

CRANFIELD UNIVERSITY

RAUL PRIETO FORT

**ASSESSMENT OF TERTIARY REED BEDS IN CHEMICALLY-DOSED
WASTEWATER TREATMENT PLANTS FOR PHOSPHORUS REMOVAL**

SCHOOL OF APPLIED SCIENCES
DEPARTMENT OF ENVIRONMENTAL SCIENCE AND TECHNOLOGY
CRANFIELD WATER SCIENCE INSTITUTE

MSc BY RESEARCH
Academic Year 2012 - 2013

Supervisors: Prof. Bruce Jefferson & Dr Gabriela Dotro

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ABSTRACT

Eutrophication is one of the problems affecting the environmental quality standards of fresh waters. Phosphorus (P) is considered a main nutrient contributing to this. In the UK, the Water Industry is responsible for c. 50% of the total phosphorus load to freshwater ecosystems. Within this, small wastewater treatment plants (WwTPs) (<2,000 population equivalent) have a significant role since they represent 75% of all WwTPs in the UK.

The current option for P removal from wastewater is chemical precipitation through the dosing of iron (Fe) salts in combination with a tertiary filtration treatment step. This study aims to determine the transformation processes whereby tertiary reed beds permanently store or release iron and phosphorus in chemically-dosed sites to provide recommendations regarding the conditions where reed beds can be used as such final filtration treatment in small WwTPs. This was carried out through sampling campaigns in 14 full-scale tertiary reed beds.

Chemically-dosed WwTPs with tertiary reed beds can perform satisfactorily achieving phosphorus removals above 85% and average P and Fe final effluent concentrations of 0.7 mg P/L and 0.2 mg Fe/L, respectively, both well below consents (2 mg TP/L and 4 mg Fe/L). The majority of the total phosphorus in the reed bed influents was associated to either suspended solids or dissolved fractions, whereas 60-90% of the effluent TP is in the dissolved form. Occasional episodes of phosphorus release from the reed bed can occur, as evidenced in an increase in soluble reactive phosphorus in the effluent. The main mechanism for trapping of Fe and P in mature beds was settlement of suspended particles, with phosphorus and iron concentrations in the accumulated sludge being up to 55.9 g P/kg dry matter and 246.6 g Fe/kg DM. The removal of particulate pollutants was successful in the reed beds studied, but colloidal and dissolved particles passing through the beds untreated. This could compromise the use of reed beds with future tightening P consents if the current chemical dosing practices are unchanged.

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1. INTRODUCTION

Eutrophication is one of the most serious problems affecting the environmental quality standards of fresh waters in the UK and elsewhere. Nutrient enrichment in rivers can degrade the ecosystem by causing oxygen depletion and altering the competitive balance between different aquatic plant and animal species. Phosphorus (P) is considered one of the main nutrients contributing to this, and so P concentrations in fresh water need to be maintained as near to background levels as possible (Mainstone and Parr, 2002).

In the UK, the Water Industry is responsible for c. 50% of the total phosphorus load to freshwater ecosystems, whereas the remaining 50% comes from diffuse sources such as agricultural runoff (Environment Agency, 2012a). Wastewater treatment plants (WwTPs) outfalls are particularly important as they represent the major point source into rivers and discharge predominately bioavailable orthophosphate (Mainstone et al., 2000). Consequently, technology upgrades that addresses this are of interest. Currently, the preferred option for the removal of P from wastewater in the UK is chemical precipitation through the dosing of iron (Fe) salts. This method is cost effective and is usually applied in combination with a tertiary filtration treatment step (Environment Agency, 2012a). Out of the 5,952 WwTP owned by the ten big water utilities in the UK, 657 WwTPs are applying Fe dosing for P removal in the *Asset Management Plan 2010-2015 (AMP5)* (UKWIR, 2010). Within this, small WwTP (<2,000 population equivalent (PE)) have a significant role since they represent 75% of all WwTPs in the UK (OFWAT, 2011).

In this context, this study analyses the performance of *reed beds* as final filtration treatment in small WwTPs with chemical dosing of iron salts for phosphorus removal. Due to their proven solids trapping ability, their mechanical simplicity, and low operation and maintenance (O&M) requirements, reed beds are the preferred choice for polishing secondary effluents pre-treated with iron salts. In this application, the role of the reed beds would be the long term entrapment of particulate solids containing Fe and P. This approach was put in practice by Severn Trent Water in 2006,

with successful initial results (Sulley, 2007). However, the long term behaviour of the P and Fe precipitates entering these systems has not been tested to date.

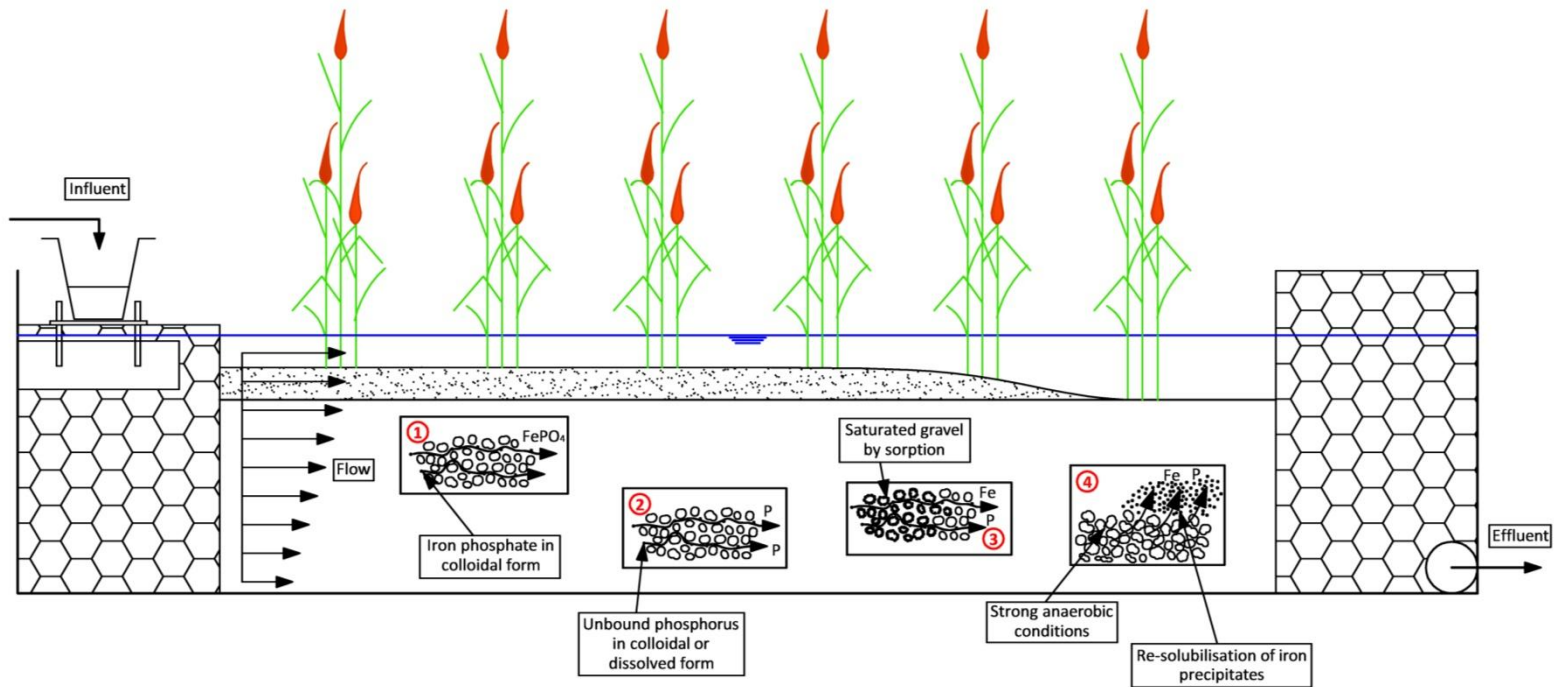
As the need for improving the quality of the water bodies in the UK gains momentum, additional phosphorus discharge standards in small WwTPs are expected to come in force in the near future. With this, having appropriate, resilient technologies for small WwTPs will become key to environmental compliance in the UK. For reed beds to be considered a suitable treatment technology in this scenario, it is necessary to understand the long term behaviour of trapped particulate phosphorus and iron.

