44	1.04	1.76	1.27	1.50	1.66	1.85	2.20	2.09	2.22	1.42
12/3/08	1.64	1.45	1.57	0.97	1.48	1.08	1.89	1.92	1.18	1.25	0.74

Table 3.1: ICP-MS metals and TP analysis in river water, %RSD of instrument drift. (n/a: not analysed on this date)

3.5.2.4. Total P and metals in sediment

- All sediment samples prepared in triplicate, data and LOD are shown in Appendix V.
- Triplicates of certified river sediment reference materials and blanks digested and analysed alongside samples (Table 3.2).
- Other quality control procedures as detailed in P and metals in water (3.5.2.3).

NBS River Sediment 2704	P	Cr	Ni	Cu	Zn	As	Cd	Pb
Certified concentration	n/c	89±1	44±2	100±2	427±5	n/c	n/c	146±1
Measured, concentrated mean	885.64	81.56	36.95	91.31	403.72	18.61	3.10	144.44
% recovery	n/c	91.64	83.98	91.31	94.55	n/c	n/c	98.93

Table 3.2: Comparison of measured & certified concentrations in reference material (mg kg^{-1}) (n/c: not certified).

3.5.2.5. P release in water

- All sediment samples prepared in triplicate, % co-efficient of variation between triplicate samples is acceptable at 7.52%.
- Two blanks of $CaCl_2$ solution and one of de-ionised water processed alongside samples, the absorbance reading was the same for all three blanks (0.008) and any samples falling below this reading were deemed to be < LOD.
- Other quality control procedures as detailed in SRP analysis (3.5.2.1).

3.6. Data manipulation

Data was stored in Microsoft® Excel 2007 worksheets and manipulated using statistical functions within Excel and MINITAB®15. Charts were produced using Excel and MINITAB®15. Students T-test results were calculated in Excel and verified using GraphPad software (GraphPad Software Inc. © 2005).

4. The river hydrology, wastewater discharges and phosphorus levels

4.1. Introduction

The detrimental role of excess P concentrations in riverine ecosystems is widely documented and, although agricultural sources were initially held responsible for the majority of inputs, it is now agreed that STW wastewaters supply significant quantities of P to rivers, particularly in heavily populated, urban areas (Jarvie *et al.*, 2006; Neal *et al.*, 2005; Wade *et al.*, 2004).

In addition to elevating P concentrations, inputs of STW wastewaters to second or third order rivers can substantially increase water volume downstream of outflows. Headwater flows generally reduce during the summer months but flows downstream of STW frequently remains high as wastewaters contribute proportionately greater quantities of water to rivers (Wade *et al.*, 2004). During periods of low base flow, the impact of wastewaters contaminants such as P are likely to be greatest as they are less diluted by headwaters although exceptional rainfall events may interrupt this cycle (Hilton, 2006; Johnes, 2007). Therefore, to thoroughly assess the impact of changes in P concentrations up and downstream of an input source, it is important to obtain river flows or discharge volumes, to provide context for changes in nutrient concentrations.

River water samples up and downstream of STW discharging into the rivers Bourne and Hogsmill have been analysed for TP and SRP, to determine differences in concentrations and calculate contributions from their respective STW source. Changes in the proportion of SRP to TP up and downstream of the source are also investigated to determine whether the dominant species alters as a result of wastewaters inputs. Increased ratios of SRP to TP are indicative of STW derived P inputs and, as SRP is considered more bioavailable than TP, the potential effect on riverine biota is greater when proportions of SRP within TP are elevated (Neal *et al.*, 2005).

4.2. Materials and methods

River water samples were collected up and downstream of STW outfalls discharging into the rivers Bourne and Hogsmill over an eighteen month period between February 2007 and

August 2008, 49 (Hogsmill) and 47 (Bourne) sampling campaigns were undertaken to cover a range of weather and river flow conditions.

For TP, unfiltered river water samples were first digested with potassium persulphate and for SRP, samples were filtered through 0.45 μm cellulose nitrate filters, both batches were analysed using an ascorbic acid modified molybdate reagent, as described in 3.5. (Allen, 1974; Rowland *et al.*, 1997). Optical density of the samples was read with an HACH DR2500 colorimeter at 880 nm.

The Meteorological Office (Met Office) supplies rainfall data for each 24 hour period, commencing 0900 hours, from the closest recording station at Heathrow (latitude 51,479, 0.449) a distance, on a direct line, of less than 11 km from both rivers. Using daily flow data from the E.A., the correlation between daily rainfall and downstream river discharge was 0.655 for the Hogsmill and 0.288 for the Bourne, suggesting that daily rainfall is a contributory factor in terms of the downstream Hogsmill flow, but less so for the Bourne. Long term average (LTA) figures indicate that rainfall in February and July 2007 was exceptional at 145% and 185% greater than LTA's respectively (Appendix VIII). Whilst downstream mean monthly river flows increased, it was the February increase of 145% which equated to greatest downstream river flows in both rivers not the July increase of 185%.

As well as the 11 km distance between the monitoring station and sampling sites over which precipitation patterns may change, catchment specific features such as ground cover and moisture deficit influence the volume of rainfall entering rivers, so it is not surprising that the relationship between rainfall and river flow is weak; this being so, rainfall data was not included in this project.

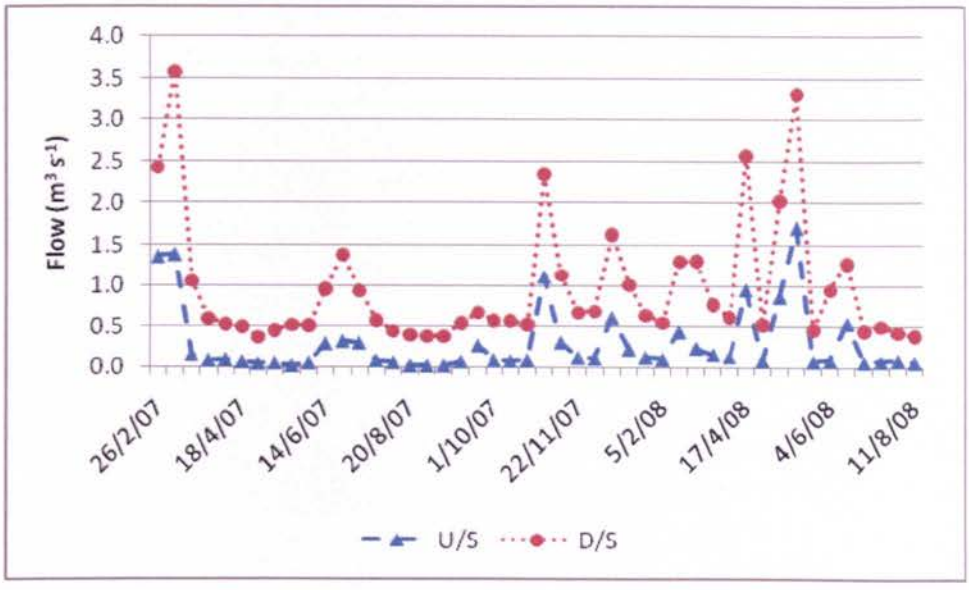

Figure 4.1 River Bourne estimated flow (U/S (1)) and E.A. Discharge (D/S (2)) for the sampling period (m3 s-1).

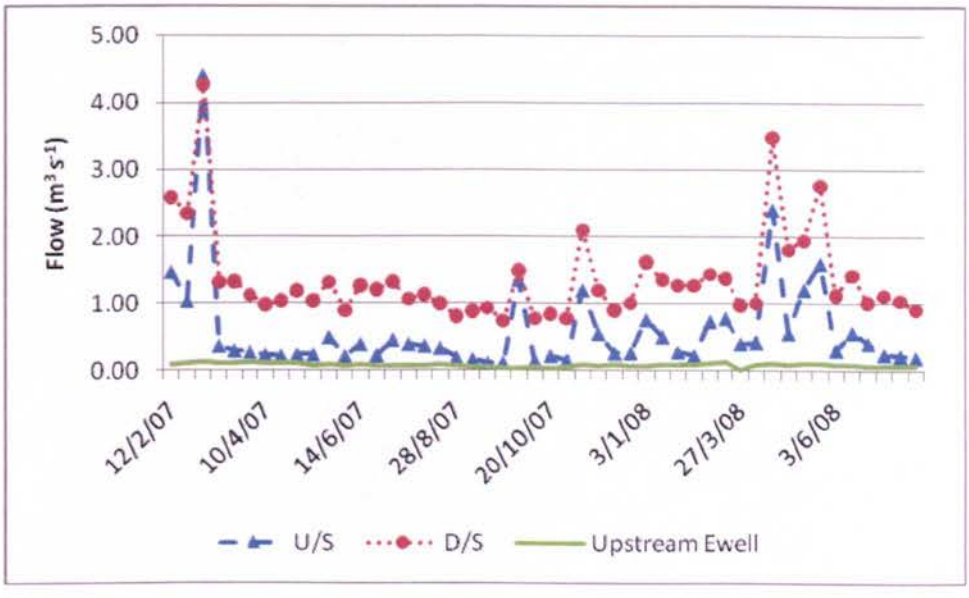

Figure 4.2 River Hogsmill, estimated flow (U/S (1)), E.A. auto-sampler derived data upstream at Ewell and downstream (D/S (2)) of the STW for sampling dates. Discharge ($m^3 s^{-1}$).

The E.A. supplied daily river flow data, readings at 15 minute intervals averaged over 24 hours, commencing 0.900 hours, for the rivers Bourne and Hogsmill downstream of the STW outflows, as illustrated in Figures 4.1 and 4.2. The E.A. does not record flows on the upstream Bourne and, although it records upstream flows on the Hogsmill the sampler is located at Ewell, more than 6 km from the sewage outflow and is not representative of flows immediately upstream of the STW (Figure 4.2). To overcome the lack of upstream flow data the upstream stage height was measured using a plumb line and flow estimated using the float method, as described in 3.4, the results are shown in Figures 4.1 and 4.2 (Shaw, 1994).

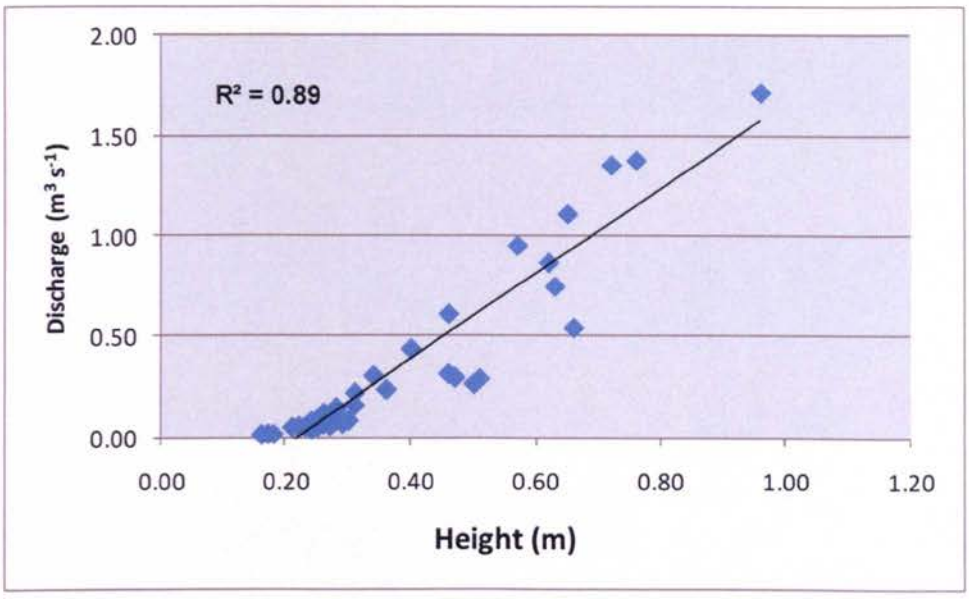

Figure 4.3 River Bourne rating curve of estimated upstream flow against stage height

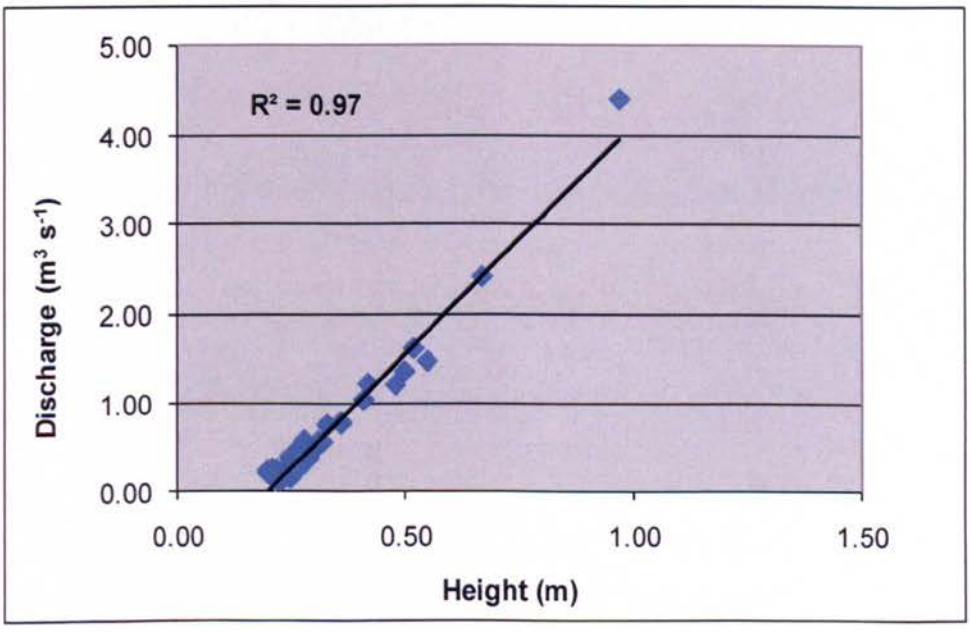

Figure 4.4 River Hogsmill rating curve of estimated upstream flow against stage height

Upstream stage heights were plotted against river discharge to obtain rating curves, as shown in Figures 4.3 and 4.4, the regression coefficients of 0.89 and 0.97 respectively indicate strong relationships between stage height and estimated flow calculations. Mean daily discharges to the receiving rivers were 70,871 m^3 day^{-1} (2007) and 62,817.42 m^3 day^{-1} (2008) for the Hogsmill and 27,893 m^3 day^{-1} (2007) and 26,970.27 m^3 day^{-1} (2008) for the Bourne (A.Wallis, Thames Water plc. pers. comm. 2008; T. Ghilespy, Thames Water plc. pers. comm. 2009). In dry weather, approximately 80% of the Hogsmill STW discharges to

the River Hogsmill, the remaining 20% going to Beverley Brook, a nearby stream, to maintain river flow during seasonal periods of low rainfall. Discharges to Beverley Brook are fixed at 20% of dry weather discharge, averaging 11,683 m^3 day^{-1} in 2007 and 11,719 m^3 day^{-1} in 2008, excess wastewater volume, e.g. from precipitation, is discharged to the Hogsmill (A.Wallis, Thames Water plc. pers. comm. 2007; T. Ghilespy, Thames Water plc. pers. comm. 2009).

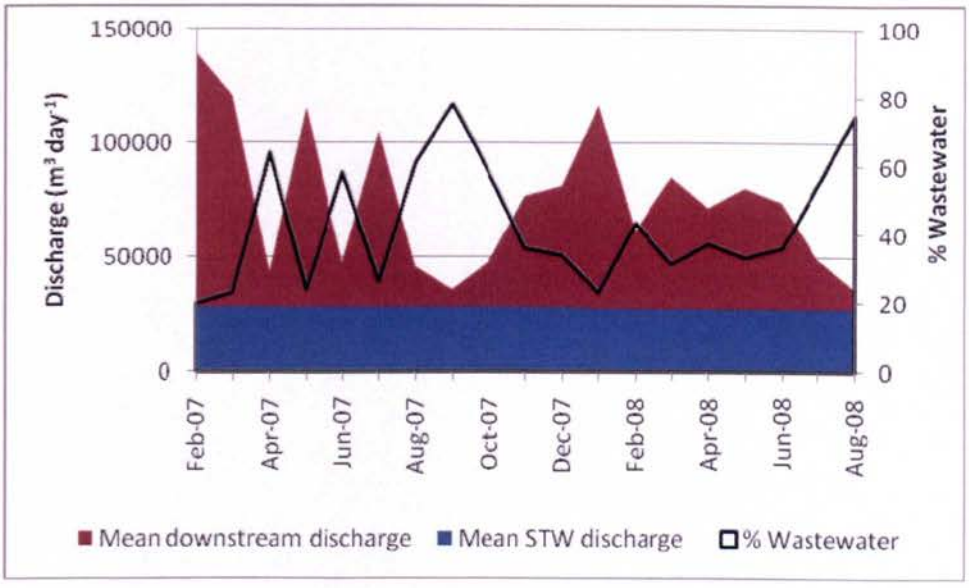

Figure 4.5 River Bourne mean downstream: effluent comparison to show estimated volume of downstream river water derived from treated STW wastewaters.

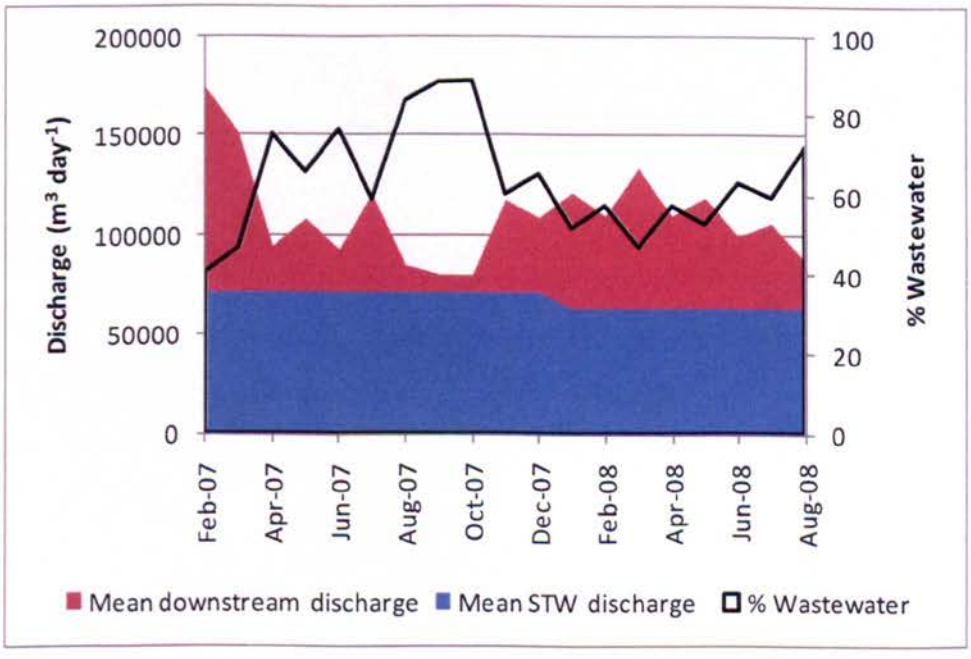

Figure 4.6 Hogsmill mean downstream: effluent comparison to show estimated volume of downstream river water derived from treated STW wastewaters.

Figures 4.5 & 4.6 use mean daily STW wastewaters discharge figures provided by Thames Water and E.A. flow data to show the potential volume of downstream river water derived from STW output. The mean wastewaters discharge figures supplied by Thames Water ignore seasonal changes and operational variation at the works so Figures 4.5 and 4.6 are intended to provide only a broad overview.

4.3. Results and Discussion

4.3.1. River Bourne

4.3.1.1. Soluble Reactive Phosphorus (SRP)

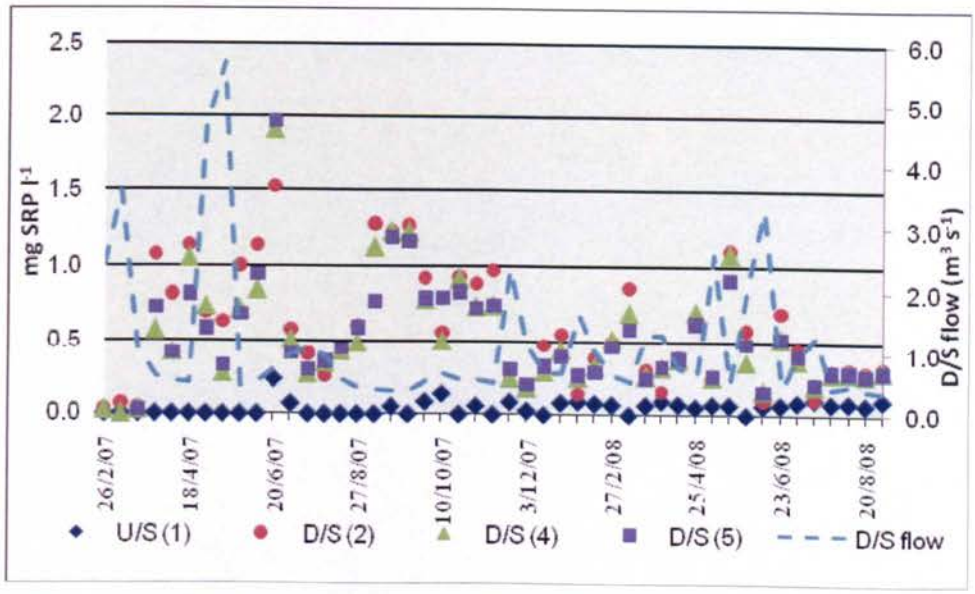

Figure 4.7 River Bourne SRP concentrations at all sampling locations and downstream river flow (mg SRP l^{-1}) and downstream river flow (m^3 s^{-1}). Sampling site D/S (3) is excluded as it relates to sediments only, locations shown in section 3.2.2.

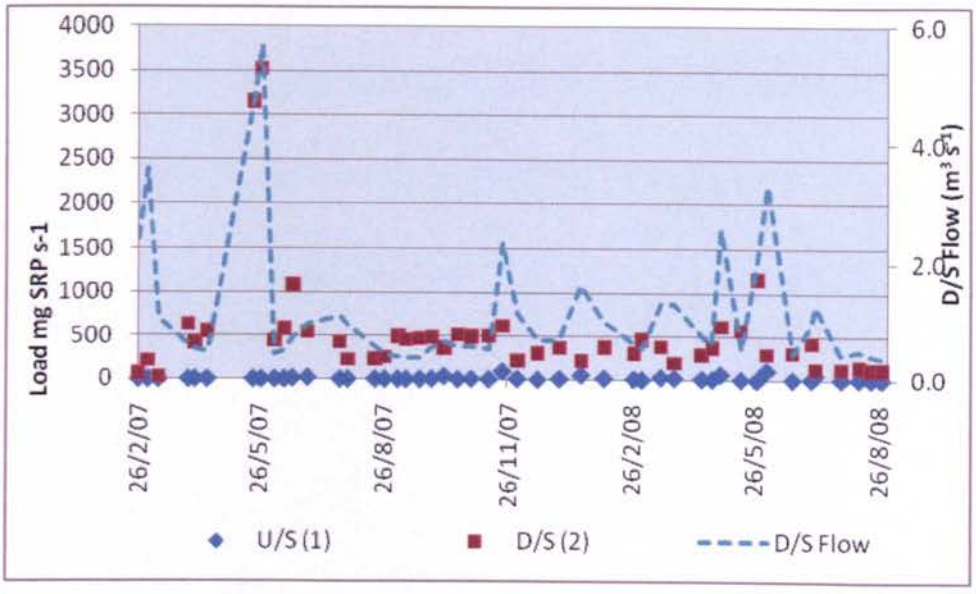

Figure 4.8 River Bourne SRP loads at U/S (1) and D/S (2) (mg SRP s^{-1}) and downstream river flow (m^3 s^{-1}). Sampling locations shown in section 3.2.2.

Sampling period	U/S (1)	D/S (2)	D/S (4)	D/S (5)	Estimated STW contribution at D/S (2)
SRP	0.08	0.45	0.39	0.39	0.37
TP	0.11	0.61	0.61	0.63	0.50

Table 4.1 Bourne flow weighted mean concentrations and estimated contribution from SWT (mg P l^{-1}). See section 3.2.2 for sampling locations and section 3.4 for the flow weighting equation.

Upstream concentrations for the River Bourne range from below the limit of detection (LOD) to 0.243 mg SRP l^{-1}, with a flow weighted mean of 0.08 mg SRP l^{-1} (LOD = 0.033 mg P l^{-1}). Upstream concentrations exceeded the E.A. target figure of 0.20 mg SRP l^{-1} for lowland rivers on clay substrates on just one sampling date, 26th June 2007 (Mainstone *et al.*, 2000). As shown in Figure 4.7, downstream concentrations were < LOD on one occasion but were generally higher than upstream with flow weighted means of 0.45 mg SRP l^{-1} at D/S (2), nearest the outflow and 0.39 mg SRP l^{-1} at the sampling points further downstream. The maximum downstream concentration was 1.96 mg SRP l^{-1}.

P concentrations in the samples taken 0.3 km, D/S (4) and 0.7 km, D/S (5) downstream of the outflow sampling point are similar to those at the D/S (2) sampling point; where there are differences in SRP concentrations between downstream river sampling points, these may result from improved mixing as the river flows away from the wastewaters discharge stream or retention of P in riverbed sediments. On occasions when P concentrations are higher at D/S (5) it is possible that a field drain downstream of D/S (4) or run-off from manure or fertiliser in adjacent fields provides additional P inputs. The peak in downstream SRP loads

on 22nd and 28th May 2007 (Figure 4.8) is due to downstream flows being an order of magnitude higher than those on other sampling dates.

On 10/7/08 the SRP concentration at the outflow was 6.3% lower than the upstream value; when raised with the STW operator, Thames Water, they explained that an additional application of phosphate stripping chemicals had been used at the STW that day to counter exceptional rainfall conditions which had increased the volume of incoming effluent (C. Newman, Thames Water plc. pers. comm. 2008).

	U/S (1)	D/S (2)	D/S (4)	D/S (5)	t-test result	P < 0.05
SRP	1.07	45.09	39.37	40.25	2.14E-06	P < 0.0001
TP	2.79	49.05	48.88	50.05	2.81E-13	P < 0.0001

Table 4.2 Bourne calculated daily P loads based on mean concentrations (kg P day^{-1}) and significance between up and downstream concentrations, P is significant at < 0.001. Sampling locations shown in section 3.2.2.

Downstream flow figures supplied by the E.A. and upstream flow figures calculated as described in 3.4, were used to estimate SRP loads in mg P s^{-1} over the sampling period, as shown in Figure 4.8 and over a 24 hour period as shown in Table 4.2. Calculated daily loads provide only an indication of the quantity of P transported downstream each day; it cannot be assumed that flow measurements or P concentrations remain constant over 24 hours because precipitation, catchment drainage output, wastewater inputs and P inputs may vary (Johnes, 2007). Discharge figures are least likely to be accurate in respect of the upstream measurements taken during a 15 – 30 minute period on the day of sampling, downstream E.A. figures, being the mean of automated flow measurements recorded at 15 minute intervals over 24 hours are more likely to be representative. Similarly, P inputs over a 24 hour period are likely to vary due to chemical changes within STW discharges. Despite these caveats, the data in Table 4.2 indicates that SRP loads in the Bourne downstream of the STW are significantly greater than those upstream, with a mean increase in SRP concentration of 0.37 mg P l^{-1} at the D/S (2) sampling point potentially increasing the daily SRP load to more than 40 kg.

4.3.1.2. Total phosphorus (TP)

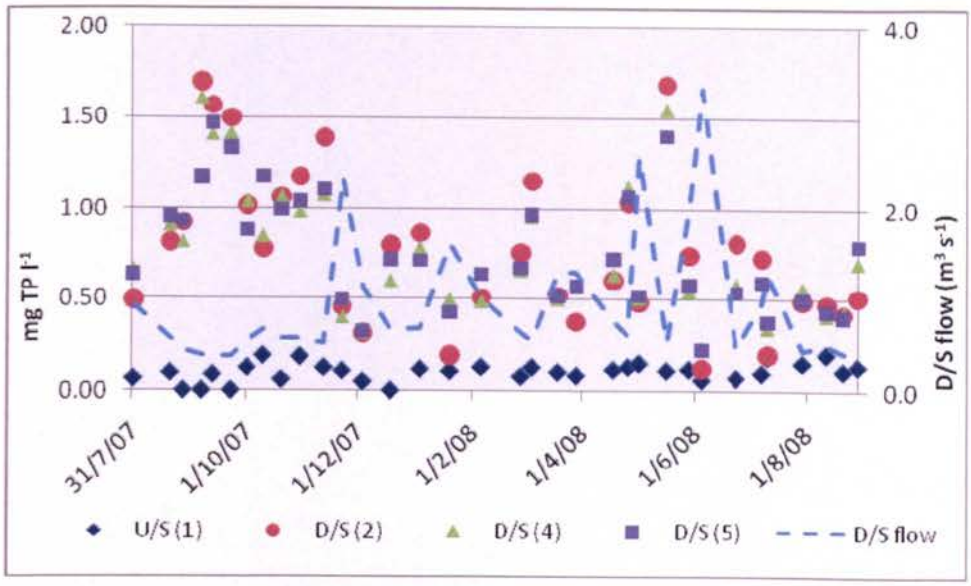

Figure 4.9 River Bourne TP concentrations at all sampling locations (mg TP l^{-1}) and downstream river flow (m^3 s^{-1}). Sampling site D/S (3) is omitted as it related to sediments only; sampling locations are shown in section 3.2.2.

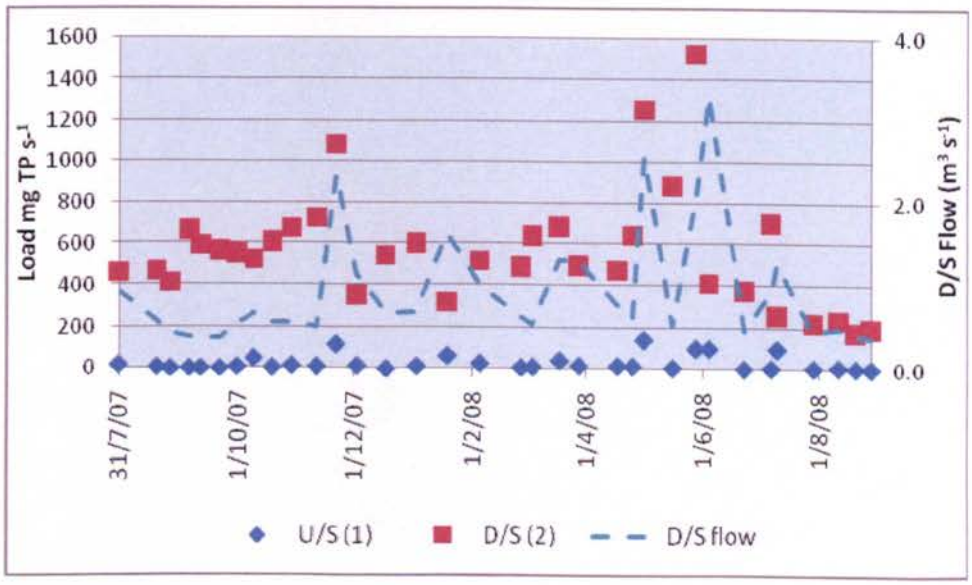

Figure 4.10 River Bourne TP loads at U/S (1) and D/S (2) (mg TP s^{-1}) and downstream river flow (m^3 s^{-1}). Sampling locations shown in section 3.2.2.

Due to analytical problems at the start of the project there are fewer results for TP; data from 34 sampling events commencing 31/7/07 are discussed in this section. Upstream TP concentrations range between < LOD and 0.196 mg l^{-1} with a flow weighted mean of 0.11 mg TP l^{-1}. Downstream concentrations range between 0.0261 and 1.697 mg TP l^{-1} with flow weighted means of 0.61 mg TP l^{-1} at D/S (2) and 0.63 mg TP l^{-1} at D/S (5), as shown in Figure 4.9 and Table 4.1. The maximum TP concentration is less than maximum SRP concentration because of the difference in sampling periods, the maximum value for SRP

concentrations occurred before results from the TP analysis were considered sufficiently robust to include in this project. A discernable elevation in P levels occurs periodically between D/S (4) and D/S (5) where the Bourne passes through a field accommodating eight Shetland ponies and it may be that manure inputs contribute TP to the river here.

Figure 4.10 and Table 4.2 describe the potential TP loads and downstream river flow, as the issues raised in section 4.3.1.1 regarding SRP concentrations and loads apply similarly to TP they are not discussed further in this section.

4.3.1.3. TP: SRP comparison

During the period when river water samples were successfully analysed for both TP and SRP, 31/7/07 – 28/8/08, upstream TP concentrations in the Bourne were greater than SRP concentrations by up to 69% except for samples collected on 23/3/08 and 4/6/08 when the SRP was greater than TP by 14% and 11% respectively. As SRP is a component of TP this should not be the case, but authors have reported this finding for a variety of reasons including water turbidity, trace element interference and analytical error (Neal *et al.*, 2000c; Jarvie *et al.*, 2002a). The coefficient of variation (R^2), suggests a lack of dependency between TP and SRP, perhaps due to a mixture of P sources, the paired t-test shows that they are significantly different at $P < 0.001$ (Figure 4.11).

As expected, downstream TP concentrations are consistently greater than SRP during the sampling period 31/7/07 – 28/8/08 when river water samples were analysed for both species. The relationship between TP and SRP is stronger downstream than upstream, as shown in Figure 4.12, the regression coefficient being more than 0.84, the difference between the P species ranges from 4.14 – 63.48%. On average, TP is 35.10% greater than SRP in river water collected from the downstream sampling sites, a similar result to that of Jarvie *et al.*, (2005), who found TP contained an average of 67% SRP in U.K. rivers receiving sewage wastewaters inputs, with the proportion of SRP increasing during periods of low base flow.

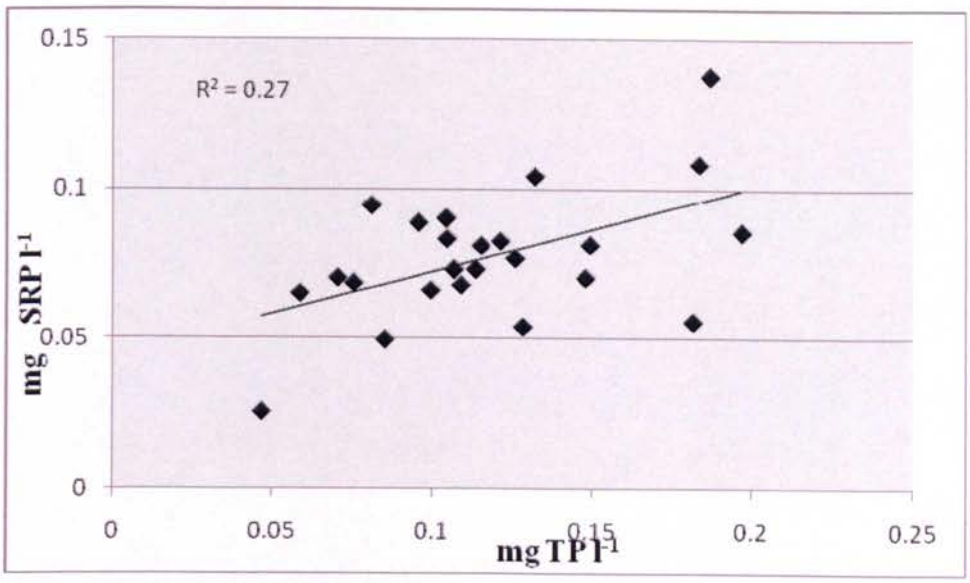

Figure 4.11 TP and SRP at Bourne U/S (1) are significantly different, most probably because of a variety of input sources of P to the river and there is little dependency between the two P species. P is significant at < 0.001 (P value - 3.17E-07)

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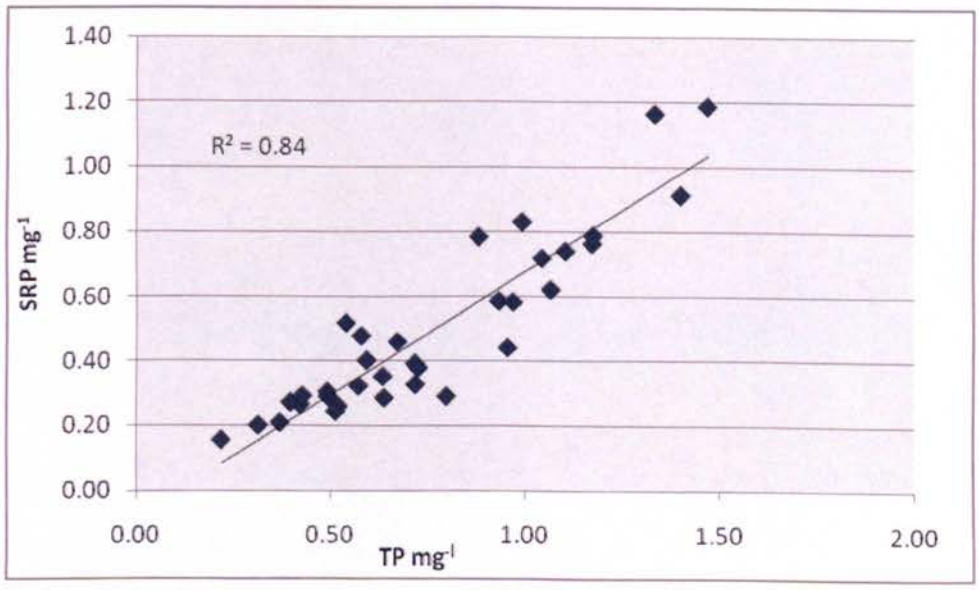

Figure 4.12 Downstream of the STW at D/S (5) TP and SRP are still significantly different but there is a greater dependency between the species, indicative of a dominant single source of P. P is significant at < 0.001. (P value - 2.61E-13)

4.3.1.4. Concentration and flow relationship

Figures 4.8 and 4.10 suggest a strong link between downstream flow and P but this is because downstream discharge figures are used to calculate the estimated P load. Figures 4.7 and 4.9, depicting P concentrations against sampling dates and downstream flow on those dates, does not show such a relationship. It may appear that in figures 4.7. and 4.9 a time lag

occurs between an increase in river flow and subsequent increase in P concentration, this is likely to be spurious as temporal scale is too great, being weekly rather than hourly.

4.3.2. Hogsmill River

4.3.2.1. SRP

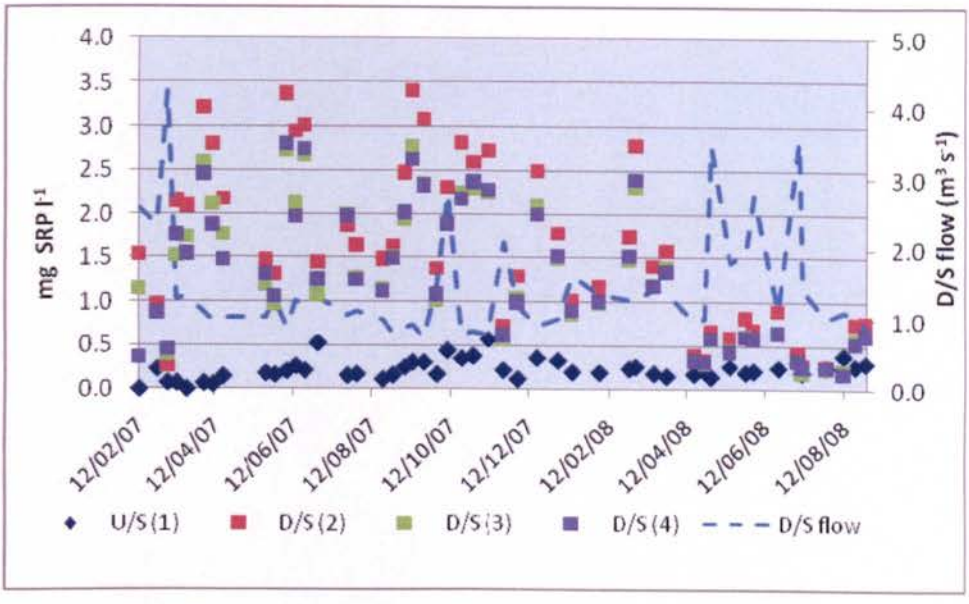

Figure 4.13 Hogsmill SRP concentrations (mg SRP l^{-1}) and downstream river flow (m^3 s^{-1}). Sampling locations shown in section 3.2.1.

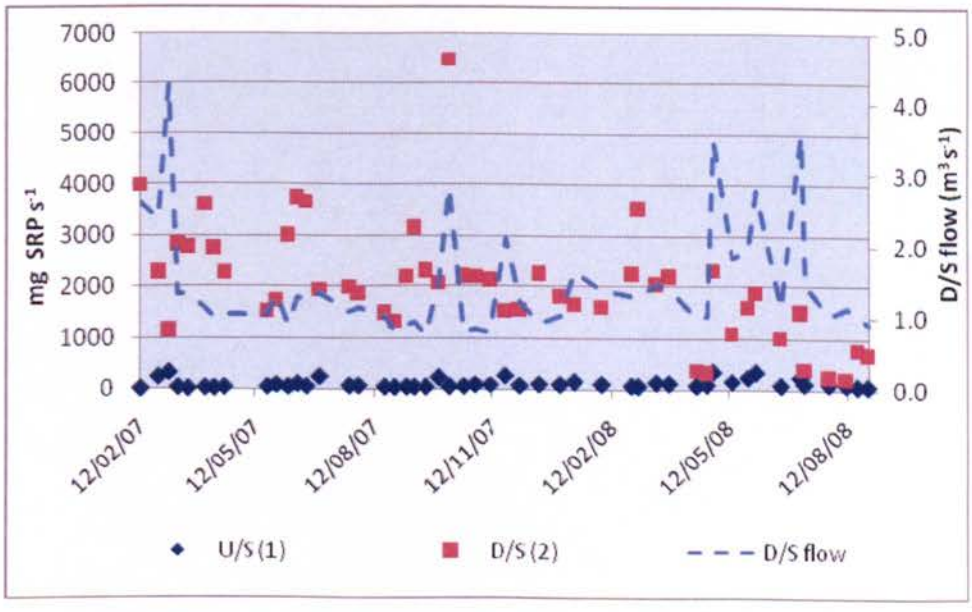

Figure 4.14 Hogsmill SRP loads at U/S (1) and D/S (2) (mg SRP l s^{-1}) and downstream river flow (m^3 s^{-1}). Sampling locations shown in section 3.2.1.

Sampling period	U/S (1)	D/S (2)	D/S (3)	D/S (4)	Estimated STW contribution at D/S (2)
Pre P-stripping 12/2/07 – 31/3/08	0.19	1.78	1.83	1.78	1.61
Post P-stripping 1/4/08 – 28/8/08		0.56	0.57	0.57	0.35

Table 4.3 Hogsmill flow weighted SRP mean concentrations and estimated contribution from SWT (mg SRP l^{-1}). See section 3.2.1. for sampling locations and section 3.4 for flow weighted mean equation.

Sampling period	U/S (1)	D/S (2)	D/S (3)	D/S (4)	t-test result	P < 0.05
Pre P-stripping 12/2/07 – 31/3/08	9.19	208.42	214.54	208.74	2.36E-15	P < 0.0001
Post P-stripping 1/4/08 – 28/8/08		83.01	84.06	84.19	3.29E-04	P < 0.001

Table 4.4 Hogsmill calculated daily SRP loads (kg SRP day^{-1}), difference between U/S (1) and D/S (2) is significant at $P < 0.001$. Sampling locations shown in section 3.2.1.

Upstream SRP concentrations for the Hogsmill range from 0.050 – 0.564 mg SRP l^{-1}, as shown in Figure 4.13, with a flow weighted mean for the entire sampling period of 0.19 mg SRP l^{-1} (Table 4.3). The upstream sampling point is approximately 7 km downstream of the rivers source at Ewell so, when it reaches U/S (1), it is likely to have accumulated P from urban sources such as the continuous discharge consents mentioned in section 3.2.1.

During the sampling campaign P-stripping was introduced at the Hogsmill Valley STW, therefore results fall into two sampling periods, before and after the introduction of P-stripping at the STW, which commenced 1 April 08. Before P-stripping, downstream SRP ranged from 0.27 – 3.49 mg SRP l^{-1} with a flow weighted mean of 1.78 mg SRP l^{-1} at D/S (2) (Table 4.3). Pre-P-stripping, SRP concentrations are similar to those reported in literature for U.K. rivers receiving STW wastewaters treated to secondary level only (Neal *et al.*, 2005; Neal *et al.*, 2008).

Following the introduction of P-stripping, SRP ranged from 0.21 – 0.90 mg SRP l^{-1} with a flow weighted mean of 0.56 mg SRP l^{-1} at D/S (2) (Table 4.3). The E.A. requires a mean annual discharge concentration of less than 1.0 mg P l^{-1} at this STW from 1st April 2008 (A. Wallis, Thames Water Plc., pers. comm., 2008). The effect on downstream concentrations is visible in Figures 4.13 and 4.14 from the sampling date of 17 April 08 onwards. As P-stripping analyses comprise 12 sampling occurrences in the final six months of the sampling

campaign, its long-term effectiveness has yet to be tested. However, the probable effect on the quantity of SRP downstream of the STW can be seen in Table 4.4 where the daily load is estimated to have reduced by more than 100 kg day^{-1}.

The effect of P-stripping on mean SRP concentrations can be seen in Table 4.3 where estimated flow weighted means reduced by more than 66%. Even with P-stripping, SRP levels remain above the E.A. guideline of 0.20 mg P l^{-1} for lowland rivers on clay substrates (Mainstone *et al.*, 2000). The reduction in SRP concentrations in the Hogsmill following introduction of P-stripping at the STW is similar to that reported in literature, for example, Jarvie *et al.* (2002b) found in-stream reductions of ≈66% on the River Kennet and ≈50% on the Thames. In a more comprehensive study, Neal *et al.* (2005) concluded that, with the introduction of P-stripping, in-stream SRP reductions of more than 50% were likely.