1.1. Project aim and hypothesis

This project aimed to determine the transformation processes whereby tertiary reed beds permanently store or release iron and phosphorus in chemically-dosed sites to provide recommendations regarding the conditions where reed beds can be used as tertiary solids filters in small WwTPs. This was carried out through sampling campaigns in full-scale tertiary reed beds in *Severn Trent Water*.

In order to assess tertiary reed beds in chemically-dosed sites a total of four hypotheses were tested:

- 1) Iron phosphate precipitates enter the reed bed as colloidal particles that pass through the bed media, resulting in high levels of both Fe and P in the effluent.
- 2) High unbound phosphorus enters the reed bed in colloidal or dissolved form, thus pass through it, resulting in high final effluent P levels.
- 3) Poor initial mixing conditions when adding ferric solution produces higher levels of colloidal and dissolved particles in the secondary effluent that would not be trapped in the tertiary reed bed.
- 4) Anaerobic conditions within the reed beds re-solubilise iron precipitates, releasing iron and phosphorus into the effluent.



- **Hypothesis**

- ① Colloidal iron phosphates are not captured by the media
- ② Unbound phosphorus in colloidal or dissolved form are not captured by the media
- ③ Phosphorus and iron passes through gravel media after it becomes saturated by sorption
- ④ Strong anaerobic conditions re-solubilise iron precipitates

Figure 1.1 Scheme of the four hypothesis tested in the tertiary reed beds at chemically-dosed sites.

1.2. Thesis structure

This thesis is organized by chapters. Chapter 2 presents a literature review of the main subjects related to the topic of this project to facilitate the understanding of the obtained results. Chapter 3 describes the materials and methods used for the experimental and analytical work. Results obtained are presented in Chapter 4. Finally, Chapter 5 and 6 present the discussion and conclusions of this project, respectively.

2. LITERATURE REVIEW

2.1. Phosphorus as a pollutant

The European legislation concerning wastewater treatment (*Urban Wastewater Treatment Directive 91/271/EEC*) defines eutrophic waters as a sensitive area where waters are affected by the addition of nutrients, mainly nitrogen (N) and phosphorus. Presence of excess nutrients in water bodies stimulates the biological growth. This phenomenon is called eutrophication and can result in an increase of visible cyanobacteria, algal blooms, or floating plant mats leading to damage of the natural environment. Whilst in the past nitrogen received the most attention due to its high solubility and leachability through field drains and groundwater, along with its potential for conversion to harmful gaseous emissions (McGechan and Wu, 1998), efforts to avoid eutrophication are currently moving towards the less soluble and non-volatile nutrient phosphorus (McGechan and Lewis, 2002).

Major sources of phosphorus are derived from human (orthophosphates plus other biological compounds containing phosphorus), industrial (condensed phosphates), agricultural wastes (synthetic fertilisers) and domestic (detergents and cleaning compounds) (Yeoman et al., 1988).

The *Urban Wastewater Treatment Directive 91/271/EEC* that was adopted on 21 May 1991 and amended on 27 February 1998 by the *Directive 98/15/EC*. This legislation regulates the requirements for discharges from WwTPs into both sensitive and non-sensitive areas, defining sensitive areas as those where discharge requires additional treatment before discharge (*Environment Agency, 2012b*). Hence, WwTP discharge standards vary according to the sensitivity of the area receiving the treated effluent and the volume of water discharged. In the case of England and Wales, this directive is implemented through the *Urban Waste Water Treatment Regulations (1994)*.

The quality requirements set out in the EU and UK legislation are 2 mg TP/l for 10,000 – 100,000 population equivalent and 1 mg TP/l for WwTPs treating more than 100,000 PE. Small WwTPs, defined as treatment facilities receiving wastewater equivalent to less than 2,000 PE are only required to meet specific P consents when particular sensitive area is identified as their discharge water body. In the UK, out of 5,952 sewage WwTPs owned by the ten big water utilities, 75% of them fall in this category (OFWAT, 2011). Phosphorus consents in small WwTPs can also be covered by other relevant UK regulations such as the classification of *Sites of Special Scientific Interest* protected under the *Countryside and Rights of Way Act (2000)*. In England, there are over 4,100 of these sites covering around 8% of the country's land area, and more than 70% (by area) are designed as special areas of conservation, special protection areas or ramsar sites (wetlands of international importance) (*Natural England, 2012*).

2.2. Phosphorus removal from wastewater

Two main strategies are used in domestic WwTP where phosphorus removal is required: (1) biological phosphorus removal and (2) chemical phosphorus removal. The biological removal pathway relies on the growth of a particular microbial population known as phosphate-accumulating organisms that under certain operational conditions are capable of storing orthophosphate in excess of their biological growth requirements. The main limitation of this approach is the requirement of high strength wastes, which are needed to enable the microbial populations to thrive in the WwTP. As such, its application for P removal in the UK is limited to sites where a significant additional organic load is present in the sewage. In contrast, chemical phosphorus removal relies on the physical-chemical transformation of soluble phosphorus to particulate form by addition of a coagulant such as iron or aluminium (Al) salts. This approach works in a range of wastewater compositions and thus is the most used method for the removal of phosphorus in the UK (Environment Agency, 2012a).

The ideal selected chemical to act as coagulant should produce as small sludge quantities as possible; be required in small amounts to remove large quantities of P;

and present minimal operational and maintenance problems associated with storage, handling and feeding. Divalent or trivalent metal salts are the most common chemicals used for P removal, particularly iron and aluminium salts. Reactions between phosphorus and metal salts mainly depend on the wastewater characteristics and the phosphorus speciation. Phosphorus in domestic wastewater may be present as organic or inorganic fractions. Typical concentrations are between 1-5 mg/L of particulate organic P, and 3-10 mg/L of soluble inorganic P (Tchobanoglous et al., 2003; WEF, 2009). Inorganic phosphorus is the primary form in wastewater with above 75% of total phosphorus, primarily as orthophosphates (PO_4^{-3}) which are the primary phosphorus species affected by chemical addition to form an insoluble precipitate.

With the Environment Agency preferring iron over aluminium salts for P removal from domestic wastewater in the UK (Environment Agency, 2012a), both ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions can be used in typical forms of ferric chloride (FeCl_3), ferrous chloride (FeCl_2), ferric sulphate ($\text{Fe}_2(\text{SO}_4)_3$) and ferrous sulphate (FeSO_4). Ferric iron is most frequently used in wastewater treatment as the ferrous ion depends on its oxidation to ferric ion to act as a coagulant (Thistleton et al., 2001). Rapid iron hydrolysis occurs when a ferric solution is added to wastewater, and thus removal of orthophosphates takes place in parallel by either *precipitation* of iron-bound-phosphates, *coprecipitation*, or *adsorption* of phosphate onto existing ferric hydroxides (Figure 1).

The most effective pathway is through the generation of iron phosphates, but is complicated by the reactivity of iron (III) towards hydroxide ions (OH^-) as well as phosphates. The balance of the two reactions is related to the ratio $\text{PO}_4^- / \text{OH}^-$ (Stumm, 1962). The type of precipitant formed during dosing has consequences over the cost of chemical treatment. For instance, where adsorption onto ferric hydroxide dominates the pathway, dose requirements can be up to five times those observed when precipitation controls (Thistleton et al., 2002). Thus, it is important to reduce the formation of iron hydroxides by applying sufficient mixing during the addition of iron salts to facilitate the proximity between phosphates and iron (III) ions for its bonding.

The chemical reaction between ferric sulphate and orthophosphates for the formation of ferric phosphates can be approximated as follows:

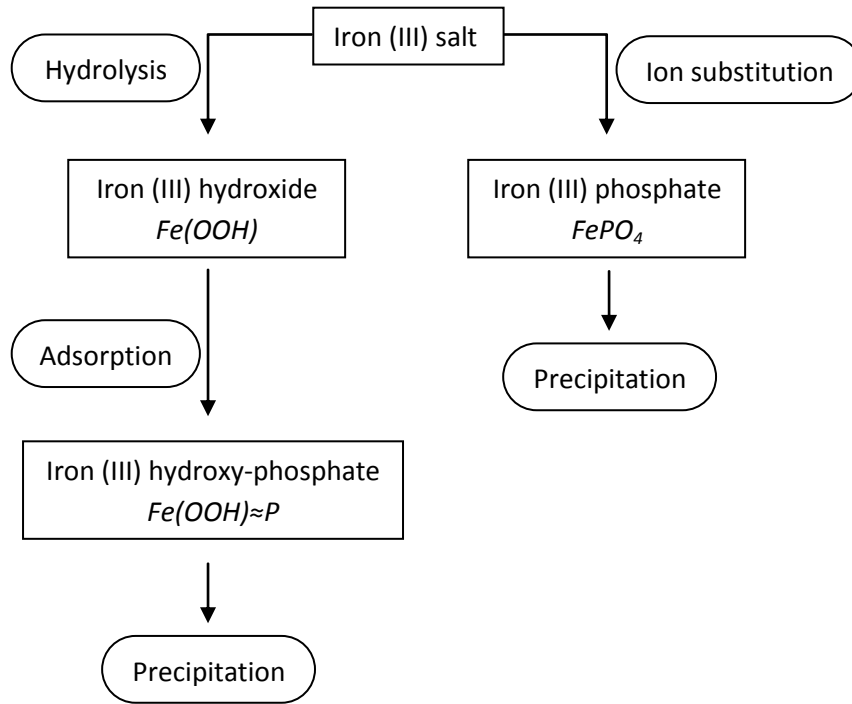
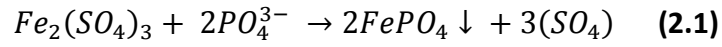


Figure 2.1 Simplified diagram of possible iron (III) reactions pathways for phosphorus removal in wastewater (adapted from Thistleton et al., 2001).

Since ferric hydrolysis is completed in less than one second (Thistleton et al., 2002), initial mixing conditions when adding ferric solution into wastewater become of high relevance for efficient P removal (Gillberg et al., 1996; Pearce, 1998). Poor mixing conditions may need greater chemical addition and will subsequently cause extra sludge production affecting the downstream treatment processes. Rather than mixing within structures specially designed for this proposal, it is a standard practice to use existing facilities within the treatment flowsheet for chemical mixing such as drop manholes, aerated grit chambers, hydraulic jumps, and discharge side of pumps).

The dosage required for phosphorus removal can vary substantially between facilities, the time of day and the season of the year. In general, iron (III) dose required for P removal is higher than indicated by FePO_4 stoichiometry (equation 2.1), with reported optimum ratios varying from 1 to 7.5 (Nesbitt, 1969) and being closely affected by the wastewater's pH. Iron salts are most effective at an acidic pH range from 3 to 5 for a constant molar ratio between ferric ion and phosphorus (Fettig et al., 1990; Gillberg et al., 1996). Formation of ferric phosphate requires a lower pH of 3.5 (Smith et al., 2008), and sorption capacity of orthophosphates is reduced with the increase in pH due to competition between PO_4^{3-} and OH^- . However, significant removal of phosphorus can be also achieved at the pH 6 to 8, typically found in wastewater (Takács et al., 2006).

Chemical addition can take place in different points within treatment stages. The most common are the upstream primary sedimentation tanks or within aeration basins in secondary treatment. Chemical dosing at primary treatment stages achieves greater suspended solids and BOD removal that generates additional sludge compared to chemical addition in secondary treatment. The main disadvantage of primary dosing is a reduced efficiency in the removal of P as the presence of particulate material reduces the orthophosphate adsorption capacity (Fettig et al., 1990; Szabó et al., 2008). Iron (III) hydroxides will keep removing orthophosphate downstream of the dosing point (Thistleton et al., 2002), but in general higher levels of phosphorus removal can be achieved by chemical addition into secondary process (US EPA, 1987).

2.3. Reed beds for wastewater treatment with chemical phosphorus removal

Subsurface flow constructed wetlands (here called "*reed beds*") are engineered systems that are specially designed to reproduce the processes that occur in natural wetlands for the removal of pollutants from wastewater. They consist of a bed of granular media (usually gravel or sand) planted with emergent macrophytes (common reed, *Phragmites australis*), through which wastewater is passed for treatment. Reed beds operate under permanently saturated soil conditions, with a horizontal flow

regime in which the water level is located 5-10 cm below the surface of the granular media.

Reed beds are used worldwide due to their mechanical simplicity and low operations and maintenance requirements in comparison to other wastewater technologies (Nivala et al., 2012). There are more than 5,000 reed beds in Europe for wastewater treatment (Vymazal, 1998), and more than 1,000 reed bed systems in the UK (Cooper, 2007). They are primarily used for secondary treatment after primary sedimentation and for tertiary filtration before discharging the treated effluent to the receiving water body.

In the UK, reed beds are widely used for tertiary treatment of municipal wastewater (Cooper, 2007). These are used in small WwTP of less than 2,000 PE as a suitable and cheaper alternative to conventional sand filters used in larger WwTPs. Removal of suspended organic matter and solids within reed beds takes place by settlement of particles due to low flow velocity within the system and the sieve effect of the granular media along with other physico-chemical mechanisms, such as coagulation of smaller colloids into larger particles, and the sorption capacity of the media through repulsive and attractive forces between particles in suspension and media surfaces (Knowles et al., 2011). Reed beds may achieve removal percentages of suspended solids above 90% and effluent concentrations below 20 mg/L (Garcia et al., 2008).

At sites with chemical dosing of iron salts for phosphorus removal, tertiary filters may be required to achieve phosphorus and iron compliance on sites where existing secondary sedimentation processes are not effective (Chappel, 2008). Reed beds can be used as such tertiary filtration treatment for trapping iron-bound phosphate particles and iron hydroxide flocs that may remain after secondary settlement. The trapping of these solids results in the accumulation of such particles within the bed and can cause reduction of pore space and a gradual clogging of the granular media. Problems associated with clogging are hydraulic malfunctions (e.g., surface ponding, reduction of hydraulic conductivity of the media), which can limit the asset life of the

system (Knowles et al., 2011). For non-dosed sites, this is currently estimated to be 8 years in the UK (Griffin et al., 2008).

Performance of reed beds has a strong dependence over loading rates and specific hydrological and ecological characteristics of the system. In general, high removal percentages of COD, BOD and bacterial pollution are achieved (80-99%), but removal rates for phosphorus are mostly too low to be relied upon as a P removal system (Verhoveven and Meuleman, 1999). Vymazal (2008) reported removal percentages of 40% in horizontal SSF CWs with inlet concentrations above 8 mg/L of total phosphorus. The main mechanism of phosphorus removal is adsorption of phosphates to media particles. Adsorption capacity of the media may be enhanced in chemically-dosed sites because of the presence of iron or aluminium salts added during treatment that are retained and accumulated within the reed bed. However, phosphorus-binding capacity of iron (III) salts is compromised under anaerobic conditions. Flooding as a result of clogging may result in anaerobic conditions, causing the reduction of iron adsorption capacity and even release of phosphates (Patrick et al., 1973; Faulkner and Richardson, 1989). Minimal phosphorus removal is achieved by plant uptake, although for it to be permanent the biomass needs to be harvested to prevent release back to the water during the decomposition of plant litter (Vymazal, 2007). In general, phosphorus removal in reed beds is greater during the first two years because of media adsorption, but it may decrease rapidly once the system reaches equilibrium (Environment Agency, 2012a).

2.4. Retention of iron and phosphorus in reed beds

Iron is a common constituent in municipal wastewaters with concentration levels varying between 0.1 and 1.9 mg/L and a mean value of 0.9 mg/L (Kadlec and Knight, 1996). Iron salts are also added in wastewater treatment plants for chemical phosphorus removal, in which particulate iron-bound-phosphates are removed either in sedimentation tanks or tertiary filters. Within this process reed beds can act as tertiary filters to retain $\text{Fe}(\text{OOH})\approx\text{P}$ and FePO_4 particles, but presence of certain

physico-chemical conditions may compromise storage of this compounds within reed bed.

2.4.1. Iron accumulation in bed media

Accumulation of iron in reed beds with upstream chemical dosing for P removal is a very particular scenario where almost no research has been undertaken. However, the existence of several studies of metal retention -including iron- in constructed wetlands for either industrial or domestic wastewater treatment may explain accumulation and retention of iron in such scenario.

Possible mechanisms of metal retention in the granular media of the reed bed include ion exchange and precipitation, along with presence of organic and inorganic components in the media that act as an effective sink for metals (Dunbabin and Bowmer, 1992). Iron and other metals are distributed in the sediment as a function of three factors: (i) distance from the inlet, (ii) position across the width of the reed bed (left, middle or right) and (iii) bed depth.