4.3.2.2. Hogsmill TP

Sampling period	U/S (1)	D/S (2)	D/S(3)	D/S (4)	Estimated STW contribution at (D/S 2)
Pre P-stripping 12/2/07 – 31/3/08	0.28	1.99	2.00	1.98	1.71
Post P-stripping 1/4/08 – 28/8/08		0.81	0.75	0.75	0.47

Table 4.5 Hogsmill flow weighted TP means (mg TP l^{-1}). See section 3.2.1 for sampling locations and section 3.4 for flow weighted mean calculation

Sampling period	U/S (1)	D/S (2)	D/S(3)	D/S (4)	t-test result	P < 0.05
Pre P-stripping 12/2/07 – 31/3/08	12.81	211.31	211.99	209.87	1.76E-08	P < 0.0001
Post P-stripping 1/4/08 – 28/8/08		119.47	110.64	111.42	7.03E-03	P < 0.01

Table 4.6 Hogsmill calculated daily TP loads (kg TP day^{-1}), difference between U/S (1) and D/S (2) is significant at $P < 0.01$. Sampling locations shown in section 3.2.1.

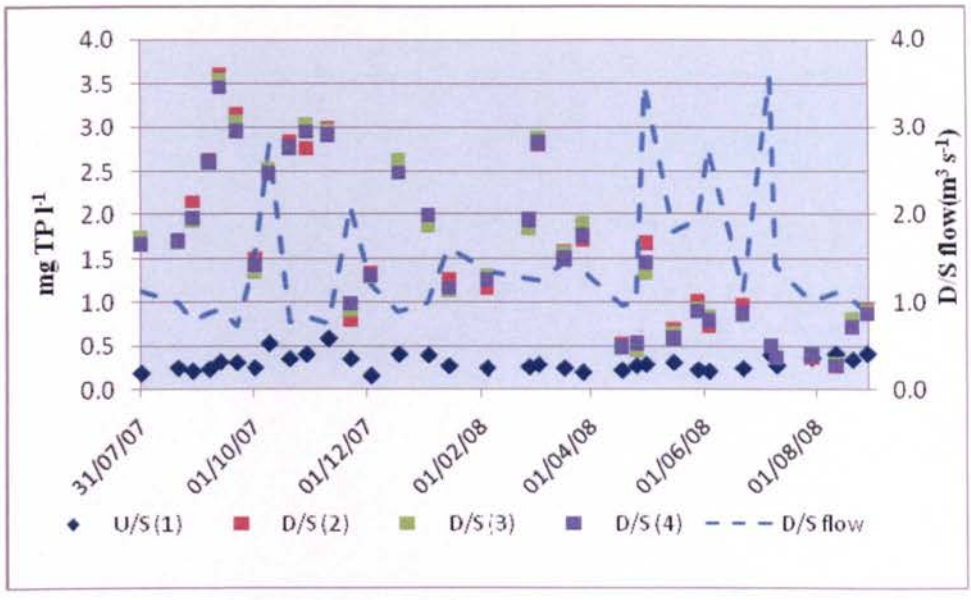

Figure 4.15 Hogsmill TP concentrations (mg l^{-1}) and downstream river flow (m^3 s^{-1}). Sampling locations shown in section 3.2.1.

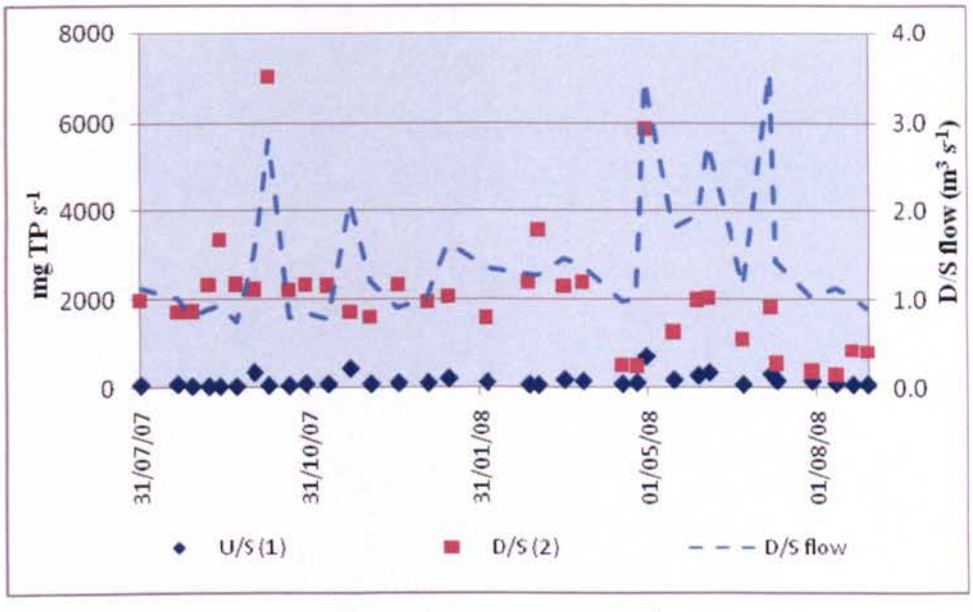

Figure 4.16 Hogsmill TP loads at U/S (1) and D/S (2) (mg TP s^{-1}) and downstream river flow (m^3 s^{-1}). Sampling locations shown in section 3.2.1.

Upstream Hogsmill TP concentrations range from 0.070 – 0.593 mg TP l^{-1} with a flow weighted mean of 0.28 mg TP l^{-1} (Figure 4.15). Downstream, TP concentrations range from 0.81 – 3.59 mg TP l^{-1} with a flow weighted means of 1.99 mg TP l^{-1} (before P stripping) and 0.27 – 1.68 mg TP l^{-1}, flow weighted mean 0.81 mg TP l^{-1} (with P stripping) at D/S (2). The spike in TP concentrations and loads on 9/10/07 and 30/4/08, are due to increased river flows on these dates, the mean downstream flow during the project period was 1.35 m^3 s^{-1} but on 9/10/07 it was 2.81m^3 s^{-1} and on 30/4/08 it was 3.48 m^3 s^{-1}. These increases in flow are likely

to be associated with exceptional rainfall as values of 15.2 mm on 9/10/07 and 26.4 mm over 29 – 30/4/08 were recorded by the Meteorological Office at their Heathrow data station (Anon, 2008).

The effect of P-stripping from 1/4/08 is seen in Figures 4.15 and 4.16 where TP concentrations and loads no longer increase in tandem with river flow, thereby maintaining lower downstream P concentrations during periods of high flows.

4.3.2.3. Hogsmill TP: SRP comparison

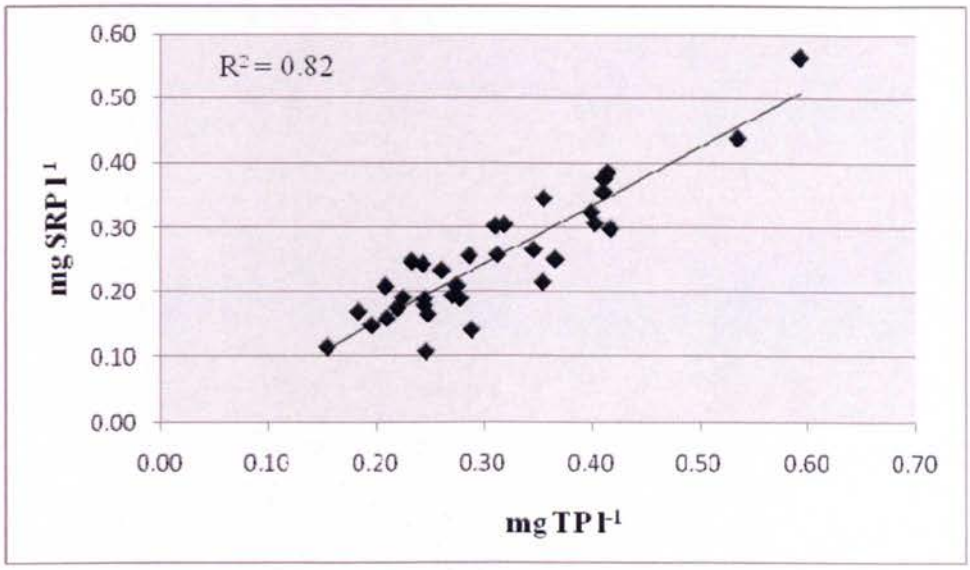

Figure 4.17 Hogsmill U/S (1) showing TP: SRP (mg P l^{-1}) relationship, they are significantly very well correlated at $P < 0.001$ (P value - 9.06E-05).

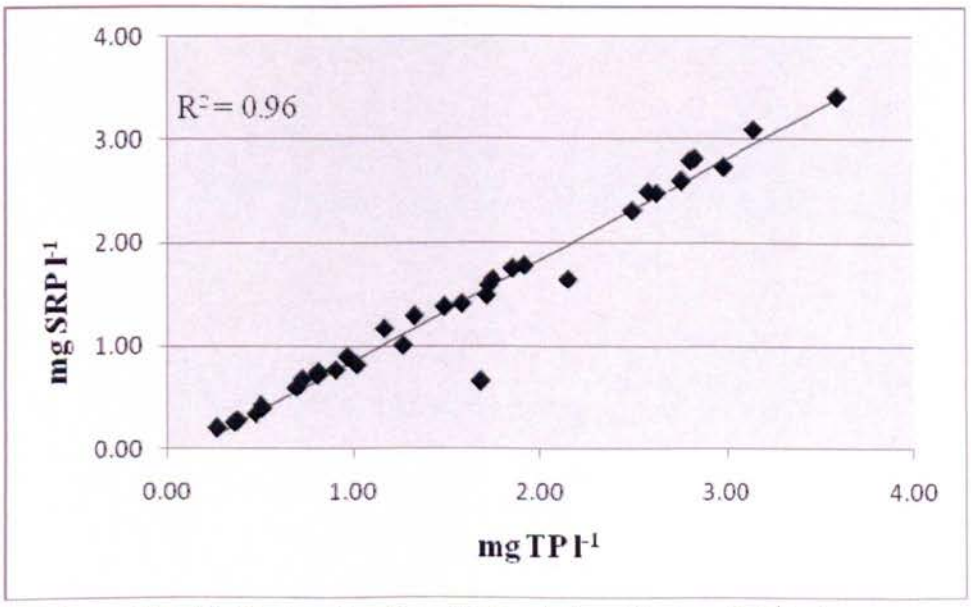

Figure 4.18 Hogsmill D/S (2) showing TP: SRP relationship (mg P l^{-1}), they are significantly different at $P < 0.001$ (P value - 4.03E-05).

Both up and downstream scatter-plots show strong relationships between SRP and TP (Figures 4.17 and 4.18). Upstream, the major P source is likely to be the continuous discharge consents (section 3.2.1) with additional contributions from fertilisers and geogenic P. The strength of the relationship between SRP and TP, as described by the regression co-efficient (R^2), for the upstream Hogsmill is stronger than that for the upstream Bourne and this is probably because of continuous minor sewage inputs mentioned previously (Figure 4.17). Downstream, there is particularly good correlation between P species because of the dominant STW source (Figure 4.18).

	Mean			Flow weighted mean		
	U/S (1)	D/S (2)	U/S:D/S % Difference	U/S (1)	D/S (2)	U/S:D/S % Difference
SRP	0.25	1.43	82.52	0.21	1.25	83.20
TP	0.31	1.59	80.50	0.28	1.45	80.69
TP:SRP % Difference	19.35	10.06		25.0	13.79	
T-test	< 0.001	< 0.001				
P <0.05	9.06E-05	4.03E-05				

Table 4.7 Hogsmill U/S (1) and D/S (2) mean and flow weighted mean and percentage differences between TP and SRP for all sampling dates. T-test indicates differences between TP and SRP both up and downstream are significant. See section 3.4 for flow weighted mean equation.

Table 4.7 shows that at U/S (1) mean TP concentrations are larger than SRP concentrations by an average of 19%; the maximum difference between these species is 55.8%. At D/S (2), TP exceeds SRP by an average of 10.8%, the maximum difference is 60.6%. Flow weighted mean figures follow a similar pattern although the percentage differences are slightly higher, due to substantially increased downstream flows. The TP and SRP means are more alike downstream of the STW, supporting the hypothesis of a single dominant source of sewage derived P (Neal *et al.*, 2000b).

Exceptionally high % ratios of SRP: TP, as seen in the downstream Hogsmill, are reported in literature, for example Jarvie *et al.* (2008a) found up to 83% of TP as SRP in streams which were heavily impacted by STW wastewaters and Neal *et al.* (2008) found SRP ratios of between 35 – 97% in the River Humber, U.K. Hogsmill P concentrations are much greater than E.A. recommended thresholds but this is not unusual in U.K. rivers as excessive P concentrations are frequently reported, for example, maximum SRP concentrations in the Froxfield and Shalbourne streams were 9.13 and 9.65 mg P l^{-1} respectively and

concentrations of up to 11.8 mg P^{-1} have been recorded for the River Humber (Neal *et al.*, 2005; Neal *et al.*, 2008).

4.3.2.4. River Hogsmill concentration and flow relationship

D/S (2) SRP and TP loads in the Hogsmill, Figures 4.14 and 4.16, suggest river flow strongly influences P downstream of the STW outflow before P-stripping commence on 1st April 2008. As discussed in relation to the River Bourne, 4.3.1.4, this is due to the use of downstream flow figures in the load calculations as Figures 4.13 and 4.15 depicting concentration only do not seem influenced by flow.

4.3.3. Comparison of P in STW and agricultural catchments

P species	U/S(1)	D/S(2)	D/S(4)	D/S(5)
SRP kg ha^{-1}	0.29	6.90	6.31	6.28
TP kg ha^{-1}	0.40	7.71	7.42	7.45

Table 4.8 River Bourne annual catchment outputs calculated using mean annual flows (kg P ha^{-1} $year^{-1}$). (D/S (3) is omitted as it relates to sediment samples only).

P species	Sampling period	U/S(1)	D/S(2)	D/S(3)	D/S(4)
SRP	Before P-stripping	0.40	11.80	12.07	11.86
	P-stripping	0.66	2.93	2.95	2.94
TP	Before P-stripping	0.51	11.32	11.32	11.18
	P-stripping	0.90	3.84	3.63	3.62

Table 4.9 Hogsmill river annual P catchment outputs calculated using mean annual flows (kg P ha^{-1} $year^{-1}$).

	Upper Hampshire Avon	Warwickshire Avon	Pevensey Levels	River Ant
Agriculture	0.31	1.06	0.88	0.80
SWT	0.28	2.25	5.12	0.18
Catchment size (km^2)	1249	2892	56	49.3

Table 4.10 Reported annual TP outputs from four U.K. catchments (kg P ha^{-1} $year^{-1}$). (Mainstone *et al.*, 2000).

Hard copy catchment maps for Hogsmill Valley and Chertsey STW, supplied by Thames Water plc. produced estimated catchment areas of 71.08 km^2 and 25.11 km^2 respectively. By applying these catchment area figures to the calculated daily STW P load figures, Tables 4.8 and 4.9, it is possible to compare STW outputs with those from agricultural sources. Hogsmill, prior to P-stripping, showed the highest P export figures. Since P stripping, the Hogsmill P export figures dropped below those of the Bourne, this is unsurprising as its

revised discharge consent permits a mean annual concentration of 1.0 mg P l^{-1} in wastewaters whilst for the Bourne it is 2.0 mg P l^{-1} (sections 3.2.1. and 3.2.2.).

TP outputs for the Bourne and Hogsmill are similar to those reported in literature (Table 4.10). Hogsmill outputs prior to P-stripping may be high in comparison to the examples in Table 4.10, because of its densely populated urban catchment. The Pevensey Levels, with a catchment of 56 km^2 and 84% of its TP budget originating from STW wastewaters is probably most similar to the rivers in this project (Mainstone *et al.*, 2000). STW derived P appears to be the dominant source in all but the most rural catchments, for example the River Ant where more than 80% of TP output is agricultural (Table 4.10).

4.4. Discussion and conclusions

Results from this study show significant differences in P concentrations up and downstream of the suspected input source for both rivers, the high ratios of SRP: TP downstream are consistent with STW derived P (Neal *et al.*, 2000b; May *et al.*, 2001). In the Bourne, treated wastewaters account for more than 80% of SRP concentrations, on average, during the study period. As upstream SRP was < LOD on 44% of sampling occasions, 100% of discernable SRP in the Bourne downstream of the STW on these sampling dates is derived from treated sewage wastewaters. Calculated TP loads in the Bourne are 2.79 kg TP day^{-1} upstream of the STW, increasing to 50.05 Kg day^{-1} downstream due to input of treated wastewaters which exceeded 26,900 m^3 day^{-1} during the study period.

In the Hogsmill, treated wastewaters supplied 89% SRP, on average, to the downstream Hogsmill before P-stripping was introduced from 1st April 2008. From 1st April 2008, downstream SRP concentrations fell from 1.78 mg SRP l^{-1} to 0.56 mg SRP l^{-1}. As the Hogsmill Valley STW discharged more than 62,800 m^3 day^{-1} of treated wastewaters to the receiving river, upstream calculated loads of 9.19 kg SRP day^{-1} increased to 208.42 kg day^{-1} before P-stripping, falling to 83.01 kg day^{-1} once P-stripping commenced. Almost 80% of TP upstream of the STW occurs as SRP, an unexpected finding which suggests additional sewage type inputs before the river reaches the STW.

Downstream P concentrations for the Hogsmill exceeded E.A. recommended limits for calcareous waters by some considerable margin until the introduction of P-stripping in April 2008. In the five month sampling period subsequent to the introduction of P-stripping there were significant reductions to P concentrations. Increased river flow, following heavy

rainfall, in June and July 2008 may be responsible for elevated P concentrations during this period, but they do not reach pre-P stripping levels. A longer sampling period would provide a more robust data set for assessment. The high proportion of wastewaters to downstream river water indicates that removal of even more P during sewage treatment would greatly benefit the riverine environment as concentrations remain high in comparison to the E.A guide value for rivers of this type, 0.20 mg P l^{-1} (Mainstone *et al.*, 2000).

The STW discharging to the River Bourne used a P-stripping process during the entire sampling period but P concentrations in the Bourne exceeded E.A. guidelines on three occasions. However, as the mean annual discharge consent for this river is 0.20 mg P l^{-1}, a greater P allowance than the Hogsmill, it remains within its current regulatory parameters (A. Wallis, Thames Water plc. pers. comm., 2007). The proportion of wastewaters to river water in the downstream Bourne is generally lower than the Hogsmill, but during periods of low base flow this ratio may increase to ≈80%.

Agricultural sourced P, from manure and fertilisers, remains a major contributor of P to U.K. rivers (Hooda *et al.*, 1997; McGrechan *et al.*, 2005). In terms of nutrient contributions to rivers it differs from STW derived P, being generally diffuse in origin, and major inputs are seasonal, occurring as major run-off events following applications of fertilisers or slurries to land and subsequent rainfall (Edwards & Hooda, 2008). However, field drains may provide lesser, continuous, point source inputs (Hooda *et al.*, 1999). Agricultural sourced P usually occurs in particulate form and is less immediately bioavailable that STW derived SRP (Salvia-Castellví *et al.*, 2005). The majority of agricultural P enters the river system during periods of storm related high river flows, so its ecological impact is greatly reduced as it is rapidly transported downstream (May *et al.*, 2000).

As agricultural derived P is frequently diffuse in origin and may not discharge directly into rivers it can be difficult to compare with point source inputs such as STW wastewaters. Edwards & Withers (2008) found farmyard run-off ranged between 0.02 – 247 mg TP l^{-1} and pig slurry between 39.4 – 43.6 mg TP l^{-1} with mean concentrations of 30.80 and 41.10 mg TP l^{-1} respectively. In comparison, they found P concentrations reported in literature for STW wastewaters of < LOD – 13.10 mg TP l^{-1} with a mean of 2.90 mg TP l^{-1} (Edwards & Withers, 2008). If P concentrations are considered in isolation, agricultural inputs are greatest but, unlike SWT derived P, the agricultural sources were not continuous and not all TP would reach nearby rivers, being removed in the farmyard to bunded storage or adsorbed to soils during the run off process (Edwards & Withers, 2008). However, agricultural P

inputs may be continuous, Edwards & Hooda (2008) found TP of between 0.13 – 51.0 mg TP l^{-1} in open farmyard drains discharging continuously into a second order stream, providing 30% of the annual TP load from that catchment.

A better comparison may be obtained by expressing P in terms of catchment outputs and it seems logical that the relationship between STW and agricultural derived P is inverse; rural catchments, with lower population densities, discharge less treated STW wastewaters and more agricultural source P whilst in more urban areas where fertiliser or livestock derived P inputs are low, STW contributions are the main source of P to rivers.

There are no nutrient concentration limits within the WFD Directive but P levels should not unbalance the ecosystem and water-bodies must meet specified biological quality requirements deemed necessary to achieve "good ecological status" (E.C., 2000). U.K. guidelines categorise rivers like the Bourne and Hogsmill as good if mean annual concentration levels are 0.12 – 0.25 mg SRP l^{-1}, moderate at 0.25 – 1.0 mg SRP l^{-1} and poor at more than 1.0 mg SRP l^{-1} (UKTAG, 2006). Using these parameters, both the Bourne and Hogsmill are good upstream and the Bourne is moderate downstream. Downstream, the Hogsmill was poor at the start of this project but, following the introduction of P-stripping, it looks likely to achieve moderate status. Moderate status is insufficient in terms of compliance with the WFD, to achieve good status it will be necessary to further reduce the amount of P in discharged wastewaters.

5. Phosphorus speciation and fractionation

5.1. Introduction

Chapter 4 quantified the effect of treated sewage wastewaters on receiving river TP and SRP concentrations and the relationship between them. The aim of this chapter is to examine differences in P speciation and size fractionation in the water column up and downstream of STW wastewaters discharge points on the Rivers Bourne and Hogsmill.

Bioavailability of P depends on its speciation and dominance of one species aids identification of its source and potential impact on the receiving water body. It is therefore appropriate to differentiate between P species within the water column when investigating the environmental effect of nutrient rich treated sewage wastewaters. However, it can be misleading to discount P species which are not immediately bioavailable as they (e.g. organic-P, particulate-P) may undergo chemical transformation which renders them bioavailable e.g. through mineralisation and desorption/dissolution (Benitez-Nelson, 2000). Also, certain compounds within organic, soluble unreactive or non-reactive phosphorus (SUP/SNP) such as phospholipids and glucose-6-phosphate are readily digested by species of marine bacteria to the extent that almost all of SNP becomes bioavailable (Benitez-Nelson, 2000). SRP is considered the most bioavailable species, being easily assimilated by phytoplankton and bacteria. Particulate P (PP) may mineralise, becoming bioavailable, but the proportion of PP that does so can be highly variable and difficult to quantify (Ellison & Brett, 2006). Therefore, SRP is not the only bioavailable P species within the water column, the area of water above the channel bed, as P from the species described above (SNP, PP etc.) may remobilise. In this study, river water samples were collected from one depth of water, Section 3.3.1.1. Both Ellison & Brett (2006) and Hilton *et al.* (2006) promote the use of SRP over TP as an indicator of nutrient status as do other authors cited within this thesis e.g. Jarvie (2006), Neal (2008), House (1997) and Withers (2002) . Individual authors adopt a range of descriptors to define P species within their research, those utilised within this study are:

- Total phosphorus (TP): comprising all forms of phosphorus present in a sample; in this project it is determined by digesting unfiltered river water with sulphuric acid and potassium persulphate before colorimetric analysis (USEPA Standard

Methods for the Examination of Water and Wastewater; HACH DR2500 instruction manual). As TP concentrations include species of P which are not readily available to biota, researchers additionally use more selective analysis of P species to demonstrate potential bioavailability.

- Total dissolved phosphorus (TDP): contains organic and inorganic forms of dissolved P and is determined by filtering river water samples through 0.45 μm cellulose nitrate filters before digestion and analysis as per TP.
- Particulate P (PP): undissolved organic and inorganic P fractions too large to pass through a 0.45 μm filter, i.e. associated with particulate (organic and inorganic) material ≥ 0.45 μm; usually determined by subtracting TDP from TP.
- Soluble reactive phosphorus (SRP): monomeric inorganic phosphorus in solution: SRP concentrations are obtained by filtering a water sample, usually through 0.45 μm, to remove particulates, subsequent analysis identifying the reactive soluble component (Jarvie *et al.*, 1988).

5.2. Materials and methods

River water samples were collected up and downstream of STW outfalls discharging into the rivers Bourne and Hogsmill (Figures 3.2 and 3.4) over an eighteen month period between February 2007 and Augusts 2008, 49 (Hogsmill) and 47 (Bourne) sampling visits took place to cover a range of weather and river flow conditions.

For TP, unfiltered river water samples were first digested with potassium persulphate and for SRP samples were filtered through 0.45 μm cellulose nitrate filters before both batches were analysed using an ascorbic acid modified molybdate reagent, as described in Section 3.5. (Allen 1974; Rowland *et al.*, 1997). Optical density of the samples was obtained using an HACH DR2500 colorimeter at 880nm. Analysis for TDP was carried out on filtered water samples, digested as for TP, using VG PlasmaQuad Inductively Coupled Plasma Mass Spectrometer (ICP-MS). The difference between TP and TDP was assumed as PP, and that between TDP and SRP as dissolved organic P (DOP).

When considering results for individual P species in this study, it is important to note that whilst SRP and TP were determined by colorimetry, TDP values were obtained using ICP-

MS. It is possible that operational differences between the analyses may render comparisons at low concentration levels unreliable.

5.3. Results and Discussion

5.3.1. P species data for Bourne and Hogsmill

	SRP	TDP	TP	PP
U/S (1)	0.078	0.023	0.104	0.081
D/S (2)	0.45	0.49	0.72	0.28
D/S (4)	0.39	0.44	0.71	0.27
D/S (5)	0.39	0.44	0.73	0.29

Table 5.1: River Bourne flow-weighted mean concentrations (mg P l^{-1}). PP concentrations do not represent the difference between the TP and TDP values shown in this table, being the TP and TDP flow weighted means are for the maximum number of sampling occasions for each species. PP was calculated on sampling dates when both TP and TDP were analysed, n=18. See section 3.2.2. for sampling locations and section 3.4 for flow weighted mean calculation.

Species	Location	No of samples	R^2	t-test result	$P < 0.05$
SRP:TDP	U/S (1)	31	0.15	2.79E-04	< 0.001
	D/S (2)	31	0.78	0.1600	N/S
	D/S (5)	31	0.66	0.1501	N/S
TP:TDP	U/S (1)	18	0.09	8.11E-06	< 0.0001
	D/S (2)	18	0.83	4.39E-07	< 0.0001
	D/S (5)	18	0.77	9.65E-08	< 0.0001
TP:SRP	U/S (1)	34	0.27	3.17E-07	< 0.0001
	D/S (2)	34	0.80	2.30E-13	< 0.0001
	D/S (5)	34	0.84	2.61E-13	< 0.0001

Table 5.2: River Bourne comparison between P species (results < LOD are excluded). R^2 provides an indication of the strength of interdependency between the two variables. Paired t-tests show the likelihood of significant difference between P species, $P < 0.05$. Sampling locations shown in section 3.2.2.2.

	SRP	TDP	TP	PP
U/S (1)	0.22	0.21	0.29	0.084
D/S (2)	1.99	1.96	2.23	0.27
D/S (3)	2.03	2.02	2.21	0.19
D/S (4)	2.03	2.01	2.20	0.19

Table 5.3: River Hogsmill flow weighted mean concentrations (mg P l^{-1}) for sampling period (31/7/07 – 27/2/08), n=18. See section 3.2.1. for sampling locations and section 3.4 for flow weighted mean calculation.

Species	Location	No. of samples	R^2	t-test result	$P < 0.05$
SRP:TDP	U/S (1)	33	0.55	0.7747	N/S
	D/S (2)	33	0.87	0.4510	N/S
	D/S (4)	33	0.83	0.5420	N/S
TP:TDP	U/S (1)	18	0.63	0.0024	< 0.005
	D/S (2)	18	0.78	0.0549	N/S
	D/S (4)	18	0.83	0.1895	N/S
TP:SRP	U/S (1)	35	0.82	0.0001	< 0.001
	D/S (2)	35	0.96	4.03E-05	< 0.0001
	D/S (4)	35	0.98	4.76E-04	< 0.0005

Table 5.4: River Hogsmill downstream comparison between P species (results < LOD are excluded). R^2 provides an indication of the strength of interdependency between the two variables. Paired t-tests show the likelihood of significant difference between P species, $P < 0.05$. Sampling locations shown in 3.2.1.2.

A summary of results and statistical analysis is displayed in Tables 5.1 – 5.4 for the Rivers Bourne and Hogsmill. Like TP and SRP discussed in Chapter 4, TDP and PP increase by an order of magnitude downstream of the STW outflow. The comparative relationship between individual species is considered in further detail in the sections below.

5.3.2. Total dissolved phosphorus

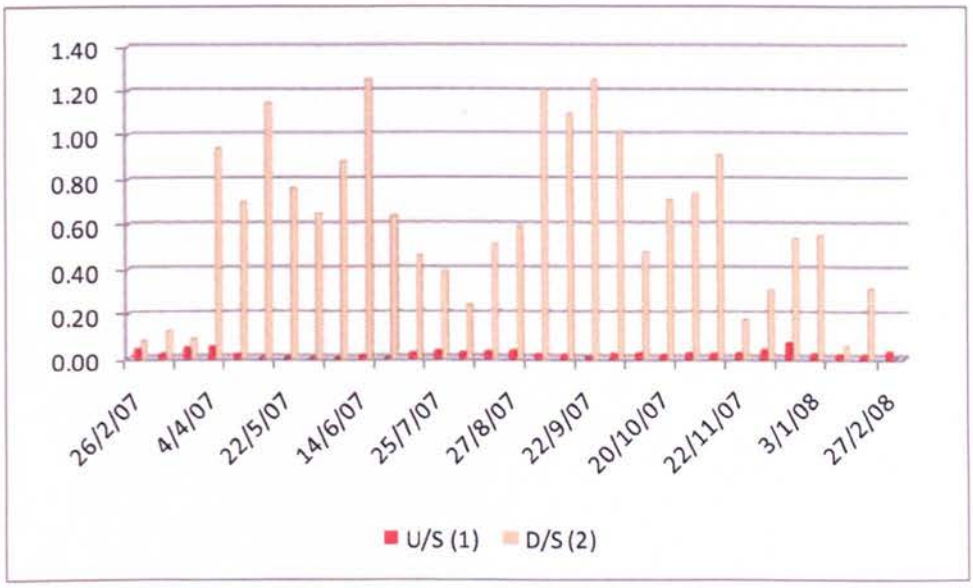

Figure 5.1: River Bourne TDP U/S (1) and D/S (2) (mg TDP l^{-1}). TDP concentrations in samples from the upstream Bourne may be understated due to low concentrations close to the ICP-MS LOD of 0.033 mg P l^{-1}. Sampling locations shown in section 3.1.2.2.

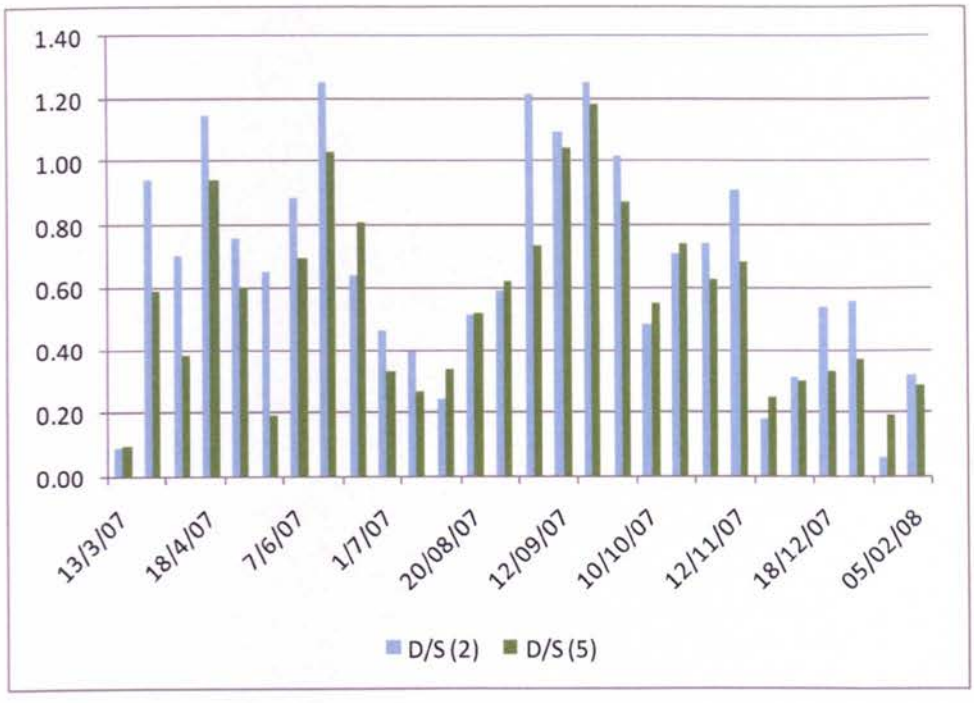

Figure 5.2: River Bourne TDP comparison of D/S (2) and D/S (5) (mg TDP l^{-1}). On 20 of 28 sampling occasions D/S (2) TDP was greater than D/S (5). Sampling locations shown in section 3.2.2.2.

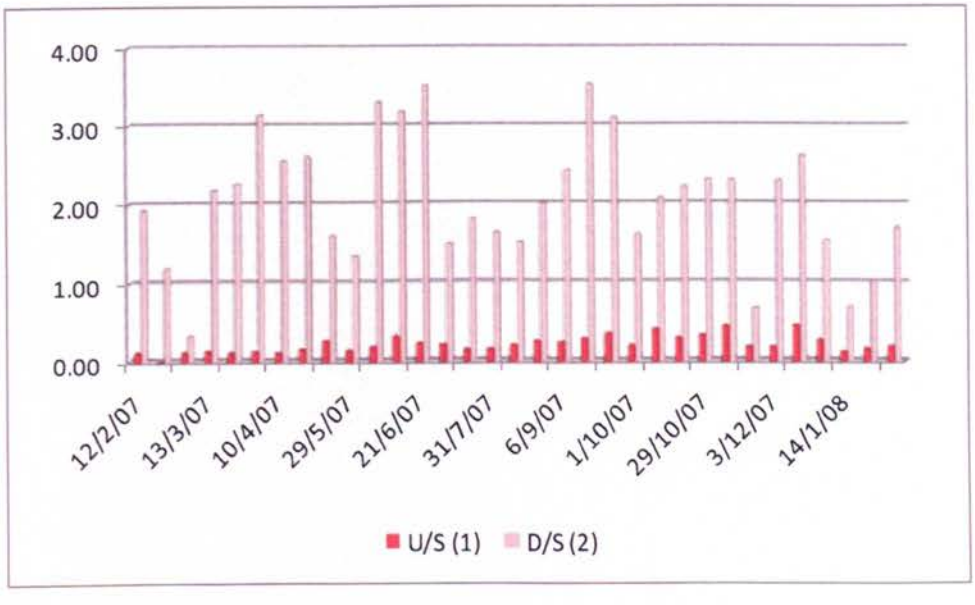

Figure 5.3: River Hogsmill upstream TDP U/S (1) and D/S (2) (mg TDP l^{-1}), downstream concentrations are an order of magnitude greater than upstream. Sampling locations shown in section 3.2.1.2.

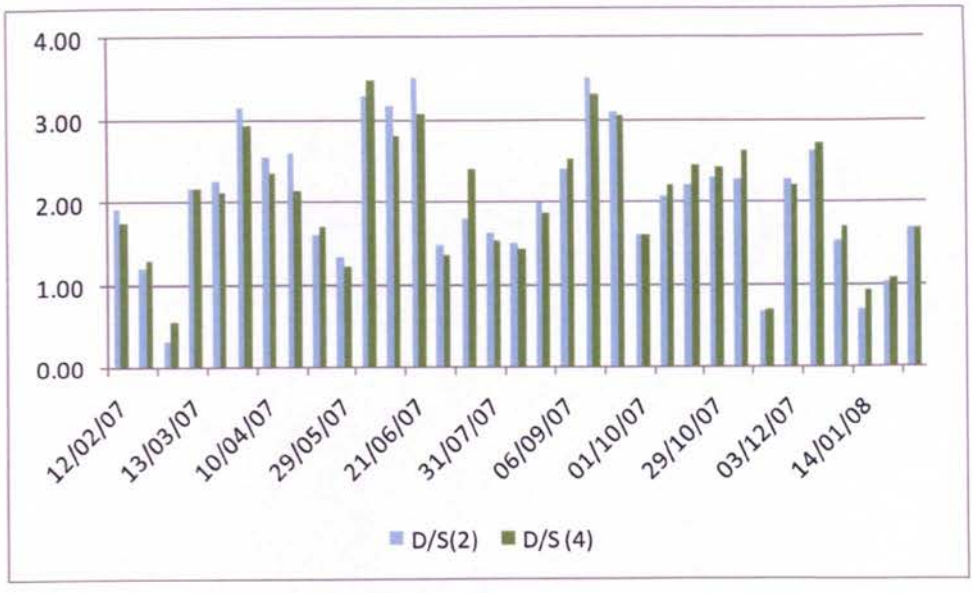

Figure 5.4: River Hogsmill TDP comparison of D/S (2) and D/S (4) (mg TDP l^{-1}). For 22 of 33 samples, D/S (4) TDP was greater than D/S (2). Sampling locations shown in section 3.2.1.2.

As stated previously, downstream TDP concentrations are an order of magnitude greater than those upstream of the STW outflow for both rivers (Figures 5.1 and 5.3). The discrepancy between Bourne upstream TDP and SRP flow-weighted means, where TDP should be greater than SRP but is significantly less, may be due to analytical error when P concentrations are close to the LOD of 0.033 mg P l^{-1} as TDP is greater than SRP on the Hogsmill, where upstream concentrations are greater by an order of magnitude (Tables 5.1. & 5.3.).

Flow weighted means for P species in the upstream Hogsmill are up to an order of magnitude greater than those in the Bourne (Tables 5.1. & 5.4.) except for PP which, although similar, is likely to be inaccurate in the Bourne for reasons discussed in the preceding paragraph. Unlike the upstream Bourne, SRP and TDP flow-weighted means for the upstream Hogsmill are similar and the T-test result in Table 5.4 indicates that there is no significant difference between these species. TP is up to 34% greater than either TDP or SRP in the upstream Hogsmill, suggesting that the ratio of dissolved to particulate P found in this river is 2:1.

For around two-thirds of sampling occasions, TDP concentrations are greatest at the downstream sampling point, D/S (2), closest to the STW outflow on the River Bourne (Figure 5.2) but for the Hogsmill only one-third of samples are highest at D/S (2) (Figure 5.4).

River Bourne flow-weighted means in Table 5.1 show similar decreases in concentration for TDP and SRP of 0.05 – 0.06 mg P l^{-1} by D/S (4) although flow weighted TP concentrations remain similar. The increasing difference in the Bourne between TP and SRP or TP and TDP concentrations downstream indicates that dissolved P is adsorbing to particulate matter downstream of the outflow. It is possible that dissolution of PP occurs in the Hogsmill as the river flows away from the STW because SRP and TDP increase downstream whilst TP decreases, reducing overall concentrations of PP.

The comparative similarity between SRP and TDP for both rivers (Tables 5.1– 5.4) and the high proportion of dissolved P species within TP, indicates that the majority of P discharged from these STWs is in dissolved inorganic form. This finding, which has been reported in literature, indicates that the majority of P in STW wastewaters comprises the most bioavailable species (May *et al.,* 2001; Jarvie *et al.,* 2005; Neal *et al.,* 2005). This is a major difference from agricultural derived P, where TP may be upwards of five times that of SRP or TDP with PP, a less bioavailable species, the dominant fraction (Hooda *et al.,* 2000).

As discussed in Chapter 4, the effect of phosphorus stripping at the Hogsmill Valley STW from 1st April 2008 is visible in the Hogsmill results after this date but, as TDP analysis ceased before P stripping commenced, the effect on TDP and PP cannot be quantified here (Table 5.5). It is probable that TDP has diminished in proportions similar to SRP and TP.

Species	Location	Pre-P stripping	Post-P stripping	% reduction
SRP	D/S (2)	2.01	0.54	73%
TDP	D/S (2)	2.05	n/a	n/a
TP	D/S (2)	2.13	0.72	66%
PP	D/S (2)	0.27	n/a	n/a

Table 5.5: River Hogsmill flow-weighted means before and after P-stripping was introduced at STW from 1/4/08 (mg P l^{-1}). (Analysis for TDP was not carried out after 27/2/08). See section 3.2.1. for sampling locations and section 3.4 for flow weighted mean calculation.

5.3.3. Particulate phosphorus

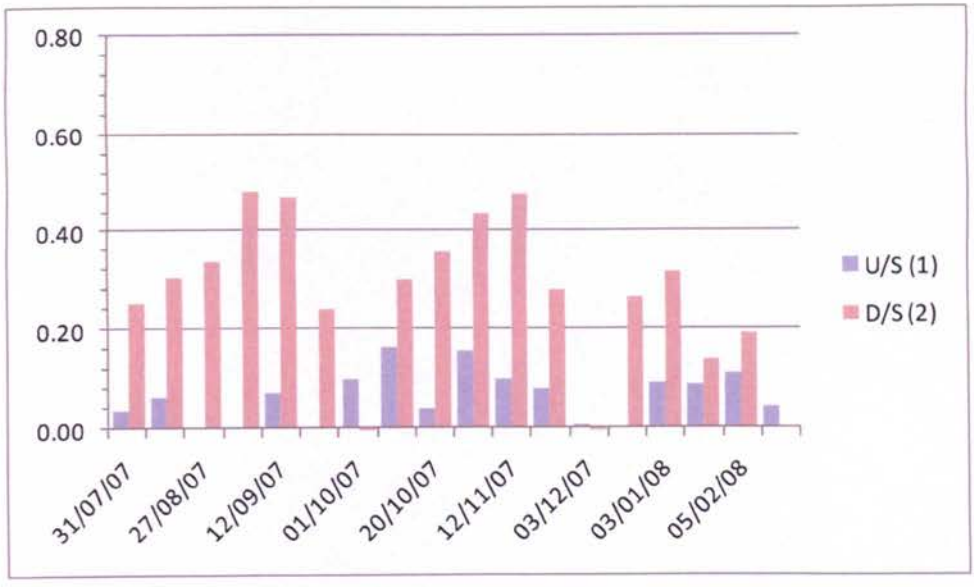

Figure 5.5: River Bourne calculated PP concentrations (PP = TP - TDP), upstream and downstream point closest to STW outflow (mg PP l^{-1}). Upstream PP concentrations may be overstated because upstream TDP concentrations were close to the ICP-MS LOD of 0.033 mg l^{-1} (see text below). Sampling locations shown in section 3.2.2.2.

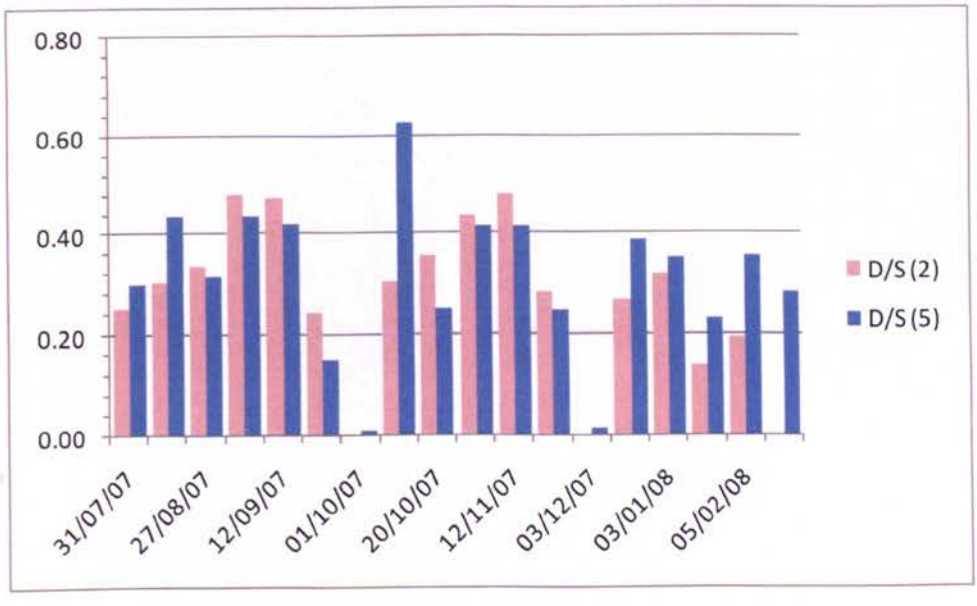

Figure 5.6: River Bourne calculated PP concentrations, comparison of downstream points closest to and furthest from STW outflow (mg PP l^{-1}). Sampling locations shown in section 3.2.2.2.

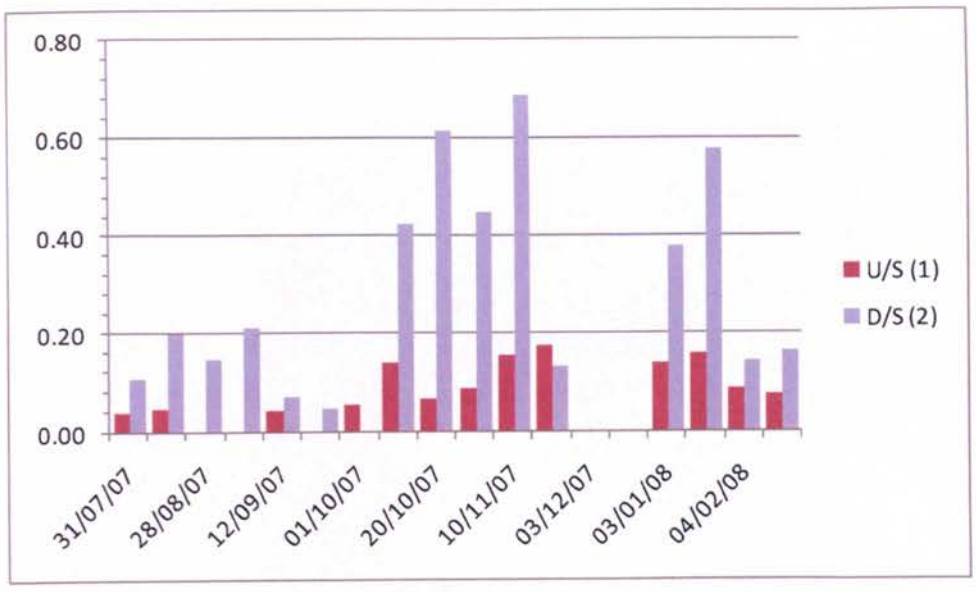

Figure 5.7: River Hogsmill calculated PP concentrations (PP = TP - TDP), upstream and downstream point closest to STW outflow (mg PP l^{-1}). On the sampling date 14/12/07, TDP concentrations are similar to TP concentrations, so PP is zero. Sampling locations shown in section 3.2.1.2.

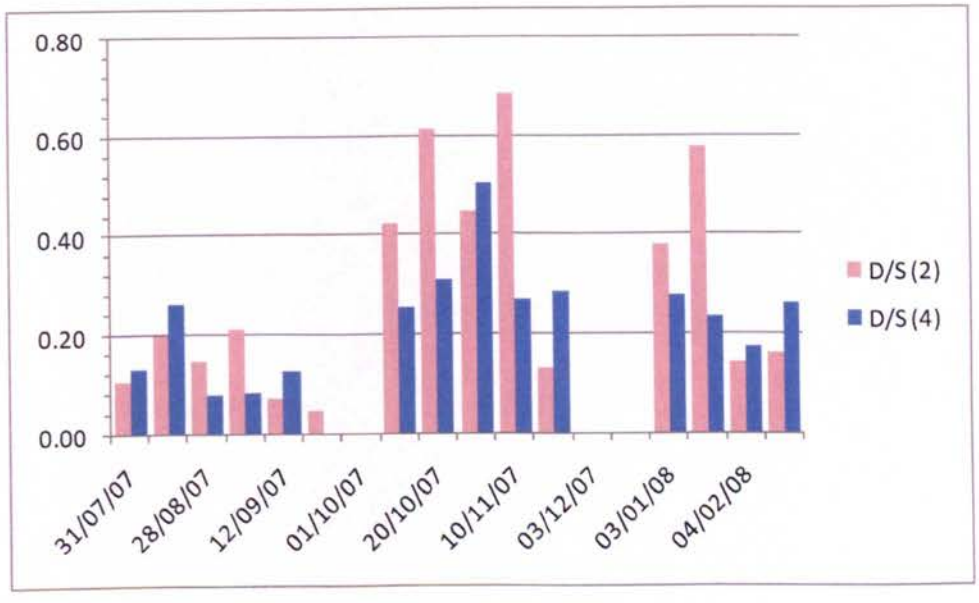

Figure 5.8: River Hogsmill calculated PP concentrations, comparison of downstream points closest to and furthest from STW outflow (mg PP l^{-1}). On sampling dates 1/10/07 & 14/12/07, TDP concentrations are similar to TP concentrations, so PP is zero.Sampling locations shown in section 3.2.1.2.

PP concentrations for this study are calculated as the difference between TP and TDP; they are not a separately analysed P species. The weakness in this approach is apparent in upstream flow weighted mean for the Bourne where PP is 79% of TP, SRP is 63% of TP and TDP is 21% of TP (Table 5.1 and Figure 5.5). Assuming upstream SRP and TP flow-weighted are accurate, the maximum possible Bourne PP value is 0.029 mg P l^{-1}, being the

difference between TP and SRP assuming all dissolved P is inorganic. The possibility of using SRP instead of TDP for PP apportionment is explored in 5.3.8. Upstream, the Hogsmill P fraction is compatible with other the P fractions (Table 5.3 and Figure 5.7), comprising around one third of TP.

Downstream of the STW Bourne PP concentrations, which are more closely allied to both SRP and TDP, increase with distance from the outflow and it is likely that dissolved P species are adsorbed to particulate matter in the water column as the river flows downstream (Figures 5.6 & 5.10). It is also possible that some P from the water column may be retained by the riverbed and bank materials. Unlike the Bourne, the Hogsmill flow-weighted PP means decreased by a third between the first and third downstream sampling sites as TDP increases and TP decreases, reducing the difference between these species (Figures 5.8 & 5.11). Reasons for the different pattern of P species between the rivers include the nature of sewage input, type of wastewater processing before discharge, river flow, underlying levels of particulate matter in the water column, composition of particulate and channel bed sediment and distance of downstream sampling points from the outflows.

5.3.4. TDP and PP

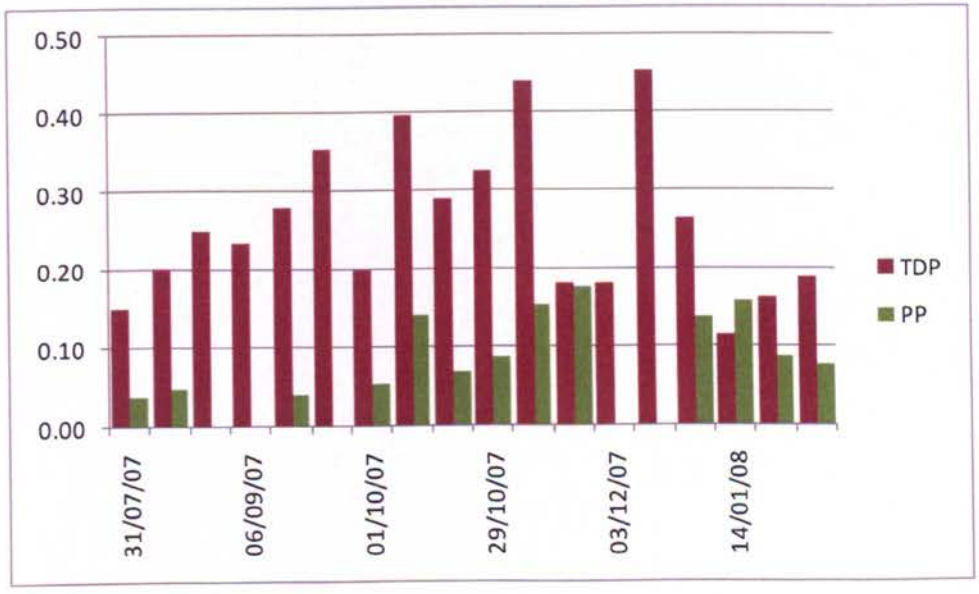

Figure 5.9: River Hogsmill U/S (1) TDP and PP comparison for period 31/7/07 – 28/2/08 (mg P l^{-1}). On a number of sampling occasions, TDP was similar to TP, so PP concetrations are zero. Sampling locations shown in section 3.2.1.2.

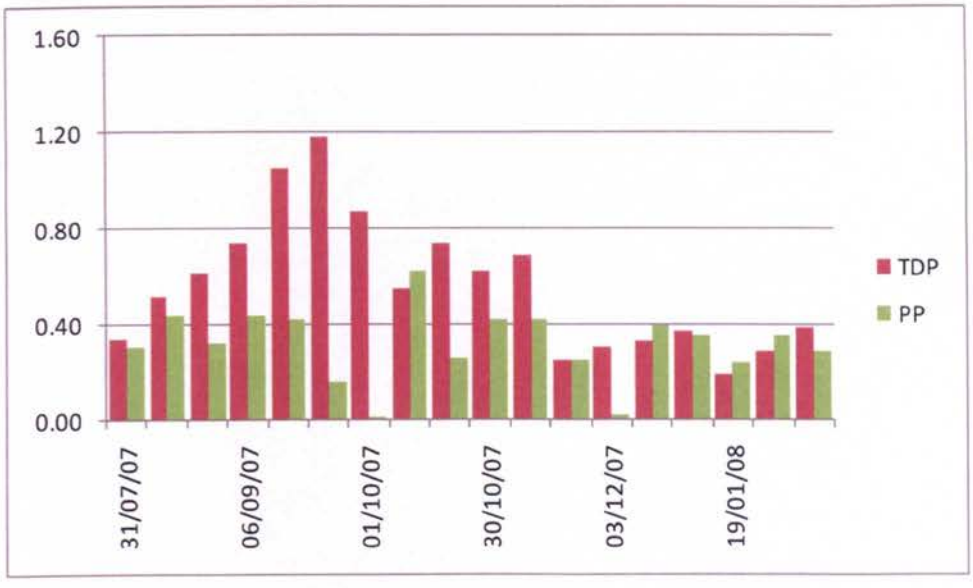

Figure 5.10: River Bourne D/S (5), TDP and PP comparison for period 31/7/07 – 28/2/08 (mg P l^{-1}). Sampling locations shown in section 3.2.2.2.

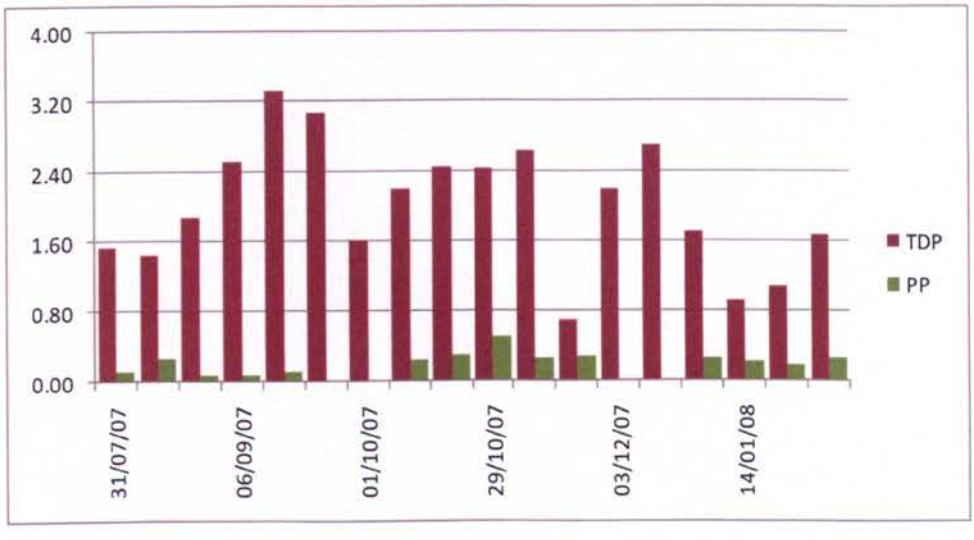

Figure 5.11: River Hogsmill D/S (4), TDP and PP comparison for period 31/7/07 – 28/2/08 (mg P l^{-1}). It is likely that P in treated wastewaters from the STW are filtered before discharge, hence the low concentrations of PP downstream of the outflow. Sampling locations shown in section 3.2.1.2.

As discussed in 5.3.3., because calculated PP data is dependent on accurate TP and TDP results the chart for River Bourne upstream TDP: PP comparison is omitted. The proportion of PP to TDP in the upstream Hogsmill is higher than that downstream (Figures 5.9 & 5.11), around 30% PP, which is similar to that reported for the River Dun in the Upper Thames area but lower than those of more pristine headwaters in the upper Cherwell basin where PP was 75% – 90% of the P fraction (Neal *et al.*, 2005; May *et al.*, 2001). In the downstream Hogsmill the proportion of PP falls from 12% to 9% of the TP fraction over the course of the three downstream points, whilst in the Bourne it increases from 34% to above 42% (Figures 5.10 and 5.11). The proportions of downstream PP:TDP for both rivers differs from that

reported in literature for rivers downstream of SWT outflows, both Neal *et al.* (2005) and May *et al.* (2001) report TDP as > 95% of the P fraction. Possible reasons for the difference between this project results and those published include underreporting of TDP concentrations in this project, greater quantities of particulate matter in this project's rivers, closer proximity of literature sites to the outflow than were accessible in this project and differences in the sewage treatment wastewater process affecting the propensity for wastewater derived P to adsorb to particulates.

5.3.5. TDP and SRP

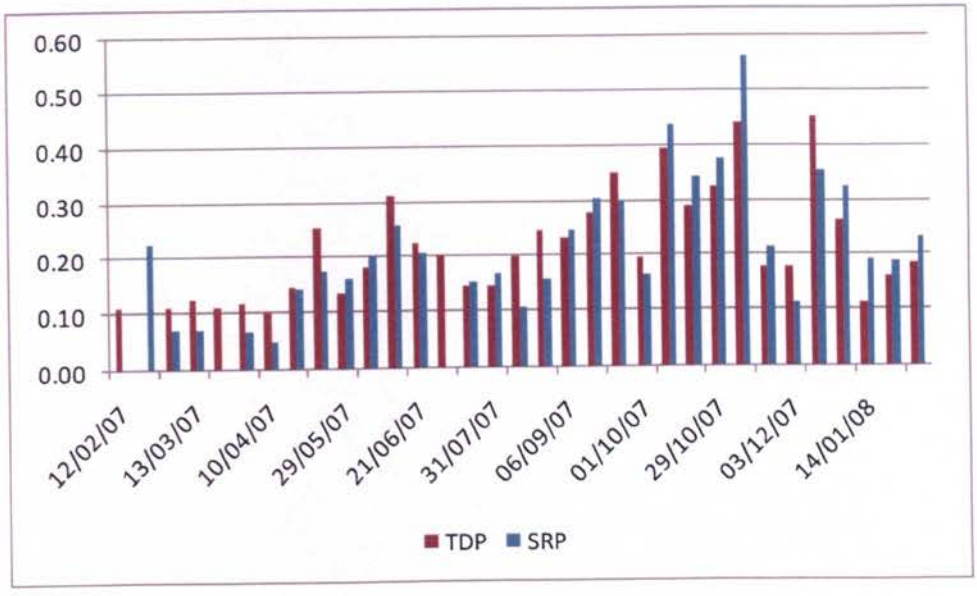

Figure 5.12: River Hogsmill upstream TDP and SRP comparison for period 12/2/07 – 27/2/08 (mg P l^{-1}). SRP and TDP flow weighted means are within 10% of each other and T-test indicates that concentrations are similar (t-test result is not significant at 0.7447). Sampling locations shown in section 3.2.1.2.

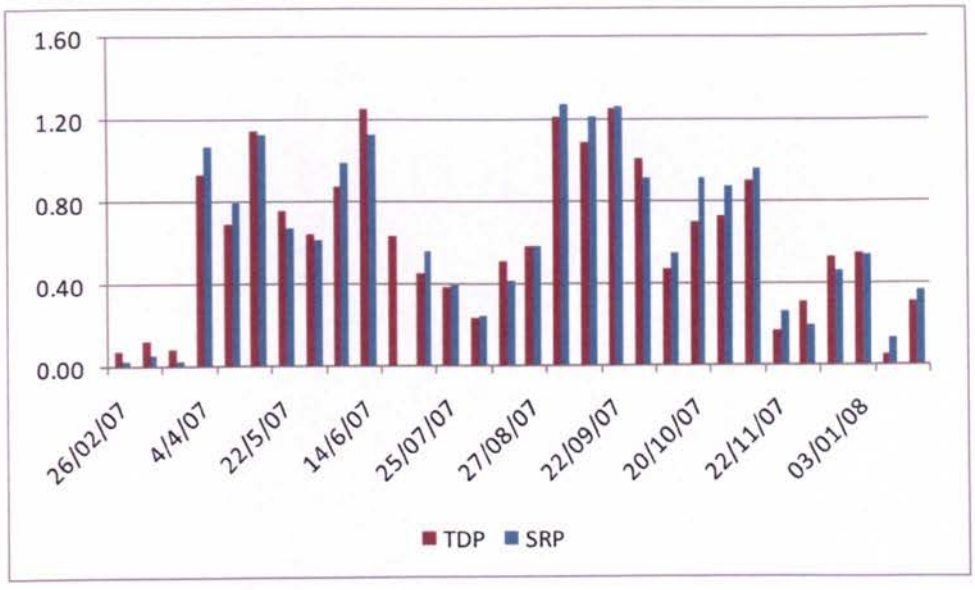

Figure 5.13: River Bourne D/S (2) TDP and SRP comparison for period 26/2/07 – 5/2/08 (mg P l^{-1}). T-test indicates that concentrations are similar (t-test result is not significant at 0.1600). Sampling locations shown in section 3.2.2.2.

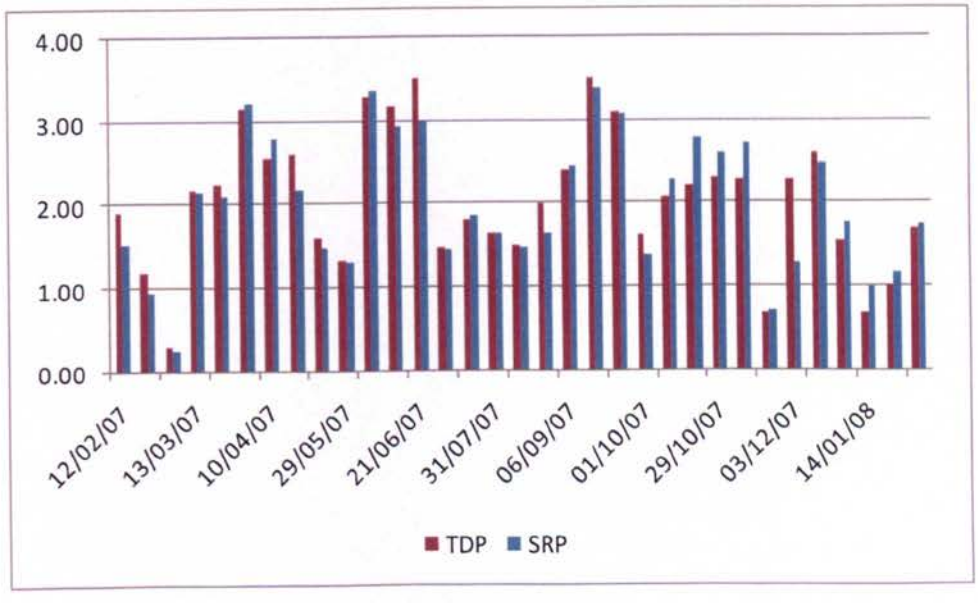

Figure 5.14: River Hogsmill D/S (2) TDP and SRP comparison for period 12/2/07 – 27/2/08 (mg P l^{-1}). T-test indicates that the concentrations are similar (t-test result is not significant at 0.4510). Sampling locations shown in section 3.2.1.2.

The upstream chart for River Bourne TDP/SRP comparison is omitted as data appears to be unreliable, most probably due to the proximity of upstream P concentrations to the LOD, as discussed in section 5.3.3. The River Hogsmill upstream data indicates TDP and SRP are not significantly different, and for individual sampling occasions concentrations are generally within 10% of each other (Figure 5.12). The similarity between SRP and TDP concentrations, along with cyclical changes to SRP and TDP concentrations, i.e. lower

concentrations January – April, increasing between July – October when underlying river flow is reduced, are consistent with patterns of STW wastewaters indicating a minor sewage source upstream although there is no operational STW upstream of the Hogsmill Valley plant (A. Wallis, Thames Water plc. pers. comm., 2009; Bowes *et al.*, 2009). The scatter plot of upstream Hogsmill concentrations (Figure 5.25) supports the conjecture that there are sewage inputs further upstream. The most likely source is an area comprising independently owned sports fields and a mobile home park in Tolworth, less than 3.5 km from the upstream sampling point, with E.A. discharge consents totaling $33m^3$ day^{-1} (J. Smith, E.A., pers. comm., 2009). In addition, intermittent discharge consents apply to 7 storm sewage overflows in Ewell and Chessington, close to the river's source and one close to this project's upstream sampling point at the Green Lane recreation ground (J. Smith, E.A., pers. comm., 2009).

Downstream, the similarity between TDP and SRP in both rivers is shown in Figures 5.13 and 5.14 where SRP and TDP concentrations are similar and t-tests are not significant.

5.3.6. TDP and TP

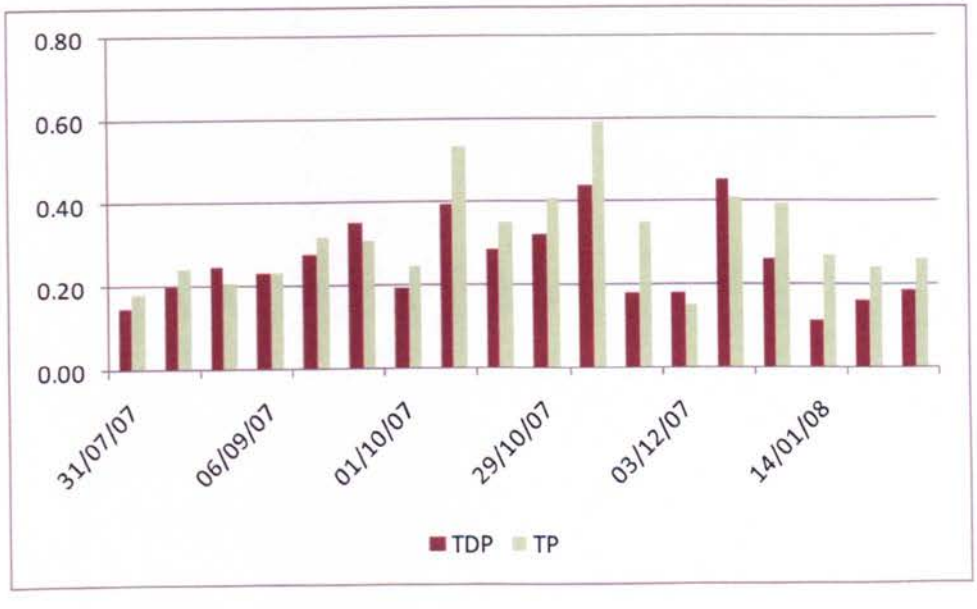

Figure 5.15: River Hogsmill U/S (1) TDP and TP concentrations (mg P 1^{-1}). T-test indicates significant difference between the species (t-test result is 2.37E-03, $P < 0.05$). Sampling locations shown in section 3.2.1.2.

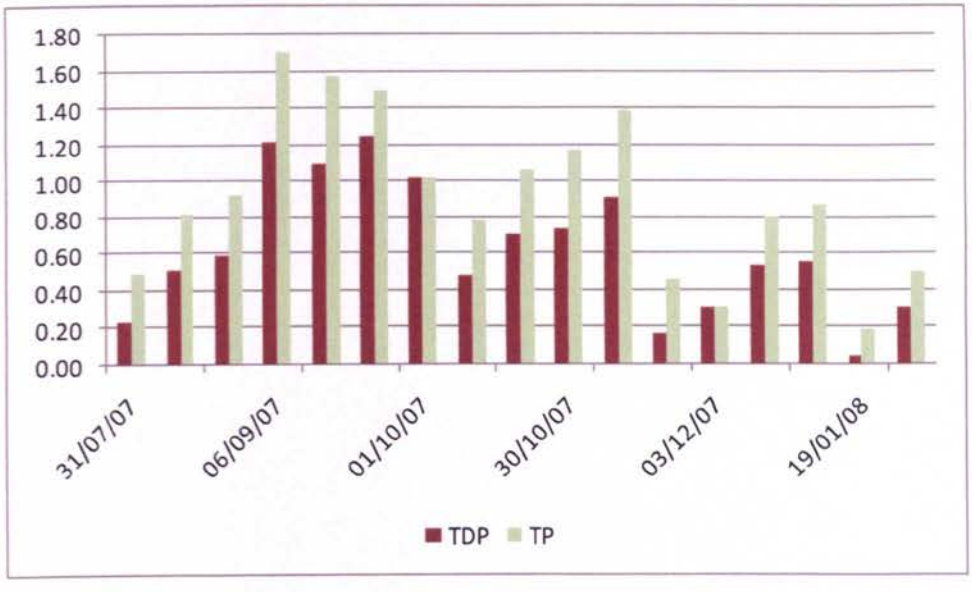

Figure 5.16: River Bourne D/S (2) TDP and TP comparison for period 31/7/07 – 5/2/08 (mg P l^{-1}). T-tests show a significant difference between TDP and TP at all downstream sampling sites (t-test result is 4.39E-07, $P < 0.05$). Sampling locations shown in section 3.2.2.2.

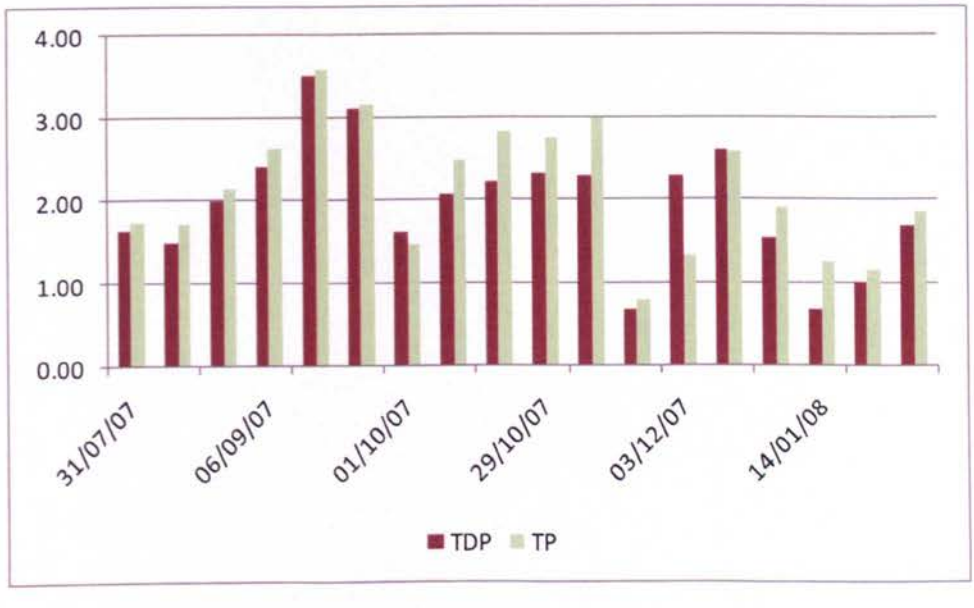

Figure 5.17: River Hogsmill D/S (2) TDP and TP comparison for period 31/7/07 – 5/2/08 (mg P l^{-1}). Unlike the Bourne, T-tests show no significant difference between TDP and TP at any downstream sampling sites (t-tes result is 0.0549, $P < 0.05$). Sampling locations shown in section 3.2.1.2.

Statistical analysis suggests that there is significant difference between TDP and TP in the upstream Hogsmill despite the fact that on a number of occasions concentrations appear similar (Figure 5.15). As discussed in 5.3.5, results indicate that there are additional sewage inputs upstream of this sampling point. Downstream, there is no significant difference

between TDP and TP at any of the sampling points, as results are similar just D/S (2) is shown (Figure 5.17).

T-tests indicate a significant difference between TDP and TP at all downstream Bourne sampling points with TDP accounting for around 79% of TP in the River Bourne (Table 5.2 & Figure 5.16). As discussed in 5.3.5., the majority of the dissolved P fraction is bioavailable SRP (Figure 5.13). The presence of additional particulate P in the Bourne may be linked to the physical characteristics of the channel bed, which is comprised of geogenic matter, except where it passes under the M3 and M25 motorways when it is concrete.

5.3.7. PP and SRP

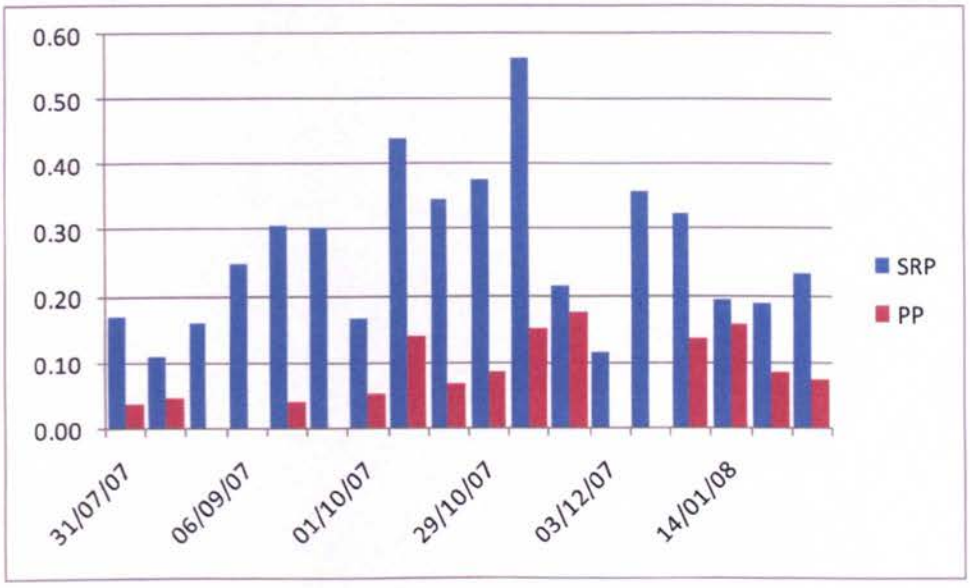

Figure 5.18: River Hogsmill U/S (1) PP and SRP comparison for period 31/7/07 – 5/2/08 (mg P l^{-1}). It is possible that sewage inputs upstream of the STW contribute SRP to the river. Sampling locations shown in section 3.2.1.2.

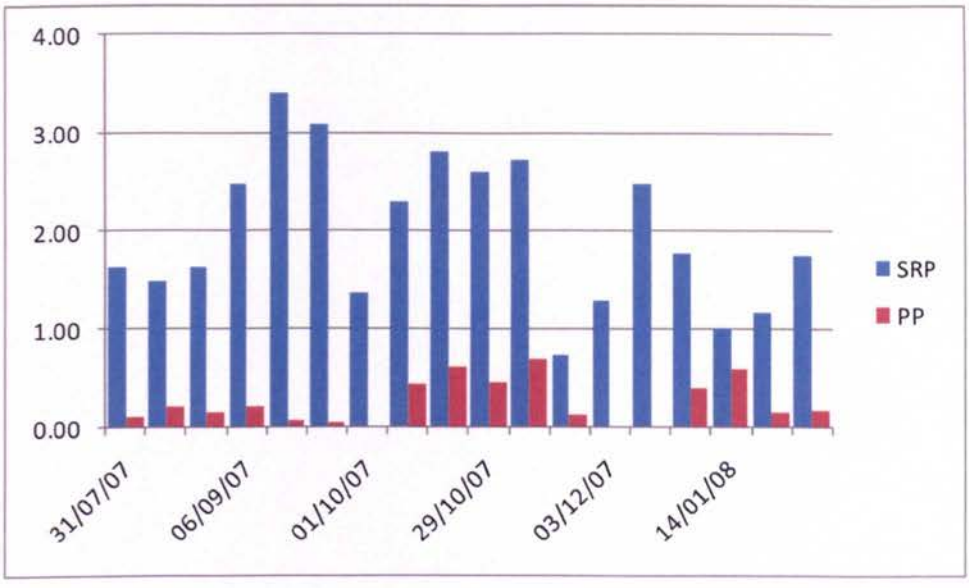

Figure 5.19: River Hogsmill D/S (2) PP and SRP comparison for period 31/7/07 – 5/2/08 (mg P l^{-1}). It is likely that treated wastewaters are filtered before discharge, resulting in high ratios of SRP to PP. Sampling locations shown in section 3.2.1.2.

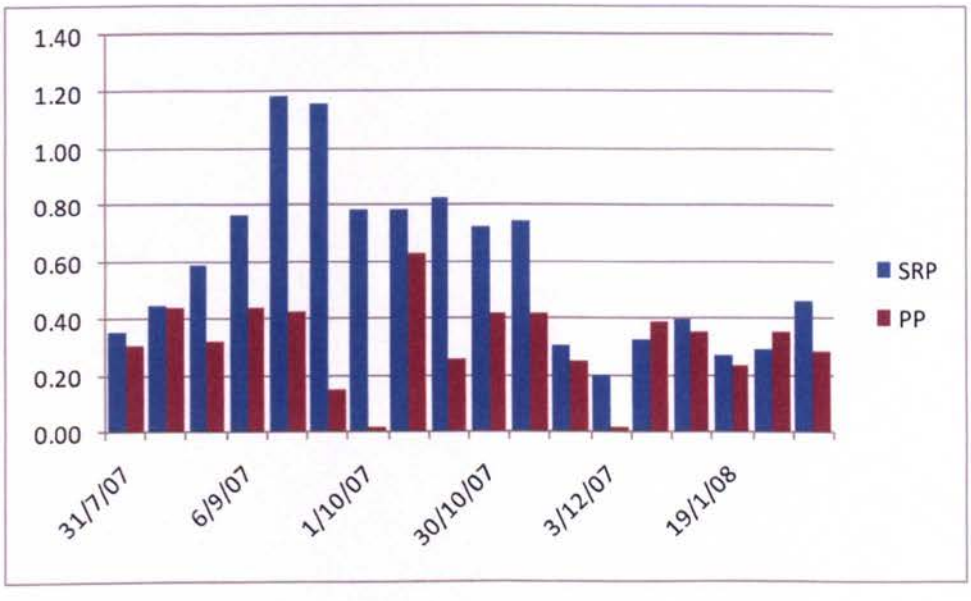

Figure 5.20: River Bourne D/S (5) PP and SRP comparison for period 31/7/07 – 5/2/08 (mg P l^{-1}). Higher ratios of PP to SRP in this river may be due to a more rural location and natural channel bed (than the Hogsmill). Sampling locations shown in section 3.2.2.2.

The proportion of PP to SRP in the Hogsmill downstream of the STW is lower than upstream (Figures 5.18 & 5.19). Unlike the Bourne, the Hogsmill is contained within a concrete channel for the majority of the stretch between D/S (2) and D/S (4), so river bed erosion is less likely to contribute particulate matter to the water column. In contrast, the concentrations of PP in relation to SRP in the Bourne increases downstream and D/S (5) where this is highest, is shown in Figure 5.20.

5.3.8. Use of SRP to calculate PP fraction for the River Bourne

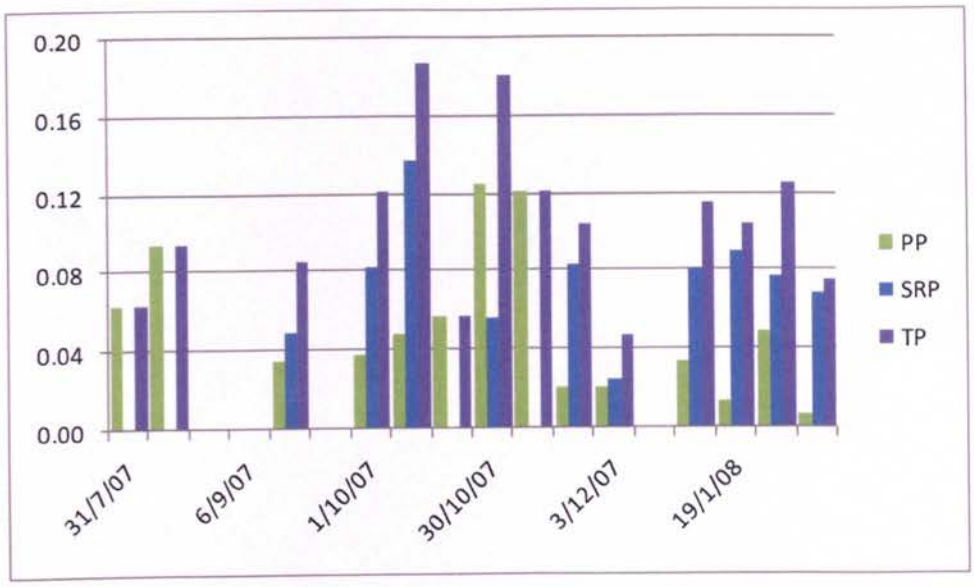

Figure 5.21: River Bourne U/S (1) P species (mg P l^{-1}). PP was calculated as the difference between TP and SRP to overcome the issue of analytical error in the upstream TDP results. On eight of eighteen sampling occasions SRP was < LOD. Sampling locations shown in section 3.2.2.2.

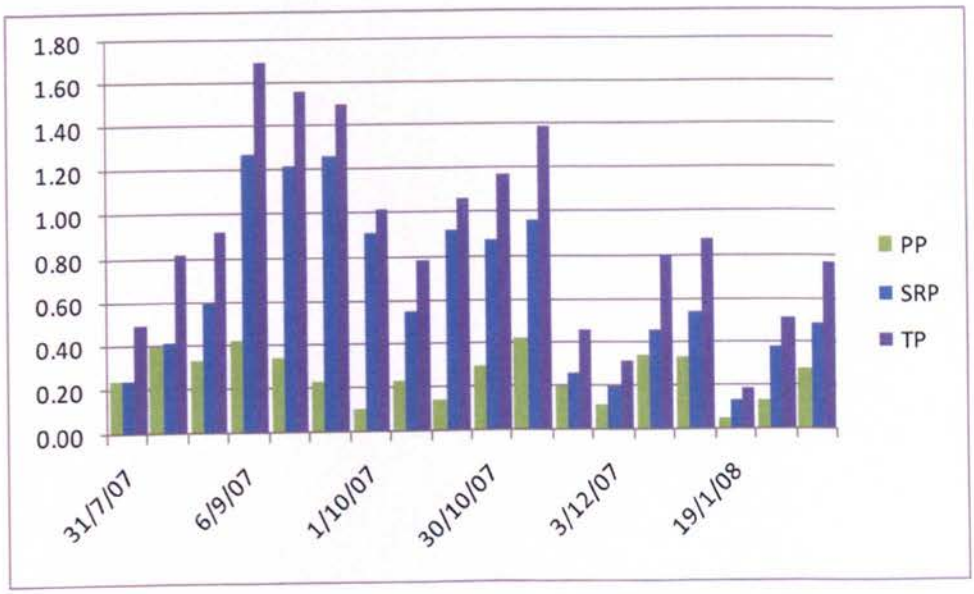

Figure 5.22: River Bourne D/S (2) P species (mg P l^{-1}). PP was calculated as the difference between TP and SRP to provide a direct comparison with the upstream results in Figure 5.21. Sampling locations shown in section 3.2.2.2.

To overcome the issue of inaccuracy in upstream TDP results for the River Bourne and to provide a comparison with the species pattern downstream, PP was calculated as the difference between TP and SRP to obtain the data presented in Figures 5.21 and 5.22. Justification for this approach can be found in literature, where SRP and TDP concentrations downstream of STW are frequently reported as being within 10% of each other, for example

Neal *et al.* (2005) found TDP between 4.7 – 10% greater than SRP at six sampling sites downstream of STW outflows, the mean being 6.6%. Results from a study of 22 sites in the River Cherwell catchment found TDP was 5 – 11% greater than SRP at sites downstream of STW, whilst PP < 2% (May *et al.*, 2001).

Site	PP 1	PP 2	PP3
U/S	0.085	0.04	0.04
Outflow	0.24	0.26	0.24
D/S 1	0.27	0.28	0.25
D/S 2	0.29	0.32	0.27

PP1 calculated as TP minus TDP
PP2 calculated as TP minus SRP for same sample dates as TDP (18 samples)
PP3 calculated as TP minus SRP for all TP sample dates (34 samples)

Table 5.6: Comparison of three different methods for calculating flow weighted mean PP (mg PP l^{-1}). See section 3.4 for flow weighted mean calculation.

Whilst unconventional, PP calculated using SRP produces an upstream flow weighted annual mean which is compatible with TP and SRP upstream means whilst not overly distorting downstream data (Table 5.6).

5.3.9. Interspecies relationships

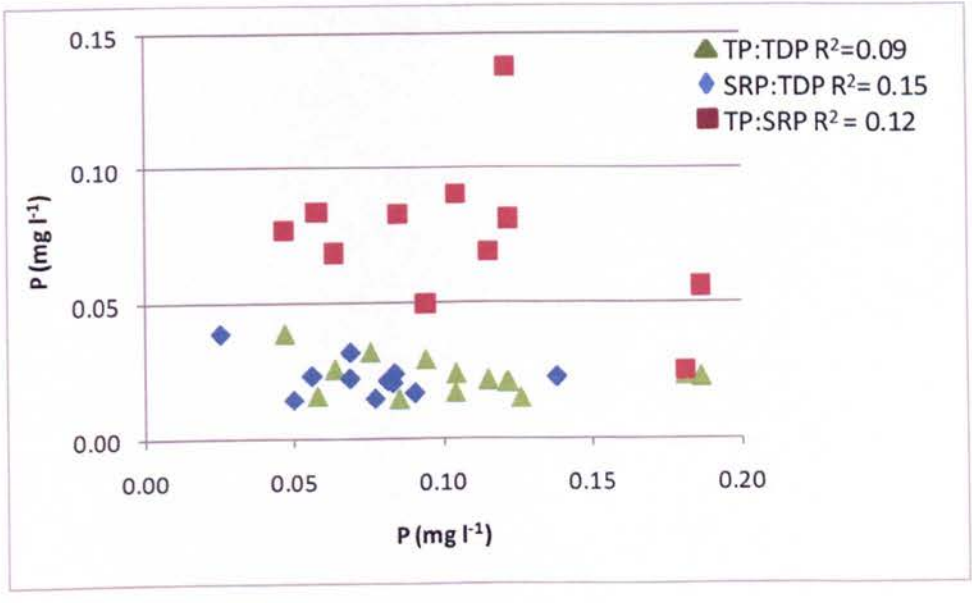

Figure 5.23: Scatter plot showing species relationships for Bourne U/S (1). Concentrations for the first comparator species are plotted on the X-axis, the second species on the Y-axis e.g. for TP: TDP the TP concentrations are read from the X-axis. (The data set is limited to 10 sampling occasions as values < LOD are omitted.) There does not appear to be a relationship between the species.

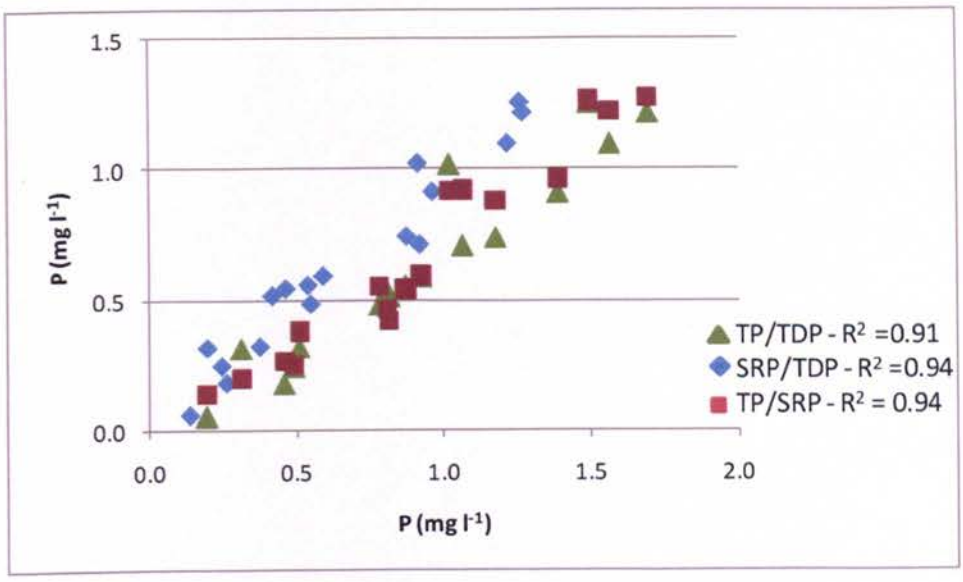

Figure 5.24: Scatter plot of River Bourne D/S (2) showing strong positive relationship between P species,inidcative of treated sewage wastewater inputs.

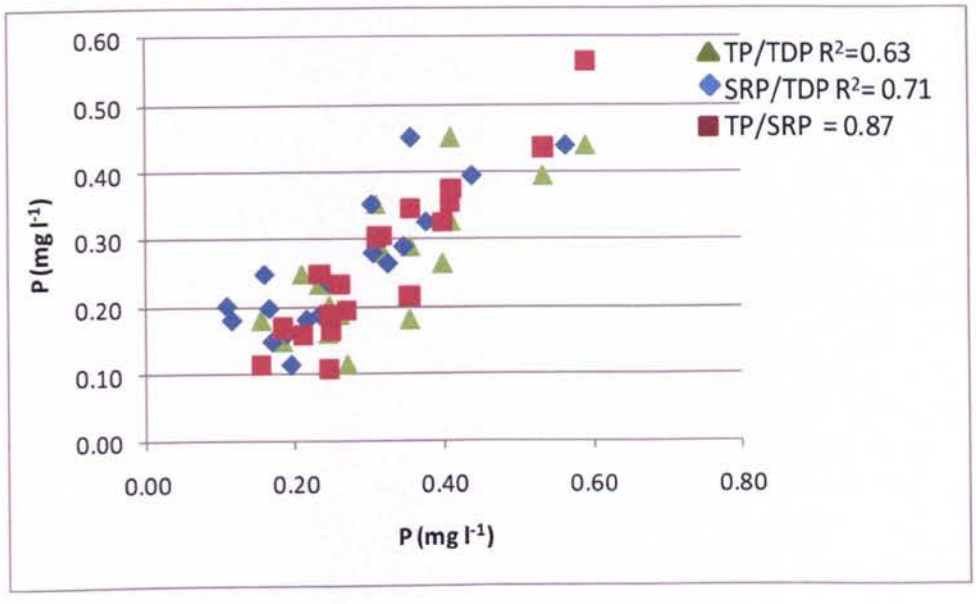

Figure 5.25: Scatter plot showing species relationships for the Hogsmill U/S (1). Interspecies relationships are strongly positive and indicative of sewage input.