The concentration of iron decreases with increasing distance, being higher in the wetland inlet than in the outlet (Mays et al., 2001; Di Luca et al., 2011). In the particular case of Fe, the concentration profile along the reed bed may show a less pronounced decrease than other metals such as zinc, cadmium and copper (Lesage et al., 2007). This gradual decrease of Fe in sediment along the bed can be related to four main factors: (i) Fe as colloidal complexes may migrate through the bed and be retained by filtration further along the treatment path, (ii) reducing conditions in the inlet area along with high organic load may lead to the reduction of Fe^{3+} to the more soluble form Fe^{2+} , (iii) change of redox conditions from reducing to oxidising along the bed length may produce precipitation of iron hydroxides, and (iv) the Fe accumulated in the plant biomass becomes buried within the sediment when no harvesting is done and thus increases the Fe content in the sediment.

Higher accumulation of metals in the inlet area rather than in the middle and outlet is only significant in reed beds with short length of operation. Vymazal and Švehla

(2012) reported that the amount of sediment in seven horizontal subsurface flow reed beds was usually greater in the inflow zone as compared to outflow zone, but the difference was statistically significant only in systems with short length of operation. Thus at the end of the operational lifetime of a reed bed, the accumulation of iron may not be higher in the inlet zone than in the outlet.

There is a correlation between metal concentrations in belowground biomass and sediment. Increasing metal concentrations in sediment has a subsequent increase in belowground biomass but not in aboveground biomass in beds planted with *Phragmites australis* (Lesage et al., 2007). This plant species restricts the translocation of iron from the roots to the stems and leaves (Windham et al., 2003; Weis and Weis, 2004). Iron accumulates mainly in the roots coating with up to 90% of the metal accumulation on the surface of the roots (Mays and Edwards, 2001). The decomposition of the reed biomass may lead to release of the iron into the sediment of the bed, increasing the iron concentration in the sediment and allowing the Fe to be exported from the CW. However, the total iron content in the plant component may correspond to only 1% of the total iron load received by the reed bed as observed by Mays and Edwards (2001).

The placement and correct operation of the flow distribution system affects iron concentration across both width and depth of the reed bed. Differences on the metal content along the bed width can indicate an unequal distribution of the influent wastewater in the inlet area (Lesage et al., 2007). These differences typically are more significant in the first meters of the bed than the rest. If the distribution system is situated above the surface of the filtration bed iron particles will tend to be retained in the upper layer of the bed, but if buried near the bottom, particles will settle at the bottom and will not flow up to the upper layers of bed (Vymazal and Švehla, 2012).

2.4.2. Phosphorus accumulation in bed media

Phosphorus removal in reed beds is performed by several factors including plant uptake, precipitation in the water column, microbial immobilization, and retention by

the granular media. However, since sub-surface flow is in permanent contact with the media, the performance of reed beds for P removal depends mainly on the retention capacities of the bed, and thus to sorption capacity of the media (McGechan and Lewis, 2002). Phosphorus removal efficiency can vary depending on the type of media in the reed bed and its selection can be crucial. Media particle size distributions influence sorption, where a high proportion of small-size particles results in higher specific surface area. Presence of iron and aluminium oxide minerals in high proportions also enhances P removal by ion adsorption of phosphates (Bowden et al., 1977). These chemicals are used as amendments for P retention in soil. Aluminium amended soils are less sensitive to changes in redox conditions than iron amended soils, but a much higher amount of aluminium (12 g/Kg) than iron (1-2 g/Kg) is required to immobilize P under anaerobic conditions (Ann et al., 2000b).

Higher sorption capacities of soils do not assure a better effluent quality in terms of P removal. This is because phosphorus concentration at equilibrium (i.e., influent P concentration in which no net sorption or desorption of phosphorus occurs in media) increases with time, and so P removal efficiency of reed beds decreases with increasing influent P concentration and loading (Pant et al., 2001). Measurements of the phosphorus concentration at equilibrium for the media used should be considered as key criteria to determine when the media must be replaced.

Most research to date has described phosphorus sorption as a fast reversible process onto solid surfaces. However, later work has suggested the existence of a second process for P accumulation in soil. This is a slow and almost irreversible process consisting of diffusion through the soil water to sites within the soil matrix, followed by precipitation or deposition below the sorption surfaces (McGechan and Lewis, 2002).

Table 2.1 Iron and phosphorus concentrations in sediment from different types of wetland (mg kg⁻¹ dry mass). (CW: constructed wetland; HSSF: horizontal subsurface flow; FWS: free water surface; VF: vertical flow).

Type of wetland		Iron	Phosphorus	Fe:P	Reference
		mg·kg ⁻¹ DM			
Coastal lagoon in sea water (brackish lagoon)	Annual mean	18,000	729	25	Gomez et al. (1999)
Agricultural soil converted to wetland	Mean	7,035	557	13	Ann et al. (2000a)
FWS CW for mine drainage	Range	176 - 617	-	-	Mays and Edwards (2001)
VF CW treating sewage lagoon wastewater with different medias	Range	258 - 1,273	190 - 1200	0.3 - 6	Pant et al. (2001)
Lakes in former open cut coal mines	Range	1,160 - 21,500	14 - 154	37 - 827	Samecka-Cymerman et al. (2001)
Natural lakes	Range	115 - 178	5 - 11	11 - 36	Samecka-Cymerman et al. (2001)
Rivers in the Thames catchment	Mean	74,939.4	1,915.8	39	House and Denison (2002)
River used as a drinking water source	Range	-	230 - 1860	-	Kim et al. (2003)
Lakes affected by copper mining	Range	101,000 - 158,000 - 120,000 - 121,000	60 - 880 42 - 59	115 - 2633 2034 - 2881	Samecka-Cymerman et al. (2004)
CW treating farmyard dirty water	Mean ± SD	-	450±29 867±33	-	Dunne et al. (2005)
Anoxic sediments from six lakes	Range	8376 - 59,748	1,238 - 7,428	7 - 8	Lake et al. (2007)
HSSF CW for domestic wastewater treatment	Mean ± SD	35,351 ± 9325 (inlet) 23,458 ± 7221 (outlet)	-	-	Lesage et al. (2007)
FWS CW for wastewater in a metallurgical plant	Mean	19,700	383	51	Maine et al. (2007)
Eutrophic marshes	Mean	32,000	1,546	21	Lai and Lam (2008)
CW treating storm water from urban catchment	Range	16,793 - 21,994	333 - 354	47 - 66	Lai and Lam (2009)

Type of wetland		Iron	Phosphorus	Fe:P	Reference
		mg·kg ⁻¹ DM			
Marsh natural wetlands	Range	-	159 - 825	-	Dunne et al. (2010)
HSSF CW for domestic wastewater treatment	Range	8,659 - 21,567	-	-	Vymazal and Švehla (2012)

2.5. Release of phosphorus from sediment to water

Phosphorus release from sediment to the overlying water has been observed in very different natural water bodies including rivers, impoundments, and natural wetlands. This phenomenon depends on different environmental conditions and media characteristics such as oxidation reduction potential (Eh), dissolved oxygen (DO) content in water, pH, temperature, phosphorus concentration in water, hydrological conditions, and aluminium and iron concentrations in sediment.

Most research studies suggest reduction of Fe³⁺ to the more soluble form Fe²⁺ to be the main contributing factor to P release. It is known that iron hydroxides are a very reactive fraction in anoxic environments. The use of iron as electron acceptor causes the breakdown of iron-bound-phosphates with subsequent release of dissolved phosphates and iron into water column (Olila and Reddy, 1997; Gomez et al., 1999; Lake et al., 2007; Lai and Lam, 2008).

Microbial reduction of ferric minerals occurs under certain redox and DO conditions indicating anaerobic environments. Iron reduction takes place when redox potential is between 100 and -100 mV. Low oxidation reduction potential may explain iron (III) reduction and concomitant release of sorbed P (Lai and Lam, 2008). Phosphorus release is also a function of the DO concentration in water. Kim et al. (2003) proved P flux rates as high as 120 mg/m² at 0.5 mg DO/L (i.e. close to anaerobic conditions) and minor fluxes as 40 mg/m² at 6 mg DO/L (aerobic conditions). Concentrations of dissolved reactive phosphorus and dissolved iron in water column and pore water at Eh -100 mV have been observed to be up to 10 times higher than those in aerobic conditions (Ann et al., 2000b). Although strong anaerobic conditions may explain high

P fluxes to the overlying water, phosphorus release can be also present under aerobic conditions although in lower rates (Table 2). Also, re-adsorption of phosphates into iron hydroxides may occur once oxic conditions are re-established.