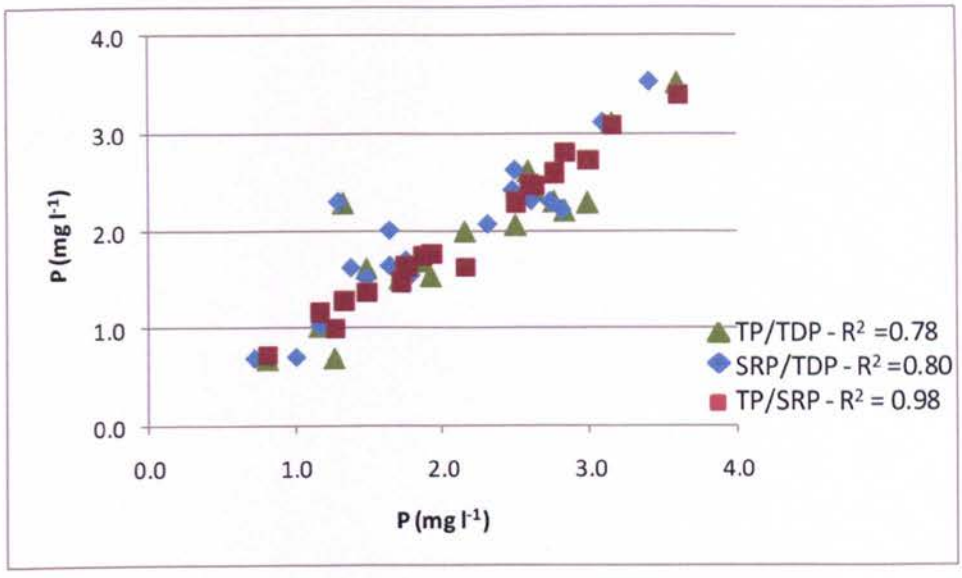

Figure 5.26: Scatter plot of River Hogsmill D/S (2) sampling site showing strong positive relationship between P species, indicating inputs of treated sewage wastewaters.

The scatter plot for the River Bourne U/S (1) (Figure 5.23) shows all P species concentrations below 0.15 mg P l^{-1}, yet these are high in comparison to unpolluted U.K. river concentrations of around 0.030 mg P l^{-1} (Mainstone & Parr, 2000). The absence of correlation between the three P species may indicate that a variety of small, diffuse inputs contribute P to the river e.g. agricultural run-off, septic tanks and storm overflows. In Figure 5.24, P concentrations increase by an order of magnitude and the relationship between them is highly dependent at $R^2 > 0.90$, indicating sewage wastewaters input.

The pattern of P species in the Hogsmill U/S (1) indicates sewage inputs, the most likely continuous source being sports fields and a mobile home park less than 3.5km upstream supplemented by intermittent inputs from storm sewage overflows (section 5.3.5). In the downstream Hogsmill the relationship between P species is highly dependent, P concentrations increase by an order of magnitude and the positive relationship between dissolved P species and TP is clear.

5.4. Size Fractionation

As manufacturing capabilities improve, utilisation of increasingly sensitive filtration equipment, to micro-filter samples, becomes feasible. Use of 0.45 μm cellulose nitrate filters is widespread, being a U.S.E.P.A. standard method for water quality, and facilitates comparison between research projects. However, some authors argue that this is an arbitrary boundary, claiming smaller filter pores provide a more accurate picture of solubility because some colloidal material passes through 0.45 μm filters (Hens & Merckx, 2002).

A further weakness, applicable to filtration generally, is that P fractions smaller than the filter pore size can become trapped on the filter, potentially underestimating concentration values although this may be reduced by sequential filtration, filtering small volumes and replacing filters regularly or by centrifuging samples (Shand, 2000; Lead *et al.*,1999).

	Hogsmill		Bourne	
	0.45 μm	0.10 μm	0.45 μm	0.10 μm
Mean (mg SRP l^{-1})	1.3238	1.3223	0.4395	0.4216
T-test , $P < 0.05$	not significant t-test result = 0.7868		not significant t-test result = 0.1343	
No. of samples	10	10	10	10

Table 5.7: Comparison of mean SRP concentrations within 0.45 and 0.10 μm filtered river water

Within this project, the intention was to filter river water samples from a random selection of ten site visits sequentially through 0.45 μm, 0.2 μm and 0.1 μm cellulose nitrate filters. It became apparent after four sets of water samples that 0.2 μm and 0.1 μm analyses were indistinguishable and the 0.2 μm filtration was discontinued. Table 5.7 summarises the results, the mean SRP concentration figures include upstream and downstream values for each river as t-tests for individual sample sites were not significant. Comparison of the complete data sets of forty values for the two filter sizes within each river showed similar concentrations, there being no significant difference between 0.45 μm and 0.10 μm filtrates.

5.5. Discussion

5.5.1. Species

Other researchers have encountered issues with analytical reliability and lack of distinction between P species (Neal *et al.*, 2000a & c; Haygarth *et al.*, 1997; Hans & Merckx, 2002; Shand, 2000). May *et al.* (2001) found anomalies in river water from one site on the Cherwell, although results for other sampling locations on the same river displayed P in the expected hierarchical sequence. The most likely reasons for a lack of species definition within this research project, which are most apparent in the upstream results, are lack of analytical sensitivity at low P concentration levels and incompatibility of inter-species comparison when using different analytical methods, although in most cases there is no option but use different methods.

The river Cherwell paper, cited above, found SRP contributed up to 93% TP at sampling sites downstream of STW (May *et al.*, 2001). Neal *et al.* (2000a) found mean concentrations

of TP comprised 94% TDP, the majority of which was SRP (93% of TP), and concluded that SWT wastewaters influenced SRP:TP ratios downstream of the outfall, upstream the ratio was 50:50. Salvia-Castellvi *et al.* (2005) also found high SRP: TP ratios downstream of STW inputs although this is not quantified in their publication. Domination of dissolved P species, particularly inorganic SRP, in the water column is a specific trait of STW wastewaters in comparison to agricultural inputs which carry high levels of particulate P (Jarvie *et al.*, 2006; Hooda *et al.*, 1997). Increased bioavailability of dissolved P species in receiving waters is a particular concern, causing overgrowth of macrophytes and unbalancing the riverine environment as discussed in Chapter 2.

Few research papers compare SRP and TDP, an exception, Haygarth *et al.* (1997), found similar values for SRP and TDP in water from the River Swale when analysis for both species was carried out using flow injection analysis (FIA). SRP analysis of the same sample, using the Murphy and Riley procedure similar to this project, did not correspond to SRP-FIA results and the authors concluded that this was due to operational differences between the two methods and because concentration levels were close to LOD.

5.5.2. Fractionation

Studies comparing P fractions are more frequently concerned with soils than water, Hens and Merckx (2002) analysed P in 1:10 soil solutions and found 2 – 4 times less SRP in samples filtered through 0.025 μm pore filters than 0.45 μm, but the difference between samples filtered through 0.45 μm and 0.22 μm was < 10%. Similarly, Shand (2000) found 4% less SRP in soil solutions filtered through 0.22 μm than 0.45 μm filters.

Haygarth *et al.* (1997) found no significant difference between SRP in river water samples filtered through 0.45 μm and 0.22 μm filters but did find a significant difference between 0.45 μm and filter sizes < 0.10 μm despite mean concentration values being within 10% of each other. P concentrations within Haygarth's study did not always decrease sequentially with filter pore size, for example 0.025 μm = 127 μg P l^{-1} but > 0.01 μm = 124 μg P l^{-1} (Haygarth *et al.*, 1997). Unsurprisingly, the greatest reductions occurred when samples were passed through 1,000 molecular weight (MW) filters, producing a mean concentration of 119.85 μg P l^{-1} (Haygarth *et al.*, 1997).

It has proved difficult to locate further research regarding microfiltration of water samples for P, perhaps because P is not a toxic element and the concentration differential between filtrates from varying filter pore sizes seems to be marginal in relation to the resource required for processing, so these results are considered alongside published finding for metals. Lead *et al.* (1999) report Cd and Cu concentrations in fraction sizes 0.005 – 0.5 μm, 0.5 – 1.0 μm and 1.0 μm metals from samples of water from the River Mersey (U.K.) to be more similar than they had anticipated. Yet in a study of boreal rivers in Siberia, Pokrovsky *et al.* (2006) found alkali and alkali earth metals were in a truly dissolved phase with < 30% concentration difference between ultrafiltrates but rare earth elements (REE) with a strong positive relationship to Fe and Al colloids showed concentration differences of > 50% between filtrates. Other papers report differences in the behaviours of individual elements over a range of fraction sizes linked to variables such a dissolved organic carbon (DOC), clay and humic substances and pH (Sigg *et al.*, 2000; Schäfer *et al.*, 2003; Lead *et al.*, 1999). This brief critique of literature demonstrates that it is difficult to use the results from ultrafiltration of other elements as comparators for this study because of their variability.

These findings, that neither the Hogsmill or Bourne display significant differences between filtrates, supports the hypothesis that P discharged in these treated wastewaters is primarily in dissolved form and has not greatly adsorbed to particulate matter at the sampling locations, as discussed in Chapter 2. Resource issues such as lack of sterile sampling and laboratory facilities and equipment shortfalls made filtration < 0.1 μm pore size impractical for this project, it may be that more conclusive results would have been obtained if this had been feasible.

5.6. Conclusion

Analysis of P by both colorimetry and ICP-MS, shows that SRP, TDP and TP increase downstream of the STW by an order of magnitude. In the Bourne, the flow weighted mean SRP concentration of 0.45 mg SRP l^{-1} is similar to the flow weighted mean TDP concentration of 0.49 mg TDP l^{-1} (Table 5.1). In the Hogsmill, flow weighted SRP and TDP concentrations are similar at between 1.96 – 1.99 mg P l^{-1} (Tables 5.3). Similarity between SRP and TDP concentrations downstream of a suspected point source input has been reported by other authors as indicative of treated sewage wastewaters discharge.

There is no significant difference between SRP and TP or TDP and TP in the Hogsmill (Table 5.4), a finding consistent with previous research in urban rivers receiving treated sewage wastewaters. Flow weighted mean PP concentrations decrease with distance from the Hogsmill STW; from 0.27 to 0.19 mg PP l^{-1}which may be the result of particulates becoming incorporated within channel bed sediments (Table 5.3). The high levels of dissolved, bioavailable P downstream of the Hogsmill Valley STW are likely to have a much greater impact on the receiving river in terms of excessive plant growth than similar quantities of agricultural derived P which occur predominantly in the less bioavailable, particulate form. The results used in this section of the study cover the period before P-stripping was introduced at the Hogsmill and it is possible that there is a greater proportion of PP in the river since P-stripping commenced as 90% of TP in the downstream Hogsmill before P-stripping was in the form of SRP, reducing to 66% of TP once P-stripping commenced.

In the Bourne, the flow weighted mean TDP concentration is around 32% lower than TP at all downstream sampling points (Table 5.1). PP concentrations are similar at all downstream points (Table 5.1). The difference in the proportions of PP to TP in the Bourne and the Hogsmill may be due to a number of factors such as P stripping being carried out at the Lyne Lane STW for the entire sampling period, because the Bourne catchment is more rural with organic inputs from field run-off and overhanging foliage or because the downstream Bourne is channelized for only a small section (100m, between sampling points D/S 3 &4, Figure 3.4) and remobilisation of some channel bed sediments occurs.

An unexpected finding is the high ratio of dissolved P to TP in the upstream Hogsmill, indicative of wastewaters input, which appears to be linked to a series of small discharge consents less than 3.5 km upstream of the STW.

A number of samples from both rivers were filtered through 0.45 μm and then 0.10 μm to establish whether colloidal material, which may reduce the bioavailability of SRP, was present in the 0.45 μm filtrate. SRP concentrations in these filtrates were similar, suggesting that there was no colloidal material in the 0.45 μm filtrate (Table 5.7). In his discussion of the sewage treatment process, Sutherland (2007) states that wastewaters undergo ultrafiltration before discharge, which may account for the result from this study.

In summary, it is clear that as the main species of P from treated sewage wastewaters are predominantly soluble and bioavailable they are likely to have a greater impact on the receiving river than P derived from agricultural sources where particulate P, a less bioavailable species, predominates.

6. Dissolved metals concentrations up and downstream of sewage wastewater outflows

6.1. Introduction

The purpose of this chapter is to consider concentrations for a range of metals up and downstream of STW sources and to assess whether wastewaters inputs increase underlying metals concentrations or, conversely, dilute upstream concentrations. The range of metals was selected on the basis of potential toxicity to biota (e.g. Pb, Cd, Cr, As) or possibility of increased concentrations from STW processing (Al, Fe or Ni) (Buzier *et al.*, 2006; Sörme & Lagerkvist, 2002). Some of the metals analysed (e.g. Cu, Mn, Zn, Fe) are micro-nutrients at low concentration but may be harmful in excess (Fraga, 2005). A number of samples were passed through 0.45 μm and 0.1 μm filters to see whether metals concentrations were significantly altered between the fraction sizes, i.e. to assess their association with colloidal material (< 0.45μm).

It is expected that some trace metals are naturally present in river water, being scoured from the river bed and endemic riverine biota are able to tolerate these underlying conditions including such metals. However, this does not mean that geogenic source metals cannot adversely affect biota, or render river water unpotable e.g. As, which mobilises in water between pH 6.5 – 8.5 is one of the most widely reported and problematic geogenic water contaminant metals worldwide (Mukherjee *et al.*, 2008). In the U.K. mobilisation of geogenic metals is not problematic in terms of drinking water, but anthropogenic metals inputs may alter the environment e.g. reducing numbers of more sensitive biota, allowing pollution tolerant species to thrive and, through bioaccumulation, increasing metals uptake in the food chain (Carvalho *et al.*, 1999). For example, following accidental discharge of metal rich acid mine-waters into the River Cannon, a study of the Fal estuary (U.K.) into which it flows, reports the absence of metals sensitive crustaceans *Corophium volutator* and *Cyathura carinata* which are usually common in U.K. estuaries and an exceptionally high abundance of small opportunistic annelid species (segmented worms) which are pollution tolerant (Warwick, 2001).

The sewage treatment process is not specifically designed to remove dissolved metals, but their propensity to adsorb to particulate matter results in removal of some metals during the

secondary stage of treatment when they become incorporated in cellular material during flocculation process (Lester, 1983). Efficiency of metals removal during sewage treatment is dependent upon many variables such as the physical properties of the metal, metal concentrations, species, plant technology and efficacy and processing period (Lester, 1983; Buzier *et al.*, 2009). Metals removal rates and concentrations in discharged wastewaters are variable, as discussed in the Literature Review, Chapter 2 and it is inarguable that some proportion of the dissolved metals intake is released in the treated effluent. A study of nine STWs in Paris concluded that whilst more than 70% of Cr and over 80% of total Al, Cu, Fe and Pb concentrations were removed from influent, and all dissolved Pb was removed, less than 47% dissolved Cr, Cu and Fe and less than 22% dissolved Al were removed. There was no reduction for dissolved Ni between the influent and effluent (Buzier *et al.*, 2008). It is reported that some tertiary treatments increase dissolved metals concentrations; Buzier *et al.*, (2006 & 2008), found dissolved Fe, Cu, Cr, Co and Ni concentrations increased following the addition of $FeCl_3$ reagent used to precipitate flocculation during the tertiary treatment and Sörme & Lagerkvist (2002) report increases in dissolved Ni, Cr and Zn during the treatment process.

6.2. Materials and methods

River water samples were collected up and downstream of STW outfalls discharging into the rivers Bourne and Hogsmill over a twelve month period between February 2007 and February 2008, 33 sampling campaigns for the Hogsmill and 31 for the Bourne were undertaken to cover a range of weather and river flow conditions. Samples were collected in acid washed bottles and, for dissolved metals analysis, approximately half of each sample was filtered through 0.45 μm cellulose nitrate filters; samples from 7 of the sampling campaigns were additionally passed through 0.1 μm filters. All filtered samples were transferred to 60 ml acid washed polyethylene bottles and acidified to < pH 2 using Aristar grade HNO_3 for storage at < 5°C until batch testing using inductively coupled mass spectrometry (ICP-MS), described in 3.5.1.

It is necessary to treat the results for Zn with caution as, partway through the sampling period, it became apparent that cellulose nitrate filter membranes are prone to irregular Zn contamination, although they were soaked in dilute HNO_3 and rinsed with deionised water once this issue had been identified the issue was not entirely resolved.

	Ni		As		Cd		Pb	
$\mu g\ l^{-1}$	Dissolved	Total	Dissolved	Total	Dissolved	Total	Dissolved	Total
U/S (1)	6.56	10.66	0.55	< LOD	0.11	< LOD	0.60	< LOD
U/S (1)	7.13	14.18	0.58	< LOD	0.36	< LOD	0.62	< LOD
U/S (1)	8.26	128.40	0.53	2.00	1.37	1.67	0.78	4.31
D/S (2)	5.96	4.71	0.60	< LOD	0.18	< LOD	0.62	< LOD
D/S (2)	5.92	16.09	0.60	< LOD	0.28	< LOD	0.25	< LOD
D/S (2)	7.54	< LOD	0.60	< LOD	0.68	< LOD	0.16	2.85
D/S (4)	5.64	< LOD	0.57	< LOD	0.16	< LOD	0.44	5.73
D/S (4)	6.57	14.34	0.58	< LOD	0.34	< LOD	0.37	< LOD
D/S (4)	6.80	8.62	0.62	1.34	0.34	0.93	0.15	23.92

Table 6.1: River Bourne, comparison of dissolved and total metals concentrations in river water from three sampling occasions ($\mu g\ l^{-1}$). Sampling locations are shown in 3.2.2.2, LOD are shown in Appendix III.

The remaining unfiltered river water samples were prepared for total metals (particulate and dissolved) analysis using the potassium persulphate/H_2SO_4 digestion method described in 3.5.1. ICP-MS analysis was undertaken using digested river water samples diluted 1:99 with milli-pore deionised water to reduce the possibility of interference from sulphur (S) contained in the digestion agents. Comparison of digested ('total') metals results to filtered ('dissolved') results showed the relationship between total and dissolved metals was often inconsistent, as total metals concentrations were frequently less than those for dissolved metals, so total metals data has been excluded from this project (Table 6.1.).

6.3. Results

6.3.1. Metal concentrations and loads

6.3.1.1. River Bourne

Flow weighted mean µg l^{-1}	Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
U/S (1)	30.79	0.95	123.87	862.54	6.26	1.77	224.23	0.56	0.32	0.62
D/S (2)	7.86	0.81	49.23	454.78	5.10	1.76	296.74	0.90	0.93	0.32
D/S (4)	6.41	0.96	56.64	419.19	5.50	1.55	248.84	0.84	0.52	0.36
D/S (5)	4.02	1.07	53.71	417.14	5.10	1.62	101.60	0.87	0.32	0.30
Arithmetic mean µg l^{-1}										
U/S (1)	16.96	0.88	143.38	900.38	6.08	1.51	195.29	0.55	0.34	0.58
D/S (2)	5.97	0.75	47.65	436.59	4.94	1.70	296.74	0.87	0.93	0.32
D/S (4)	6.41	0.85	56.64	419.19	5.50	1.55	248.84	0.84	0.52	0.36
D/S (5)	3.14	1.03	53.71	417.14	5.10	1.62	101.60	0.87	0.32	0.30
T test										
U/S :D/S (2)	5.7E-08	0.37	5.0E-12	4.3E-09	1.7E-05	0.13	0.53	7.5E-07	0.86	1.9E-04
t-test result	< 0.0001	N / S	< 0.0001	< 0.0001	< 0.0001	N/S	N/S	< 0.0001	N / S	< 0.001
U/S:D/S (5)	6.2E-08	0.42	6.4E-13	2.5E-09	2.5E-08	0.13	1.9E-02	4.3E-09	0.49	1.9E-04
t-test result	< 0.0001	N / S	< 0.0001	< 0.0001	< 0.0001	N/S	<0.05	< 0.0001	N / S	< 0.001

Table 6.2: River Bourne flow weighted and arithmetic means. 2-tailed paired t-tests for U/S (1) & D/S (2) and U/S (1) & D/S (5), ($P < 0.05$), n=31 (See section 3.2.2. for sampling locations and section 3.4 for flow weighted mean calculation.)

Table 6.2 shows that for a number of metals, Al, Mn, Fe, Ni, Zn and Pb there is a significant reduction in arithmetic mean concentrations and corresponding flow weighted mean concentrations downstream of the STW outflow. Zn concentrations are exceptionally high in comparison to major U.K. rivers analysed during the Land Ocean Interaction Study (LOIS) whose flow rated means range from 4.70 – 83.66 µg Zn l^{-1}, suggesting that the Bourne samples are affected by Zn in the cellulose nitrate filters, therefore they are included in Table 6.2. to illustrate the issue and excluded from River Bourne data thereafter (Neal & Robson, 2000).

There is no significant difference between Cd for up and downstream mean concentrations, despite the fact that the flow weighted and arithmetic means at the downstream sampling location closest to the outfall are almost three times greater than upstream. The D/S (2) mean concentration is skewed by a single result of more than 16 µg l^{-1} on 22nd May 2007 which, as it is not seen in the subsequent downstream concentrations for this date, may be a spurious result. Overall, as these are low concentrations, Cd is broadly similar up and downstream.

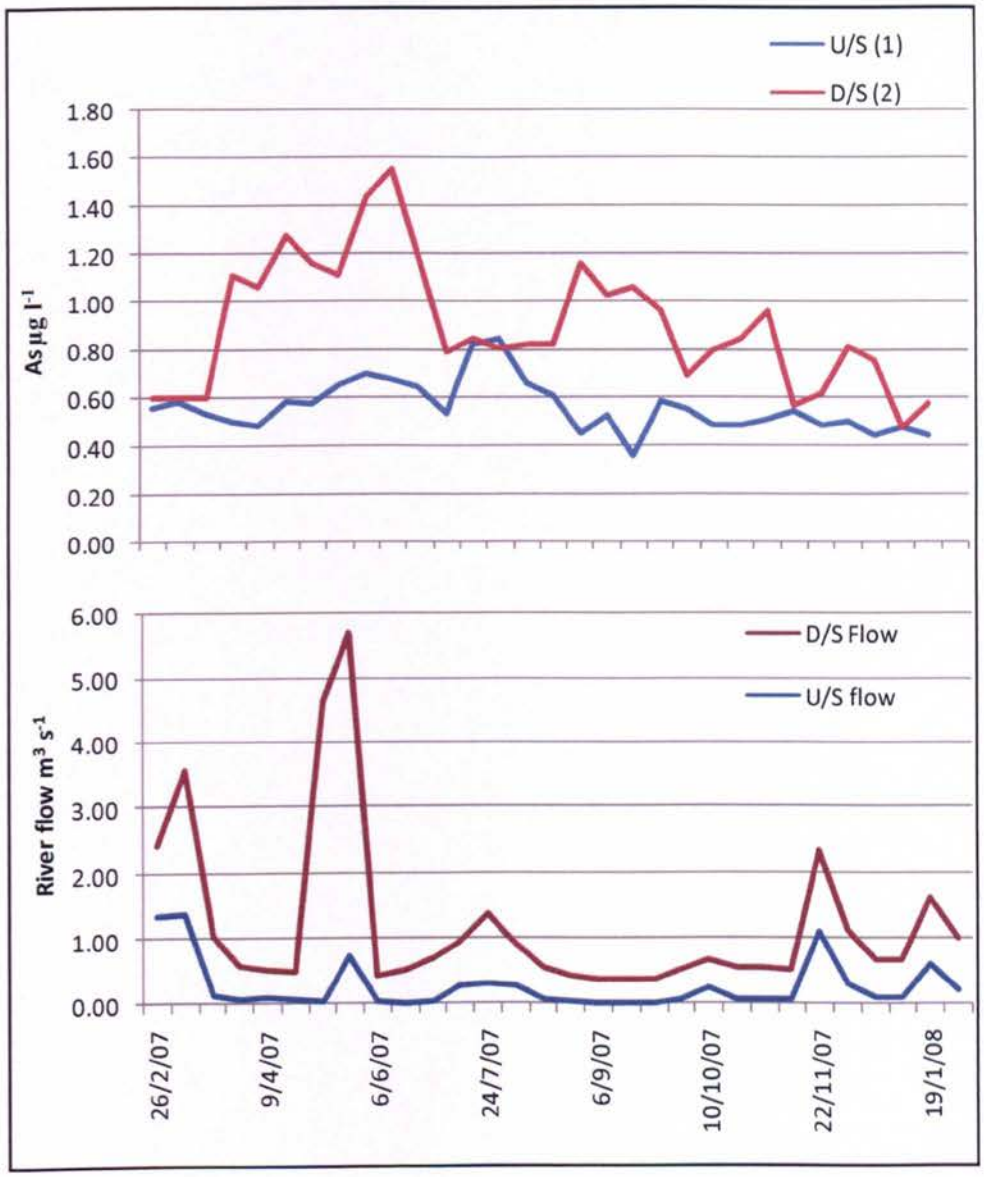

Figure 6.1: River Bourne As concentrations and downstream flow, n=30. As concentrations do not appear to be linked to river flow.

Only As mean concentrations increase significantly downstream of the STW, there is no obvious reason why this metal concentration alone is greater (Figure 6.1). As concentrations do not seem to be influenced by river flow as downstream As concentrations are not dependent on upstream (R^2=0.057), upstream As concentrations are not dependent on upstream flows (R^2=0.006) and downstream As concentrations are not dependent on downstream flows (R^2=0.015).

Cave *et al.* (2005) found As concentrations in the River Humber (U.K.) reduced substantially following closure of a tin smelting works, but the Bourne catchment is not heavily industrial. Mighanetara *et al.* (2009) found elevated As concentrations in the River Thrushel, (U.K.), which receives run-off from abandoned mines but Mn, Cu, Ni, Pb and Zn levels were also

elevated and the Bourne catchment is not a mining area. The use of compounds containing As in herbicides and insecticides, particularly those used in poultry farming is reported in literature, and this is a more feasible source in the Bourne Catchment which is more rural than the Hogsmill and a number of farms, including a large poultry farm, are located within the catchment (Peltier *et al.*, 2008). It is also possible, given the proximity of the M3 and M25 motorways, that inputs are not linked to STW wastewaters, emanating instead from road dust deposition and run-off from the two motorways spanning the Bourne, although it is expected that many of the other metals analysed in this study would have elevated concentrations too (Smedley & Kinniburgh, 2002). It is possible that As is leaching from the motorway bridges and river channel lining as Portland concrete and other construction materials usually include a proportion of arsenic rich industrial waste such as cement kiln ash (Siddique, 2006). Studies into the stability of concrete products containing arsenic generally conclude that it does not leach from the finished building product when it has just been manufactured but it was not possible to find information about the integrity of the structure over a period of years, the M3 motorway bridge was constructed before 1974 (Anon, 2004).

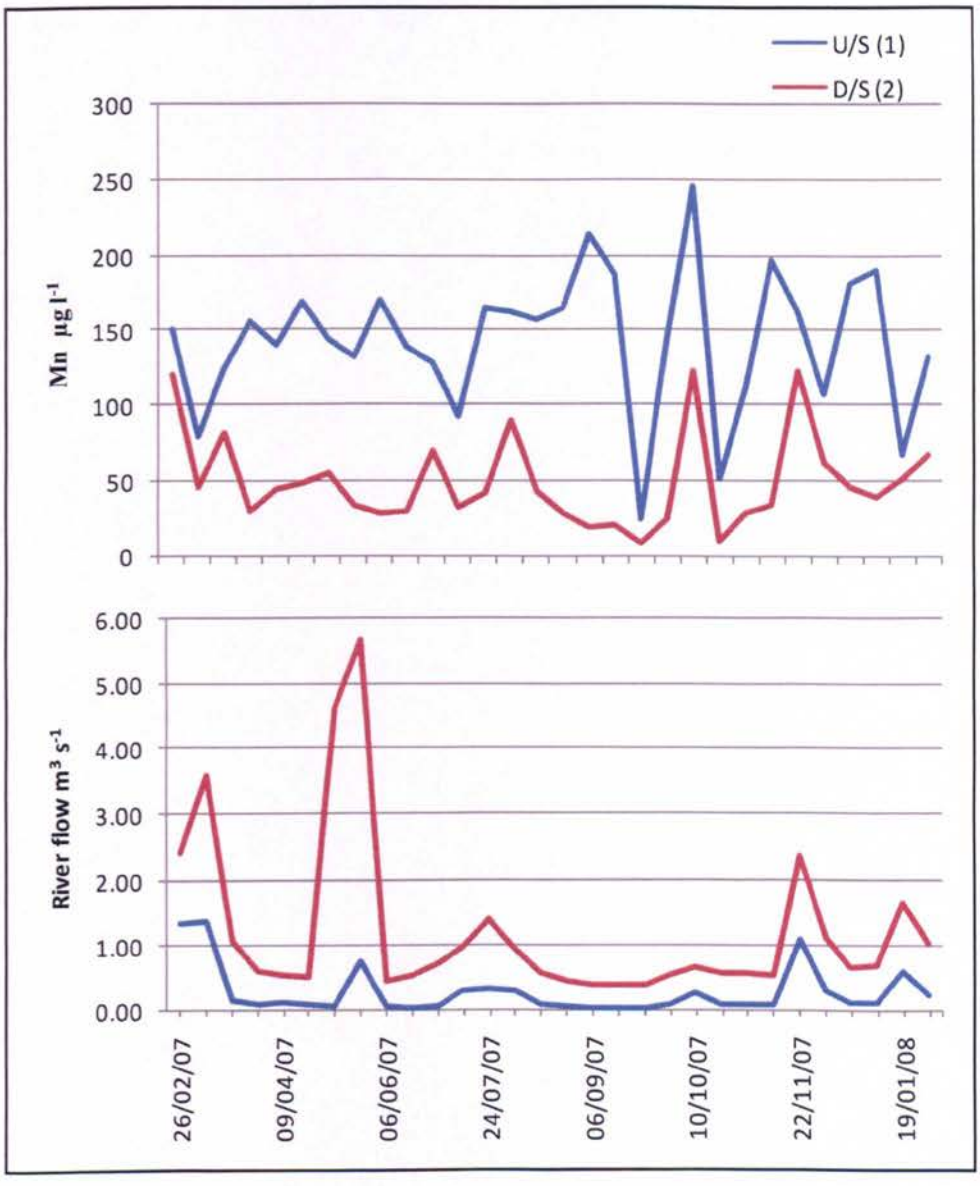

Figure 6.2: River Bourne Mn concentrations and downstream flow, n=24. Concentrations do not seem linked to river flow.

Unlike As, Mn concentrations reduce significantly downstream as STW wastewaters dilute upstream concentrations (Figure 6.2). A similar pattern occurs for other metals which reduce significantly downstream, such as Fe, Al, Ni and Pb indicating that wastewaters contain lower levels of these dissolved metals than the underlying river or that wastewaters are diluting metals inputs from a source upstream of the STW. It is unlikely, given the close proximity of the first D/S sampling site to the outflow that metal concentrations reduce because they adsorb to particulate matter. If the concentration of metals upstream is assumed to be geogenic rather than anthropogenic it is possible that inputs of treated wastewaters may unbalance the ecosystem, but literature on this subject was not identified.

Mean load mg s^{-1}	Al	Cr	Mn	Fe	Ni	Cu	As	Cd	Pb
U/S (1)	17.40	0.33	63.48	487.52	3.21	0.91	0.29	0.17	0.32
D/S (2)	16.71	0.80	66.05	494.20	6.57	2.60	1.03	0.66	0.49
D/S (4)	13.23	0.69	75.52	468.53	6.45	2.02	0.96	0.68	0.44
D/S (5)	6.25	0.92	66.35	423.17	6.17	2.04	1.00	0.48	0.32

Table 6.3: River Bourne flow weighted mean metals loads, n=31. (See section 3.2.2. for sampling locations and section 3.4 for flow weighted mean calculation.)

Mean load kg day^{-1}	Al	Cr	Mn	Fe	Ni	Cu	As	Cd	Pb
U/S (1)	1.50	0.03	5.48	42.12	0.28	0.08	0.02	0.01	0.03
D/S (2)	1.44	0.07	5.71	42.70	0.57	0.22	0.09	0.06	0.04
D/S (4)	1.14	0.06	6.52	40.48	0.56	0.17	0.08	0.06	0.04
D/S (5)	0.54	0.08	5.73	36.56	0.53	0.18	0.09	0.04	0.03

Table 6.4: River Bourne mean daily loads (kg day^{-1}), n=31.

The metals loads figures, based on flow weighted means, (Tables 6.3 and 6.4) show the potential for a substantial increase in the quantity of Cr, Ni, Cu, As and Cr in the downstream Bourne. This is caused by the increased mean flow downstream, 0.94 m^3 s^{-1}, against the estimated flow upstream, 0.30 m^3 s^{-1}. Although only As concentrations increase significantly downstream of the STW, if loads for other metals increase significantly downstream then i). this is also attributable to sewage wastewaters inputs and ii). it may have a detrimental effect on the receiving river environment. Due to suspected contamination of filter papers, discussed earlier in this section, Zn is excluded from Tables 6.3 and 6.4.

Downstream sampling location D/S (5) was not identified at the start of the sampling regime and there is no data from this site for the first two sampling dates, 26/2/07 and 6/3/07, as the two highest Al concentrations and the fastest and third fastest river discharges were recorded on these dates, the substantially lower means at D/S (5) reflects the exclusion of these results. Loads calculations for other metals, particularly Zn and Cd are similarly affected.

6.3.1.2. River Hogsmill

Flow weighted mean (µg l^{-1})	Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
U/S (1)	13.15	1.08	12.62	578.20	3.20	4.31	363.44	1.24	0.37	0.50
D/S (2)	5.28	0.96	11.72	584.06	3.13	2.41	134.48	1.11	0.59	0.64
D/S (3)	5.13	1.31	13.69	590.13	3.32	2.62	182.36	1.12	0.35	0.61
D/S (4)	5.93	1.28	13.15	594.05	3.30	2.69	209.62	1.14	0.48	0.71
Arithmetic Mean µg l^{-1}										
U/S (1)	5.93	1.05	10.51	652.81	3.14	3.36	222.37	1.18	0.44	0.48
D/S (2)	5.28	0.96	11.72	584.06	3.13	2.41	134.48	1.11	0.59	0.64
D/S (3)	5.13	1.37	13.69	590.13	3.32	2.62	182.36	1.12	0.35	0.61
D/S (4)	5.93	1.23	13.15	594.05	3.30	2.69	209.62	1.14	0.48	0.71
T test										
U/S (1):D/S (2)	0.95	0.66	0.67	0.017	0.18	3.0E-06	0.21	3.2E-03	0.37	9.76E-03
t-test results	N/S	N/S	N/S	< 0.05	N/S	< 0.0001	N/S	< 0.005	N/S	< 0.05
U/S (1):D/S (4)	0.85	0.84	0.51	0.019	0.91	5.9E-03	0.50	2.5E-02	0.54	2.14E-02
t-test results	N/S	N/S	N/S	< 0.05	N/S	< 0.01	N/S	< 0.05	N/S	< 0.05

Table 6.5: River Hogsmill flow weighted and arithmetic means. 2-tailed paired t-tests between U/S (1) and D/S (2) and U/S (1) and D/S (4), ($P < 0.05$). (See section 3.2.1. for sampling locations and section 34. for flow weighted mean equation), n= 33.

In terms of arithmetic mean concentrations for the Hogsmill, Table 6.5 shows that the paired t-test for six metals (Al, Mn, Cr, Ni, Zn, Cd) exhibits no significant difference downstream and that Fe, Cu and As are significantly reduced downstream. Elevated Zn levels are probably the result of Zn contamination from cellulose nitrate filters, and this metal is excluded in subsequent data analysis, as discussed in 6.3.1.1 and 3.5.1.2.2.

The most likely explanation for similarity between up and downstream metals concentrations or reduced concentrations downstream of the STW is dilution of dissolved metals by wastewaters; the downstream mean flow of 1.3 m^3 s^{-1} being much greater than the upstream mean flow of 0.58 m^3 s^{-1}, a comparable finding is reported by Nyamangara *et al.* (2008) in respect to Zn, Cu, Pb and Cd concentrations in a Zimbabwean river downstream of sewage outfall.

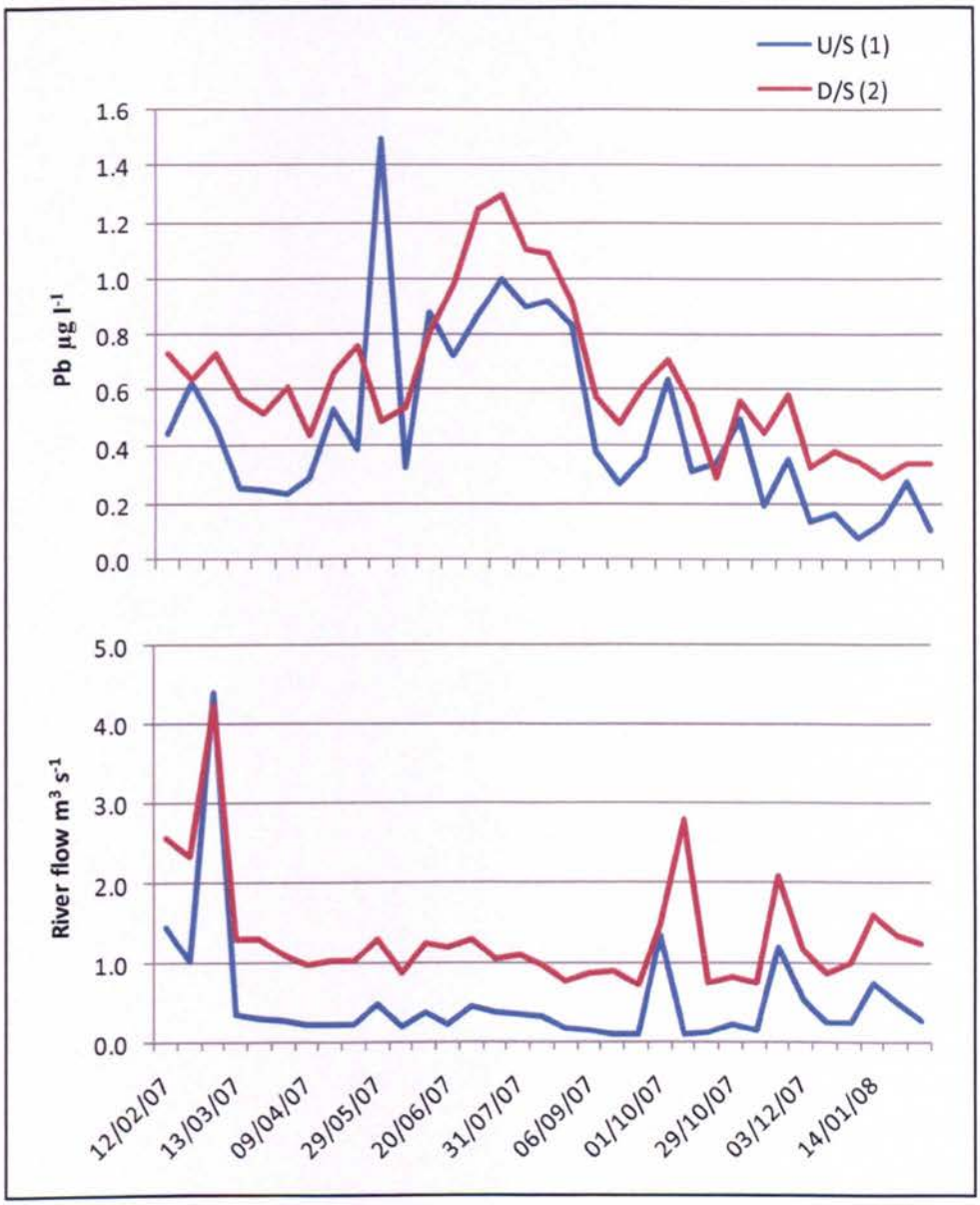

Figure 6.3: River Hogsmill Pb concentrations and river flow, n=33. Peaks in Pb concentration do not generally coincide with peaks in river flow, suggesting that Pb is not mobilised by river bed sediments.

In the Hogsmill, Pb is the only metal which increases significantly downstream. According to Thames Water, lead pipes are unlikely to be the source as $CaCO_3$ build-up in pipes in this hard water (>200 mg $CaCO_3$ l^{-1}) region results in a protective coating which substantially reduces leaching (Thames Water, 2009). Potential sources to the STW include car brake linings and tyres and industrial discharge as reported by Sörme and Lagerkvist (2002) and Rule *et al.* (2006) which, given the urban nature of this catchment, is possible. Studies into the deposition of metals within an urban environment usually find elevated levels of other metals such as Fe, Mn, Cd, Zn, Cu, Cr which is not the case for the Hogsmill, and Sörme and Lagerkvist (2002) attribute less than 15% of Pb input to the STW as traffic and atmospheric deposition derived, the major source being businesses, although it was one of the least

understood metals in their study and they were able to account for only 50% of Pb entering the STW (Fang *et al.*, 2007).

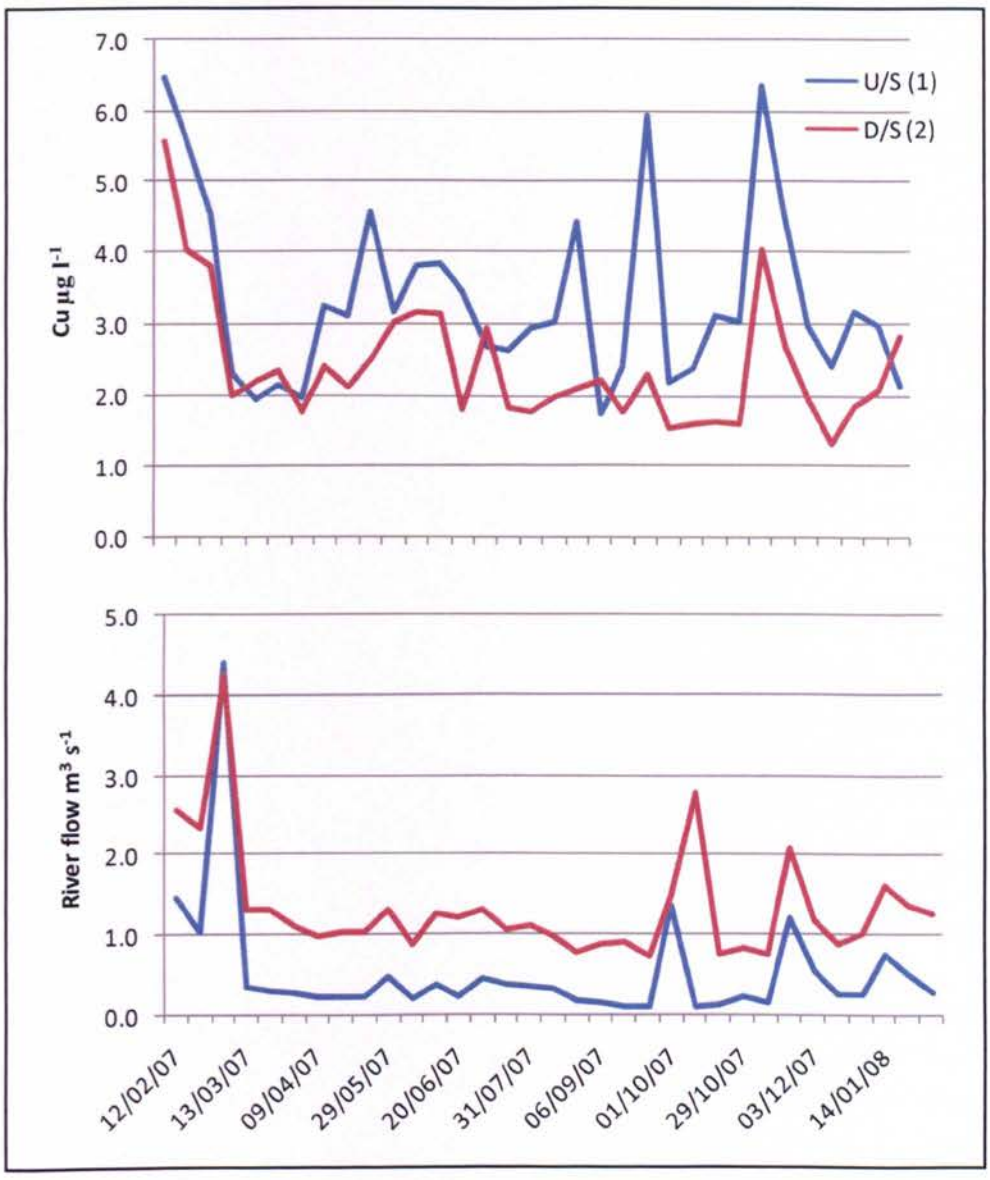

Figure 6.4: River Hogsmill Cu concentrations and downstream flow, n=33. Peaks in Cu concentration almost always coincide with increased river flow suggesting Cu inputs are mobilised during channel bed scouring and diluted by STW wastewaters.

In the Hogsmill, Cu, like Fe and Al, reduces significantly downstream, Figure 6.4. Peaks in Cu concentration almost always coincide with increased river flow suggesting Cu inputs, which may be geogenic or from sediment, are mobilised during channel bed scouring and diluted by STW wastewaters (Neal *et al.*, 2000a).

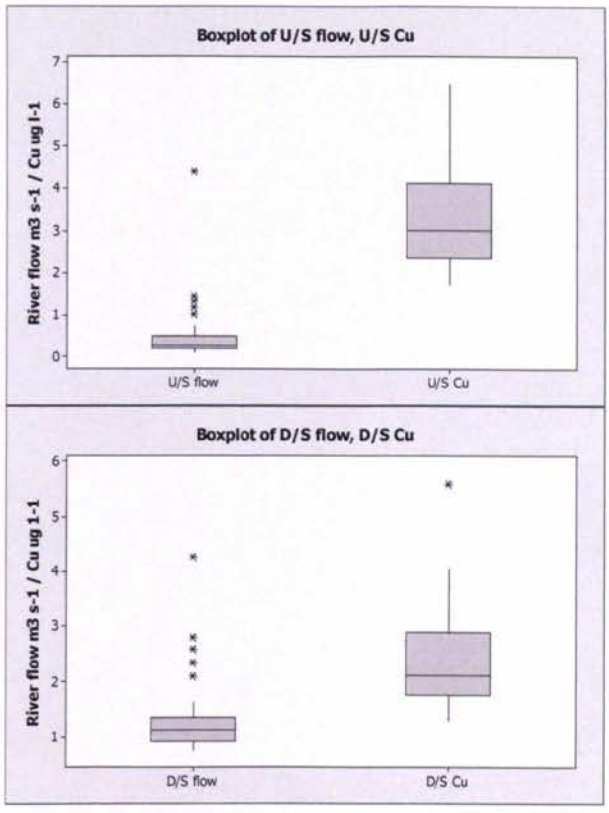

Figure 6.5: Box-plots of Cu flow and concentration up and downstream of the Hogsmill Valley STW. The box-plot is based on median data values, outliers are indicated by asterisks. U/S and D/S river flows contain a number of outliers, indicating peak flows. Cu concentrations do not show similar outliers, suggesting that whilst river flow may mobilise Cu from channel bed sediments, the relation is not linear during peak river flow

However, using linear regression, river flow accounts for only 27% (upstream) and 33% (downstream) of dissolved Cu concentrations in the Hogsmill. As Figure 6.5 boxplots show, river flow data up and downstream contain a number of outliers at high flow values which may distort the linear relationship; this would correspond with findings from Neal *et al.* (2000a) who suggest that although geogenic metals concentrations are correlated to river flow, the relationship is not necessarily linear for the entire data-set as extreme values may distort the equation.