Iron hydroxides are dependent of pH. Whereas at acid pH iron hydroxides have a large adsorption capacity, phosphorus release under aerobic conditions increases with higher overlying water pH. This increase at high pH (pH 9.5-10.5) is probably as result of solubilization of iron phosphates (Seitzinger, 1991). Liberation of P adsorbed onto iron complexes is increased by pH because of competition with hydroxide (OH^-) ions, since phosphates can be exchanged with OH^- (Bostrom, 1988). Kim et al. (2003) observed that P release under anaerobic conditions is affected by extreme pHs, and found that flux rates are lowest in the range pH 7-10, increase fourfold at pH 2 and doubles at pH 13. Gomez et al. (1999) noticed an existing relation between redox potential and pH, since the necessary Eh for iron reduction and the subsequent P release had to decrease with an increase in pH, i.e. from pH 7 and -50 mV to pH 9 and -150 mV. In addition, microbial activity is enhanced with pH up to 7 and so it produces a decrease in Eh due to the reduction of inorganic electron acceptors.

Many studies have observed a clear correlation between P release and temperature. The highest release rates usually take place in summer (Kim et al., 2003; Lai and Lam, 2008; Zhou et al., 2010), when high temperatures intensify microbial activity causing a decrease in Eh on sediment and developing the appropriate conditions for iron reduction and P release. Kim et al. (2003) found that phosphorus release rate was increased fivefold between 2 and 25-35°C. In addition, temperature derived changes in water density can cause stratification leading to stagnant bottom layers which develop anoxic environments and a reducing environment which can cause the breakdown of iron-bound-phosphates (Lake et al., 2007).

Hydrological factors can influence phosphorus dynamics between media and water. Water level drawdown and re-flooding can result in significant P release (Olila et al., 1997; Moustafa et al., 2012). Mineralized inorganic P may be rapidly released to the overlying water column when re-flooding after drained periods. Olila et al. (1997)

observed high and rapid P fluxes in re-flooded soils whereas continuously flooded wetlands had lower and constant release rates. Therefore, maintaining moist media minimize P oxidation and P flux to surface water after re-flooding (Moustafa et al., 2012).

Phosphorus release rates also decrease with increasing P concentration in water since it is a diffusion process controlled by P concentration gradient between soil and overlying water (Reddy et al., 1999; Pant and Reddy, 2003). Dune et al. (2005) showed that P retention capacity of soil is higher as P load in water increases, and Pant and Reddy (2003) that P flux is greater in soils with high P concentrations.

Table 2.2 Phosphorus release rates ($\text{mg}\cdot\text{m}^{-2}\cdot\text{day}$) from sediment to water in different types of water bodies.

Type of wetland		P release $\text{mg}\cdot\text{m}^{-2}\cdot\text{day}$		Reference
River Seine downstream Paris (France)	Range	14.3 - 29.3	Anaerobic conditions	Garban et al. (1995)
CW to treat water from a hypereutrophic lake (USA)	Mean \pm SD	1.5 \pm 0.6	Continuously flooded	Olila et al. (1997)
		33.4 \pm 4.5	3 weeks drained and re-flooded	
		334 \pm 14	6 weeks drained and re-flooded	
River used as drinking water source (South Korea)	Mean	5.7	Aerobic conditions	Kim et al. (2003)
		15	Anaerobic conditions	
Wetland constructed in agricultural land (USA)	Mean \pm SD	25 \pm 9	Flux during four 28- days hydraulic retention cycles.	Pant and Reddy (2003)
Lower St. Johns River (USA)	Mean	0.13	Aerobic conditions	Malecki et al. (2004)
		4.77	Anaerobic conditions	

Type of wetland		P release		Reference
		mg·m ⁻² day		
Lowland river (Poland)	Mean ± SD	7.6 ± 2.5	Low flow conditions in summer-early autumn.	Banaszuk and Wysocka-Czubaszek (2005)
Small impoundment in a river (USA)	Range	0.4 - 3.6	Aerobic conditions	Haggard and Soerens (2006)
		14.5 - 15.5	Anaerobic conditions	
Eutrophic marshes (Hong Kong)	Mean ± SD	9.4 ± 3.3	Aerobic conditions	Lai and Lam (2008)
		31.7 ± 5.8	Anaerobic conditions	
Marsh natural wetlands (USA)	Range	-20 - 77	-	Dunne et al. (2010)

The competition between nitrate reducers and ferric iron reducers for electron donors is known for soil systems and anaerobic sediments. The presence of nitrates minimises the dissolution of ferric P compounds since nitrates are preferred over iron (III) as electron acceptors by facultative anaerobic microbes (Sondergaard et al., 2000), and so nitrates addition may be a strategy to reduce P release to overlying water under anaerobic conditions.

2.5.1. Variability of oxidation reduction potential in reed beds

Reed beds are characterized by operating permanently saturated with water. Saturated media are liable to have low concentrations of dissolved oxygen leading to establish an anaerobic environment in the system. Anaerobic conditions are defined as a combination of two factors: absence of dissolved oxygen and low oxidation reduction potential. The system is considered to be under anaerobic conditions when dissolved oxygen and redox potential are lower than 0.5 mg/L and +400 mV, respectively (Rowell, 1981).

In an anaerobic environment, the microbial and chemical processes causing the removal of organic matter are governed by redox potential. Redox reactions depend

on the electron acceptor that is used, differentiating between aerobic and anaerobic conditions if oxygen is the electron acceptor or not, respectively. In the absence of dissolved oxygen, there are different electron acceptors in the form of combined oxygen. These are nitrates (NO_3^-), manganese dioxide (MnO_2), ferric hydroxide ($\text{Fe}(\text{OH})_3$), sulfates (SO_4^{2-}) and carbon dioxide (CO_2) (Ponnamperuma, 1972; Richardson and Vepraskas, 2000). Electron acceptors are reduced in anaerobic soils and specific redox values are related to each of them. The activity of denitrifying bacteria using NO_3^- as electron acceptor is performed under E_H values compressed between +400 mV and +100 mV, values below +100 mV indicate reduction of Fe^{3+} to Fe^{2+} , lower than -100 mV indicate the reduction of sulfates and organic substances (fermentation), and values below -200 mV are related to activity of methanogenic bacteria reducing CO_2 .

Redox potential is widely used for characterization of oxidation-reduction conditions in wetland media. It is influenced by different physical and biological parameters that may produce a variability of E_H values in both spatial and temporal terms. For instance, Dušek et al. (2008) established a fluctuation of 800 mV within the same day, being regular in some periods, and also showed that E_H had fewer fluctuations near the inflow and in deeper layers of the bed.

This variability of redox potential in a reed bed may be influenced by several factors, some of the most important being the following:

- *Intense activity of microorganisms* can lead to low E_H values, due to the intensive use of electron acceptors present in the system.
- *Accumulation of organic matter* in media is expected to produce a lower and more stable E_H . The concentration of pollutants in the wastewater is not uniform and thus the organic matter will not be uniformly distributed in the wetland media (Richardson and Vepraskas, 2000), leading to different redox values across media depth.
- *Water level fluctuations* along with *variable hydraulic loading rates* can alter media redox conditions (Ann et al., 2000b) and pH of wetland media. Most

existing research considers that media redox potential is mainly controlled by the water level fluctuation (Catallo, 1999; Dwire et al., 2006).

- *Presence of plants* in reed beds provides oxygen to the water in close proximity to the roots, through the roots by diffusion, and may change the redox conditions in the rhizosphere. Brix (1997) reported oxygen diffusion values for *Phragmites australis* varying from 0.02 to 12 g m⁻²d⁻¹. Other studies suggest that redox potential is related to the oxygen transfer to the media from plant roots due to favourable light conditions (Flessa, 1994; Wießner et al., 2005). However, plant roots may release exudates to the rhizosphere (Bertin et al., 2003) which are easily decomposable organic substrates that can accelerate microbial processes and thus use of electron acceptors, resulting in a decrease of the redox potential (Dušek et al., 2008).
- *Pore water temperature* is closely correlated with E_H as temperature affects the solubility of oxygen in water, which is depleted with increasing temperature. Temperature also influences redox indirectly through the acceleration of microbial activity and plant growth during warm periods (e.g., summer) consuming the oxygen present. Zhou et al. (2012) confirmed a negative correlation between E_H and temperature and a positive correlation with dissolved oxygen.

3. MATERIALS AND METHODS

3.1. Stage 1: Profiling of all 14 small WwTPs with chemical phosphorus removal

The first phase of the project consisted in the profiling of 14 chemically-dosed small WwTPs for phosphorus removal in *Severn Trent Water* that use reed beds as their final (tertiary) filtration step. Initial profiling included gathering historic performance data and conducting site visits and interviews with operators and site managers.