Neal *et al.* (2000b & 2006) report that dissolved Fe and Al concentrations in the rural Thames and the River Thame exhibit similar behaviours to the upstream Hogsmill, increasing in tandem with river flow, although mean Al concentrations were higher, 21– 87 $\mu g\ l^{-1}$ and Fe lower, 64 –160 $\mu g\ l^{-1}$; these differences are most likely due to variance in the underlying bedrock between this projects rivers and those from Neal's study.

Flow weighted loads mg l^{-1}	Al	Cr	Mn	Fe	Ni	Cu	As	Cd	Pb
U/S (1)	8.53	0.41	6.75	340.13	1.71	2.30	0.66	0.20	0.27
D/S (2)	10.78	1.12	18.16	671.65	4.33	3.64	1.56	0.69	0.87
D/S (3)	8.45	1.57	19.83	682.71	4.68	3.94	1.55	0.40	0.80
D/S (4)	8.85	1.46	19.64	687.26	4.56	3.96	1.58	0.64	1.21

Table 6.6: River Hogsmill flow rated mean metal loadings (mg l s^{-1}), n=33 See section 3.2.1. for sampling locations and section 3.4 for flow weighted mean calculation.

Flow weighted loads kg day^{-1}	Al	Cr	Mn	Fe	Ni	Cu	As	Cd	Pb
U/S (1)	0.74	0.04	0.58	29.39	0.15	0.20	0.06	0.02	0.02
D/S (2)	0.93	0.10	1.57	58.03	0.37	0.31	0.13	0.06	0.08
D/S (3)	0.73	0.14	1.71	58.99	0.40	0.34	0.13	0.03	0.07
D/S (4)	0.77	0.13	1.70	59.38	0.39	0.34	0.14	0.05	0.10

Table 6.7: River Hogsmill flow rated mean daily loads (kg day^{-1}), n=33.

Metals load figures, shown in Tables 6.6 and 6.7, for the Hogsmill show substantial increases downstream of the STW for all metals except Al, Zn is excluded from these tables because of suspected contamination, see section 6.3.1.1. Like the Bourne, the volume of water in the downstream Hogsmill is greatly increased by sewage wastewaters; the measured mean downstream flow for the eighteen month sampling period is 1.30 m^3 s^{-1} whilst the mean upstream flow for the same period is estimated at 0.55 m^3 s^{-1}. Whilst metals concentrations up and downstream of the STW are often similar, discharged wastewaters elevate the downstream flow and so, because of STW inputs, the metals load to the river is substantially increased. Apart from Al and Cd, there is no reduction in metals loads between downstream sampling sites D/S (2) and D/S (4), suggesting most of these metals remain dissolved and potentially available to biota.

Although load calculations based on sporadic sampling and flow measurements must be treated with caution, as described in 4.3.1.1., Tables 6.6 and 6.7, provide a useful illustration of the likely quantities of dissolved metals being transported towards the River Thames by just two of its tributaries each day. Inter-river processes usually remove some of the dissolved metals from water to particulate matter and then to channel bed sediment, but this does not necessarily render them immobile, an aspect which will be explored in subsequent chapters on sediments.

6.4. Fractionation

On seven occasions during the sampling campaign, water samples were passed through 0.10 μm filters to establish whether significant differences in metals concentrations between 0.45 μm and 0.10 μm filtrate could be discerned. Once accepted as the barrier between particulate and dissolved matter, more recently 0.45 μm filters have become the starting point for a series of filtration stages to investigate the quantity of colloidal material present in water systems. Although definitions of colloid vary between scientific and engineering disciplines, in this project they are considered as fractions with at least one dimension between 1 nm – 1 μm (Lead & Wilkinson, 2007). Colloidal material has a high specific surface area, thus increasing its capacity to adsorb pollutants such as metals, in fact colloids less than 0.1 μm may have a greater metals binding capacity than particles greater than 0.1 μm because of their larger surface area, so understanding how individual metals interact with colloids can assist in assessing potential bioavailability (Dai *et al.*, 1995; Lead *et al.*, 1999; Lead & Wilkinson, 2007).

Colloidal material remains suspended in the water column for long periods of time, i.e. from more than a few hours to a number of days, due to Brownian motion (water molecules impacting the colloids and keeping them suspended), so they are important in terms of metal transportation downstream of a pollution source as they do not readily settle to channel bed sediment like particulate matter (Tuccillo, 2006; Lead & Wilkinson, 2007).

In this project, the distinction between filtrates is physical, speciation, chemical structure or behaviours of different sized metal fractions has not been investigated, so it is only possible to speculate on the impact to biota in the receiving river.

	Al	Cr	Mn	Fe	Ni	Cu	As	Cd	Pb
Mean 0.1μm	1.46	0.92	55.28	465.83	4.05	1.91	0.83	0.30	0.44
Mean 0.45 μm	3.18	0.99	41.06	472.74	4.05	1.85	0.85	0.27	0.44
t-test results (P < 0.05)	2.15E-05	0.69	0.32	0.52	0.97	0.46	0.04	0.30	0.83
	< 0.0001	N/S	N/S	N/S	N/S	N/S	< 0.05	N/S	N/S

Table 6.8: Comparison of 0.45 and 0.1 μm filtrate for rivers Hogsmill & Bourne across all sampling sites (μg l^{-1}). N=48 (max), P < 0.05.

The area of interest in this section is difference between 0.45 and 0.10 μm filtrates, so results from both rivers and all sampling sites are pooled to provide a larger data set (Table 6.8). As

mentioned in Section 6.3.1.1., due to Zn contamination of filter papers, results for this metal are excluded as they are elevated in comparison to concentrations found in literature for U.K. rivers.

Only Al and As show a significant reduction in metals concentration between 0.45 and 0.10 μm filtrates, although the difference for As is marginal. There is no significant difference between the remaining filtrates. It is possible that the lack of significant difference between the other seven metals occurred because the majority of metal bearing colloids in these rivers are less than 0.1 μm and therefore pass through both filters, more conclusive results might be obtained if a range of finer filters had been available for this project or if access to other methods for classifying colloids such as field flow fractionation, or microscopy (electron, atomic force, confocal, etc.) had been possible (Buffle *et al.*, 1998; Lead & Wilkinson, 2007). Like the results from this project, Shkinev *et al.*, 1996 found similar concentrations of Ni, Mn and Cu in river water which had been passed through 0.45 and 01 μm filters although Al showed a significant reduction. One issue identified by these authors was that subsequent filtration through 0.025 μm filters increased Mn and Al concentrations, this they attributed to desorption or disassociation of metals due to acidification of river water samples for storage, pH was reduced from ≈ 7.6 to 2.7 using HNO_3 (Shkinev *et al.*,1996).

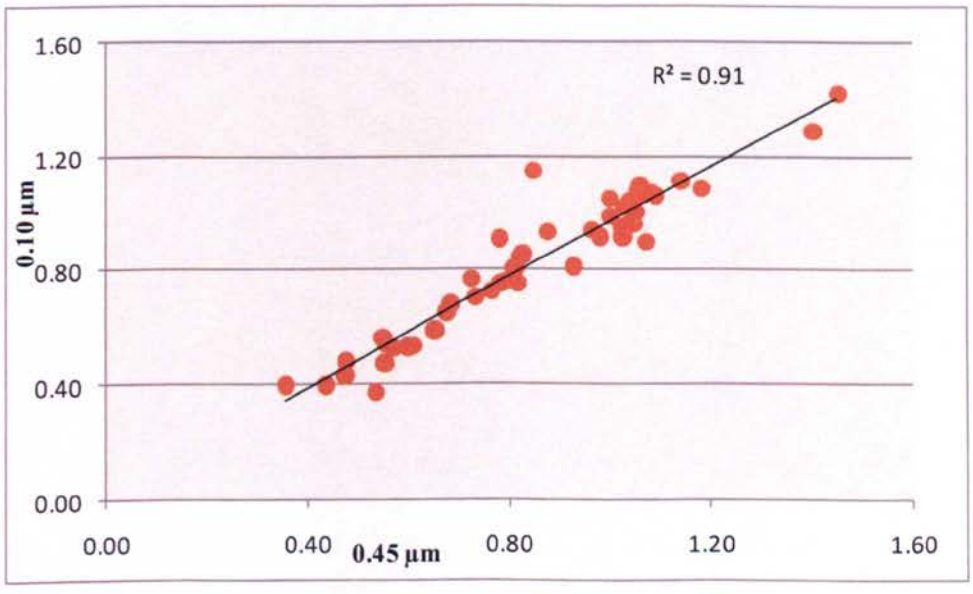

Figure 6.6: Scatterplot of relationship between As in 0.45 and 0.10 μm filtrate (μg As l^{-1})

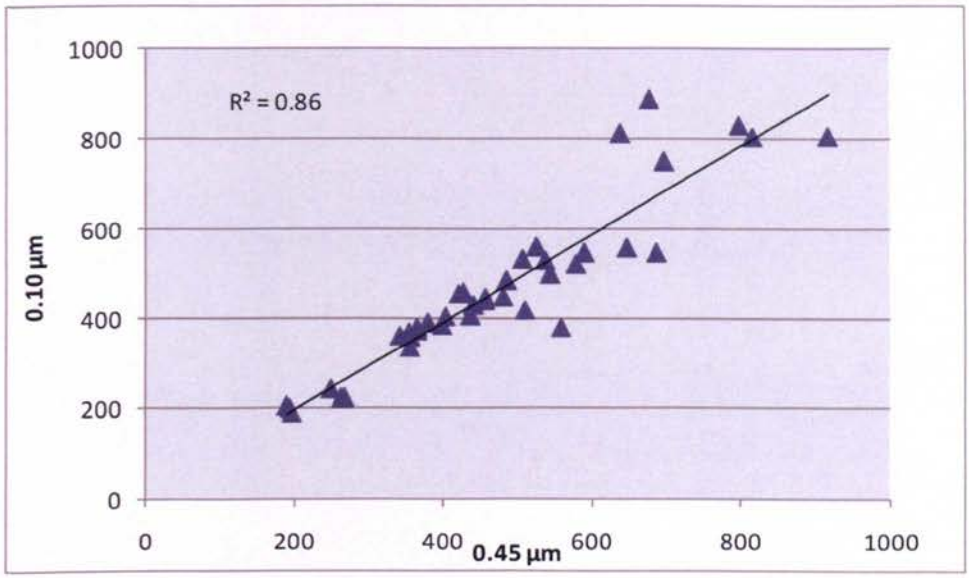

Figure 6.7: Scatterplot of relationship between Fe concentrations in 0.45 and 0.10µm filtrates (µg Fe l^{-1})

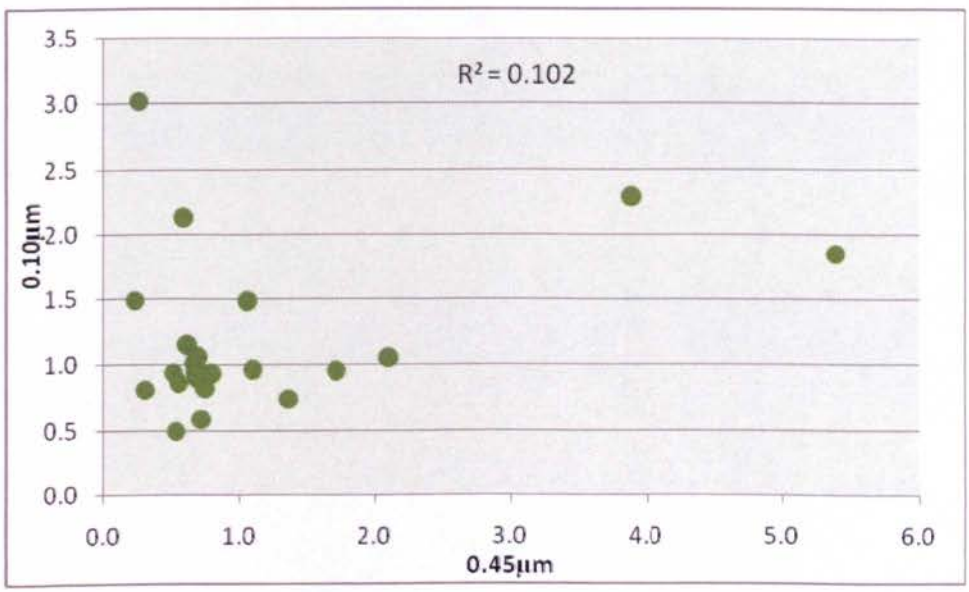

Figure 6.8: Scatter plot of Cr concentrations in 0.45 and 0.10µm filtrates (µg Cr l^{-1}) shows no relationship between the filtrates. The scatter plots for Al, Mn, Ni, and Cd are similar, with low regression coefficients.

When considering the relationship between the same elements in 0.45 and 0.10µm filtrates, As and Fe show strong correlation between the 0.45 and 0.10 µm filtrates (Figures 6.6 & 6.7) but this is not apparent for other metals such as Cr (Figure 6.8). Where poor correlations exist between individual metals in the different sized filtrates, the causes may be low concentration values, but as the strongest correlation occurs for As where concentrations are less than 0.2 µg l^{-1}, it is likely that other factors are involved.

These may include adsorption of smaller colloids to dissolved organic matter (DOM) or precipitation with other elements such as Ca, Fe or Al (Wells *et al.*, 2000).

6.5. Discussion and Conclusion

This project established that dissolved concentrations for As on the River Bourne and Pb, on the Hogsmill increase downstream of the STW wastewaters outfall and, with the exception of Al, all metal loads increase downstream, this is not surprising given the increased volume of water contributed by these discharges. Therefore, it is appropriate to consider whether these changes to the underlying river breach legislative water quality standards and if an adverse effect on riverine biota is likely to occur.

Generally, metals content of river water is covered in the Water Framework Directive (200/60/EC) which requires individual EC members to set targets to achieve "good ecological status" (E.C., 2000). As, Cd, Zn and Cu are more specifically covered by the Integrated Pollution Prevention and Control Directive (IPPC) (96/61/EC) applicable to discharges from STW, the Cadmium Discharges Directive (83/513/EEC) and the Freshwater Fish Directive (87/659/EEC & 2006/44/EC). The IPPC does not set a maximum concentration limit for As, it requires the use of best available techniques to control discharges and the WHO recommended maximum concentration of 10 $\mu g\ l^{-1}$ in drinking water is not exceeded in either the Bourne or Hogsmill (Mandal & Suzuki, 2002). Recently the U.K. Technical Advisory Group on the Water Framework Directive recommended a mean annual limit of 50 As $\mu g\ l^{-1}$ as an environmental quality standard (EQS) for rivers (U.K.T.A.G., 2008), the As concentrations from this project fall well below these limits.

The Cadmium Discharges Directive limit is 5 $\mu g\ l^{-1}$, although concentrations in both rivers meet this target, it is not possible to confirm whether wastewaters from the STW outfalls are compliant as Thames Water denied access to the outfall for sampling due to Health and Safety issues (E.C., 2000; A. Wallis, Thames Water plc. pers. comm., 2006). Currently, there are no legislative parameters for metals loadings which, given the extremely dilute but high volume characteristics of wastewater discharges might be considered a more appropriate measure of pollution. It may be that the effect of increased metal loadings is discernable in channel bed sediments, an aspect investigated in the following chapter.

The Freshwater Fish Directive defines a range for Cu dependent upon $CaCO_3$ concentrations in the receiving river water, the Hogsmill and Bourne are both below the lower limit of 0.005 mg l^{-1} (5 $\mu g\ l^{-1}$). For Zn, the same Directive's range for Cyprinid waters is 0.3 – 2.0 mg l^{-1} and whilst several mean Zn concentration values are close to or exceed the lower value, the issue of filter contamination makes it likely that the analysed data values are higher than

those in the rivers the samples came from. Overall, where regulatory limits exist for metals concentrations in rivers, values obtained for the Hogsmill and Bourne do not exceed them.

$\mu g\ l^{-1}$	Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
Aire	37.1	2.75	124.6	173.6	7.35	6.04	24.35	3.45	0.10	1.48
Thames	29.0	0.39	6.8	51.4	2.69	3.36	4.99	1.67	0.075	0.33
Tweed	47.2 – 160.2	0.44 – 1.24	4.5 – 8.1	86.7 – 135.7	1.47 – 2.29	2.44 – 3.11	4.70 – 5.93	0.53 – 0.64	0.02	0.26 – 0.31
Hogsmill	6.66	1.16	14.18	591.6	3.34	2.84	177.5	1.15	0.43	0.71
Bourne	8.87	0.95	59.94	448.6	5.23	1.67	219.7	0.83	0.55	0.34

Table 6.9: Flow weighted mean concentrations from LOIS study compared with mean flow weighted mean concentrations for the downstream sampling sites of the study rivers ($\mu g\ l^{-1}$) (Neal & Robson, 2000).

So far as the remaining metals are concerned, as the quality standard is the subjective descriptor "good ecological status", rather than specific concentrations, the flow weighted mean concentrations from this study were compared to data from UK rivers draining into the North Sea which form part of the Land-Ocean Interaction Study (LOIS), Table 6.9, (Neal & Robson, 2000). The comparator rivers are the Tweed, considered by the Environment Agency to represent good water quality, the Aire, being urban/industrially impacted and the Thames at Day's Lock, approximately 90 miles downstream of its source. The Thames was selected as both the Bourne and Hogsmill are tributaries, albeit approximately 50 – 60 miles downstream of Days lock in a more urban catchment. Generally, flow weighted mean metals concentrations for the study rivers exceed those of the Tweed and fall below those of the Aire. High Fe concentrations in the study rivers are due to the parent bedrock, upstream Fe concentrations being similar to downstream and high Zn concentrations are associated with the filter contamination issue described in 6.3.1.1. Ni and Mn concentrations for the downstream Bourne are high in comparison to the LOIS study rivers, they are elevated upstream too. Pb concentrations in the Hogsmill are also high, possibly due to lead supply pipes, although Thames Water plc. deny this (Rule *et al.*, 2006; Thames Water plc., 2009). However, it is Cd levels in both study rivers which is most notably greater than those of the LOIS report. The most likely impact of these heavy metals on the receiving river is bioaccumulation in biota. Cd, Ni, As, and Cr (VI) are human carcinogens and Pb is toxic to humans, therefore, it is probable that these metals are similarly harmful to riverine organisms in the study rivers and it is possible that they will become incorporated into the food chain (Jarup, 2003). As investigation into the impact of dissolved metals on riverine biota from the study rivers did not form part of this project, a number of questions remain unanswered, e.g. do low concentrations of a number of metals present more of a risk to biota than an

individual metal at greater concentrations and do other compounds reportedly present in STW wastewaters but not investigated here, such as pharmaceutical drugs, adversely affect biota in conjunction with increased metals concentrations (Ellis, 2005). Studies of metals toxicity in biota are usually based on lethal concentrations (LC) in a laboratory environment for one specific toxin rather than for a number of toxins which act as stressors to species (Madoni, 2000). An alternative assessment method which might be more appropriate here uses species counts within a study area, this might provide an indication of whether pollution intolerant species are absent or excessive numbers of pollution tolerant species are present up and downstream of the STW outflow.

With reference to fraction size, the similarity between concentrations in the 0.45 and 0.1 μm filtrates for many of the metals analysed suggests that there is merit in investigating this further, to establish what proportion of smaller metals fractions exists in rivers receiving cleaned STW wastewaters and whether they present a greater risk to biota because they may be in a more bioavailable form. It may be that sewage waste processing, where particulates are separated from liquid waste during several stages, is more likely to result in smaller dissolved metals fractions than are present in wastewaters from other sources and that the environmental impact on the receiving river is greater despite overall concentrations falling within regulatory limits. However, it would be necessary to have the use of a completely clean sample collection and processing facility and access to alternative methods of identifying fraction size in order to investigate this satisfactorily.

7. Phosphorus and metals in river bed sediments

7.1. Introduction

Sediments, particulate matter in river flows which settle in layers on the river bed, are a reservoir of contaminants in the river system acting either as sink or source, depending on physical, geological and chemical conditions in the overlying water course (Taylor & Boult, 2007; Jarvie *et al.*, 2008b).

A number of studies have established that the majority of contaminants in freshwater aquatic systems occur in channel bed sediments and Golterman *et al.* (1983) suggests that up to 70% phosphorus within a water system may end up in sediments (Taylor & Boult, 2007; Cotman *et al.*, 2001; Cave *et al.*,2005; Jarvie *et al.*, 2005). Thus it is important to examine sediments in conjunction with river water in order to gain a more complete understanding of the impact of pollutants on the aquatic system (Cotman *et al.*, 2001; Owens *et al.*, 2001). River sediments are an important habitat and food source for aquatic plants and organisms, so contaminants from this source may enter the food chain (Förstner, 2004; Cave *et al.*, 2005).

The rate at which particulate matter may settle as sediment is affected by factors including the rate of river flow, morphology, seasonality, underlying geological composition of particulates and particulate grain size (Gurnell & Petts, 1995). The likelihood of chemicals from treated wastewater discharges settling as sediments in the river system depends on whether they are discharged in dissolved or particulate form, their propensity to adsorb to suspended sediment, the quantity of particulates in the river stream and the underlying chemistry of the water column (Golterman *et al.*, 1983).

River bed sediments are not immobile and are transported downstream during periods of increased flow following heavy rain, re-suspension following anthropogenic activity or from erosion (Golterman *et al.*, 1983). Changes in water chemistry e.g. pH levels, reducing P or metals concentrations in the overlying water column, may also allow remobilisation of metals and P adsorbed to sediments (Förstner, 2004).

7.2. Materials and methods

Samples were collected during September 2007 and, like the water sampling programme, sediments were collected from the Hogsmill and Chertsey Bourne rivers; an additional downstream sampling site was included for each river, Figures 3.3 and 3.4 (Chapter 3). Two more rivers, the Blackwater and Mole, selected for their proximity to STW's, were sampled to provide additional sediment data, locations are shown in Figures 3.5 and 3.6 (Chapter 3).

Distance from STW Outflow	Blackwater	Bourne	Hogsmill	Mole
D/S 1	At confluence	At confluence	200 m	50 m
D/S 2	150 m	200 m	750 m	300 m
D/S 3	400 m	300 m	1250 m	600 m
D/S 4	800 m	700 m	1550 m	Not sampled

Table 7.1: Downstream sediment sampling points, distances from STW outflow

In total, sediment was collected from nineteen locations, four upstream and fifteen downstream (Table 7.1). Lack of access restricted sampling in the downstream Mole, only three downstream samples were taken from this river.

Sediment was obtained by wading into the river and collecting from four or five discrete points across the riverbed using a trowel which was covered as it was bought up through the water column (Stutter *et al.,* 2007). Sampling depth varied according to riverbed sediment deposition; however the maximum depth was about 5 cm. Sediment was mixed in a polythene bag to provide a homogeneous sample, transferred to acid washed open porcelain dishes and placed in a drying oven heated to 50°C for up to seven days until all moisture had evaporated then lightly crushed to break up sediment clumps and sieved to less than 2 mm fraction.

7.2.2. Total metals and phosphorus

Triplicate sediment samples weighing ~1.5 g were prepared for total metals and total P analysis using Method 3050B, Acid digestion of sediments, sludges, and soils (USEPA, 2003. Certified reference materials and blanks were included in each batch. Analysis was undertaken twice, using the VG PlasmaQuad Inductively Coupled Plasma Mass Spectrometer (ICP-MS) and Inductively Coupled Atomic Emission Spectrometer ICP-AES as described in Chapter 3.

As the percentage recovery from certified reference materials was highest for ICP-MS, it is these results that are discussed here. The exceptions are Al and Fe which were only analysed using ICP-AES as they occur in concentrations too high for ICP-MS analysis at the solution strength necessary to detect the other elements.

7.2.3. SRP release from sediment

Using the method described by House *et al.* (1995) and Jarvie *et al.* (2005), triplicate river bed sediment samples weighing ~0.5 g were placed in 250 ml polypropylene bottles with 200 ml of 2 mmo l^{-1} $CaCl_2$ solution to mimic the hard-water conditions of the rivers studied. Samples were agitated overnight at 150 rpm, the laboratory temperature was reduced to 10 °C and the samples covered to exclude light in order to limit microbial action. A 25 ml subsample from each 250 ml bottle was centrifuged for 15 minutes. The supernatant was analysed for SRP using the ascorbic acid method described in section 3.5.1.1 to ascertain whether P would release into water without the use of reagents.

7.3. Results and discussion

7.3.1. Total phosphorus in sediment

River	Blackwater	Bourne	Hogsmill	Mole
U/S (1)	694.41	1246.62	812.57	2050.55
D/S (2)	1121.95	1441.12	1827.82	1539.54
D/S (3)	1125.82	1758.87	956.84	1768.42
D/S (4)	1669.41	2516.80	777.29	2332.03
D/S (5)	2830.98	3776.39	1239.03	Not sampled

Table 7.2: Total phosphorus in sediment (mg kg^{-1}). See Table 7.1 for distances from STW outflow

	U/S (1) & D/S (2)		U/S (1) and D/S (5)	
	t-test result	significance	t-test result	significancee
Blackwater	0.0097	< 0.01	0.0190	< 0.05
Mole	0.0048	< 0.005	0.1002	N/S (D/S(4))
Bourne	0.2359	N/S	0.0054	< 0.01
Hogsmill	0.0300	< 0.05	0.0800	N/S

Table 7.3: 2-way paired t-test results for ICP-MS data. $P < 0.05$, n=3. (N/S: not significant.)

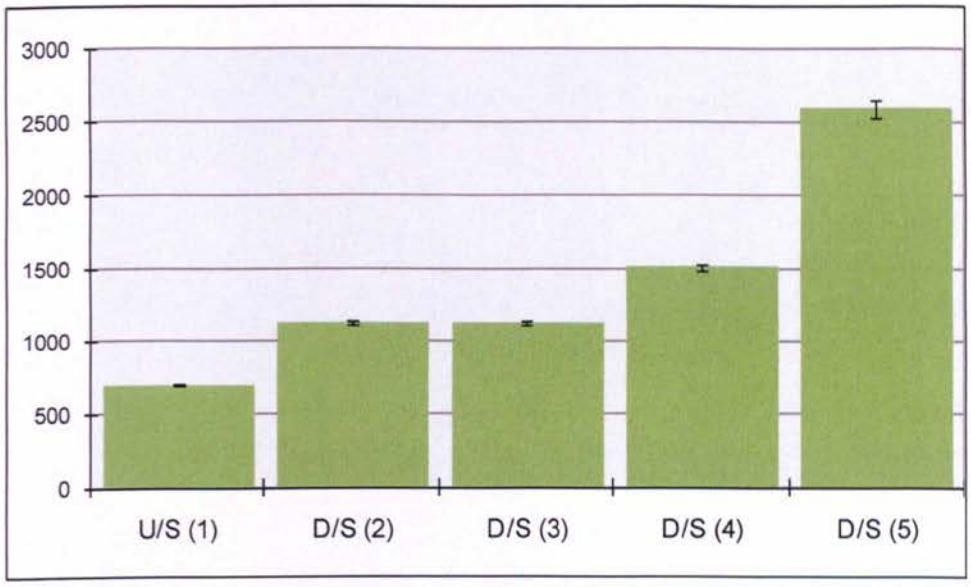

Figure 7.1: River Blackwater TP concentrations in sediment (mg TP kg^{-1}), ICP-MS analysis. Error bars are 3 x S.D.

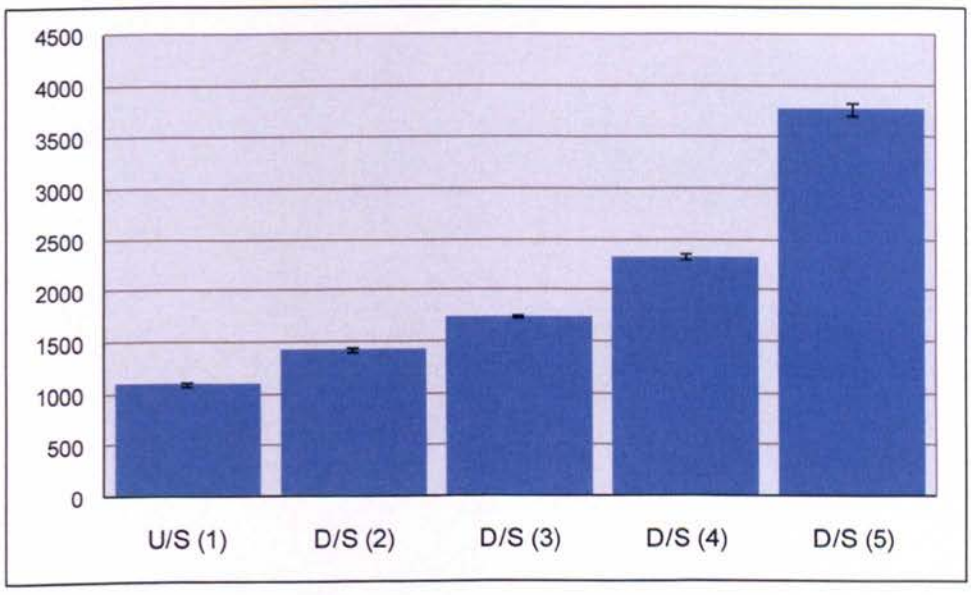

Figure 7.2: River Bourne TP concentrations in sediment (mg TP kg^{-1}), ICP-MS analysis. Error bars are 3 x S.D.

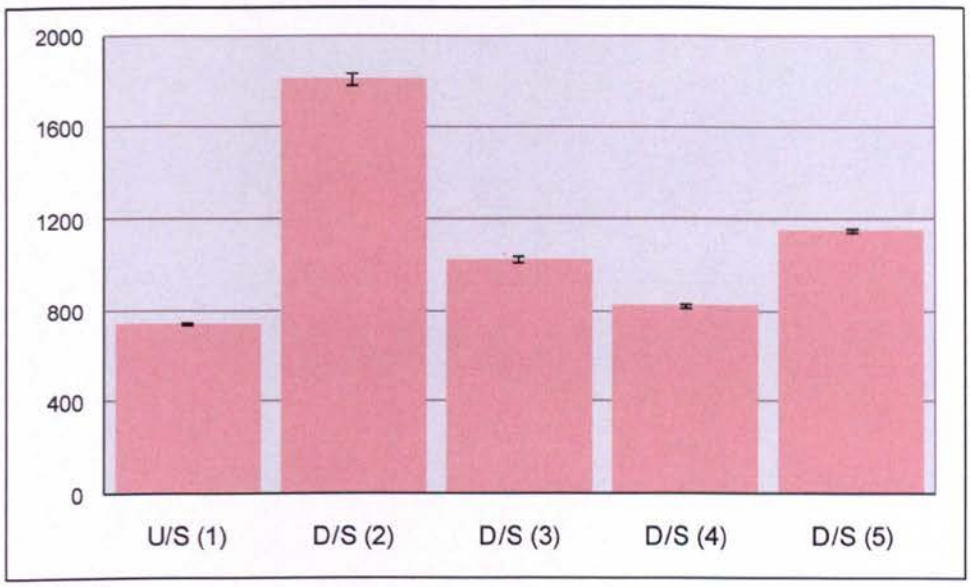

Figure 7.3: River Hogsmill TP concentrations in sediment (mg TP kg^{-1}), ICP-MS analysis. Error bars are 3 x SD

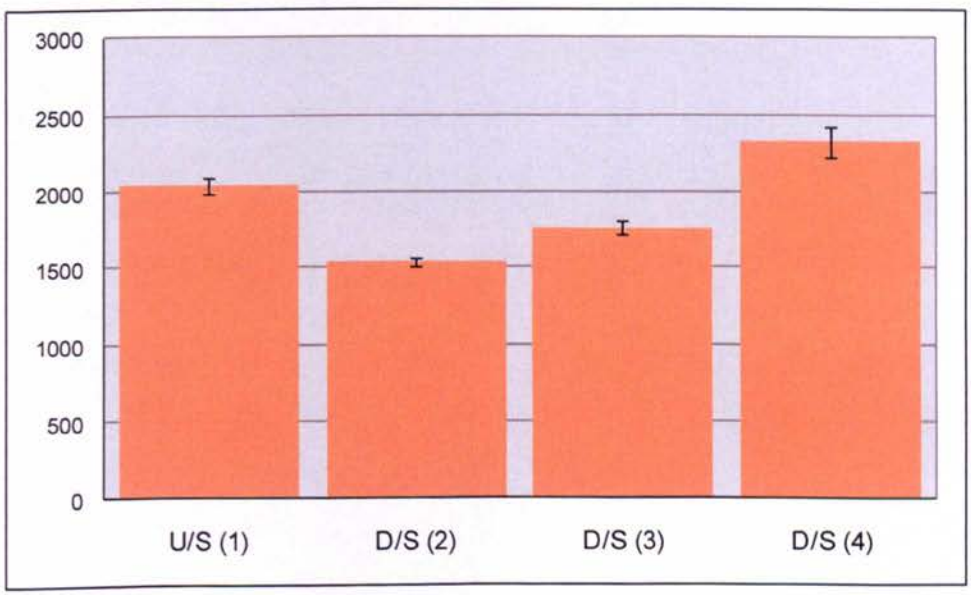

Figure 7.4: River Mole TP concentrations in sediment (mg TP kg^{-1}), ICP-MS analysis. Error bars are 3 x SD

As Tables 7.1 & 7.2 and Figures 7.1 – 7.4 shows, the pattern of TP concentration in sediments is inconsistent between rivers, a finding reported in literature (Clarke & Wharton, 2001). Variation in the location and number of wastewater outflow points, discharge rate of wastewaters entering the river, river flow and site access affect the results for this project, for example the closest downstream Hogsmill sampling point is 200m from the most downstream STW outflow on the Hogsmill, whilst for the Bourne it is possible to sample within 10 m of the outflow/river confluence. The primary reason for the inconsistency of sampling positions in relation to STW outfalls is the policy of Thames Water plc. to restrict

access to authorised in the vicinity of the outfall, as discussed in Sections 3.2.1.2 and 3.2.2.1. In the case of the Mole, it was not possible to access the river further than 600 m from the outflow as it became private land beyond this point and the river was too deep to wade (Section 3.2.4.2).

Trends for individual rivers are similar whether ICP-MS or ICP-AES results are used. Certified reference materials used for quality control during analysis did not state recovery figures for P. As the most accurate recoveries for certified metals were obtained from ICP-MS, it is assumed that this trend would apply if values for P had been certified, so just ICP-MS results are discussed here.

Rivers Bourne and Blackwater (Figures 7.1 & 7.2) exhibit a similar steady increase in TP over distance from the outfall although TP concentrations in the Bourne are greater, the highest concentration of TP in sediment from all project rivers is found at the furthest downstream point of the Bourne, 3776.39 mg TP kg^{-1}. It may be that sediment transported downstream begins to accumulate where river morphology changes, e.g. the river channel widens, reducing river flow, leading to deposition of suspended sediments.

The Bourne is not significantly different from upstream at the first sampling point close to the outflow, but it is significantly higher from D/S (3), 200 m downstream (Table 7.2). Wastewaters from the Lyne Lane STW enter the Bourne in a fast flowing stream via a narrow concrete culvert which may inhibit settling of contaminants until the river flow decreases further downstream. Geogenically, sediment may differ from U/S (1) and D/S (2) at D/S (3) and D/S (4) where the river is encased in concrete as it flows underneath the motorway bridges. Although it is reported that river channelization generally reduces the capacity for nutrient retention within sediments because river flow is constant and there is less opportunity for the deposition of particulate matter, this does not seem to be the case with the Bourne as TP concentrations in sediments from D/S (3) and (4) are greater than D/S (2) (Withers & Jarvie, 2008). Increased TP concentrations in sediments at the furthest downstream point may be due to the combination of a natural channel bed and a reduction in river velocity which allow P-rich particulates to settle out of the water column.

TP concentrations in sediments from the Hogsmill increase by more than 100% 200 m downstream of the STW outflow, falling to less than the upstream concentration by D/S (4) (1300 m from the outflow), an increase at the final downstream sampling point, D/S (5) is

due, most probably, to inputs from a combined sewer outflow (CSO) close by (Table 7.2, Figure 7.3) (J. Smith, E.A., pers. comm., 2009).

The Mole exhibits the highest upstream TP concentrations, 2050 mg TP kg^{-1}, it is only river where TP within sediments decrease significantly at the first downstream (outflow) sampling point (Table 7.2, Figure 7.4). Possible explanations for the downstream reduction are explored in section 7.3.2 in conjunction with P-release data.

Overall, concentrations of TP in sediment for this project's dataset are a similar order of magnitude to those reported in literature. Owens *et al.* (2001) report channel bed sediments of less than 1280 mg TP kg^{-1} from the River Swale (U.K) a relatively unpolluted river flowing through a mainly rural catchment, whilst Clarke & Wharton (2001) found 154 – 2247 mg TP kg^{-1} in a study of 17 lowland rivers in the south-east U.K. Their highest TP concentrations are low in comparison to those reported by Rose (1995) of up to 6158 mg TP kg^{-1} in the Rivers Welland (U.K.) and Morava (Czech Republic) and Owens & Walling (2001) who found between 1002 – 5870 mg TP kg^{-1} in sediment from the Rivers Aire and Calder (U.K.) . The high concentrations of TP in sediment reported by Owens & Walling (2001) are attributed to the 69 STWs and 1734 consented discharges these rivers, the highest P concentration in sediments was found after the confluence of these rivers, downstream of major conurbations encompassing Leeds and Huddersfield (U.K.).

7.3.2. Phosphorus release from sediment

Site/River	Blackwater	Bourne	Hogsmill	Mole
Upstream	2.63	< LOD	4.21	5.50
Downstream 1	5.61	< LOD	19.83	< LOD
Downstream 2	2.50	4.84	6.49	6.49
Downstream 3	2.33	4.17	6.31	5.87
Downstream 4	4.50	4.59	10.78	not sampled
t-test U/S & D/S1 (n=3)	0.060	< LOD	0.002	< LOD
	N/S	n/a	< 0.005	n/a
t-test U/S & furthest D/S (n=3)	0.008	< LOD	0.03	4.69E-05
	< 0.01	n/a	< 0.05	< 0.0001

t-tests - combined data-set	t-test result	significance
U/S & D/S 1 (n=12)	0.19	N/S
U/S & D/S 2 (n=12)	0.0070	< 0.01
U/S & D/S 3 (n=12)	0.0110	< 0.05
U/S & D/S 4 excluding Mole (n=9)	0.0002	< 0.0005

Table 7.4: SRP release from sediment in 2mmol-^{1} $CaCO_3$ solution (mg kg^{-1}) and t-test ($P < 0.05$)

Whilst acid digestion quantifies TP concentrations within sediments, the results do not necessarily relate to desorption of bioavailable P from sediment *in situ*. Desorption of P from sediment is influenced by factors such the extent to which the overlying water column is saturated in respect of P and the ability of sediment to retain P, which is itself affected by physical and chemical characteristics such as sediment fraction size, composition of river bed and the presence of Al, Fe, Mn, $CaCO_3$ and organic matter which increase sediment binding capacity (House & Denison, 2000; House & Denison, 2002; Jarvie *et al.*, 2005; Jarvie *et al.*, 2008b).

Authors use a variety of analytical and modeling processes to explore the relationship between total P in sediment and impact on water quality such as sorption tests to determine equilibrium P concentration (EPC_0) as discussed in Chapter 2, release experiments to ascertain P release or uptake from sediments and sediment pore-water analysis to establish P concentrations at the sediment-water interface in order to gain a greater understanding of P behavior (House & Denison, 2000; Jarvie *et al.*,2004; Jarvie *et al.*, 2008b).

Results from SRP release experiments carried out for this project, like the acid digestion analyses for sediments, vary between rivers (Table 7.4). In total, fifty-seven samples were analysed. The only river to show a statistically significant increase in P release at the downstream point closest to the outflow is the Hogsmill. When the combined data-set of all four rivers is used to calculate t-tests, there is no significant difference between U/S (1) and D/S (2), although sampling points further downstream are all significantly different from upstream (Table 7.4).

SRP release from River Mole sediment was < LOD at the downstream sampling point closest to the STW outflow, this result may be linked to the TP reduction of ≈25% in comparison to upstream sediment as it is possible that wastewaters dilute upstream P concentrations in the water column, and that mobilisable SRP in sediment desorbs in situ to make up this deficit (Jarvie *et al.*, 2005). Further down the Mole, as TP concentrations in sediment increase, SRP desorption is detectable at a similar rate to upstream.

P release at U/S (1) and D/S (2) on the Bourne was < LOD and, although t-tests did not verify that SRP release rates increased downstream, from D/S (3) onwards they are clearly greater than upstream. Possible explanations for the lack of significant difference between U/S (1) and D/S (2) are discussed in 7.3.1.

When comparing SRP release at U/S (1) with the furthest downstream sampling points for individual rivers, desorption on the Hogsmill (D/S (5)), Blackwater (D/S (5)) and Mole (D/S (4)) are significantly different and this also the case when the combined data-set is used. The quantity of sediment storage relative to sediment binding capacity is influenced by sediment mineralogy and the presence of Al, Fe, Ca and organic matter (House & Denison, 2002; Wang *et al.*, 2008).

It has not been possible to compare these project findings with those in literature, as SRP release figures are rarely quoted in isolation; they are usually modeled in conjunction with other measurements to produce EPC_0 figures and this project lacks the data to proceed to this stage (Jarvie *et al.*, 2005) . Therefore, the following section considers relationships between SRP released in water and TP in sediments to provide context.

7.3.3. Comparison of Phosphorus release relative to total phosphorus in sediments

Site/river	Blackwater		Bourne		Hogsmill		Mole	
	mg kg^{-1}	%	mg kg^{-1}	%	mg kg^{-1}	%	mg kg^{-1}	%
U/S (1)	0.0038	0.38	< LOD	—	0.0056	0.56	0.0027	0.27
D/S (2)	0.0050	0.50	< LOD	—	0.0109	1.09	< LOD	—
D/S (3)	0.0022	0.22	0.0028	0.28	0.0063	0.63	0.0037	0.37
D/S (4)	0.0015	0.15	0.0018	0.18	0.0076	0.76	0.0025	0.25
D/S (5)	0.0017	0.17	0.0012	0.12	0.0093	0.93	not sampled	
R^2 P release/TP								
	0.10		0.48		0.97		0.46	

Table 7.5: SRP-released in water as a proportion of TP in sediment (mg kg^{-1}) and ratio (%) and R^2

Site/River	Blackwater	Bourne	Hogsmill	Mole
U/S (1)	264.28	n/a	177.98	373.05
D/S (2)	200.06	n/a	91.50	n/a
D/S (3)	450.51	363.07	159.13	272.41
D/S (4)	649.26	562.44	131.66	397.42
D/S (5)	575.13	822.94	107.31	not sampled

Table 7.6: Partition co-efficient (Kd) of P in sediment

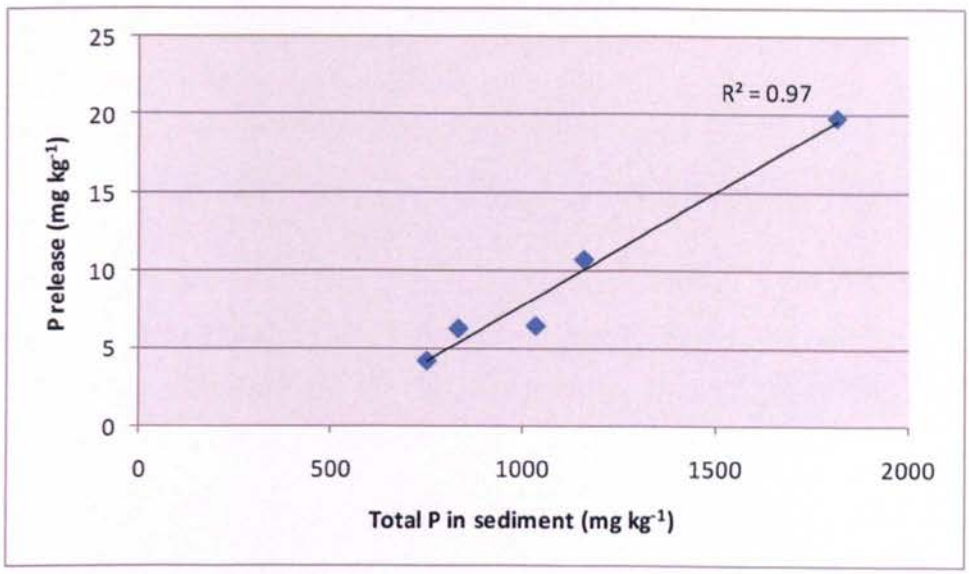

Figure 7.5: River Hogsmill scatterplot of relationship between mean SRP release and TP in sediments. T-test result is 0.004, P is significant at $P < 0.005$.