Site data was facilitated by *Severn Trent Water* and included data records of the main wastewater constituents and characteristics (i.e. biodegradable organics (BOD, COD), total suspended solids, phosphorus, phosphates, iron, ammonia, nitrites, nitrates, pH, daily flow, etc.) for the fully treated effluent and some eventual data at other stages of treatment (i.e. crude, settled, humus effluent). Data records began in 1993 and were taken in a frequency that varied from weekly to monthly basis depending on each site. Data review consisted mainly in analysis of the wastewater consent compliance data to assess site performance, and an analysis of residual iron and phosphorus concentrations in the fully treated effluent before and after reed bed refurbishments and dosing start dates.

Site visits were conducted in order to determine the actual conditions of each site, treatment process and any operational issues. Other information gathered included the dosing strategy (i.e. dosing point, dosing rates, etc.) and reed beds characteristics. Reed beds were measured for bed dimensions, distribution channel characteristics, freeboard, gravel size, sludge accumulation levels, water level, status of the effluent pipe, and any deviations from the standard design.

In addition, the content of iron and phosphorus in the sludge accumulated on the surface of the reed beds was determined.

Individual site reports were produced and can be found in Appendix.

3.1.1. Phosphorus and iron content in reed bed sludge

Spot samples of sludge accumulated over the bed of each of the 14 studied reed beds were collected for analysis of iron and phosphorus content. A representative sludge amount of 300 mL was taken per sample point. Samples were collected from 15 points within the reed bed area in those sites with apparent risk of failure and from 3 points where such risk did not exist. In the first case, sampling points were distributed according to a 3x5 grid (reed bed width divided in 3 transects and length in 5 rows), whereas in the second case a single sample was taken for each inlet, middle and outlet zone (each zone corresponding to a third of the reed bed area) (Figure 3.1).

Samples were held in sealed plastic bags until treated in the laboratory on the same day. Sludge samples were then weighted and oven-dried at 105°C during 48 hours. Total solids and water content were measured following APHA (2005) procedures. Once dried each sample was ground for digestion. Each sample was extracted with a hydrochloric/nitric acid mixture using a microwave digestion system. The extract was then clarified and made to volume with deionised water. Iron was determined by atomic absorption, whereas phosphorus content was determined by a spectrometric measurement in solution. Analytical replication was carried out to ensure the reliability of results. The procedure was based on US EPA Method 3051 and British Standard BS 7755: Section 3.13:1998 which is identical to ISO 11047:1998.

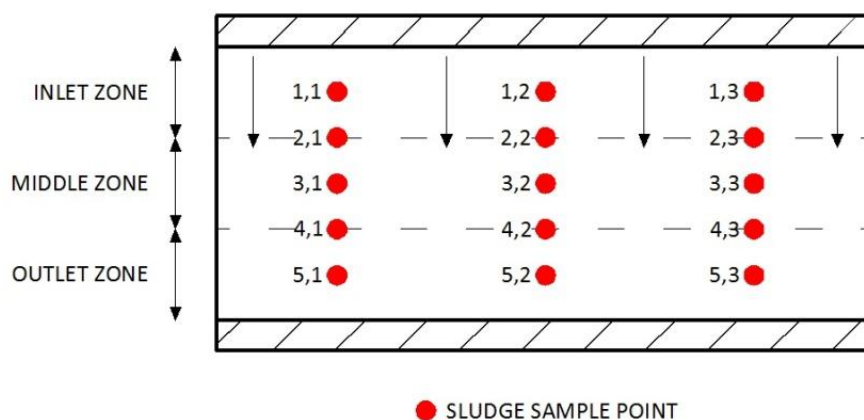


Figure 3.1 Scheme of the location of the sludge sample points within the reed bed area and the inlet, middle and outlet zones.

3.2. Stage 2: Detailed profiling of three small WwTPs with chemical phosphorus removal

The second phase of the project consisted in doing a more detailed profiling of three key WwTPs, namely: two sites as suspected problematic works (sites P1 and P2) and one as a reliable works (site R1).

3.2.1. Particle size fractionation

Wastewater samples were obtained as 24-hour composite samples (200 mL per hour; ISCO 3700, Teledyne Isco, UK) from the influent and effluent of the studied reed beds at sites P1, P2 and R1 during a two-weeks sampling period. All samples were processed to separate suspended, colloidal, and dissolved fractions as described on Martin (2010). Briefly, samples were progressively filtered through three separate membranes of pore sizes: 1.2 μm , 100 KDa (kiloDalton) and 1 KDa. The pore sizes of the last two membranes are defined by a non SI measurement known as Daltons (Da) that refers to the atomic mass unit. Suspended particles corresponded to particles bigger than 1.2 μm , colloidal phase between 1.2 μm and 1 KDa, and dissolved phase below 1 KDa (Figure 3.2). Membranes used for collection of suspended solids were made of glass microfiber binder free (Whatman papers Grade GF/C, WhatmanTM, GE Healthcare, UK). Suspended solids fractionation was conducted in a standard vacuum filtration equipment following APHA (2005) procedures. Membranes used to fractionate the samples for colloidal and dissolved phases were made from a low protein binding modified polyethersulfone (OmegaTM, PALL Life Sciences, UK). Before and after use of the membranes these were washed with sequences of ultrapure water, 0.1 M NaOH and 0.1 M HCl. The colloidal and dissolved fractionations were conducted in an Amicon 8400 stirred pressure cell driven by nitrogen gas at a pressure of 3.7 atm. After fractionation, each filtered was analysed for total phosphorus, orthophosphates, total iron, iron (II) and iron (III) using analytical test kits (cuvette tests LCK349, LCK 321, and LCK 320, Hach Lange Ltd., UK).

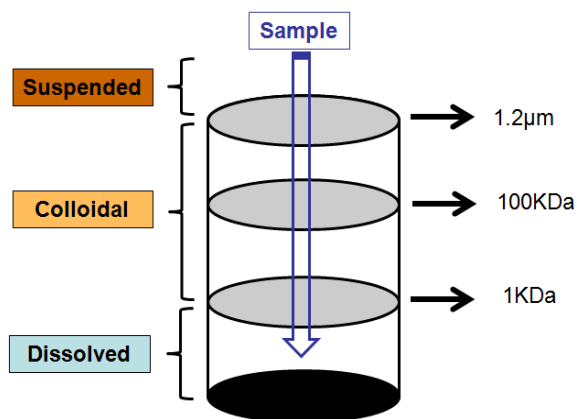


Figure 3.2 Scheme of the fractionation process for classifying particles between suspended solids, colloidal and dissolved phases.

3.2.2. Mass balances and removal rates

Mass balances for iron and phosphorus were calculated for the tertiary reed beds at sites P1, P2 and R1. It was calculated as the difference between mass input and mass output during the period from the start date of chemical dosing for phosphorus removal to the last sampling day at each site. It corresponded to a period of six years at site R1, seven months at site P1, and five months at site P2. Mass input and output resulted from multiplying average concentrations at influent and effluent by the average daily flow treated during the considered period. Mean P and Fe concentrations at reed bed influent and effluent were obtained through both the database at Severn Trent Water and the results from the two-weeks sampling period carried out in this study. Influent data for sites P1 and P2 was limited to samples collected in the current study as no additional data was available. Average daily flow treated at each site was obtained as the sum of the daily flows divided by the number of days of the considered period. Daily flow was monitored by flow meters at each site by *Severn Trent Water*. This approach ignored the effects of precipitation and evapotranspiration on the flow balance.

Removal rates for phosphorus, orthophosphates, total iron, iron (II), iron (III), nitrates and suspended solids at sites P1, P2 and P3 were calculated for the two-weeks sampling period. Daily removal rates were obtained from the difference between

effluent and influent concentrations multiplied by the daily flow and divided by the bed area. Influent and effluent samples were obtained as 24-hour composite samples. Analytical test kits were used to measure phosphorus, orthophosphates, total iron, iron (II), iron (III) and nitrates (cuvette tests LCK 349, LCK 321, LCK 320, LCK 339, and LCK 340, Hach Lange Ltd., UK). Suspended solids were measured as previously described.