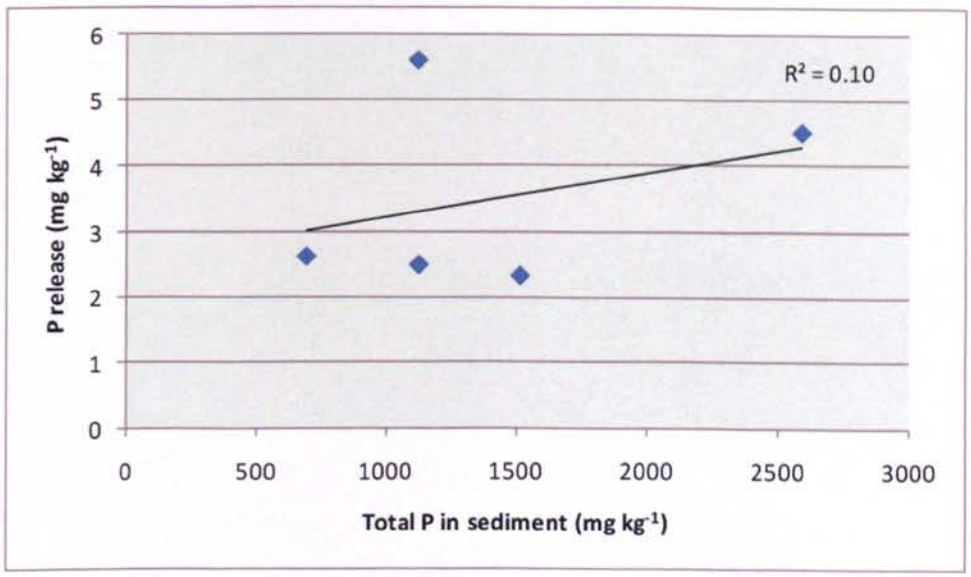

Figure 7.6: River Blackwater scatterplot of relationship between mean SRP release and TP in sediments. T-test result is 0.012; P is significant at $P < 0.05$.

Greatest SRP desorption from sediments occurred in the Hogsmill, particularly at the downstream sampling point closest to the STW outfall where more than twice as much P is mobilized than upstream (Tables 7.5 & 7.6). The R^2 figure of 0.97 shows that the relationship between TP in sediment and SRP released in water is very strong (Table 7.5, Figure 7.5). TP concentrations in Hogsmill sediment are greatest at D/S (2), and it is unsurprising that SRP desorption is highest there, but even at D/S (5) where the mean TP concentration in sediment is lower than comparable rivers, Hogsmill SRP desorption is considerably more.

These findings are supported by the partition coefficient (Kd) figures shown in Table 7.6 which demonstrate the strength with which P is retained in sediment, the higher the figure

the greater the retention strength. The lowest Kd occurs in Hogsmill D/S (2), closest to the STW, where the greatest desorption and highest ratio of desorbed SRP: TP in sediment occurs and the highest Kd result is in the River Bourne D/S (5) where the ratio of desorbed SRP: TP in sediment is lowest.

These findings demonstrate the importance of using contaminant desorption measurements in conjunction with total contaminant analysis to determine the impact on the receiving river as, if considering sediment TP concentrations in isolation, sediment in the Bourne and Blackwater would seem most contaminated for P downstream of the STW when in reality these two rivers seem most effective at retaining it.

7.3.4. Relationship between Fe or Al and total phosphorus

	Blackwater		Bourne		Hogsmill		Mole	
	r	t-test value	r	t-test value	r	t-test value	r	t-test value
TP/Fe	0.80*	0.0009	-0.23*	0.0006	-0.91*	0.0010	-0.16*	0.0015
TP/Al	0.55	0.201	-0.11	0.624	0.06	0.0390	-0.83*	0.0004
SRP/Fe	0.06*	0.001	-0.40	0.0055	-0.91*	0.0003	0.30*	0.0005
SRP/Al	0.20	0.009	0.24	0.004	-0.05	0.006	-0.84	0.011

Table 7.7: Linear correlation (r) between TP in sediment and SRP released from sediment with Al or Fe, n=5. *Significant at $p < 005$.

Fe and Al are frequently used in wastewater treatment to reduce P levels in the final effluent, e.g. the Hogsmill Valley STW has been using Al salts since April 2008 (see Chapter 3) and the main Paris STW, Seine-Aval, uses a tertiary $FeCl_3$ flocculation process (Wallis, 2007; Buzier *et al.,* 2006) . $Fe_2(SO_4)_3$ may be used to remove P from eutrophic water bodies (Perkins & Underwood, 2001). Therefore, the affinity of these two metals for P is well known.

A number of studies have examined the relationship between Fe or Al and the behaviour of P in river sediments (Perkins & Underwood, 2001; House & Denison, 2002; House, 2003; Coelho *et al.,* 2004; Withers & Jarvie, 2008). Frequently, they involve detailed examination of P, Fe and Al species and fraction size, which has not been possible here. Interaction between P and minerals in the water column is complex and requires investigation of pH, microbial action, bioturbation, reactive fractions of metals etc. It is also necessary to understand how individual rivers are affected by STW wastewater inputs (Withers & Jarvie, 2008). For this project, analysis of the relationships between TP or released SRP and total Fe

or Al was undertaken although, given the small data set (n=5), this is a limited investigation (Table 7.7).

The strongest positive dependencies in any of the four project rivers occurs in the Blackwater, particularly between Fe and TP , the t-test indicates that this relationship is significant. This result is supported by research from House & Denison (2002) who found total Fe content in sediment to be a significant, positive, predictor of TP in sediment some rivers, including the Blackwater. They also identified vivianite within sediment from the Blackwater channel bed, frequently linked to STW inputs, formed by the precipitation of Fe oxides where O_2 levels are low and SRP concentrations in pore water are high (House, 2003;Withers & Jarvie, 2008).

Without additional sampling and analyses of sediments, to establish the proportions of reactive Fe and Al within the total fraction of these metals, and quantification of Ca concentrations as this also plays an important role in the precipitation of P to sediment, it is only possible to highlight the fact that the storage or release of P within sediment from these rivers seems to be influenced by either Fe or Al (Withers & Jarvie, 2008).

7.3.5. Total metals in sediments

Bourne	Al	As	Cd	Cr	Cu	Fe	Ni	Pb	Zn
U/S (1)	2143.49	7.74	0.09	7.14	4.13	46719.12	7.65	11.19	41.90
D/S (2)	3359.71	13.09	0.08	11.84	6.62	64150.06	12.96	17.52	60.47
D/S (3)	2005.91	6.50	0.08	7.01	7.59	37987.07	8.56	13.76	62.16
D/S (4)	1950.76	6.73	0.12	6.98	14.30	42615.20	9.81	16.78	86.24
D/S (5)	2450.94	6.60	0.23	8.33	31.19	46750.98	13.85	23.40	129.88
Blackwater									
U/S (1)	1299.87	4.16	0.12	5.49	3.86	10872.20	2.58	8.61	34.88
D/S (2)	712.84	3.31	0.16	5.13	6.53	9311.90	6.36	9.77	45.82
D/S (3)	581.79	2.17	0.10	3.69	3.51	8018.05	3.28	7.15	36.94
D/S (4)	713.57	3.39	0.12	4.10	3.98	13480.76	3.48	9.21	50.60
D/S (5)	1671.39	4.47	0.33	6.62	13.44	15509.97	4.86	26.45	97.91
Mole									
U/S (1)	4544.37	7.68	1.06	23.88	21.69	39004.46	46.30	31.38	300.59
D/S (2)	6766.24	8.19	1.19	27.43	24.46	32385.35	40.91	30.83	180.78
D/S (3)	5545.01	7.50	1.55	24.68	26.25	35968.87	46.37	49.67	265.49
D/S (4)	4975.24	7.33	1.41	25.20	32.76	30047.83	37.89	49.91	297.07
Hogsmill									
U/S (1)	4651.98	3.96	0.73	16.60	59.41	12218.98	15.20	146.15	208.66
D/S (2)	3152.18	2.20	0.28	10.24	31.93	6981.58	8.52	52.35	107.40
D/S (3)	2084.49	3.02	0.22	14.02	17.60	10519.31	10.58	189.90	100.78
D/S (4)	1797.65	2.16	0.18	11.08	104.27	10158.56	18.09	133.98	556.96
D/S (5)	2334.98	2.90	0.20	12.98	80.77	10880.92	13.52	132.48	366.63

Table 7.8: Total metals concentrations in sediments (mg kg^{-1}) determined by digestion with acid (USEPA method 3050B)

River	T test	Cr	Ni	Cu	Zn	As	Cd	Pb	Al	Fe
Black-water	U/S (1) & D/S (2)	0.709	0.137	0.223	0.027	0.300	0.235	0.058	0.003	0.654
		N/S	N/S	N/S	< 0.05	N/S	N/S	N/S	S/L	N/S
	U/S (1) & D/S (5)	0.135	0.020	0.012	0.005	0.622	0.003	0.003	0.004	0.007
		N/S	< 0.05	< 0.05	< 0.005	N/S	< 0.005	< 0.005	< 0.005	< 0.01
Mole	U/S (1) & D/S (2)	0.251	0.010	0.052	0.0004	0.022	0.081	0.391	0.0048	0.002
		N/S	S/L	N/S	S/L	N/S	N/S	N/S	< 0.005	S/L
	U/S (1) & D/S (4)	0.610	0.021	0.014	0.760	0.464	0.012	0.153	0.031	0.004
		N/S	S/L	< 0.05	N/S	N/S	< 0.05	N/S	< 0.05	S/L
Bourne	U/S (1) & D/S (2)	0.047	0.006	0.010	0.023	0.004	0.340	0.212	0.008	0.016
		< 0.05	< 0.01	< 0.05	< 0.05	< 0.005	N/S	N/S	<0.01	< 0.05
	U/S (1) & D/S (5)	0.840	0.036	0.003	0.004	0.041	0.036	0.0009	0.069	0.99
		N/S	< 0.05	< 0.005	< 0.005	S/L	< 0.05	< 0.001	N/S	N/S
Hogs mill	U/S (1) & D/S (2)	0.001	0.009	0.023	0.048	0.004	0.004	0.035	0.009	0.013
		S/L	S/L	S/L	S/L	S/L	S/L	S/L	S/L	S/L
	U/S (1) & D/S (5)	0.009	0.911	0.317	0.398	0.097	0.0002	0.768	0.002	0.049
		S/L	N/S	N/S	N/S	N/S	S/L	N/S	S/L	S/L
N/S – not significant					S/L – significantly lower					

Table 7.9: T-test results (actual value and level of significance) for metals concentrations in sediments at upstream and downstream sites closest to and furthest from STW outflow. P < 0.05, n=3.

As with P, the pattern of metals concentrations varies between rivers and metals concentrations in sediments downstream of the STW are frequently lower than upstream. In the Hogsmill, all metals decreased significantly at D/S (2) and were similar to or significantly lower than upstream concentrations at D/S (5) (Tables 7.8 & 7.9). In the River Mole Al, Cd and Cu increased downstream.

Seven of the nine metals analysed increased significantly downstream of the Blackwater STW, mainly at D/S (5) (Tables 7.8 & 7.9). In the Bourne, all nine metals increased significantly downstream of the STW and, except for Cd and Pb these increases were apparent at D/S (2), closest to the STW.

7.3.6. Relationship between metals in sediments and water

	Al	As	Cd	Cr	Cu	Fe	Ni	Pb	Zn
Bourne (r)	-0.16	0.31	-0.02	-0.22	-0.49	-0.13	-0.84	-0.92	-0.37
P value	0.72	1.65	0.71	0.73	0.81	0.71	1.29	1.85	0.76
Hogsmill (r)	0.98*	0.88	-0.26	0.38	0.33	0.71	-0.07	-0.17	0.17
P value	0.04	1.49	0.73	0.76	0.75	1.00	0.71	0.72	0.72

Table 7.10: Linear correlation (r) between metals in sediment and flow weighted mean concentrations in river water and t-test value, n=4. *Significant at p<005.

Despite strong linear correlation between metal concentrations in sediment and those in water for Ni and Pb in the Bourne and Fe, As and Al in the Hogmsill, the relationship is significant for Al only. Results must be treated with caution due to the small number of sampling sites. Combining data from the two rivers did not improve the linear correlation.

7.3.7. Quality assessment of total metals in sediments

	Guidelines		Percentage incidence of effects		
Metal	ERL	EML	< ERL	ERL–ERM	> ERM
As	8.2	70	5.0	11.1	63.0
Cd	1.2	9.6	6.6	36.6	65.7
Cr	81	370	2.9	21.1	95.0
Cu	34	270	9.4	29.1	83.7
Pb	46.7	218	8.0	35.8	90.2
Ni	20.9	51.6	1.9	16.7	16.9
Zn	150	410	6.1	47.0	69.8

Table 7.11: Sediment Quality Guideline values for trace metals (mg kg^{-1}).Percentage incidence of effects = no. of data entries for each range in which biological effects were observed divided by the total no. of entries within that range (USEPA, 1999)

There is no sediment quality protocol in the U.K., so US EPA Sediment Quality Guidelines (SQG) are used here to assess the likely impact of metals concentrations in sediment from the project rivers, two of the metals analysed during this project, Al and Fe, are not included in the guidelines (Table 7.11) (USEPA, 1999). SQG comprise two values, obtained by ranking individual metal concentration and toxicity to biota; ERL (effects range low) is equivalent to the 10th percentile and ERM (effects range median) is equivalent to the 50th percentile. Metal concentrations below ERL rarely cause adverse effects to biota but concentrations greater than ERM frequently result in adverse effects to biota, as shown in the percentage effects figures in Table 7.11 (USEPA, 1999). As SQG are not toxicity thresholds, being more an indication of hazard, there is no certainty that sediments containing metals below the ERL are completely safe so it is recommended that these guidelines are used in conjunction with other assessment methods such as benthic community analyses (USEPA, 1999).

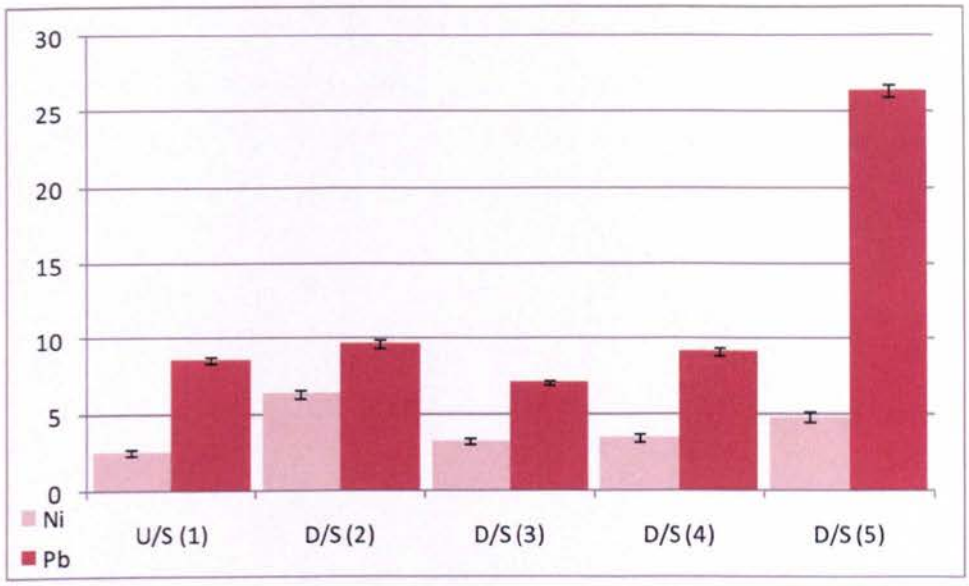

Figure 7.7: River Blackwater Ni and Pb concentrations in sediment (mg kg^{-1}). Error bars are 3 x SD.

The Blackwater is the only river where no metals concentrations exceed the quality guideline figures. For example, Ni and Pb concentrations, shown in Figure 7.7., are well within the ERL, so biota are unlikely to be adversely impacted by these metals, the risk of adverse effects is 8% for Pb and 1.9% for Ni based on samples falling within the ERL range (not the entire database of sediment samples).

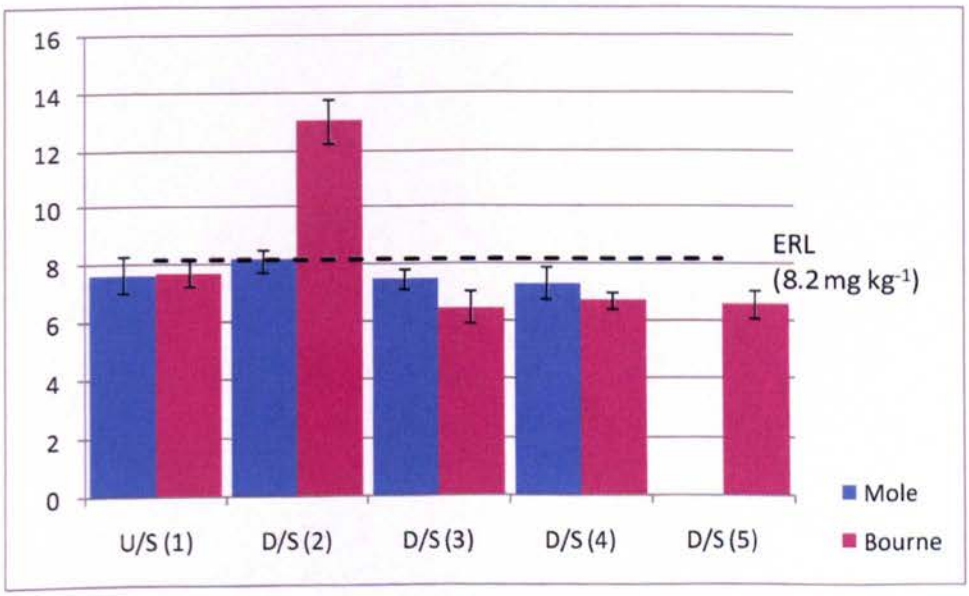

Figure 7.8: Rivers Bourne & Mole As concentrations in sediment (mg kg^{-1}). (ERL figures from U.S.E.P.A Sediment Quality Guidelines, error bars as Figure 7.7)

As concentrations in the Bourne and Mole are at least 30% higher than those in the Blackwater and Hogsmill (Figure 7.8). The Bourne is the only river to show a significant increase in As concentration in sediment downstream of the STW. As discussed in 6.3.1.1, As concentrations in river water also increased significantly increased downstream of the

SWT. The Bourne As concentration exceeds the ERL at the downstream point closest to the outflow but is well within the ERM concentration (70 mg kg^{-1}). No other metals in Bourne sediment exceed ERL levels. The potential risk to biota where the As concentration is below the ERL is 5% rising to 11.1% where concentrations are greater than the ERL but below the ERM.

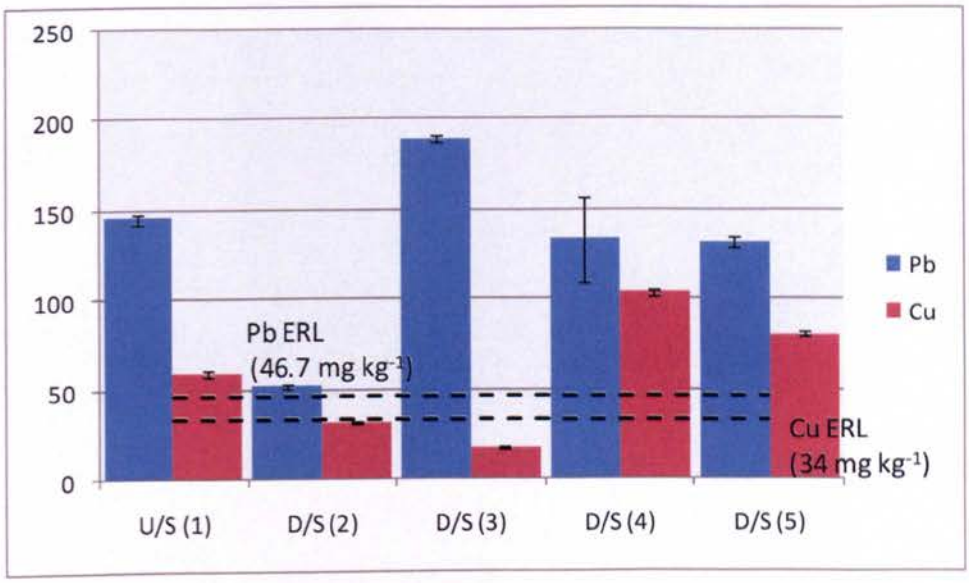

Figure 7.9: River Hogsmill Cu and Pb concentrations in sediment (mg kg $^{-1}$).(ERL and error bars as in Figure 7.8)

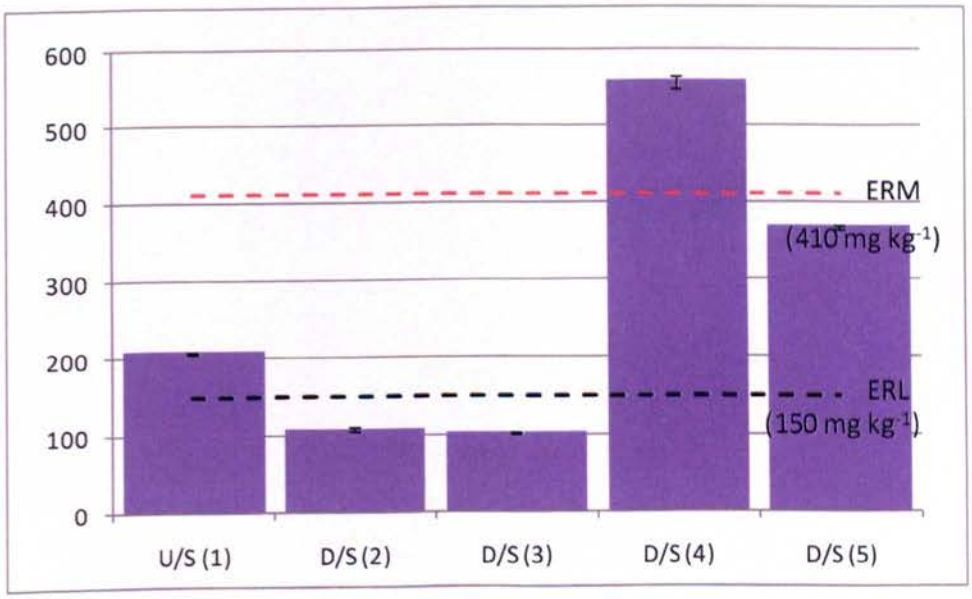

Figure 7.10: River Hogsmill Zn concentrations in sediment (mg kg-1). ERM (effects range median) & ERL) figures from U.S.E.P.A Sediment Quality Guidelines

Sediment samples up and downstream of the Hogsmill STW contain similar quantities of Pb and they all exceed the ERL (46.7 mg kg^{-1}) (Figure 7.9. Pb is the only metal in Hogsmill

river water that increased significantly downstream of the STW, possible sources are discussed in 6.3.1.2. The potential risk to biota where concentrations exceed the ERL but remain below the ERM is 35.8%, increasing to 90.2% above the ERM of 218 mg kg^{-1}. At D/S (3), the concentration of 190 mg Pb kg^{-1} indicates that biota is particularly at risk.

There is no significant difference between Cu concentrations in the Hogsmill but the U/S (1) and D/S (5) sampling sites exceed the ERL (Figure 7.9). SQG's give accumulation toxicity figures where one or more ERL is exceeded; in this case increasing the percentage incidence of effects to biota in the Hogsmill is 38% (USEPA, 1999).

In addition, Zn concentrations in Hogsmill sediment (Figure7.10) exceed the ERM at D/S (4), further increasing the risk of adverse effects to biota in conjunction with Pb and Cu to 52% (USEPA, 1999).

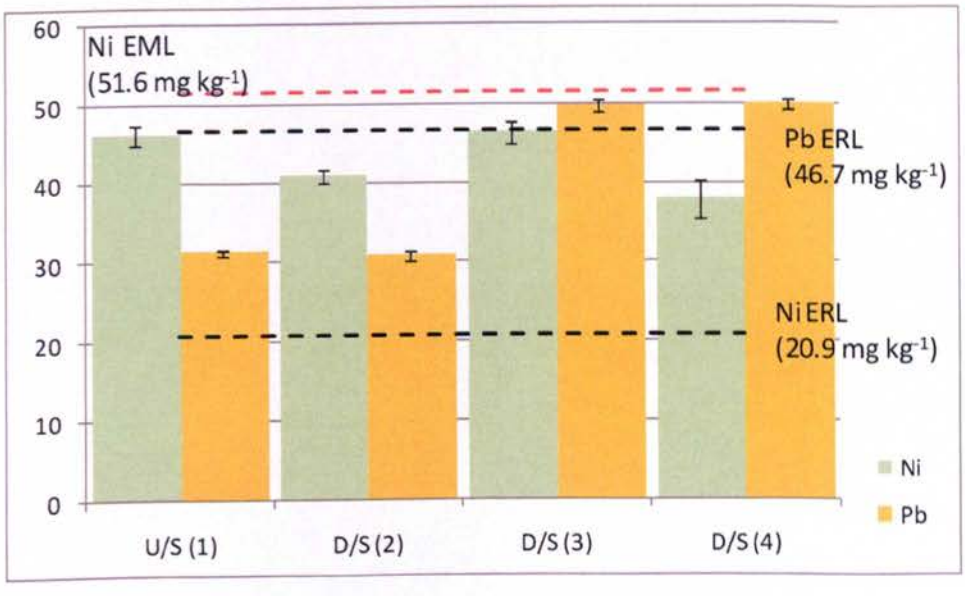

Figure 7.11: River Mole Ni and Pb concentrations in sediment (mg kg^{-1}). Error bars are 3 x SD. ERL, ERM & SD as Figure 7.10.

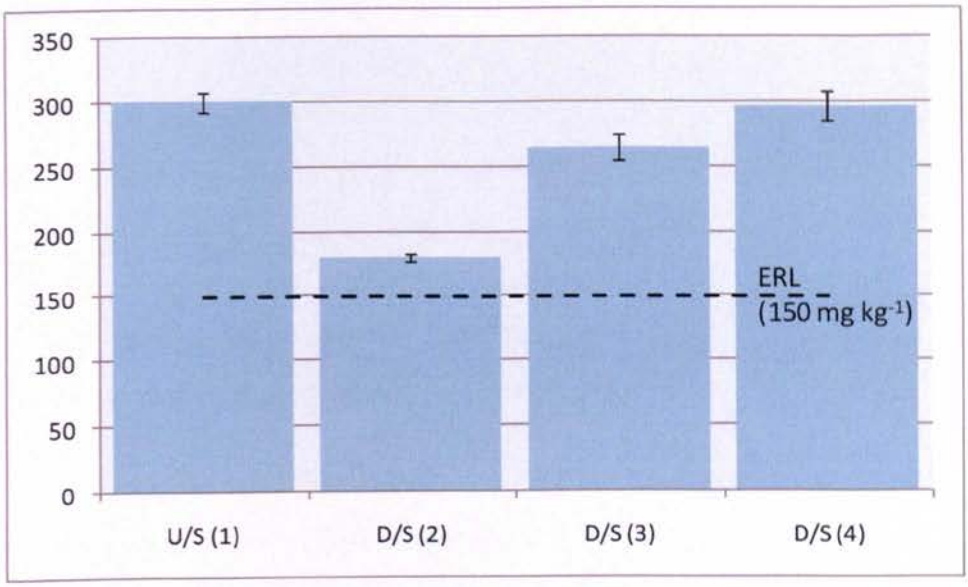

Figure 7.12: River Mole Zn concentrations in sediment (mg kg^{-1}). ERL & error bars as Figure 7.8.

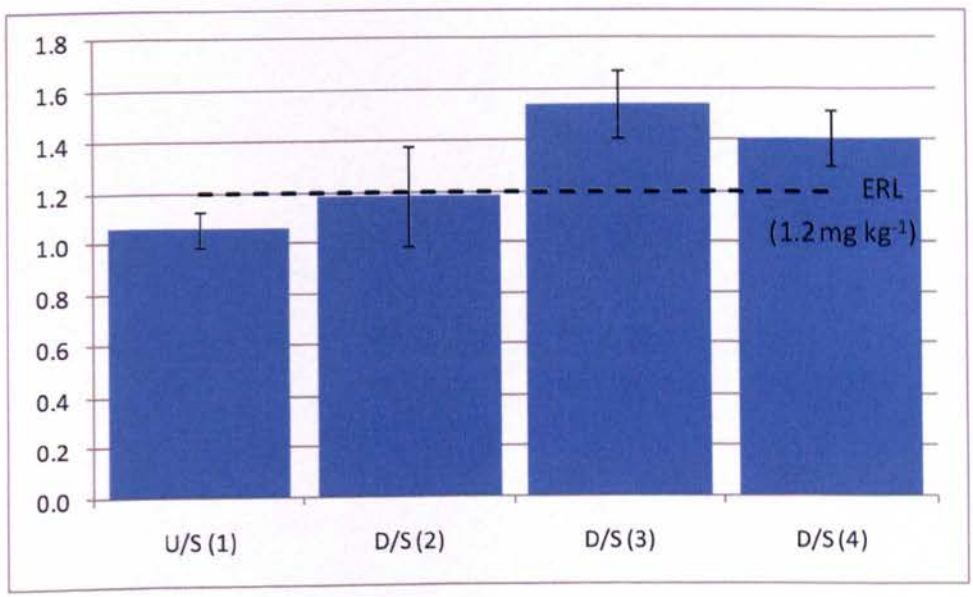

Figure 7.13: River Mole Cd concentrations in sediment (mg kg-1). ERL and error bars as Figure 7.8.

Of the four rivers analysed in this project, sediment from the River Mole contained the highest number of individual metals exceeding their ERL's (Figures 7.11, 7.12 & 7.13) and As levels which are close to the ERL (Figure 7.8). The only metal to increase significantly downstream of the STW and exceed the ERL is Cd (Figure 7.13). The risk of adverse effects to biota from an accumulation of metals exceeding ERL's is 38%, less that the Hogsmill because none of the metals in the Mole sediments exceeded their ERM.

7.4. Conclusions

Channel bed sediments from four rivers were analysed for P and metals to obtain additional information on the impact of STW wastewaters. Concentrations of TP in sediments increased downstream of STW for the Blackwater, Bourne and Hogmsill. Mole TP concentrations decreased at D/S (2), increasing to become significantly greater than U/S (1) by D/S (4), the furthest downstream sampling site. TP concentrations from all rivers were similar to those reported in literature for rivers receiving urban and STW inputs.

P release analysis indicates that desorption of SRP in water is not necessarily linked TP concentrations in sediment. Sediment from the Hogsmill shows the strongest relationship between TP and desorption and the Blackwater the weakest, factors including grain size, geology and the presence of minerals such as Ca, Fe, Al, Mn and organic matter influence desorption (House & Denison, 2002). Substantial increases to TP concentrations in sediments for the Bourne, Blackwater and Mole at sampling points further downstream did not increase the quantities of the SRP released, suggesting these rivers are acting as sinks for P, whilst the quantity of SRP released from Hogsmill sediments despite reductions in TP suggests they are a source of SRP to the river. These findings are substantiated by partition co-efficient (Kd) calculations.

This may have particular implication for the Hogsmill as P-stripping was introduced in April 2008, leading to reductions in SRP levels in the downstream water column, as discussed in Chapters 4 and 5. It is possible that reductions to downstream SRP concentrations in the water column may not be as great as anticipated whilst P desorbs from sediment so readily.

If the Hogsmill was prone to flooding, it is likely that river water downstream of the STW would deposit P and trace metals on soils in the vicinity of the river. However, to prevent flooding of the urban catchment which includes commercial property and Kingston Guildhall, the Hogsmill is heavily channelised downstream of the STW and, even when the nearby Thames is on flood alert; the Hogsmill River is contained within its concrete channel. Downstream of the STW in this project, the Bourne, Blackwater and Mole are prone to flooding, potentially depositing P and metals on the surrounding floodplains where they may be retained by topsoil but also, as floodwaters recede, taking additional quantities of these pollutants with them (Cook, 2007).

Despite the limited data set, there is strong positive correlation between Fe and TP in the Blackwater, strong negative correlation between Fe and TP and Fe and released SRP in Hogsmill and strong negative correlation between Al and TP and Al and released SRP in the Mole. These inter-element relationships appear to affect whether P adsorbs readily to sediment and it's propensity to desorb readily in water but further analysis is required to confirm this.

The relationship between metals concentrations in sediment and river water was significant for Al in the Hogsmill although several other metals showed strong linear correlation. Analysis of samples from a greater number of sediment and water sampling sites is required to confirm whether there are dependencies.

Seven of the metals analysed showed a significant increase downstream of the Bourne SWT, additionally Cd and Pb, which were not significant at D/S (2), were significant at D/S (5). Despite these increases, only As occurred in sufficient concentration to exceed the effects range low (ERL) criteria of the Sediment Quality Guidelines (SQG) (USEPA, 1999). As levels in river water from the Bourne were also elevated, as discussed in 6.3.1.1., suggesting there is a continuous input to the river.

Although only two of the metals, Zn and Pb, increased significantly at the Blackwater D/S (2) sampling site, closest to the outflow, by D/S (5) seven of the metals were higher than those in upstream sediment. However, none of the Blackwater metals exceeded SQG ERL's.

In the Mole, only Al was significantly increased downstream of the STW, with Cd and Cu being significantly increased by D/S (4). In terms of SQG's, this river has the greatest number of metals exceeding ERL's, although their source is not necessarily the Horley STW (see section 3.2.4.) and the high upstream P levels suggest that there is an upstream pollutant source e.g. agriculture, sewage effluents or industry.

The Hogsmill is the only river where none of the metals increase significantly downstream, yet Cu and Pb exceed ERL's and concentrations appear higher downstream. Zn is particularly elevated at D/S (3), being the only metal in this study to exceed the SQG effects level median (ERM). Overall, sediment from the Mole and Hogsmill seem to be most polluted in terms of metals and, using the SQG as a benchmark, the rivers most likely to cause adverse effects to biota.

Concentrations of metals in sediment downstream of STW are not consistently greater than upstream in any of the project rivers. Potential explanations for the lack of a distinct pattern include historic industrial inputs of metals to the river and anthropogenic changes such as channelization and dredging. Differences in land use, for example, inputs of metals from agricultural fertilisers, industrial discharges and urban run-off are also likely to affect the type and concentration of metals in river sediments. Overall, although several of the project rivers, particularly the Hogsmill and Mole, contain metals in sediments downstream of the STW outflow in concentrations likely to harm biota, these metals are not necessarily attributable to STW discharges.

8. Conclusion

The Water Framework Directive (WFD) (2000/60/EC) is designed to harmonise existing legislation in member countries and improve the overall quality of European waters (E.C., 2000). It states that within 15 years of its implementation date (2015), surface water bodies within all European countries must achieve "good ecological quality" (DEFRA, 2003). More specifically, the physico–chemical quality descriptors for rivers indicate that nutrient concentrations should not attain levels which adversely affect the ecosystem (E.C., 2000). For metals, quality standards vary, some, e.g. Cd, Hg, Pb and Ni appear on the list of Priority Substances (Annex VIII), Cd and Hg also have specific emission limits under Annex IX and all metals are included in Annex XIII, the indicative list of main pollutants; ultimately, the Directive's goal is to end the discharge of metals into water bodies (E.C., 2000).

The purpose of this project was to assess the impact of sewage wastewaters on P and metals concentrations in sediments from four and water from two second order rivers, to ascertain whether they are likely to achieve "good ecological status" under the WFD by the target date of 22nd December 2015. Over an eighteen month period, water samples were collected on at least 47 sampling occasions to cover a range of dates, times and weather conditions. Sediments were collected once from each river, along a reach of at least 1 km to cover upstream and a minimum of three downstream sites.

The main findings from this project are detailed below:

8.1. Phosphorus

Downstream of the STW outflows, TP concentrations in the rivers Hogsmill and Bourne occurred predominantly as SRP and were significantly increased from those upstream, frequently by an order of magnitude. This finding is consistent with those reported by Neal *et al.* (2005) and other researchers attached to the U.K. Centre for Hydrology and Ecology (May *et al.*, 2001; Bowes *et al.*, 2005; Jarvie *et al.*, 2008a; Withers & Jarvie, 2008).

Although SRP concentrations in the downstream Hogsmill reduced significantly following the introduction of P-stripping from 1st April 2008, downstream flow weighted mean SRP concentrations for both rivers are higher than the E.A. target figure of 0.20 mg SRP l^{-1} for lowland rivers on clay substrates (Mainstone *et al.*, 2000). The current E.A. target figure is

generous in comparison to that proposed by the U.K. Technical Advisory Group for the Water Framework Directive of 0.12 mg SRP l^{-1} for rivers 80 m above sea level with more than 50 mg $CaCO_3$ l^{-1} (UK TAG, 2006).

As downstream river flow is substantially increased by STW wastewaters, the impact of increased P concentrations is most noticeable when estimated loads are calculated; the Bourne upstream load of 1.07 kg SRP day^{-1} increased to 45.09 kg SRP day^{-1} at the downstream point closest to the outflow and, before P stripping processes were introduced, the Hogsmill upstream load of 7.78 kg SRP day^{-1} rose to 208.42 kg day^{-1} downstream. The benefit of P stripping to the Hogsmill River is best observed in the estimated post P-stripping figure of 83.01 kg SRP day^{-1} at the first downstream sampling site (D/S (2)).

Unexpectedly, P concentrations in samples collected from the upstream Hogsmill sampling site exhibited high ratios of SRP to TP and these were traced to a series of small discharge consents approximately 3.5 km upstream of the STW (J. Smith, E.A., pers. comm., 2009). The flow weighted mean figure of 0.19 mg SRP l^{-1} in the upstream Hogsmill, twice that of the upstream Bourne, is similar to the current E.A recommendation of 0.20 mg SRP l^{-1} for this type of river (Mainstone *et al.*, 2000). If the U.K. TAG recommendations are adopted, the upstream Hogsmill fails to be compliant before STW wastewaters are discharged to it (UK TAG, 2006). The impact of untreated or insufficiently treated sewage inputs from sources other than STW has been noted by researchers such as Withers & Jarvie (2008). SRP concentrations in the upstream Hogsmill show that in the headwaters of small rivers minor untreated sewage inputs may cause notable deterioration in water quality.

Sewage treatment processes separate solid matter from fluids and, where tertiary treatment is undertaken, effluent is micro-filtered before discharge, so it is not surprising that there was no significant difference in the P concentrations of 0.45 μm and 0.1 μm filtrates in either river (Sutherland, 2007). Dueñas *et al.* (2003) found particulate P to be the most completely removed form of P from sewage influent so, even if the pore size of STW filters is greater than 0.45 μm, this may explain why this project found downstream P mainly in soluble, more bioavailable form. Additionally, increased flows immediately downstream of the STW may prevent adsorption to suspended particulate matter.

Channel bed sediment from all study rivers were analysed for both TP and their ability to release SRP in $CaCO_3$ enriched water. Rivers Blackwater, Bourne and Hogsmill showed elevated levels of TP in sediments immediately downstream of STW outflows (D/S (2))

whilst TP in sediment from the Mole was less than upstream at the sampling point closest to the STW outflow (D/S (2)) but significantly greater by the furthest downstream sampling site (D/S (4)). Possible reasons for the high concentration of TP in sediment from the upstream Mole include its proximity to a major STW less than 10 km upstream and its rural location, surrounded by farmland, suggesting agricultural inputs. All rivers showed similar concentrations of TP in sediment to those reported in literature for urban rivers receiving STW inputs.

Whilst greatest TP concentrations in sediments were observed in the River Bourne at the furthest downstream sampling point, it is the Hogsmill that exhibits the lowest partition coefficient (Kd) and therefore the greatest potential release of SRP from sediment to the water column. Although P-stripping at the Hogsmill Valley STW commenced in 2008 to meet a revised annual mean discharge consent of 1.0 mg P l^{-1}, SRP concentrations in the receiving river may not reduce as anticipated until the source sediment is exhausted (A.Wallis, Thames Water plc., pers. comm., 2008).

8.2. Metals

Dissolved metals concentrations in the study rivers were generally similar to or less than those upstream, except for As in the River Bourne and Pb in Hogsmill. The downstream flow weighted mean concentration of 0.87 μg As l^{-1} in the Bourne is less than geogenic, background values for many rivers and well below the Environmental Quality Standard (EQS) recommended by the U.K. Technical Advisory Group on the Water Framework Directive, a maximum mean annual concentration of 50 μg As l^{-1} in freshwaters (UK TAG, 2008). Similarly, Pb concentrations in the downstream Hogsmill are less than 0.1 μg Pb l^{-1}, within regulatory limits for U.K. drinking water, but this metal is not mentioned in the UK TAG report (Drinking Water Inspectorate, 2006).

As with P, calculated loads for most metals increase downstream as a result of greater river water volume. For example the mean upstream daily load of 0.02 kg As day^{-1} in the Bourne rose to 0.09 kg As day^{-1} at the first downstream sampling point and daily loads of Pb in the Hogsmill increased similarly. Only Al in both rivers and Fe in the Bourne had lower daily loads downstream, probably because discharged wastewaters dilute geogenic concentrations. This is not necessarily beneficial to the downstream river, but the WFD does not require an evaluation of changes to underlying water chemistry as a result of high volume wastewater

inputs in isolation. Unless changes to taxa species or abundance were observed, this impact would not breach the Water Framework Directive.

There are no regulatory limits for contaminant loads in river water and, as they are modelled predictions, this is probably appropriate. The propensity for dissolved metals to adsorb to particulates, which then settle on the channel bed, makes it possible to estimate their impact in terms of metals concentrations within channel bed sediment downstream of a suspected source (Cotman *et al.*, 2001; Förstner, 2004). As the WFD does not contain specific limits for contaminants in sediment, although there is an intention that contaminant levels should not adversely affect biota, this study assessed metals concentration in sediment against US EPA sediment quality guidelines (SQGs) which exist for all metals analysed in the study except Al and Fe (E.C., 2000). SQGs use the criteria effects range low (ERL) and effects range median (ERM) to describe the likely impact of metals concentrations in sediment on biota, concentrations below ERL values are unlikely to be toxic to organisms (US EPA, 1999).

The Blackwater is the only river where all metals concentrations in sediment fall below the ERL although, of the nine metals analysed, only Cr and As concentrations in sediment are not significantly higher than upstream by the furthest downstream sampling site. In the Bourne, all metals concentrations increased significantly downstream of the STW but only As exceeds the ERL of 8.2 mg kg^{-1}, suggesting that more than 5% of biota may be adversely affected by its occurrence in sediment. Once more, the presence of As is exceptional in comparison to other metals in the Bourne, highlighting the need for further investigation into source and impact.

Although statistical testing suggests no metal sediment concentrations increase significantly downstream of the Hogsmill Valley STW, comparison of up and downstream flow weighted mean concentrations of Zn, Cu and Pb suggests that these metals do increase downstream. As Pb concentrations in river water downstream of the Hogsmill Valley STW are significantly different from upstream, it is unsurprising to find downstream sediment concentrations elevated too. Upstream and at two downstream sampling points, Zn, Cu and Pb exceed their ERL's and at the third downstream sampling point Zn exceeds the ERM too. A combination of three metals exceeding the ERL, as in the upstream Hogsmill, results in a probability of toxic effects to biota of 38%, downstream, because one metal exceeds its ERM, this likelihood increases to 52%.

In the Mole, Cu, Cd and Al concentrations in sediment increase significantly downstream, and Cd levels are close to or higher than the ERL at all downstream sampling points. Zn and Ni concentrations in the Mole exceed the ERL at all (U/S and D/S) sampling points and, at 8.19 mg Kg^{-1}, As levels at the first downstream sampling site are similar to the ERL of 8.20 mg As kg^{-1}. Overall, metal concentrations in sediment from the River Mole exceed more individual ERLs than the other rivers in this study. As no ERM's are exceeded, the SQGs indicate the probability of toxic effects in biota both up and downstream of the STW outflow as 38%, less than the Hogsmill. This may understate potential toxicity in the Mole as, unsurprisingly, Long *et al.* (1998), found likelihood of toxicity increases as more ERL's are exceeded. Of the four rivers in this study, the Mole appears most contaminated upstream of the STW outflow, potentially masking the impact of wastewaters.

8.3. Implications

When investigating P, it is relatively easy to identify the chemical species likely to cause adverse ecological impacts, with SRP being most bioavailable and other species such as TDP and PP less so, but still able to cause excessive plant growth in appropriate conditions. The WFD does not provide specific parameters for nutrient concentrations; it states that there should be no evidence of accelerated plant growth in macrophytes and phytobenthos species and only slight increases to the frequency and intensity of planktonic blooms. However, U.K. TAG recommends a mean annual figure of 120 μg SRP l^{-1}, which both the Hogsmill and Bourne fail to achieve downstream of the STW (E.C., 2000; UK TAG, 2006).

Investigating the impact of metals in river systems is not as simple as for P because, with a few exceptions such as As, Cu, and Zn, the WFD does not contain EQS for metals in river water and there are no EQS for metals in channel bed sediment. It may be argued that this is appropriate as it is insufficient to consider increased concentrations of metals in water or sediments in isolation as bioavailability of metals varies according to metal speciation, being influenced by external chemical and physical factors such as the capacity to adsorb to particulates and to bind within insoluble matrices (Borgmann, 2000). Additionally, species specific factors dictate how metals interact on the membrane surface of, or within, biota determining which organisms survive in polluted conditions (Borgmann, 2000). The situation is further complicated by other insufficiently researched factors such as how metals interact with pharmaceutical drugs, personal care products, chelating substances used during industrial processing such as EDTA, and other materials which remain in STW wastewaters,

some of which may hinder adsorption of metals to suspended particulate metals (Ridge & Sedlak, 2006; Ellis, 2006). The lack of EQS within the WFD with which to assess the majority of metals within riverine environments removes the incentive by STW operators to reduce or eliminate contaminants discharged in wastewaters until biota is affected. However, a major disadvantage of using taxa species and abundance as method of assessment is the difficulty in proving cause and effect (Borja, 2005). On the basis of data obtained during this study, none of the rivers fail to achieve "good ecological status" in terms of metals but comparison of metals concentrations in sediments with the US EPA SQG indicate that investigation into taxa species and abundance in the downstream Mole, Bourne and Hogsmill is warranted.

8.4. Analytical issues and areas for future research

Within this project some analyses failed to produce reliable results, for example TDP concentrations analysed using ICP-MS were often less than those of SRP where absorbance was read from a colorimeter and this had a subsequent impact on PP, calculated as the difference between TDP and TP. Separate analysis of PP removes reliance on TDP and investigation of the particulate fraction size may provide additional information on the fate of P discharged in wastewaters.