3.2.3. Phosphorus and iron release batch experiment

Phosphorus and iron releases from sludge collected on the reed bed were tested through a batch reactor experiment. Samples of anaerobic sludge and wastewater were collected from the studied reed bed at site P2. Representative sludge samples were taken from the sludge accumulated above the granular media at the inlet area of the reed bed. Spot wastewater samples of the reed bed influent were also collected to be used as the overlying water in the reactor. Influent wastewater was used in order to preserve similar environmental conditions such as pH, dissolved oxygen, redox potential and microbial population within the reactor than in the actual reed bed.

Two batch experiments were conducted: firstly an anaerobic reactor during a 24 hours incubation time, and secondly a two-reactor batch experiment under aerobic and anaerobic conditions for a six days incubation time. Each reactor was filled with 2 L of anaerobic sludge and 2 L of overlying water. Initial concentrations of total phosphorus, orthophosphate and total iron were measured in the water before filling in the reactor. During the incubation time reactors were kept at room temperature, approximately 18°C. The overlying water at the reactor incubated under aerobic conditions was bubbled with air during the entire incubation time in order to keep dissolved oxygen concentration in water above 6 mg/L. Anaerobic reactors remained untouched since anaerobic conditions were already present in the sludge and overlying floodwater. Water samples were removed from the overlying water at every hour during working hours for the 24 hour incubation batch reactor, and daily for the six days incubation time reactors. The same sampling frequency was used for measuring redox potential, dissolved oxygen and pH in the overlying water. The total

volume of water removed from the reactor by the end of the experiment was calculated to never exceed a 5% of the initial overlying water volume. Samples were filtered through 0.45 μm pore size using sterile syringe filters (MillexTM syringe filters, Merk Millipore Corp., UK) and analysed for total phosphorus, orthophosphate, total iron and nitrates using analytical test kits (cuvette tests LCK 349, LCK 321, LCK 339, and LCK 340, Hach Lange Ltd., UK). Measurements of redox potential, dissolved oxygen and pH in the overlying water were conducted using a standard epoxy liquid electrode for redox potential with platinum disc sensor (Intellical, Hach Lange Ltd., UK), a stainless steel lumiphore sensor for dissolved oxygen (Intellical, Hach Lange Ltd., UK), and a stainless steel glass sensor for pH (Intellical, Hach Lange Ltd., UK), with a probe reader HQ40D Digital two channel multi meter (Hach Lange Ltd., UK).

Soluble orthophosphates and total iron release rates were calculated at linear changes in the PO_4 and Fe mass in the overlying water as a function of time (i.e. incubation time) divided by the area of the sediment in the reactor (i.e. 0.035 m^2). The relation between mass and time was determined by linear regression.

3.2.4. Jar tests

The dosing system at RBC sites uses the turbulent flow generated from the rotation of biodiscs to mix the chemical into the flow. Since biodiscs rotate at a very slow pace, the initial mixing conditions were poor compared to a traditional rapid mix system. It has been reported that initial mixing conditions affect the phosphorus removal capacity of the coagulant (Gillberg et al., 1996; Pearce, 1998). A series of jar tests were conducted in order to assess the effect of poor mixing over the reed bed influent quality.

To imitate the poor mixing conditions, the rapid mix stage was discarded from the standard jar test procedure and only slow mixing and settlement stages were performed. In addition a standard jar test with rapid mixing was conducted to carry out a comparison between poor and good mixing conditions.

Jar tests were performed using a standardized apparatus and wastewater taken from each of the three key sites (P1, P2 and R1). Sewage spot samples were obtained from the dosing point feed, which was located just after the primary settlement tank and in the front end of the biological zone of the rotating biological contactors. Jar tests for good and poor mixing conditions were conducted in duplicate for each site, with wastewater samples obtained in two different days. The coagulant used was ferric sulphate (45%, 1.6 SG, Brenntag AG, UK) which was obtained from one of the studied WwTPs for a better approximation to the actual conditions on site. Before commencing jar tests, orthophosphate concentration was measured to calculate the correct coagulant dose at different molar ratios of Fe:PO₄. Coagulant was then added either at the start of the rapid mixing stage (good mixing jar test) or during the first seconds of the slow mixing phase (poor mixing jar test). The jars were stirred at 300 rpm for 1 minute rapid mix and at 30 rpm for 30 minutes slow mixing (flocculation time) (Thistleton et al., 2001). Afterwards the sewage was left to settle for 60 minutes. After settlement the supernatant was decanted and measured for orthophosphate and total iron. Analytical test kits were used to measure orthophosphates and total iron (cuvette tests LCK 349 and LCK 321, Hach Lange Ltd., UK).

3.2.5. Quantification of solids in the granular media

The granular media in the studied reed beds at sites P1, P2 and R1 was sampled in order to measure total solids accumulation. Samples were taken in two transects along the length of each bed at inlet, middle and outlet zones according to the same area division used to obtain sludge samples (as described in section 3.1.1.). A small hole was dug in the granular medium using a shovel until the water level was reached. Water level was located in the first 10 cm below the surface of the granular medium at site R1, and above the bed surface at sites P1 and P2 since the reed beds were flooded. A representative volume of approximately 1L of granular media was obtained per sampling point from the first 10-20 cm of the wetted granular media. Samples were stored in plastic bags and maintained at 4°C until processed in the laboratory. The sample analysis started with the removal of recognisable belowground biomass. A

total of 0.5L of granular medium was then mixed with 0.5L of deionised water and shaken by hand to wash it (Caselles-Osorio et al., 2007). The resulting water containing the accumulated solids was then filtered through a 1 mm metal mesh for further removal of any macroscopic plant material. Finally, the resulting water was analysed for total solids using conventional methods (APHA, 2005).

3.2.6. Measurement of redox and dissolved oxygen in reed beds

Oxidation reduction potential and dissolved oxygen (DO) concentration in the sediment-water interface were measured in the studied reed beds at sites P1, P2 and R1. Measurements were conducted in three transects along the length of each bed at inlet, middle and outlet zones according to the same area division used to obtain sludge samples (as described in section 3.1.1.). Similar to the samples obtained for total solids quantification, redox potential and DO readings were performed in the upper layer of the granular media, below the water table and within the first 10-20 cm. Measurements were taken using a standard epoxy liquid electrode for redox potential with platinum disc sensor (Intellical, Hach Lange Ltd., UK) and a stainless steel lumiphore sensor for dissolved oxygen (Intellical, Hach Lange Ltd., UK) with a probe reader HQ40D Digital two channel multi meter (Hach Lange Ltd., UK).

4. RESULTS

4.1. Initial site characterisation

The 14 treatment plants studied are classified as small WwTPs treating urban wastewater equivalent to less than 2,000 population equivalent (PE), with the exception of site 6 with a PE of 4,864, and have a dry weather flow ranging from a minimum of 60 m³/day at site 12 to a maximum of 1,800 m³/day at site 6 (Table 4.1).

Differences between the WwTP's were found within the secondary treatment and chemical dosing strategies. Primary settlement tanks and humus tanks (PST, HT) were used before and after the secondary biological treatment. Three different technologies provided secondary biological treatment. The majority of sites included rotating biological contactors (RBC) (9 sites), followed by trickling filters (4 sites) and submerged aerated filters (SAF) (1 site). Most of the sites with RBCs had the PST, RBC and HT integrated in a single system called integral RBC. Reed beds provided final tertiary filtration treatment in all sites before discharge into the receiving water body (Figure 4.1).

Chemical dosing for phosphorus removal was carried out by adding ferric sulphate (Fe₂(SO₄)₃), except in site 8 where the chemical used was aluminium sulphate (Al₂(SO₄)₃). The dosing point varied between crude, PST effluent, and HT influent depending on the technology used as secondary treatment. The dosing point in the RBC sites was located in the front end of the biological zone of the RBC and after the primary settlement zone. In this case the dosing system uses the turbulent flow generated from the discs rotation to create adequate mixing of the chemicals. At sites with trickling filters the chemical was dosed either in the crude sewage before the PST or just before the SST. Mixing in cases where the dose was applied into the crude sewage was performed within a standing wave in a flume (sites 3 and 8) and a mixing chamber and flocculation chamber were required when the SST feed was the primary dose point (site 2 and 6). The WwTP with SAFs as the secondary treatment had chemical dosing to the crude sewage in a chamber with air mixing (site 12). Chemical

dose varied according to a daily diurnal variation in phosphorus load at the dosing point, except in RBC sites where there was a fixed average dose that may be inhibited from 22h to 3h.