The results from micro-filtration for both P and metals were inconclusive; it may be that difference in fraction size between 0.45 μm and 0.1 μm filters was insufficient to make a significant difference and that comparison of 0.45 μm filtrate with that filtered through 0.05 μm or smaller would provide more useable results. In any event, in this project's budget the cost of finer filters was prohibitive and the lack of completely clean sample collection and laboratory analysis facilities made further research at this stage unviable. As finer fractions are likely to be more bioavailable and P and metals in wastewaters are usually dissolved, this is an area which merits further research although, for the reasons stated in 8.2., it is unlikely to influence compliance with the WFD.

Analysis of total metals in river water using ICP-MS was unsuccessful due to the presence of sulphur (S) in H_2SO_4 used during the digestion process, despite diluting the analyte with de-ionised water before analysis results were unusable. Some methods for digesting metals in river water do not require compounds containing S, but need additional facilities such as pressurised microwave ovens which were not available during this study. Like micro-

filtration, this data would provide additional information on wastewaters but would not affect compliance with the WFD.

Of the four rivers studied during this project, both the Bourne and Hogsmill currently fail to achieve "good ecological status" in terms of elevated nutrient levels caused by the discharge of treated sewage wastewaters. It is not clear whether increased levels of metals in river water and sediments in the Bourne, Hogsmill and Mole downstream of the wastewaters outflow impact biota to the extent that taxa species and abundance are so altered that they fail to meet the requirements of the Directive, as both the Hogsmill and Bourne exceed a number of SQG values this seems likely. Further research into the ecological status of these rivers should focus on biological quality elements, taxa species and abundance.

Appendix I: Hogsmill River P data

	Soluble Reactive Phosphorus (mg P l^{-1})				Total Phosphorus (mg P l^{-1})				Total dissolved P (mg P l^{-1})			
Date	U/S (1)	D/S (2)	D/S (3)	D/S (4)	U/S (1)	D/S (2)	D/S (3)	D/S (4)	U/S (1)	D/S (2)	D/S (3)	D/S (4)
12/02/07	< LOD	1.5395	1.4413	0.4599	< LOD	1.8503	2.0956	2.1447	0.1106	1.9274	1.6821	1.7539
26/02/07	0.2279	0.9681	1.1026	1.1026	0.2279	0.6316	0.6989	0.6989	0.1368	1.1962	1.2260	1.3077
06/03/07	0.0727	0.2711	0.4827	0.5687	0.2050	0.1852	0.3439	0.5158	0.1117	0.3180	0.5463	0.5607
14/03/07	0.0709	2.1564	1.8798	2.2061	0.0709	1.8088	1.2981	1.8940	0.1269	2.1785	2.0958	2.1803
21/03/07	< LOD	2.0982	2.1854	1.9374	< LOD	2.5474	2.2591	1.8636	0.1096	2.2617	2.2783	2.1111
03/04/07	0.0669	3.2242	3.2465	3.0756					0.1188	3.1516	2.9235	2.9422
10/04/07	0.0504	2.7998	2.6559	2.3176	TP analysis suspended whilst investigations				0.1037	2.5529	2.5598	2.3662
18/04/07	0.1443	2.1798	2.2119	1.8512	into analytical issues undertaken				0.3136	3.1884	2.5984	2.8271
22/05/07	0.1773	1.4778	1.4926	1.6477					0.1489	2.6084	2.4605	2.1543
29/05/07	0.1608	1.3167	1.2172	1.3244					0.2262	3.5157	3.3703	3.0871
07/06/07	0.2086	3.3751	3.4123	3.4943					0.2566	1.6089	1.6667	1.7093
14/06/07	0.2589	2.9446	3.4123	2.5451					0.1366	1.3436	1.1668	1.2222
21/06/07	0.2094	3.0190	3.3365	3.4243					0.1825	3.3066	3.1644	3.5010
01/07/07	0.5199	1.4515	1.3576	1.5743					0.2063	1.4963	1.4599	1.3778
25/07/07	0.1529	1.8715	2.5050	2.4759					0.1470	1.8113	2.4438	2.3999
31/07/07	0.1694	1.6447	1.5953	1.5600	0.1835	1.7506	1.7365	1.6659	0.1484	1.6464	1.5646	1.5355
20/08/07	0.1087	1.4855	1.4421	1.3986	0.2464	1.7174	1.6957	1.7102	0.2012	1.5196	1.4906	1.4462
28/08/07	0.1593	1.6440	1.8831	1.8686	0.2100	2.1583	1.9410	1.9627	0.2486	2.0086	1.9300	1.8854
06/09/07	0.2476	2.4759	2.4335	2.5325	0.2334	2.6315	2.5679	2.6032	0.2334	2.4201	2.4492	2.5243
12/09/07	0.3052	3.4068	3.4636	3.2790	0.3194	3.5984	3.5488	3.4494	0.2801	3.5280	3.5962	3.3244
21/09/07	0.3033	3.0908	2.9392	2.9103	0.3105	3.1558	3.0691	2.9536	0.3536	3.1100	2.9580	3.0669
01/10/07	0.1657	1.3805	1.2866	1.3584	0.2485	1.4909	1.3639	1.4302	0.1976	1.6257	1.6376	1.6260
10/10/07	0.4382	2.3044	2.3693	2.3693	0.5355	2.4991	2.5316	2.4748	0.3968	2.0735	2.1675	2.2213
20/10/07	0.3460	2.8115	2.8187	2.7250	0.3532	2.8331	2.7755	2.7683	0.2893	2.2209	2.4417	2.4587
29/10/07	0.3766	2.6011	2.8801	2.9219	0.4114	2.7615	3.0335	2.9498	0.3266	2.3120	2.4223	2.4430

Appendix I: Hogsmill River P data

10/11/07	0.5640	2.7320	2.8273	2.8492	0.5933	2.9884	2.9664	2.9078	0.4416	2.3001	2.5298	2.6377
22/11/07	0.2158	0.7241	0.7102	0.7728	0.3551	0.8146	0.9191	0.9887	0.1802	0.6834	0.6963	0.7016
03/12/07	0.1151	1.2915	1.2987	1.2483	0.1547	1.3311	1.2987	1.3131	0.1803	2.2991	2.3016	2.2168
18/12/07	0.3561	2.4930	2.6232	2.4999	0.4109	2.6917	2.6300	2.4862	0.4543	2.6215	2.8046	2.7128
03/01/08	0.3252	1.7817	1.8698	1.9104	0.3997	1.9240	1.8765	1.9917	0.2642	1.5453	1.6027	1.7148
14/01/08	0.1945	1.0070	1.0834	1.1320	0.2709	1.2709	1.1251	1.1668	0.1134	0.6939	0.9325	0.9332
05/02/08	0.1891	1.1695	1.2395	1.2535	0.2451	1.1695	1.3026	1.2605	0.1606	1.0276	1.1130	1.0861
27/02/08	0.2336	1.7520	1.8619	1.9031	0.2611	1.8619	1.8550	1.9375	0.1877	1.6987	1.6411	1.6769
03/03/08	0.2568	2.7899	2.8870	2.9911	0.2915	2.8107	2.8801	2.8246				
17/03/08	0.1790	1.4056	1.4785	1.4719	0.2453	1.5846	1.5647	1.5050				
27/03/08	0.1485	1.5863	1.7483	1.6808	0.1958	1.7280	1.9035	1.7685				
17/04/08	0.0734	0.3870	0.3803	0.3803	0.2202	0.5205	0.4938	0.4938				
25/04/08	0.2096	0.3380	0.3650	0.3853	0.2749	0.4800	0.4529	0.5340				
30/04/08	0.1409	0.6622	0.7115	0.7327	0.2888	1.6838	1.3386	1.4513				
15/05/08	0.2584	0.5984	0.5644	0.5440	0.3128	0.7004	0.6528	0.5916				
28/05/08	0.1912	0.8196	0.7650	0.7513	0.2254	1.0245	0.9289	0.9084				
03/06/08	0.2088	0.6786	0.7308	0.7373	0.2088	0.7330	0.8352	0.7961				
22/06/08	0.2436	0.8974	0.8141	0.8141	0.2436	0.9743	0.8654	0.8846				
07/07/08	0.3076	0.4238	0.4238	0.4169	0.4033	0.5126	0.5126	0.5126				
10/07/08	0.1900	0.2782	0.2443	0.3189	0.2782	0.3800	0.3732	0.3732				
29/07/08	0.2512	0.2580	0.3056	0.3123	0.3667	0.3667	0.3938	0.4074				
11/08/08	0.3862	0.2074	0.2718	0.2288	0.4148	0.2718	0.3075	0.2861				
20/08/08	0.2664	0.7526	0.7326	0.6593	0.3463	0.8192	0.8125	0.7259				
28/08/08	0.2992	0.7723	0.7723	0.7793	0.4175	0.9115	0.8976	0.8767				

ICP-MS analysis undertaken for 12 month period only

Appendix I: Hogsmill River P data

SRP analysis of river water filtered through 01 µm cellulose nitrate filters (mg P l^{-1})

Date	U/S (1)	D/S (2)	D/S (3)	D/S (4)
21/09/07	0.2672	3.0547	2.8669	2.8958
10/10/07	0.4382	2.2232	2.4504	2.4180
20/10/07	0.3388	2.8043	2.8115	2.7322
03/12/07	0.1079	1.2663	1.2879	1.2519
14/01/08	0.2084	1.0140	1.0904	1.1112
03/03/08	0.2568	2.8454	2.8940	2.9842
17/03/08	0.1790	1.5315	1.4387	1.4056
03/06/08	0.2088	0.6721	0.7373	0.7439
22/06/08	0.2436	0.8974	0.8077	0.8269
07/07/08	0.3144	0.4238	0.4238	0.4169

Key

<LOD	Below limit of detection
n/a	Not analysed on this date

Limit of detection (LOD) calculation for P analysis by colorimeter

Date	Mean Absorbance	P mg l^{-1}
06/03/07	0.00235	0.003
14/03/07	0.004	0.005
21/03/07	0.003	0.028
04/04/07	0.0024	0.003
10/04/07	0.002	0.003
18/04/07	0.003	0.005
Mean	0.003	0.010
Standard deviation (SD)	0.0007	0.01
LOD (3 x SD)	0.0020	0.03

Appendix II: River Bourne P data

	Soluble Reactive Phosphorus (mg P l^{-1})				Total Phosphorus (mg P l^{-1})				Total dissolved P (mg P l^{-1})			
Date	U/S (1)	D/S (2)	D/S (4)	D/S (5)	U/S (1)	D/S (2)	D/S (4)	D/S (5)	U/S (1)	D/S (2)	D/S (4)	D/S (5)
26/02/7	< LOD	0.0261	0.0261	no data	0.0261	0.0934	0.0261	no data	0.0401	0.0784	0.1009	no data
05/03/7	< LOD	0.0595	< LOD	no data	< LOD	0.1719	< LOD	no data	0.0196	0.1247	0.0736	no data
14/03/7	< LOD	0.0297	0.0297	0.0223	< LOD	< LOD	< LOD	< LOD	0.0466	0.0858	0.0985	0.0974
04/04/7	< LOD	1.0698	0.5646	0.7206					0.0503	0.9424	0.5477	0.5917
09/04/7	< LOD	0.8061	0.4175	0.4103					0.0158	0.7031	0.3742	0.3801
18/04/7	< LOD	1.1300	1.0819	0.8094	TP analysis suspended whilst investigations				< LOD	1.2574	0.9371	1.0319
22/05/7	< LOD	0.6798	0.7315	0.5763	into analytical issues undertaken				< LOD	1.1449	1.0419	0.9408
28/05/7	< LOD	0.6201	0.2756	0.3215					< LOD	0.6417	0.7717	0.8111
07/06/7	< LOD	0.9984	0.7152	0.6780					< LOD	0.7633	0.7201	0.6035
14/06/7	< LOD	1.1320	0.8434	0.9470					0.0136	0.6518	0.2395	0.1904
20/06/7	0.2344	1.5186	1.9044	1.9630					< LOD	0.8843	0.6703	0.6964
01/07/7	0.0686	0.5657	0.5057	0.4114					0.0220	0.4646	0.4213	0.3307
24/07/7	< LOD	0.4005	0.2549	0.2986					0.0326	0.3929	0.2627	0.2675
31/07/7	< LOD	0.2471	0.3388	0.3530	0.0635	0.4941	0.6635	0.6353	0.0254	0.2412	0.3397	0.3330
20/08/7	< LOD	0.4203	0.4275	0.4420	0.0942	0.8189	0.8551	0.9565	0.0288	0.5142	0.4965	0.5201
27/08/7	< LOD	0.5939	0.4852	0.5866	< LOD	0.9270	0.8184	0.9343	0.0358	0.5905	0.5048	0.6183
06/09/7	< LOD	1.2733	1.1248	0.7640	< LOD	1.6978	1.6058	1.1743	0.0163	1.2154	1.0030	0.7359
12/09/7	0.0497	1.2208	1.2279	1.1853	0.0852	1.5685	1.4053	1.4479	0.0142	1.0967	1.0066	1.0475
22/09/7	< LOD	1.2638	1.2204	1.1627	< LOD	1.4976	1.4124	1.3343	0.0070	1.2544	1.1950	1.1824
01/10/7	0.0828	0.9167	0.7786	0.7841	0.1215	1.0216	1.0437	0.8835	0.0203	1.0189	0.9622	0.8727
10/10/7	0.1379	0.5518	0.4950	0.7871	0.1866	0.7952	0.8520	1.1765	0.0223	0.4813	0.4573	0.5496
20/10/7	< LOD	0.9228	0.9155	0.8290	0.0577	1.0669	1.0669	0.9948	0.0155	0.7093	0.7009	0.7422
30/10/7	0.0558	0.8787	0.7322	0.7183	0.1813	1.1785	0.9833	1.0460	0.0230	0.7409	0.6096	0.6260
12/11/7	< LOD	0.9668	0.7398	0.7398	0.1245	1.3917	1.0767	1.1060	0.0203	0.9116	0.6987	0.6872
22/11/7	0.0836	0.2646	0.2507	0.3064	0.1044	0.4595	0.3969	0.4943	0.0236	0.1760	0.2269	0.2460
03/12/7	0.0252	0.1979	0.1799	0.2015	0.0468	0.3130	0.3130	0.3166	0.0386	0.3118	0.3143	0.2996

Appendix II: River Bourne P data

18/12/7	< LOD	0.4657	0.2945	0.3288	< LOD	0.8082	0.6027	0.7191	0.0691	0.5407	0.2858	0.3282
03/01/8	0.0813	0.5420	0.4403	0.3929	0.1152	0.8739	0.7723	0.7181	0.0211	0.5552	0.3794	0.3660
19/01/8	0.0903	0.1389	0.2570	0.2639	0.1042	0.1945	0.4931	0.4236	0.0167	0.0542	0.2116	0.1893
05/02/8	0.0770	0.3782	0.3291	0.2871	0.1261	0.5112	0.4832	0.6373				
27/02/8	0.0687	0.4878	0.5153	0.4603	0.0756	0.7558	0.6596	0.6733				
04/03/8	< LOD	0.8536	0.6940	0.5830	0.1249	1.1590	0.9577	0.9716				
18/03/8	0.0663	0.2984	0.2652	0.2453	0.0995	0.5238	0.4973	0.5171				
28/03/8	0.0945	0.1553	0.3240	0.3240	0.0810	0.3780	0.5670	0.5738				
17/04/8	0.0734	0.3870	0.3803	0.3803	0.1134	0.6139	0.6472	0.7273				
25/04/8	0.0541	0.6219	0.7030	0.6219	0.1284	1.0410	1.1222	1.0681				
01/05/8	0.0705	0.2395	0.2607	0.2607	0.1479	0.4861	0.5049	0.5213				
16/05/8	0.0680	1.1016	1.0812	0.9112	0.1088	1.6864	1.5436	1.4008				
28/05/8	< LOD	0.5737	0.3620	0.4781	0.1161	0.7513	0.5396	0.5806				
04/06/8	0.0653	0.0914	0.1697	0.1566	0.0587	0.1240	0.2284	0.2219				
23/06/8	0.0705	0.6923	0.5256	0.5192	0.0705	0.8205	0.5833	0.5416				
07/07/8	0.0889	0.4579	0.3759	0.4033	0.0957	0.7382	0.6015	0.5946				
10/07/8	0.1086	0.1018	0.2036	0.2103	0.1832	0.2036	0.3415	0.3732				
29/07/8	0.0815	0.2852	0.2920	0.2920	0.1494	0.4957	0.5636	0.4957				
11/08/8	0.0858	0.3075	0.2932	0.2932	0.1969	0.4753	0.4074	0.4300				
20/08/8	0.0733	0.2864	0.2797	0.2731	0.1066	0.4196	0.4262	0.3996				
28/08/8	0.1044	0.3131	0.3062	0.2922	0.1322	0.5149	0.7028	0.8002				

ICP-MS analysis undertaken for 12 month period only

Appendix II: River Bourne P data

SRP analysis of river water filtered through 01 µm cellulose nitrate filters (mg P l^{-1})

Date	U/S (1)	D/S (2)	D/S (4)	D/S (5)
22/09/07	< LOD	1.2421	1.2060	1.1554
10/10/07	0.0811	0.5274	0.4625	0.6410
20/10/07	< LOD	0.9228	0.9083	0.8362
03/12/07	0.0324	0.2051	0.1907	0.1799
19/01/08	0.0903	0.1320	0.2431	0.2639
04/03/08	0.0555	0.8606	0.6871	0.5899
18/03/08	0.0995	0.3116	0.3116	0.2851
04/06/08	0.0653	0.0914	0.1566	0.1436
23/06/08	0.0705	0.6218	0.5064	0.5320
07/07/08	0.0889	0.4511	0.3759	0.3964

Key

< LOD	Below limit of detection
n/a	Not analysed on this date

Limit of detection (LOD) calculation for P analysis by colorimeter

Date	Mean Absorbance	P mg l^{-1}
06/03/07	0.00235	0.003
14/03/07	0.004	0.005
21/03/07	0.003	0.028
04/04/07	0.0024	0.003
10/04/07	0.002	0.003
18/04/07	0.003	0.005
Mean	0.003	0.010
Standard deviation (SD)	0.0007	0.01
LOD (3 x SD)	0.0020	0.03

Appendix III: Hogsmill River dissolved metals concentrations

27 Al	52Cr	55 Mn	57 Fe	60 Ni	65 Cu	68 Zn	75 As	111 Cd	208 Pb
13.99	n/a	7.89	660.96	2.67	6.46	12.71	1.10	1.46	0.45
27.92	n/a	23.30	954.02	4.74	5.60	13.46	1.58	0.23	0.63
22.56	n/a	18.38	426.77	3.56	4.53	806.01	1.34	0.11	0.48
1.39	n/a	16.69	1089.47	4.28	2.32	1.40	1.29	0.16	0.25
4.79	n/a	12.05	1089.20	3.54	1.92	845.63	0.83	0.24	0.25
4.67	n/a	5.27	1096.63	3.27	2.15	16.25	0.83	1.52	0.23
1.78	n/a	15.04	1011.50	3.08	1.96	12.16	0.76	0.38	0.29
n/a	1.01	8.64	n/a	5.07	3.24	505.58	0.96	0.27	0.53
n/a	1.86	8.60	n/a	5.57	3.10	64.19	1.33	0.37	0.39
n/a	1.45	17.08	n/a	4.04	4.55	1784.92	1.52	0.18	1.49
n/a	0.84	12.87	n/a	4.90	3.16	227.88	1.16	0.27	0.33
n/a	2.21	13.86	n/a	4.79	3.81	249.18	1.53	0.60	0.88
n/a	2.59	10.71	n/a	3.88	3.82	749.06	1.56	0.26	0.72
7.79	1.54	8.37	248.42	2.11	3.43	12.13	1.24	0.47	0.87
< LOD	0.60	4.93	371.73	2.28	2.67	3.62	1.15	0.09	1.00
0.22	1.32	14.11	483.72	3.49	2.61	268.52	1.12	0.25	0.90
< LOD	0.55	6.88	364.69	2.12	2.93	8.49	1.18	0.23	0.92
< LOD	0.53	14.47	478.45	2.35	3.03	11.50	1.09	0.28	0.83
2.66	0.49	11.07	523.58	2.67	4.42	22.57	0.99	0.65	0.38
0.82	0.59	12.10	502.46	2.40	1.73	31.18	1.08	0.19	0.27
0.42	0.55	0.75	506.05	2.58	2.39	61.67	1.45	1.20	0.36
6.12	1.31	6.07	217.18	1.84	5.92	69.56	1.12	0.27	0.64
1.21	1.57	14.80	543.20	2.68	2.17	49.38	1.40	0.13	0.31
5.14	0.43	3.92	414.95	2.27	2.37	67.24	1.05	1.64	0.34
< LOD	0.74	4.96	351.77	2.62	3.10	35.29	1.17	1.06	0.50
0.39	< LOD	2.78	868.00	1.78	3.01	< LOD	1.21	0.44	0.19

Appendix III: Hogsmill River dissolved metals concentrations

12.63	0.17	16.92	699.37	2.44	6.36	< LOD	1.62	0.23	0.35
1.22	0.72	5.76	435.70	2.82	4.43	< LOD	1.29	0.53	0.14
3.79	0.18	18.55	1297.50	3.19	2.96	< LOD	1.26	0.16	0.16
4.30	0.63	15.87	1061.49	2.66	2.40	< LOD	0.99	0.08	0.08
5.43	1.72	1.15	676.46	3.29	3.16	47.64	0.85	0.06	0.13
0.00	1.64	7.84	589.39	3.38	2.96	26.88	0.93	0.15	0.28
1.19	< LOD	5.28	663.13	1.33	2.13	0.00	0.86	0.23	0.11
5.36	n/a	20.67	770.29	3.24	5.59	23.36	1.38	0.41	0.73
10.65	n/a	27.59	862.38	3.90	4.05	18.94	1.67	0.47	0.64
31.43	n/a	19.66	409.57	3.95	3.81	701.86	1.13	0.18	0.73
6.87	n/a	30.40	947.85	6.52	1.96	10.26	1.14	1.12	0.58
3.87	n/a	11.90	876.98	4.25	2.19	643.72	1.00	0.64	0.52
6.27	n/a	3.49	856.54	3.55	2.35	25.85	1.10	0.51	0.61
4.95	n/a	13.75	774.08	3.24	1.75	56.13	0.98	0.37	0.45
n/a	0.84	8.27	n/a	4.68	2.40	83.00	1.16	0.24	0.66
n/a	0.66	13.76	n/a	4.43	2.11	146.33	1.25	0.19	0.76
n/a	1.38	17.78	n/a	3.71	2.48	236.90	1.53	0.64	0.49
n/a	2.05	7.01	n/a	4.59	3.01	233.09	1.33	0.31	0.54
n/a	2.07	10.95	n/a	4.52	3.16	318.98	1.37	0.22	0.81
n/a	2.29	8.48	n/a	3.79	3.14	331.51	1.23	0.36	0.98
3.17	1.20	6.24	276.77	1.81	1.77	10.71	1.09	0.38	1.25
5.50	1.75	5.27	364.24	3.72	2.94	15.91	1.33	0.62	1.30
3.11	1.73	14.98	411.23	3.55	1.80	417.71	1.18	0.27	1.11
0.76	0.61	15.94	326.56	2.23	1.75	15.46	0.98	0.13	1.09
5.05	0.74	8.88	398.30	2.60	1.96	22.73	1.00	0.33	0.92
5.49	0.99	6.36	414.08	2.56	2.09	23.72	0.90	0.32	0.58
3.84	1.14	7.96	437.80	2.84	2.20	77.62	0.94	0.28	0.49
4.86	1.10	0.91	420.36	2.74	1.75	24.99	1.00	0.29	0.62

Appendix III: Hogsmill River dissolved metals concentrations

4.86	0.69	8.46	360.03	2.34	2.28	29.42	1.07	0.25	0.71
4.67	1.00	11.86	440.01	2.73	1.53	65.76	1.04	0.20	0.55
2.66	0.67	3.28	354.97	2.48	1.57	37.76	0.80	6.65	0.30
1.01	1.02	6.44	334.79	2.62	1.61	41.36	0.91	0.61	0.56
3.56	< LOD	5.94	986.79	1.56	1.59	< LOD	0.91	0.26	0.45
7.92	0.08	18.54	694.83	2.22	4.04	< LOD	1.53	1.28	0.58
1.34	0.62	4.97	398.05	2.49	2.68	4.79	1.25	0.25	0.33
4.23	0.03	13.88	1077.11	2.77	1.96	< LOD	1.37	0.32	0.38
4.15	0.12	18.53	840.58	1.71	1.30	< LOD	0.81	0.29	0.35
2.03	0.86	2.62	637.43	2.35	1.85	13.11	0.78	< LOD	0.30
1.51	0.17	8.67	536.65	1.92	2.06	< LOD	0.78	0.19	0.34
3.35	0.10	23.24	561.35	1.60	2.83	< LOD	0.82	0.17	0.34
8.03	n/a	21.18	735.34	3.05	5.36	27.73	1.20	0.18	1.03
9.71	n/a	28.64	862.78	3.57	6.35	13.10	1.53	0.11	0.43
10.81	n/a	18.66	438.87	5.63	4.00	179.85	1.20	0.19	0.44
5.69	n/a	30.58	941.58	4.33	1.89	10.96	1.10	0.26	0.47
5.27	n/a	10.71	922.77	4.02	2.55	16.43	1.04	0.30	0.49
7.30	n/a	4.00	841.16	3.47	2.49	26.03	1.05	0.72	0.59
7.01	n/a	16.36	854.41	3.84	2.04	782.78	1.00	0.27	0.52
n/a	1.71	10.37	n/a	6.22	2.95	1331.80	1.13	0.19	0.69
n/a	0.30	8.39	n/a	4.19	2.21	78.90	1.31	0.27	0.79
n/a	0.77	18.02	n/a	3.67	2.72	902.92	1.39	0.26	0.50
n/a	1.82	6.66	n/a	4.43	2.83	235.97	1.30	0.25	0.57
n/a	0.79	10.18	n/a	3.89	3.29	218.92	1.33	0.25	0.76
n/a	1.86	7.21	n/a	3.75	2.75	691.91	1.21	0.22	0.69
5.10	2.11	4.28	284.79	1.80	1.88	11.64	1.07	0.29	1.03
4.25	1.00	5.97	376.67	3.74	2.71	55.38	1.46	0.80	1.33
2.67	1.01	11.78	399.53	2.79	1.72	143.22	1.14	0.22	1.03

Appendix III: Hogsmill River dissolved metals concentrations

1.03	0.93	94.84	338.31	2.32	1.94	16.23	0.96	0.21	1.05
2.38	0.68	8.53	405.44	2.58	2.04	18.00	1.03	0.28	0.94
6.69	0.82	8.39	413.21	2.56	1.81	27.75	0.92	0.41	0.65
5.76	3.04	5.60	428.67	2.87	2.00	97.07	0.95	0.43	0.56
5.69	0.67	0.80	426.54	2.73	1.78	24.23	1.08	0.18	0.53
5.85	0.81	7.28	350.53	2.39	2.45	23.42	1.10	0.31	0.67
6.41	0.79	8.47	455.81	2.64	1.55	46.48	1.06	0.13	0.44
4.50	0.79	3.02	367.58	2.66	1.78	42.99	0.97	2.22	0.49
1.20	1.13	6.94	313.20	2.67	4.56	45.44	0.91	0.33	0.42
4.21	< LOD	4.17	780.09	1.74	1.73	0.00	0.98	0.26	0.35
7.37	< LOD	17.81	662.43	1.73	3.60	0.00	1.42	0.30	0.52
2.12	0.68	5.28	402.53	2.60	2.83	2.74	1.30	0.38	0.35
4.27	0.80	14.54	1117.47	3.23	2.03	0.00	1.38	0.14	0.39
4.81	2.28	18.70	887.70	2.64	1.38	0.00	0.93	0.58	0.26
5.17	1.17	2.85	814.76	2.95	2.38	15.13	1.02	0.07	0.37
2.95	5.39	8.88	578.34	6.30	2.01	198.92	0.76	0.24	0.35
2.13	1.44	22.66	533.01	2.61	2.84	2.63	0.76	0.23	0.30
7.27	n/a	23.79	733.91	3.50	5.52	27.08	1.24	0.29	0.85
10.49	n/a	32.93	907.97	3.72	3.66	14.33	1.69	0.07	0.70
8.33	n/a	19.52	432.31	4.68	3.64	167.06	1.21	1.01	3.38
8.59	n/a	30.51	927.83	4.90	1.83	820.75	1.09	0.45	0.48
5.33	n/a	11.49	888.93	3.94	2.29	94.02	1.07	0.21	0.45
10.13	n/a	5.92	917.65	5.72	2.80	1360.77	1.07	0.20	0.64
6.55	n/a	16.03	836.97	3.56	2.27	461.57	0.99	0.57	0.43
n/a	1.76	11.52	n/a	5.14	2.89	1128.06	1.07	0.17	0.52
n/a	0.43	7.41	n/a	4.38	2.52	166.52	1.29	0.38	0.61
n/a	1.25	22.69	n/a	4.17	8.19	200.82	1.51	0.15	0.53
n/a	0.71	6.61	n/a	4.69	2.53	183.01	1.37	0.20	0.52

Appendix III: Hogsmill River dissolved metals concentrations

n/a	0.54	10.29	n/a	4.15	3.70	133.51	1.39	0.50	0.76
n/a	1.20	6.29	n/a	3.46	2.48	239.44	1.19	0.29	0.69
2.94	4.88	4.17	296.51	1.86	1.78	16.23	1.04	0.16	1.14
7.15	0.75	7.18	369.83	2.81	2.43	15.56	1.40	0.29	1.32
5.42	1.42	11.26	422.54	3.21	1.98	413.53	1.14	0.27	1.20
8.88	1.06	68.66	348.30	2.31	2.18	16.06	1.03	0.15	1.12
3.47	2.10	8.79	407.89	3.06	2.74	124.20	1.03	0.22	1.08
7.57	0.77	7.42	433.48	2.68	2.13	27.78	0.98	0.44	0.44
5.12	0.80	4.77	406.09	2.52	1.85	49.92	0.96	0.25	0.42
7.26	0.79	1.47	426.40	2.82	1.80	35.34	1.07	0.23	0.62
6.45	0.69	6.92	346.23	2.45	2.59	27.78	1.07	0.29	0.67
5.33	0.73	6.87	480.19	2.72	1.97	41.17	1.14	0.30	0.47
6.17	0.72	2.48	375.05	2.63	1.83	31.35	0.98	2.36	0.41
2.22	1.75	6.45	342.78	3.24	1.74	119.93	0.91	0.26	0.41
5.36	< LOD	3.57	813.10	1.88	1.78	< LOD	1.00	0.24	0.49
8.51	< LOD	17.95	673.87	1.77	3.75	< LOD	1.48	0.21	0.59
2.04	0.52	5.43	378.61	2.53	2.77	11.04	1.25	0.32	0.40
6.81	1.22	13.68	1116.69	3.36	2.07	17.73	1.36	0.12	0.37
5.11	1.96	18.47	894.59	3.33	1.42	67.35	0.91	3.85	0.27
3.11	0.23	2.45	796.79	2.49	2.65	0.00	1.07	0.82	0.45
2.04	0.00	7.52	524.89	1.18	1.89	0.00	0.73	0.19	0.37
2.47	3.13	23.41	539.94	4.21	2.97	66.97	0.73	0.26	0.51

LOD µg l^{-1}	Date of Analysis	11 B	27 Al	31 P	53 Cr	55 Mn	57 Fe	60 Ni	65 Cu	68 Zn	75 As	111 Cd	208 Pb
Filtered	05/03/2007	0.247	0.283	0.589	n/a	0.007	1.439	0.008	0.034	0.102	0.006	0.008	0.020
Digested	05/03/2007	0.089	0.602	0.513	n/a	0.002	1.959	0.034	0.061	0.016	0.010	0.009	0.007
Filtered	06/03/2007	0.052	0.147	0.857	n/a	0.008	4.510	0.036	0.045	0.259	0.021	0.031	0.043

Appendix III: Hogsmill River dissolved metals concentrations

Filtered	13/03/2007	0.028	0.202	1.361		0.013	0.845	0.040	0.019	0.279	0.008	0.007	0.008
Filtered	21/03/2007	0.117	0.175	1.468	n/a	0.014	1.192	0.043	0.085	0.296	0.009	0.029	0.015
Filtered	26/06/2007	0.253	n/a	9.064	0.060	0.032	1.848	0.036	0.040	0.215	0.049	0.016	0.019
Filtered Filter_0.45um	06/02/2008	2.876	0.398	1.211	0.391	0.036	1.158	1.239	0.057	1.782	0.017	0.016	0.008
Filtered_0.1um	06/02/2008	1.860	0.045	2.270	0.033	0.025	0.871	0.079	0.055	1.635	0.011	0.023	0.015
Filtered	19/09/2007	0.182	0.871	0.067	n/a	0.004	1.382	0.028	0.028	0.123	0.015	0.002	0.006
H_2O Filtered	13/12/2007	-6.408	0.245	0.976	0.146	0.063	1.786	0.078	0.099	2.516	0.022	0.156	0.037
Filtered_0.45um	13/12/2007	-4.579	0.403	0.395	0.158	0.037	0.584	0.054	0.021	0.757	0.027	0.067	0.017
Filtered_0.20um	13/12/2007	-6.548	0.358	0.548	0.061	0.042	0.568	0.044	0.080	1.595	0.028	0.089	0.020
Filtered _0.10um	13/12/2007	-4.636	0.241	0.388	0.115	0.006	0.581	0.105	0.034	1.287	0.024	0.055	0.032
Deionised water	24/01/2008	0.054	0.106	1.270	0.036	0.005	2.184	0.085	0.038	0.157	0.012	0.003	0.005
0.45 um soaked filter	24/01/2008	0.760	0.144	1.740	0.119	0.012	0.652	0.080	0.077	1.243	0.028	0.027	0.012
0.45um unsoaked filter	24/01/2008	0.234	0.049	1.376	0.329	0.017	1.588	0.124	0.075	3.391	0.006	0.028	0.016
0.10 um soaked filter	24/01/2008	0.142	0.292	0.897	0.089	0.113	4.088	0.145	0.058	2.710	0.028	0.052	0.024
0.10um unsoaked	24/01/2008	0.191	0.090	1.114	0.056	0.056	2.250	0.094	0.103	2.418	0.044	0.055	0.012

Key	
< LOD	Below limit of detection
n/a	Not analysed on this date

Appendix IV: River Bourne dissolved metals concentrations

Dissolved metals (concentration µg l^{-1})

Date	Site	27 Al	52Cr	55 Mn	57 Fe	60 Ni	65 Cu	68 Zn	75 As	111 Cd	208 Pb
26/02/07	U/S (1)	68.53	n/a	150.65	972.16	6.56	2.12	8.64	0.55	0.11	0.60
06/03/07	U/S (1)	51.17	n/a	79.12	862.98	7.13	2.29	343.24	0.58	0.36	0.62
13/03/07	U/S (1)	37.59	n/a	124.56	1303.67	8.26	2.11	535.69	0.53	1.37	0.78
04/04/07	U/S (1)	13.87	n/a	156.60	1404.72	7.23	2.38	20.17	0.49	1.01	0.35
09/04/07	U/S (1)	9.37	n/a	140.90	1058.69	7.40	1.44	414.52	0.48	0.32	0.59
18/04/07	U/S (1)	n/a	1.41	169.47	n/a	9.09	2.01	920.82	0.58	0.53	0.81
22/05/07	U/S (1)	n/a	0.30	144.72	n/a	6.64	1.80	116.00	0.58	0.40	0.36
29/05/07	U/S (1)	n/a	0.74	133.31	n/a	6.22	2.68	583.33	0.65	0.15	0.63
06/06/07	U/S (1)	n/a	0.81	171.62	n/a	8.00	1.81	160.23	0.70	0.40	0.82
14/06/07	U/S (1)	n/a	1.16	139.06	n/a	7.14	2.14	246.88	0.67	0.64	1.79
20/06/07	U/S (1)	n/a	1.06	128.23	n/a	6.36	1.98	650.90	0.64	0.26	0.35
01/07/07	U/S (1)	13.39	0.79	93.04	717.80	4.72	2.23	5.06	0.53	0.20	1.02
24/07/07	U/S (1)	15.20	1.18	165.46	930.80	5.99	1.46	9.17	0.82	0.17	1.26
31/07/07	U/S (1)	13.70	1.25	163.60	1039.62	6.48	1.55	406.48	0.85	0.13	0.78
20/08/07	U/S (1)	4.00	0.58	158.47	1112.44	5.74	1.61	9.52	0.65	0.76	0.92
27/08/07	U/S (1)	1.93	0.69	166.23	1091.66	5.25	0.97	50.67	0.61	0.29	0.64
06/09/07	U/S (1)	11.45	0.83	214.64	810.68	5.27	0.85	40.07	0.45	0.43	0.59
12/09/07	U/S (1)	10.41	1.19	188.72	924.35	5.37	0.72	161.04	0.52	0.48	0.71
22/09/07	U/S (1)	10.67	0.74	25.44	557.96	4.96	0.69	72.68	0.36	0.50	0.69
01/10/07	U/S (1)	9.01	0.70	145.67	907.67	6.09	1.25	63.69	0.58	0.22	0.32
10/10/07	U/S (1)	13.92	0.61	246.69	915.75	5.15	1.06	15.85	0.55	0.09	0.26
20/10/07	U/S (1)	11.06	0.88	51.69	725.56	4.65	0.97	15.29	0.48	< LOD	0.27
30/10/07	U/S (1)	9.55	1.22	111.22	792.21	5.48	2.17	62.78	0.48	0.17	0.16
12/11/07	U/S (1)	5.45	0.00	198.03	779.56	4.50	0.48	< LOD	0.51	0.19	0.08
22/11/07	U/S (1)	31.23	0.00	162.58	583.27	3.97	1.53	< LOD	0.54	0.32	1.00
03/12/07	U/S (1)	13.37	0.31	107.65	509.34	4.74	0.91	13.05	0.48	< LOD	0.24

Appendix IV: River Bourne dissolved metals concentrations

18/12/07	U/S (1)	10.61	0.46	181.43	1071.04	5.68	0.99	< LOD	0.50	0.13	0.19
03/01/08	U/S (1)	12.87	0.37	190.43	1074.37	6.15	0.94	< LOD	0.44	0.58	0.23
19/01/08	U/S (1)	27.39	0.26	68.08	696.50	4.72	1.16	< LOD	0.48	0.04	0.38
05/02/08	U/S (1)	11.74	3.88	132.19	686.43	7.69	1.54	118.38	0.44	0.23	0.36
27/02/08	U/S (1)	6.64	1.56	135.18	980.31	5.74	1.10	33.35	0.34	0.13	0.26
26/02/07	D/S (2)	44.77	n/a	120.26	830.97	5.96	2.09	11.28	0.60	0.18	0.62
06/03/07	D/S (2)	20.10	n/a	46.04	588.72	5.92	2.44	533.89	0.60	0.28	0.25
13/03/07	D/S (2)	8.98	n/a	82.07	540.79	7.54	1.97	16.11	0.60	0.68	0.16
04/04/07	D/S (2)	3.58	n/a	30.05	757.01	5.30	1.79	16.25	1.11	0.16	0.16
09/04/07	D/S (2)	3.09	n/a	44.90	629.04	5.80	1.64	953.15	1.06	0.06	0.19
18/04/07	D/S (2)	n/a	0.86	47.81	n/a	6.28	2.80	541.31	1.27	0.11	0.25
22/05/07	D/S (2)	n/a	0.54	54.86	n/a	7.90	2.70	114.66	1.16	16.36	0.29
29/05/07	D/S (2)	n/a	0.99	34.08	n/a	5.58	3.97	4204.14	1.11	0.80	0.24
06/06/07	D/S (2)	n/a	0.74	28.25	n/a	6.70	1.89	192.54	1.43	0.39	0.18
14/06/07	D/S (2)	n/a	1.36	29.46	n/a	6.67	2.83	255.16	1.55	1.08	0.25
20/06/07	D/S (2)	n/a	0.39	69.96	n/a	6.45	2.97	205.40	1.18	0.72	0.27
01/07/07	D/S (2)	3.39	1.31	32.11	267.46	4.26	1.68	3.89	0.79	0.12	0.67
24/07/07	D/S (2)	< LOD	0.63	41.27	301.21	4.45	1.46	4.70	0.85	0.09	0.82
31/07/07	D/S (2)	< LOD	0.53	90.17	287.49	4.80	1.86	15.04	0.80	0.24	0.67
20/08/07	D/S (2)	< LOD	0.68	42.83	265.72	4.16	1.26	4.76	0.82	0.09	0.66
27/08/07	D/S (2)	< LOD	1.36	28.04	316.20	5.01	3.09	125.48	0.82	0.55	0.54
06/09/07	D/S (2)	2.16	1.14	19.15	419.12	4.49	1.53	15.74	1.16	0.22	0.17
12/09/07	D/S (2)	1.92	1.30	21.18	346.86	4.42	1.59	64.41	1.02	0.54	0.11
22/09/07	D/S (2)	1.04	0.91	8.53	364.15	4.23	1.34	10.89	1.06	0.12	0.06
01/10/07	D/S (2)	1.98	0.68	23.89	357.17	4.41	1.22	25.21	0.96	0.59	0.13
10/10/07	D/S (2)	2.22	0.64	123.05	266.76	4.28	0.94	22.72	0.68	0.38	0.07
20/10/07	D/S (2)	< LOD	0.54	9.85	247.86	3.72	1.01	5.97	0.79	< LOD	< LOD
30/10/07	D/S (2)	< LOD	1.25	27.86	293.78	4.44	0.83	35.45	0.84	< LOD	0.18

Appendix IV: River Bourne dissolved metals concentrations

12/11/07	D/S (2)	2.21	0.17	34.13	759.40	3.53	0.78	< LOD	0.96	0.03	0.04
22/11/07	D/S (2)	24.85	0.00	122.79	551.36	3.57	1.27	< LOD	0.57	0.33	1.67
03/12/07	D/S (2)	1.78	0.24	61.66	193.25	4.08	0.86	7.73	0.61	0.18	0.00
18/12/07	D/S (2)	3.25	0.53	45.72	681.39	4.67	1.01	< LOD	0.81	0.14	0.08
03/01/08	D/S (2)	2.49	0.44	38.91	647.53	4.03	1.04	< LOD	0.75	0.10	0.07
19/01/08	D/S (2)	19.84	1.48	51.17	646.49	5.79	1.33	32.65	0.47	1.20	0.19
05/02/08	D/S (2)	1.67	0.81	66.94	355.00	4.65	1.56	< LOD	0.57	0.24	0.04
26/02/07	D/S (4)	37.34	n/a	104.69	777.90	5.64	2.06	8.35	0.57	0.16	0.44
06/03/07	D/S (4)	26.45	n/a	51.30	629.46	6.57	2.42	202.90	0.58	0.34	0.37
13/03/07	D/S (4)	10.05	n/a	70.07	574.27	6.80	1.91	712.75	0.62	0.34	0.15
04/04/07	D/S (4)	2.40	n/a	67.60	589.69	5.70	1.48	14.87	0.88	0.16	0.22
09/04/07	D/S (4)	2.50	n/a	79.24	536.52	21.54	1.68	649.84	0.84	0.25	0.16
18/04/07	D/S (4)	n/a	2.51	53.28	n/a	6.50	2.19	1331.55	1.23	0.24	0.43
22/05/07	D/S (4)	n/a	0.26	51.40	n/a	5.81	1.49	94.43	1.18	1.27	0.26
29/05/07	D/S (4)	n/a	0.42	67.31	n/a	5.12	2.18	1718.02	0.87	0.26	0.28
06/06/07	D/S (4)	n/a	1.27	51.68	n/a	6.44	1.95	200.67	1.30	0.28	0.25
14/06/07	D/S (4)	n/a	1.39	42.30	n/a	6.54	2.21	274.88	1.24	4.56	0.19
20/06/07	D/S (4)	n/a	1.19	47.87	n/a	6.14	2.37	242.14	1.30	0.33	0.37
01/07/07	D/S (4)	6.68	1.17	29.77	347.19	4.30	1.60	5.61	0.76	0.18	0.85
24/07/07	D/S (4)	0.31	0.92	85.65	305.42	5.12	1.52	114.97	0.81	0.12	0.81
31/07/07	D/S (4)	n/a	1.33	72.73	296.79	5.29	1.68	269.38	0.86	0.36	0.60
20/08/07	D/S (4)	n/a	0.65	36.91	252.27	4.03	1.19	5.42	0.81	0.17	0.69
27/08/07	D/S (4)	n/a	1.13	35.57	286.97	4.60	1.70	87.30	0.79	0.32	0.56
06/09/07	D/S (4)	2.00	1.05	27.49	359.25	4.51	1.38	69.92	0.99	0.19	0.09
12/09/07	D/S (4)	1.32	1.51	32.05	326.50	4.80	1.55	75.89	1.00	0.91	0.09
22/09/07	D/S (4)	2.79	0.90	8.46	355.59	4.43	1.31	12.22	1.04	0.12	0.21
01/10/07	D/S (4)	1.23	0.72	24.23	344.21	4.40	1.22	16.14	0.93	0.32	0.04
10/10/07	D/S (4)	1.83	0.73	134.86	262.45	4.41	0.97	66.49	0.68	0.17	0.15

Appendix IV: River Bourne dissolved metals concentrations

20/10/07	D/S (4)	n/a	0.53	11.40	244.63	3.75	0.97	< LOD	0.81	< LOD	< LOD
30/10/07	D/S (4)	n/a	0.73	33.70	251.81	4.18	1.17	3.19	0.77	< LOD	< LOD
12/11/07	D/S (4)	2.70	0.52	58.34	685.99	3.82	0.84	< LOD	0.92	0.07	0.23
22/11/07	D/S (4)	15.14	< LOD	122.94	551.89	3.60	1.21	< LOD	0.64	1.36	0.25
03/12/07	D/S (4)	1.48	0.62	61.15	196.17	4.20	1.06	1.37	0.59	< LOD	< LOD
18/12/07	D/S (4)	2.72	0.96	87.25	554.56	5.00	0.89	18.67	0.68	1.00	0.06
03/01/08	D/S (4)	1.36	< LOD	59.56	540.90	3.76	0.97	0.00	0.68	0.07	0.42
19/01/08	D/S (4)	6.79	1.02	17.14	484.42	5.36	1.54	23.98	0.53	0.32	0.53
05/02/08	D/S (4)	2.00	0.59	71.02	340.89	4.45	1.61	< LOD	0.56	0.31	0.06
27/02/08	D/S (4)	1.02	< LOD	58.93	383.96	3.69	1.60	< LOD	0.60	0.37	1.40
13/03/07	D/S (5)	7.27	n/a	71.63	584.65	6.23	1.92	5.29	0.66	0.26	0.15
04/04/07	D/S (5)	4.39	n/a	67.36	659.16	5.89	1.58	14.40	0.95	0.12	0.27
09/04/07	D/S (5)	2.75	n/a	76.69	519.61	6.32	1.89	71.75	0.82	0.22	0.24
18/04/07	D/S (5)	n/a	0.69	73.50	n/a	7.75	3.17	207.94	1.17	0.32	0.63
22/05/07	D/S (5)	n/a	0.93	65.07	n/a	6.96	2.25	79.74	1.06	1.47	0.21
29/05/07	D/S (5)	n/a	0.25	65.09	n/a	4.69	1.91	514.05	0.77	0.25	0.28
06/06/07	D/S (5)	n/a	0.84	47.75	n/a	6.66	2.54	222.95	1.33	0.50	0.23
14/06/07	D/S (5)	n/a	0.85	33.35	n/a	6.28	2.14	214.78	1.38	1.28	0.16
20/06/07	D/S (5)	n/a	3.87	45.12	n/a	6.31	2.48	454.55	1.32	0.24	0.46
01/07/07	D/S (5)	7.38	1.32	34.61	338.65	4.26	1.48	2.97	0.81	0.08	0.94
24/07/07	D/S (5)	2.20	1.08	77.62	291.64	4.72	1.33	7.73	0.83	0.13	0.79
31/07/07	D/S (5)	< LOD	0.79	44.75	267.83	4.57	1.88	110.01	0.83	0.34	0.53
20/08/07	D/S (5)	< LOD	0.66	28.14	256.43	4.40	1.23	6.38	0.83	0.15	0.56
27/08/07	D/S (5)	< LOD	0.91	26.27	297.48	4.31	1.22	7.11	0.88	0.13	0.44
06/09/07	D/S (5)	0.99	0.77	42.26	315.77	4.48	1.88	13.92	0.83	0.61	0.07
12/09/07	D/S (5)	1.35	1.07	22.77	333.51	4.60	1.31	71.94	1.06	0.31	0.12
22/09/07	D/S (5)	1.87	1.06	6.45	353.12	4.59	1.35	69.06	1.05	0.09	0.14
01/10/07	D/S (5)	6.66	0.82	33.39	687.62	4.20	1.85	13.99	0.88	0.58	0.18

Appendix IV: River Bourne dissolved metals concentrations

10/10/07	D/S (5)	1.83	0.77	105.43	248.26	4.07	0.90	64.11	0.73	0.08	0.19
20/10/07	D/S (5)	< LOD	0.73	10.28	286.56	4.45	1.32	6.11	0.89	0.09	0.06
30/10/07	D/S (5)	< LOD	1.45	34.91	292.48	4.87	1.11	57.49	0.87	< LOD	< LOD
12/11/07	D/S (5)	1.88	0.96	60.50	704.35	4.46	0.94	< LOD	0.95	0.20	0.05
22/11/07	D/S (5)	17.76	< LOD	132.91	645.65	3.96	1.47	< LOD	0.73	0.25	0.33
03/12/07	D/S (5)	2.34	0.43	59.02	188.72	4.24	1.23	< LOD	0.57	0.17	0.28
18/12/07	D/S (5)	1.59	0.58	64.05	543.84	4.40	1.10	< LOD	0.70	0.14	0.06
03/01/08	D/S (5)	2.58	0.77	88.64	590.66	4.93	1.14	< LOD	0.79	0.19	0.06
19/01/08	D/S (5)	7.10	0.98	18.33	455.73	4.79	1.40	0.86	0.55	< LOD	0.03
05/02/08	D/S (5)	1.51	3.74	67.27	364.37	6.74	1.55	119.73	0.60	0.18	0.15
27/02/08	D/S (5)	0.84	0.47	54.31	368.16	3.82	1.40	< LOD	0.53	0.27	0.75

Key

< LOD Below limit of detection

n/a Not analysed on this date

Appendix V: Sediment analysis data

ICP-MS analysis of sediments (mg kg^{-1})

Sample	11 B	28 Si	31 P	53 Cr	60 Ni	65 Cu	68 Zn	75 As	111 Cd	208 Pb
CRM1	4.18	165.38	995.01	73.76	33.50	79.67	347.90	17.65	3.09	137.52
CRM2	4.42	122.37	879.50	67.45	30.34	74.91	317.03	15.91	2.73	132.27
CRM3	3.27	123.61	821.44	63.16	28.61	70.37	302.63	16.38	2.78	124.43
Mean	3.96	137.12	898.65	68.12	30.82	74.98	322.52	16.65	2.86	131.41
SD	0.61	24.48	88.35	5.33	2.48	4.65	23.13	0.90	0.20	6.58
%SD	15.28	17.85	9.83	7.82	8.05	6.20	7.17	5.41	6.91	5.01
CRM2	5.12	121.57	885.64	81.56	36.95	90.13	391.13	18.61	3.10	144.44

(mg kg^{-1})	11 B	28 Si	31 P	53 Cr	60 Ni	65 Cu	68 Zn	75 As	111 Cd	208 Pb
LOD Batch1	0.176	0.435	4.690	3.039	0.165	0.060	0.491	0.248	0.021	0.615
LOD Batch2	0.097	0.462	2.126	0.142	0.045	0.051	0.381	0.012	0.027	0.008

Blackwater1b	2.35	36.19	755.16	5.86	2.80	4.28	37.97	4.37	0.12	8.85
Blackwater1c	1.51	25.04	712.13	5.33	2.59	3.74	35.46	3.94	0.13	9.09
Mean	2.60	30.62	694.41	5.49	2.58	3.86	34.88	4.16	0.12	8.61
SD	0.36	7.89	71.28	0.32	0.22	0.38	3.42	0.31	0.00	0.63
%SD	13.72	25.76	10.26	5.75	8.39	9.80	9.79	7.39	2.28	7.30
Blackwater2a	2.87	37.93	1126.17	4.19	7.07	5.43	45.70	3.36	0.29	9.64
Blackwater2b	1.60	44.32	1125.69	7.16	8.69	9.91	46.23	3.33	0.16	9.74
Blackwater2c	2.49	32.59	1113.99	4.04	3.31	4.25	45.52	3.25	0.17	9.94
Mean	2.68	41.13	1121.95	5.13	6.36	6.53	45.82	3.31	0.16	9.77
SD	0.27	4.52	6.90	1.76	2.76	2.99	0.37	0.06	0.01	0.15
%SD	10.04	10.99	0.62	34.34	43.48	45.74	0.80	1.71	7.95	1.53

Appendix V: Sediment analysis data

Blackwater3a	1.29	59.88	1055.61	3.69	3.28	3.48	37.45	2.00	0.13	7.15
Blackwater3b	0.86	50.79	1123.91	2.94	2.67	3.35	36.43	2.35	0.08	6.15
Blackwater3c	3.00	39.11	1197.93	4.16	3.85	3.69	44.08	3.46	0.10	8.09
Mean	1.72	55.33	1125.82	3.60	3.27	3.51	36.94	2.17	0.10	7.13
SD	1.13	6.43	71.18	0.61	0.59	0.17	0.72	0.25	0.02	0.97
%SD	65.86	11.61	6.32	17.06	18.03	4.87	1.96	11.31	23.56	13.56
Blackwater4a	1.59	43.46	1430.49	3.98	3.58	3.80	49.21	3.25	0.09	8.80
Blackwater4b	1.29	66.36	1596.99	3.81	3.37	3.93	52.00	3.54	0.12	9.62
Blackwater4c	1.61	46.34	1980.76	4.52	4.39	4.20	61.54	6.04	0.16	11.96
Mean	1.60	44.90	1513.74	4.10	3.48	3.98	50.60	3.39	0.13	9.21
SD	0.01	2.04	117.73	0.37	0.15	0.20	1.97	0.20	0.03	0.58
%SD	0.58	4.54	7.78	9.02	4.25	5.14	3.90	5.98	26.29	6.31
Blackwater5a	3.18	41.37	3312.85	6.23	4.69	13.41	89.54	3.08	0.30	25.21
Blackwater5b	3.13	30.38	2431.02	7.00	5.03	13.47	97.14	4.18	0.32	25.22
Blackwater5c	3.42	37.71	2749.09	8.54	6.00	16.72	107.06	4.76	0.36	28.92
Mean	3.24	39.54	2590.05	6.62	4.86	13.44	97.91	4.47	0.33	26.45
SD	0.16	2.59	224.91	0.54	0.24	0.04	8.79	0.41	0.03	2.14
%SD	4.87	6.54	8.68	8.20	4.89	0.32	8.97	9.14	9.49	8.08
Mole1a	1.17	60.87	2080.01	26.33	46.26	21.63	305.08	7.52	1.08	47.71
Mole1b	1.06	29.02	1997.93	22.49	46.05	22.18	290.65	7.26	0.99	31.56
Mole1c	1.55	36.90	2073.71	22.80	46.60	21.27	306.04	8.27	1.12	31.19
Mean	1.11	42.27	2050.55	23.88	46.30	21.69	300.59	7.68	1.06	31.38
SD	0.08	16.59	45.68	2.13	0.28	0.46	8.62	0.52	0.07	0.26
%SD	6.90	39.25	2.23	8.94	0.61	2.10	2.87	6.79	6.38	0.84

Appendix V: Sediment analysis data

Mole2a	2.12	51.80	1626.01	26.44	39.88	24.14	181.40	7.98	1.15	30.85
Mole2b	2.41	62.94	1495.04	25.35	40.79	23.96	175.31	7.66	1.18	29.33
Mole2c	3.03	56.65	1497.59	30.51	42.07	25.28	185.64	8.92	1.23	32.30
Mean	2.26	57.13	1539.54	27.43	40.91	24.46	180.78	8.19	1.19	30.83
SD	0.21	5.59	74.89	2.72	1.10	0.71	5.19	0.65	0.04	1.49
%SD	9.18	9.78	4.86	9.92	2.69	2.92	2.87	8.00	3.35	4.82
Mole3a	1.96	38.12	1896.07	24.61	48.80	26.26	270.01	7.59	1.54	46.69
Mole3b	1.54	24.63	1726.45	24.24	44.84	25.67	265.46	7.53	1.46	48.08
Mole3c	1.51	31.45	1682.73	25.18	45.46	26.82	260.99	7.39	1.63	54.25
Mean	1.53	31.45	1768.42	24.68	46.37	26.25	265.49	7.50	1.55	49.67
SD	0.02	0.00	112.69	0.47	2.13	0.57	4.51	0.10	0.08	4.03
%SD	1.40	0.00	6.37	1.91	4.59	2.19	1.70	1.35	5.39	8.11
Mole4a	1.73	37.66	2193.36	23.26	35.50	30.21	285.14	6.50	1.35	49.24
Mole4b	3.01	53.85	2445.54	26.24	39.48	33.72	305.51	7.62	1.36	51.45
Mole4c	2.44	42.16	2357.20	26.09	38.69	34.34	300.55	7.86	1.51	49.04
Mean	2.39	44.56	2332.03	25.20	37.89	32.76	297.07	7.33	1.41	49.91
SD	0.64	3.18	127.96	1.68	2.11	2.23	10.62	0.72	0.09	1.34
%SD	26.73	7.14	5.49	6.67	5.56	6.80	3.58	9.87	6.56	2.68
Bourne1a	2.33	28.22	1531.58	10.16	9.52	5.01	51.24	8.15	0.09	11.65
Bourne1b	5.53	29.18	1096.77	7.15	7.75	3.87	41.18	7.44	0.05	11.25
Bourne1c	1.70	8.83	1111.53	7.14	7.55	4.40	42.63	7.64	0.09	10.66
Mean	3.19	28.70	1104.15	7.14	7.65	4.13	41.90	7.74	0.09	11.19
SD	2.05	0.68	10.44	0.01	0.14	0.37	1.02	0.37	0.00	0.50
%SD	64.36	2.37	0.95	0.10	1.80	9.04	2.44	4.73	2.75	4.43

Appendix V: Sediment analysis data

Bourne2a	3.61	22.61	1513.47	12.22	13.52	8.34	62.43	13.67	0.27	17.52
Bourne2b	3.67	14.62	1478.52	11.89	12.89	6.28	60.58	13.28	0.08	13.95
Bourne2c	2.01	18.62	1331.37	11.43	12.47	6.95	58.40	12.30	0.09	30.32
Mean	3.64	18.62	1441.12	11.84	12.96	6.62	60.47	13.09	0.08	17.52
SD	0.04	3.99	96.64	0.40	0.53	0.47	2.02	0.71	0.01	0.00
%SD	1.12	21.43	6.71	3.34	4.07	7.14	3.34	5.39	6.14	0.00
Bourne3a	3.49	20.66	1683.33	6.60	8.42	7.47	56.04	6.39	0.08	13.52
Bourne3b	4.73	24.03	1792.87	6.98	8.62	7.39	61.00	6.60	0.08	13.01
Bourne3c	2.57	17.32	1800.41	7.45	8.65	7.90	69.45	6.52	0.07	14.76
Mean	3.60	20.67	1758.87	7.01	8.56	7.59	62.16	6.50	0.08	13.76
SD	1.08	3.35	65.53	0.43	0.12	0.28	6.78	0.11	0.00	0.90
%SD	30.11	16.22	3.73	6.06	1.42	3.63	10.91	1.64	6.15	6.53
Bourne4a	3.53	35.91	2429.19	6.92	9.67	19.51	83.41	6.70	0.15	17.95
Bourne4b	3.50	5.20	2256.90	6.31	9.12	11.08	70.57	6.06	0.09	13.45
Bourne4c	4.11	34.30	2864.31	7.72	10.63	14.30	89.08	7.41	0.12	15.62
Mean	3.71	35.11	2343.05	6.98	9.81	14.96	86.24	6.73	0.12	16.78
SD	0.34	1.14	121.83	0.71	0.77	4.25	4.01	0.68	0.03	1.65
%SD	9.26	3.24	5.20	10.16	7.83	28.41	4.65	10.04	26.48	9.81
Bourne5a	5.30	21.53	3694.52	8.82	12.95	29.17	125.68	6.53	0.36	23.87
Bourne5b	3.25	11.39	3743.39	7.76	14.06	32.53	127.51	6.44	0.23	22.83
Bourne5c	3.84	13.38	3891.26	8.40	14.52	31.86	136.45	6.82	0.23	23.49
Mean	3.55	12.38	3776.39	8.33	13.85	31.19	129.88	6.60	0.23	23.40
SD	0.42	1.41	102.44	0.54	0.81	1.78	5.77	0.20	0.00	0.52
%SD	11.78	11.38	2.71	6.45	5.83	5.70	4.44	2.99	0.50	2.24

Appendix V: Sediment analysis data

Hogsmill 1a	4.98	65.19	940.72	16.94	16.25	59.20	283.58	3.96	0.80	230.85
Hogsmill 1b	7.73	92.97	775.13	16.26	13.70	41.02	209.13	4.03	0.70	145.61
Hogsmill 1c	2.34	16.95	721.84	16.62	15.65	59.63	208.18	3.88	0.69	146.68
Mean	5.02	58.37	748.49	16.60	15.20	59.41	208.66	3.96	0.73	146.15
SD	2.70	38.46	37.68	0.34	1.33	0.30	0.67	0.08	0.06	0.76
%SD	53.72	65.90	5.03	2.05	8.75	0.51	0.32	1.93	8.26	0.52
Hogsmill 2a	6.93	74.68	1814.09	10.72	8.85	32.79	114.92	2.39	0.30	55.59
Hogsmill 2b	6.00	43.68	1575.20	10.04	8.29	24.41	131.93	2.28	0.26	37.34
Hogsmill 2c	7.11	50.94	2094.18	9.94	8.42	31.07	99.87	1.93	0.28	49.11
Mean	6.68	47.31	1814.09	10.24	8.52	31.93	107.40	2.20	0.28	52.35
SD	0.60	5.13	0.00	0.43	0.29	1.22	10.64	0.24	0.02	4.58
%SD	8.92	10.85	0.00	4.16	3.44	3.82	9.91	10.93	8.15	8.75
Hogsmill 3a	3.84	77.02	1029.24	13.96	11.56	16.24	107.83	4.71	0.30	189.90
Hogsmill 3b	4.31	103.46	806.30	14.85	10.78	23.65	105.97	3.02	0.23	230.88
Hogsmill 3c	5.71	56.58	1034.97	13.26	9.40	18.95	88.55	2.12	0.22	132.09
Mean	4.08	77.02	1032.10	14.02	10.58	17.60	100.78	3.28	0.22	184.29
SD	0.33	0.00	4.05	0.79	1.09	1.91	10.64	1.07	0.00	49.63
%SD	8.12	0.00	0.39	5.66	10.34	10.88	10.55	32.65	1.33	26.93
Hogsmill 4a	15.24	87.31	670.26	43.26	18.43	127.70	757.53	2.22	0.18	1613.97
Hogsmill 4b	10.03	128.17	876.44	11.57	13.96	67.68	377.43	2.11	0.26	48.23
Hogsmill 4c	13.68	95.58	785.17	10.59	17.75	104.27	556.96	1.63	0.14	133.98
Mean	14.46	91.44	830.80	11.08	18.09	99.88	563.97	2.16	0.19	598.73
SD	1.10	5.85	64.54	0.69	0.48	30.25	190.14	0.08	0.06	880.27
%SD	7.63	6.40	7.77	6.26	2.63	30.29	33.72	3.66	31.71	147.02

Appendix V: Sediment analysis data

Hogsmill 5a	6.49	89.39	1207.44	13.53	13.82	47.29	214.99	3.45	0.30	386.85
Hogsmill 5b	11.92	191.85	1106.87	13.08	17.74	80.77	396.04	2.28	0.20	73.17
Hogsmill 5c	10.82	126.04	1402.78	12.32	13.22	156.48	337.21	2.90	0.21	132.48
Mean	11.37	135.76	1157.15	12.98	13.52	94.85	366.63	2.88	0.20	197.50
SD	0.77	51.92	71.11	0.61	0.43	55.94	41.60	0.59	0.01	166.64
%SD	6.81	38.24	6.15	4.73	3.15	58.98	11.35	20.35	3.03	84.38

ICP-AES analysis of sediments (mg kg^{-1})

NBS River Sediment 2704	Al	As	Cd	Cr	Cu	Fe	Mn	Ni	P	Pb	Zn
Certified concentration	n/c	n/c	n/c	89±1	100±2	n/c	n/c	44±2	n/c	146±1	427±5
Measured, concentrated mean	10334.03	15.37	3.40	73.35	89.78	25517.09	398.34	34.79	716.52	139.45	370.673
% recovery				**82.42**	**89.78**			**79.07**		**95.51**	**86.809**

Reference materials : Comparison of measured & certified concentrations (mg/kg)

n/c :not certified

NIST Montana Soil 2710	Al	As	Cd	Cr	Cu	Fe	Mn	Ni	P	Pb	Zn
Certified concentration	n/c	n/c	n/c	23±0.5	2910±59	n/c	n/c	7±0.44	n/c	5720±280	6230±115
Measured, concentrated mean	14483.59	581.78	25.28	16.60	2735.67	21143.51	6956.26	12.80	782.37	4803.43	6138.04
% recovery				**72.19**	**94.01**			**182.83**		**83.976**	**98.524**

Reference materials : Comparison of measured & certified concentrations (mg/kg)

n/c :not certified

Appendix V: Sediment analysis data

ICP-AES analysis of sediments (mg kg^{-1})

	Al	As	Cd	Cr	Cu	Fe	Mn	Ni	P	Pb	Zn
Bourne1	2143.49	2.689	**1.819**	8.966	5.455	46719.12	322.218	11.144	1471.70	15.125	57.742
Bourne2	3359.71	5.735	1.167	13.429	8.637	64150.06	340.120	16.852	1793.76	21.948	73.347
Bourne3	2005.91	1.901	0.718	8.438	9.230	37987.07	419.276	11.304	2273.63	16.995	75.007
Bourne4	1950.76	1.946	0.857	8.774	16.333	42615.20	452.915	13.603	3279.93	20.376	100.844
Bourne5	2450.94	0.968	1.099	10.431	**38.191**	46750.98	634.716	18.305	4770.14	30.196	**155.263**
Blackwater1	1299.87	3.812	0.262	6.361	4.073	10872.20	94.331	3.212	682.447	9.861	42.884
Blackwater2	712.842	2.631	0.270	4.516	5.011	9311.897	111.248	3.751	1000.21	9.750	50.855
Blackwater3	581.794	1.798	0.216	4.109	3.869	8018.049	145.095	3.372	986.251	6.803	40.753
Blackwater4	713.568	2.117	0.297	4.096	4.172	13480.76	141.280	3.907	1333.35	10.588	54.594
Blackwater5	1671.40	2.952	0.548	7.968	16.329	15509.97	157.750	6.108	2619.86	28.797	108.037
Mole1	4544.37	1.688	**1.721**	25.917	24.087	39004.47	4871.17	**52.037**	2082.36	37.395	**334.424**
Mole2	6766.24	3.534	**1.550**	25.418	23.574	32385.35	2526.16	**40.578**	1343.29	33.159	**167.270**
Mole3	5545.01	3.249	**2.308**	27.985	30.920	35968.87	3596.72	**55.803**	2005.19	**56.374**	**295.464**
Mole4	4975.24	3.923	**1.915**	25.748	**35.566**	30047.83	2256.88	**42.484**	2479.01	**55.450**	**304.927**
Hogsmill1	4651.98	3.172	0.833	17.758	**71.329**	12218.98	299.849	16.642	979.693	**164.329**	**240.914**
Hogsmill2	3152.18	1.783	0.287	10.001	33.600	6981.585	102.847	8.421	2013.46	**51.709**	130.324
Hogsmill3	2084.49	2.480	0.299	14.120	21.153	10519.31	134.391	10.694	1087.26	**192.756**	101.997
Hogsmill4	1797.65	0.775	0.201	22.651	**110.576**	10158.56	157.511	18.501	870.798	**616.459**	**603.586**
Hogsmill5	2334.98	2.131	0.310	13.092	**88.991**	10880.92	158.135	14.370	1193.03	**138.282**	**365.032**

ICP-AES LOD	Al	As	Cd	Cr	Cu	Fe	Mn	Ni	P	Pb	Zn
(mg l^{-1})	0.07	0.01	0.01	0.01	0.01	0.90	0.01	0.00	0.61	0.00	0.14

Appendix V: Sediment analysis data

Release of P in sediment

Sample		Location	Actual weight	Absorbance	Absorbance - blank	P mg l^{-1}	Weight corrected	P in 200 ml	P released /kg sediment
Batch 1	1	Hogsmill 1	0.5002	0.032	0.024	0.03158	0.03157	0.00631	12.63
	2	Hogsmill 1	0.5009	0.016	0.008	0.01053	0.01051	0.00210	4.20
	3	Hogsmill 1	0.5003	0.016	0.008	0.01053	0.01052	0.00210	4.21
	4	Hogsmill 2	0.5008	0.042	0.034	0.04474	0.04467	0.00893	17.87
	5	Hogsmill 2	0.5005	0.043	0.035	0.04605	0.04601	0.00920	18.40
	6	Hogsmill 2	0.5004	0.083	0.075	0.09869	0.09861	0.01972	39.44
rep 6		Hogsmill 2	0.5004	0.097	0.089	0.11711	0.11701	0.02340	46.81
	7	Hogsmill 3	0.5004	0.021	0.013	0.01711	0.01709	0.00342	6.84
	8	Hogsmill 3	0.5003	0.020	0.012	0.01579	0.01578	0.00316	6.31
	9	Hogsmill 3	0.5005	0.020	0.012	0.01579	0.01577	0.00315	6.31
	10	Hogsmill 4	0.5000	0.020	0.012	0.01579	0.01579	0.00316	6.32
	11	Hogsmill 4	0.5009	0.022	0.014	0.01842	0.01839	0.00368	7.36
	12	Hogsmill 4	0.5009	0.020	0.012	0.01579	0.01576	0.00315	6.30
	13	Hogsmill 5	0.5005	0.029	0.021	0.02763	0.02760	0.00552	11.04
	14	Hogsmill 5	0.5001	0.028	0.02	0.02632	0.02631	0.00526	10.52
	15	Hogsmill 5	0.5007	0.033	0.025	0.03290	0.03285	0.00657	13.14
	16	Blackwater 1	0.5008	0.013	0.005	0.00658	0.00657	0.00131	2.63
	17	Blackwater 1	0.5009	0.013	0.005	0.00658	0.00657	0.00131	2.63
	18	Blackwater 1	0.5006	0.013	0.005	0.00658	0.00657	0.00131	2.63
	19	Blackwater 2	0.5002	0.019	0.011	0.01447	0.01447	0.00289	5.79
	20	Blackwater 2	0.5010	0.021	0.013	0.01711	0.01707	0.00341	6.83
	21	Blackwater 2	0.5002	0.016	0.008	0.01053	0.01052	0.00210	4.21
	22	Blank batch1.1.		0.008		0.01053			
	23	Blank batch1.2		0.008		0.01053			

Appendix V: Sediment analysis data

	24	Deionised H_2O		0.008		0.01053			
Batch 2	25	Hogsmill 2	0.5003	0.048	0.041	0.05127	0.05124	0.01025	20.50
	26	Hogsmill 2	0.5004	0.048	0.041	0.05127	0.05123	0.01025	20.49
	27	Hogsmill 2	0.5005	0.044	0.037	0.04627	0.04622	0.00924	18.49
	28	Blackwater 3	0.5007	0.015	0.008	0.01000	0.00999	0.00200	4.00
	29	Blackwater 3	0.5004	0.012	0.005	0.00625	0.00625	0.00125	2.50
	30	Blackwater 3	0.5004	0.012	0.005	0.00625	0.00625	0.00125	2.50
	31	Blackwater 4	0.5007	0.012	0.005	0.00625	0.00624	0.00125	2.50
	32	Blackwater 4	0.5008	0.012	0.005	0.00625	0.00624	0.00125	2.50
	33	Blackwater 4	0.5002	0.011	0.004	0.00500	0.00500	0.00100	2.00
	34	Blackwater 5	0.5009	0.016	0.009	0.01125	0.01123	0.00225	4.49
	35	Blackwater 5	0.5007	0.016	0.009	0.01125	0.01124	0.00225	4.50
	36	Blackwater 5	0.5004	0.029	0.022	0.02751	0.02749	0.00550	11.00
	37	Mole 1	0.5002	0.018	0.011	0.01376	0.01375	0.00275	5.50
	38	Mole 1	0.5003	0.018	0.011	0.01376	0.01375	0.00275	5.50
	39	Mole 1	0.5010	0.018	0.011	0.01376	0.01373	0.00275	5.49
	40	Mole 2	0.5005	0.011	0.004	<LLD	<LLD	<LLD	<LLD
	41	Mole 2	0.5002	0.012	0.005	0.00625	0.00625	0.00125	2.50
	42	Mole 2	0.5005	0.010	0.003	<LLD	<LLD	<LLD	<LLD
	43	Mole 3	0.5008	0.020	0.013	0.01626	0.01623	0.00325	6.49
	44	Mole 3	0.5008	0.020	0.013	0.01626	0.01623	0.00325	6.49
	45	Mole 3	0.5009	0.020	0.013	0.01626	0.01623	0.00325	6.49
	46	Blank2.1		0.008		0.01000			
	47	Blank2.2		0.007		0.00875			
	48	H_2O		0.006		0.00750			
Batch3	49	Mole 4	0.5002	0.016	0.012	0.01468	0.01467	0.00293	5.87
	50	Mole 4	0.5003	0.016	0.012	0.01468	0.01467	0.00293	5.87
	51	Mole 4	0.5005	0.016	0.012	0.01468	0.01467	0.00293	5.87

Appendix V: Sediment analysis data

52	Bourne 1	0.5008	0.002	-0.003	<LLD	<LLD	<LLD	<LLD
53	Bourne 1	0.5006	0.002	-0.003	<LLD	<LLD	<LLD	<LLD
54	Bourne 1	0.5004	0.002	-0.003	<LLD	<LLD	<LLD	<LLD
55	Bourne 2	0.5001	0.004	-0.001	<LLD	<LLD	<LLD	<LLD
56	Bourne 2	0.5001	0.003	-0.002	<LLD	<LLD	<LLD	<LLD
57	Bourne 2	0.5009	0.002	-0.003	<LLD	<LLD	<LLD	<LLD
58	Bourne 3	0.5004	0.011	0.007	0.00830	0.00829	0.00166	3.32
59	Bourne 3	0.5001	0.013	0.009	0.01085	0.01085	0.00217	4.34
60	Bourne 3	0.5011	0.018	0.014	0.01723	0.01719	0.00344	6.88
61	Bourne 4	0.5008	0.013	0.009	0.01085	0.01083	0.00217	4.33
62	Bourne 4	0.5001	0.012	0.008	0.00957	0.00957	0.00191	3.83
63	Bourne 4	0.5005	0.013	0.009	0.01085	0.01084	0.00217	4.34
64	Bourne 5	0.5010	0.074	0.070	0.08872	0.08854	0.01771	35.42
64a	Bourne 5rep	0.5010	0.068	0.064	0.08106	0.08090	0.01618	32.36
65	Bourne 5	0.5008	0.014	0.010	0.01213	0.01211	0.00242	4.84
66	Bourne 5	0.5006	0.013	0.009	0.01085	0.01084	0.00217	4.33
67	Blackwater 5	0.5006	0.013	0.009	0.01085	0.01084	0.00217	4.33
68	Blackwater 5	0.5008	0.014	0.010	0.01213	0.01211	0.00242	4.84
69	Blackwater 5	0.5009	0.013	0.009	0.01085	0.01083	0.00217	4.33
70	Blank2.1		0.004		0.00511			
71	Blank2.2		0.005		0.00638			

LOD (absorbance)	0.006

Appendix VI – River Hogsmill flow

	Estimation of upstream river flow using timed float										Mean	U/S stage	D/S Flow
Float no.	1	2	3	4	5	6	7	8	9	10	time	height (m)	($m^3 s^{-1}$)
12/02/07	8.00	8.27	9.00	9.00	9.32	8.16	7.98	8.28	8.27	8.69	8.50	0.55	2.587
26/02/07	7.63	8.34	8.55	8.01	8.17	7.95	7.93	8.50	8.51	7.83	8.14	0.41	2.349
06/03/07	6.35	6.06	7.13	6.90	7.00	6.54	8.86	6.40	6.70	6.72	6.87	0.97	4.262
13/03/07	11.65	12.83	16.11	13.04	12.54	13.39	11.18	11.65	11.76	11.34	12.55	0.25	1.313
21/03/07	15.66	15.67	14.31	14.16	17.63	13.95	17.37	16.45	14.95	14.73	15.49	0.25	1.322
03/04/07	16.37	15.22	15.54	17.86	16.18	14.84	16.77	18.20	17.8	17.15	16.59	0.25	1.119
10/04/07	15.39	16.88	18.93	25.14	21.69	17.89	22.24	21.11	17.13	22.36	19.88	0.25	0.981
18/04/07	20.98	19.87	19.04	32.30	20.87	18.08	19.61	19.41	19.12	20.05	20.93	0.25	1.037
30/04/07	14.96	22.1	19.07	16.28	20.6	15.96	20.05	18.06	22.38	16.66	18.61	0.24	1.189
22/05/07	17.22	15.07	19.55	19.36	15.43	16.49	15.65	15.55	16.06	15.73	16.61	0.22	1.033
29/05/07	10.05	10.47	10.58	10.21	10.56	9.3	10.24	10.15	9.61	10.58	10.18	0.27	1.313
07/06/07	17.20	19.34	17.10	17.14	16.91	15.82	18.64	16.55	18.9	15.36	17.30	0.21	0.889
14/06/07	11.38	12.34	11.93	11.76	12.04	11.32	11.89	11.76	11.67	11.28	11.74	0.25	1.269
19/06/07	18.14	17.28	13.58	13.83	14.25	14.08	19.79	17.45	15.28	16.84	16.05	0.21	1.210
01/07/07	11.43	11.94	13.32	12.48	11.85	10.32	11.92	10.52	11.1	10.13	11.50	0.28	1.324
24/07/07	12.00	13.6	14.15	12.77	12.87	13.54	13.86	11.11	12.94	12.13	12.90	0.27	1.060
31/07/07	17.59	13.25	14.86	14.96	14.37	14.15	17.28	13.73	13.6	16.29	15.01	0.29	1.127
20/08/07	13.24	13.43	14.61	15.21	15.06	15.83	14.97	14.33	14.91	12.95	14.45	0.26	0.998
28/08/07	22.35	22.41	18.85	22.99	17.67	19.3	19.91	17.87	16.82	21.14	19.93	0.21	0.801
06/09/07	28.59	26.85	27.75	23.44	25.01	31.00	25.09	23.40	30.01	30.55	27.17	0.24	0.882
12/09/07	59.25	30.48	36.27	51.16	28.91	28.75	30.63	29.27	36.74	31.5	36.30	0.22	0.927
21/09/07	45.03	33.15	30.24	34.64	42.66	34.21	32.06	34.32	46.58	33.2	36.61	0.23	0.742
01/10/07	9.31	7.74	7.2	7.40	7.52	8.64	7.83	7.52	7.86	8.59	7.961	0.50	1.492
09/10/07	30.18	39.71	37.98	46.17	31.62	36.57	40.79	34.11	46.28	35.98	37.939	0.22	2.805
20/10/07	29.53	23.21	30.33	26.50	34.22	29.98	26.43	23.89	25.91	27.17	27.717	0.22	0.779

Appendix VI – River Hogsmill flow

29/10/07	15.85	27.1	18.81	17.4	33.81	26.24	16.72	16.02	18.64	17.95	20.854	0.25	0.841
10/11/07	43.41	25.26	26.2	34.97	28.68	39.00	26.34	35.73	26.12	38.97	32.468	0.25	0.774
22/11/07	8.43	8.82	8.03	8.82	8.7	7.82	9.13	7.70	8.47	8.99	8.491	0.48	2.1
03/12/07	11.38	11.06	11.72	11.07	13.22	11.14	9.91	11.72	11.38	11.23	11.383	0.32	1.2
18/12/07	18.38	16.55	21.51	19.78	18.51	17.79	21.08	19.23	19.10	21.90	19.383	0.27	0.899
03/01/08	15.59	15.06	18.94	17.83	19.86	15.36	17.18	18.92	16.75	16.22	17.171	0.25	1.01
14/01/08	8.69	9.65	9.08	9.31	10.36	10.06	9.66	9.57	9.78	9.36	9.552	0.36	1.63
04/02/08	12.28	11.16	10.92	12.56	14.48	11.39	11.21	11.12	11.49	11.13	11.774	0.31	1.36
27/02/08	17.42	14.87	21.09	16.01	17.82	16.80	17.74	15.89	19.48	14.92	17.204	0.26	1.28
03/03/08	22.13	21.45	22.57	22.65	18.89	19.12	21.49	17.17	20.84	25.64	21.195	0.26	1.27
17/03/08	9.22	8.41	9.23	9.43	9.29	8.41	8.86	9.04	8.88	8.52	8.929	0.33	1.45
27/03/08	9.67	9.05	9.21	10.10	9.06	8.86	9.01	9.13	9.04	9.97	9.31	0.36	1.38
17/04/08	14.20	12.96	12.59	12.29	12.98	12.67	14.04	13.57	12.6	12.79	13.069	0.28	0.977
25/04/08	12.14	11.65	13.78	12.82	12.89	12.82	11.63	11.85	12.71	12.11	12.44	0.28	1.01
30/04/08	7.17	7.38	7.26	6.92	7.00	7.04	7.06	7.45	7.21	6.73	7.122	0.67	3.48
15/05/08	11.07	10.54	9.84	11.53	10.36	10.94	11.01	10.13	10.97	9.85	10.624	0.31	1.81
28/05/08	7.87	6.87	6.90	7.17	6.76	6.80	6.93	7.53	7.30	7.35	7.15	0.42	1.95
03/06/08	7.13	6.78	7.39	6.91	7.29	6.97	6.71	7.47	7.07	6.85	7.057	0.52	2.767
22/06/08	15.06	16.02	15.16	14.04	13.62	14.74	14.97	14.13	14.88	15.06	14.768	0.25	1.129
07/07/08	8.87	9.83	8.15	10.43	7.96	8.41	8.03	9.01	7.97	8.65	8.731	0.33	3.570
10/07/08	8.91	9.05	9.08	8.98	9.21	9.5	8.45	10.11	9.51	9.43	9.223	0.28	1.430
29/07/08	11.25	11.82	11.79	11.69	12.25	12.56	12.01	11.34	13.92	13.92	12.255	0.27	1.020
11/08/08	14.19	14.34	14.9	14.41	14.05	16.69	14.68	15.85	14.69	14.96	14.88	0.21	1.12
20/08/08	16.15	14.49	13.70	15.22	15.78	15.53	13.23	15.07	16.64	15.60	15.14	0.20	1.04
28/08/08	16.68	17.81	18.55	15.00	16.36	18.22	18.16	18.44	18.7	16.53	17.445	0.20	0.907

Appendix VII – River Bourne flow

Estimation of upstream river flow using timed float

Float no.	1	2	3	4	5	6	7	8	9	10	Mean time	U/S stage height (m)	D/S Flow ($m^3 s^{-1}$)
26/02/07	18.78	18.67	17.67	18.99	16.47	19.83	22.12	19.93	20.24	20.81	19.35	0.72	2.421
05/03/07	19.24	20.4	20.8	19.12	19.71	20.22	23.1	18.03	22.53	21.95	20.51	0.76	3.577
13/03/07	44.41	46.21	51	36.56	53.79	32.95	39.74	34.22	35.45	34.88	40.92	0.28	1.054
04/04/07	52.70	67.88	58.84	67.84	58.81	53.31	68.42	79.63	65.47	60.72	63.36	0.25	0.597
09/04/07	55.47	46.79	61.18	47.02	55.37	55.66	48.69	50.75	79.72	48.05	54.87	0.25	0.526
18/04/07	75.31	73.95	78.23	109.75	68.44	81.75	64.33	74.42	65.95	63.68	75.58	0.24	0.49
30/04/07	104.60	133.9	97.94	128.9	111.13	109.15	133.88	126.26	118.08	100.59	116.44	0.24	0.365
22/05/07	69.64	70.9	60.1	69.95	68.21	107.98	74.75	76.21	78.88	70.08	74.67	0.22	4.649
28/05/07	24.00	23.8	36.5	25.8	24.80	24.9	35.6	29.08	35.8	29.9	29.02	0.63	5.685
07/06/07	72.60	81.3									76.95	0.21	0.449
14/06/07	110.00	120.01	118.8	100.3	110.30	110.4	120.2	130.2	140.1		117.81	0.17	0.515
19/06/07	119.96	75.2	93.42	92.3	115.02	99.73	135.76	91.42	77.48	85.53	98.58	0.25	0.506
01/07/07	50.35	55.56	52.95	49.83	61.54	54.26	51.91	62.48	52.29	57.63	54.88	0.51	0.956
24/07/07	40.65	38.47	42.3	43.98	52.06	38.51	50.65	42.81	38.77	44.01	43.22	0.46	1.381
31/07/07	47.82	50.42	42.85	50.49	47.08	48.42	44.4	47.93	49.44	43.46	47.23	0.47	0.934
20/08/07	103.89	63.7	49.95	61.59	92.70	61.39	64.05	73.33	58.92	63.26	69.28	0.26	0.571
27/08/07	90.61	82.3	77.42	93.97	74.17	85.99	84.29	83.58	70.76	88.47	83.16	0.23	0.443
06/09/07	172.09	109.57	116.71	150.01	134.15	139.48	124.6	100.96	110.04	144.26	130.19	0.17	0.389
12/09/07	128.53	136.29	129.94	135.44	115.56	107.17	156.8	139.57	114.01	174.42	133.77	0.16	0.377
22/09/07	151.44	122.36	140.94	106.35	120.54	143.94	156.52	189.7	122.45	123.41	137.77	0.18	0.376
01/10/07	68.00	70.59	106.69	67.03	108.80	75.32	90.32	78.84	76.88	77.09	81.96	0.26	0.540
20/10/07	65.96	72.89	68.77	58.9	55.49	64.41	59.16	67.99	58.93	64.22	63.67	0.27	0.567
30/10/07	62.22	57.70	60.86	60.77	69.12	78.18	63.58	65.01	59.5	68.22	64.52	0.25	0.569
12/11/07	58.78	57.54	58.68	61.76	61.40	59.11	51.18	56.20	65.77	54.80	58.52	0.25	0.521
22/11/07	20.46	20.39	19.540	20.03	20.00	21.70	20.5	21.02	21.69	19.67	20.50	0.65	2.350

Appendix VII – River Bourne flow

03/12/07	24.12	23.19	24.4	26.44	28.87	27.03	22	23.76	25.53	24.58	24.99	0.34	1.13
18/12/07	47.98	47.76	48.9	51.06	45.96	47.16	54.2	49.42	46.71	46.8	48.60	0.27	0.669
03/01/08	49.31	54.12	49.08	49.32	48.60						50.09	0.26	0.686
19/01/08	23.72	24.46	21.55	21.6	20.10	20.69	22.34	20.64	24.35	23.28	22.29	0.46	1.63
05/02/08	31.90	28.64	29.01	34.69	38.46	27.79	30.97	36.2	33.45	31.58	32.54	0.31	1.01
27/02/08	43.19	47.88	49.32	40.98	41.14	39.78	52.09	52.28	52.28	41.95	44.50	0.26	0.639
04/03/08	52.10	49.49	51.07	52.60	67.97	53.00	46.01	45.19	61.85	47.85	54.65	0.26	0.549
18/03/08	22.76	25.64	23.79	24.73	27.55	23.26	25.54	25.33	22.94	25.55	24.89	0.40	1.300
28/03/08	35.92	41.53	35.42	38.14	37.61	34.76	35.36	35.38	36.7	34.64	37.72	0.36	1.310
17/04/08	47.27	41.78	43.56	44.29	48.23	46.21	44.49	41.26	43.86	42.2	45.03	0.31	0.771
25/04/08	49.31	41.66	42.7	49.82	48.99	49.3	47.3	48.47	50.32	52.42	46.50	0.28	0.616
01/05/08	18.94	17.63	21.38	20.56	20.36	16.55	19.24	20.8	21.63	19.31	19.77	0.57	2.58
16/05/08	53.60	57.64	57.28	60.90	63.76	61.83	57.47	62.56	58.93	60.35	58.64	0.24	0.525
28/05/08	21.30	24.04	25.42	25.53	23.49	25.01	25.63	28.07	22.55	25.55	23.96	0.62	2.03
04/06/08	21.60	23.26	22.23	20.97	21.62	20.94	22.48	22.99	19.35	22.08	21.94	0.96	3.32
23/06/08	71.76	65.32	82.36	72.17	75.15	72.09	80.60	85.04	103.83	67.32	73.35	0.25	0.46
07/07/08	88.37	72.52	62.62	66.68	71.03	82.30	110.66	113.54	84.81	89.63	72.24	0.28	0.95
10/07/08	42.85	39.43	41.12	38.81	51.19	38.58	40.95	36.84	36.16	40.23	42.68	0.66	1.28
29/07/08	94.74	85.38	80.78	80.66	108.00	101.18	102.66	125.68	73.59	76.19	89.91	0.27	0.45
11/08/08	99.94	92.38	118.45	92.82	76.15	80.70	110.28	89.57	128.93	92.37	95.95	0.29	0.498
20/08/08	83.81	83.12	80.46	78.98	85.57	100.41	82.46	88.93	85.49	73.86	82.39	0.30	0.423
28/08/08	98.72	90.75	137.20	99.06	78.72	88.97	85.21	90.63	105.17	103.04	100.89	0.27	0.384

Appendix VIII – Long term average rainfall, monthly average rainfall and downstream river flows

Month	Long term average rainfall Jan 1977-Dec 2006 (mm)	Project year	Monthly Rainfall (mm)	% of LT average	Average D/S river flow Hogsmill $m^3 s^{-1}$	Average D/S river flow Bourne $m^3 s^{-1}$
February	37.81	2006	92.9	145.70	2.00	1.62
March	44.93	2006	43.8	-2.52	1.74	1.39
April	45.63	2006	3.6	-92.12	1.09	0.50
May	50.54	2006	80.0	58.29	1.25	1.34
June	47.61	2006	63.8	34.00	1.07	0.55
July	40.39	2006	115.2	185.22	1.39	1.21
August	51.39	2006	41.0	-20.22	0.98	0.53
September	47.31	2006	17.4	-63.22	0.93	0.41
October	69.12	2006	37.8	-45.31	0.92	0.55
November	52.67	2006	84.8	61.00	1.36	0.89
December	58.36	2006	44.6	-23.58	1.25	0.94
January	54.33	2007	69.0	27.00	1.40	1.35
February	37.81	2007	15.4	-59.27	1.26	0.71
March	44.93	2007	69.8	55.35	1.54	0.99
April	45.63	2007	63.4	38.94	1.26	0.83
May	50.54	2007	64.2	27.03	1.37	0.93
June	47.61	2007	45.6	-4.22	1.15	0.86
July	40.39	2007	76.8	90.15	1.23	0.57
August	51.39	2007	64.4	25.31	1.01	0.42
Rainfall data from Heathrow monitoring station (www.metoffice.gov.uk)			D/S river flow supplied by the Environment Agency			

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