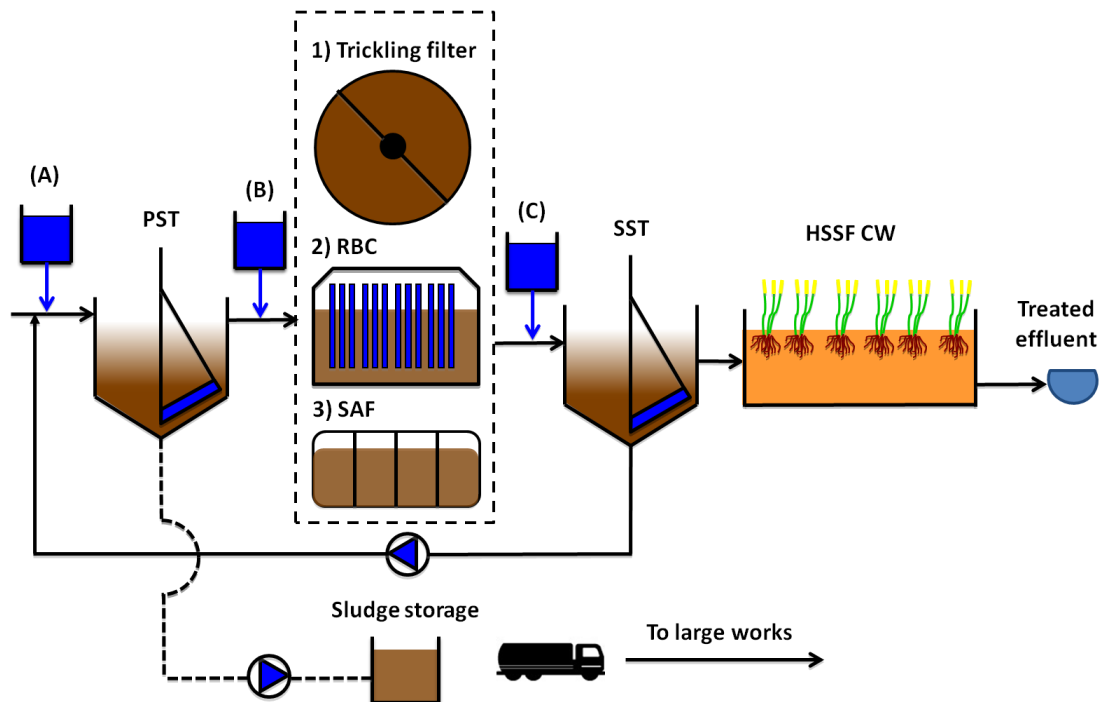


Figure 4.1 Process lay-out of the WwTPs. Within dashed line are shown the three technologies used as secondary treatment: trickling filters, rotating biological contactors (RBC), or submerged aerated filters (SAF). The three alternative dosing points are indicated by (A) crude, (B) primary settlement tank effluent, (C) secondary settlement tank influent.

The phosphorus content permitted at final effluent was a 95th percentile maximum concentration of 2 mg TP/L, along with an upper tier iron consent of 4 mg/L. Most of the consents were applicable year-round, with the exception of sites 10, 13 and 14 where consents were applied only in the period comprised between 1st April and 30th September (“summer” consent). Time of operation under dosing conditions among all sites varied between a maximum of seven years at sites 8, 10, 13 and 14 and a few months at sites 7 and 9.

Table 4.1 Main characteristics and design parameters of the 14 studied WwTPs. DWF = Dry weather flow, ADF = Average daily flow, RBC = Rotating biological contactor, TF = Tricking filters, SAF = Submerged aerated filter, T = Tertiary reed beds, C = Combined reed beds, EBCT = Empty bed contact time, HT = Humus tank, TP = Total phosphorus, TFe = Total iron, TSS = Total suspended solids.

WwTPs	Population equivalent	DWF (m ³ /day)	ADF (m ³ /day)	Secondary biological treatment	Reed beds						Dosing point	Dosing start date	Consent ² (mg/L)		
					Type	Area (m ²)	Area/P E (m ² /PE)	Hydraulic load (mm/day)	EBCT (hours) ¹	Last time refurbished			TP	TFe	TSS
Site 1	607	510	612	RBC	T	912	1.5	671	21	<2007	RBC front end	03/2007	2	4	25
Site 2	1,876	546	655	TF	C	1,400	0.7	468	31	<2007	HT influent	03/2007	2	4	25
Site 3	1,873	433	520	TF	T	1,250	0.7	416	35	<2007	Crude	01/2009	1	4	30
Site 4	1,834	692	830	RBC	C	3,000	1.6	277	52	<2007	RBC front end	03/2010	2	4	30
Site 5	1,013	294	353	RBC	C	1,175	1.2	300	48	<2007	RBC front end	03/2008	2	4	45
Site 6	4,864	1800	2160	TF	T	2,250	0.5	960	15	<2007	HT influent	03/2007	2	4	30
Site 7	526	121	145	RBC	T	364	0.7	399	22	<2007	RBC front end	03/2012	2	4	60
Site 8	1,839	440	528	TF	T	2,150	1.2	246	59	<2007	Crude	03/2005	2	1 ³	25
Site 9	795	113	136	RBC	T	480	0.6	283	51	2009-10	RBC front end	03/2012	2	4	50
Site 10	1,337	299	359	RBC	T	1,050	0.8	342	42	2011	RBC front end	04/2005	2 ⁴	4 ⁴	45
Site 11	1,297	341	409	RBC	C	1,625	1.3	252	57	<2007	RBC front end	03/2006	2	4	40
Site 12	222	60	72	SAF	T	187	0.8	385	37	2011	Crude	03/2007	2	4	45
Site 13	415	123	148	RBC	T ¹	412	1.0	358	40	2011	RBC front end	04/2005	2 ⁴	4 ⁴	40
Site 14	1,317	294	353	RBC	C	1,450	1.1	243	59	<2007	RBC front end	04/2005	2 ⁴	4 ⁴	45

¹Theoretical value. ²Total phosphorus consent is a 95%ile maximum allowable concentration whereas total iron and suspended solids are a 100%ile.

³Aluminium sulphate dosing. ⁴Summer consent (i.e. April to September).

Most tertiary reed beds had a standard bed length of 12.5 m and a maximum width with a single distribution channel of 40 m. The granular media in the beds was 14 mm single size gravel graded, with a minimum 0.5 m wide zone of coarse stone 40 to 70 mm size in the inlet and outlet zones. Common reed *Phragmites australis* were planted as vegetation. Most of the studied reed beds were refurbished before 2007 and just three of them during the last two years, resulting in a minimum operational time of 5 years on average. The water level in each bed was controlled by a rigid swivel pipe adjustable between horizontal, to fully drain the bed, and up to 250 mm above the surface of the media. The majority of reed beds were flooded by the time of sampling, indicating a potential flow short circuit was possible. Great variability of hydraulic loads and theoretical empty bed contact times (EBCT) was observed among the 14 studied reed beds. Site 6, with the highest PE and dry weather flow, had the highest hydraulic load (960 mm/day) and the lowest EBCT (15 hours), whereas site 14 had the lowest hydraulic load (243 mm/day) and the major EBCT (59 hours). Average hydraulic load for all reed beds (431 mm/day) was similar to the standard design value (400 mm/day), and the average EBCT was 39 hours.

There were two types of reed beds depending if they received secondary effluent or a combination of secondary effluent and storm flow (>6 times dry weather flow) after screening. Reed beds in the first case are called tertiary reed beds whilst in the second are known as combined reed beds. Different area per person equivalent for each tertiary and combined reed beds is applied for a standard reed bed design, i.e. 0.7 and 1.0 m²/PE respectively. However, sites 2, 6 and 9 had an area per person ratio lower than the one required.

In general, all WwTPs have been performing satisfactorily during the period with chemical dosing on site. Data analysis showed high average removal percentages for suspended solids (98%) (Table 4.2), total phosphorus (85%) (Table 4.3) and total iron (79%) (Table 4.4), meaning that the chemical dosing strategies and reed beds as the tertiary filtration step achieved good results. However, high average removals does not imply P and Fe consents compliance since these are 95%iles and upper tier consents.

Plant managers and operators indicated that certain sites experienced occasional compliance issues with both phosphorus and iron (sites 7, 9, 12 and 13).

Pearson correlations (r) were calculated between total phosphorus, total iron, and total suspended solids concentrations in the final effluent (Table 4.5). Moderate to strong correlations (significance level of $p < 0.05$) were observed between total iron and total suspended solids at all sites except sites 8, 10, 11, and 14, ranging from 0.49 (site 6) to 0.93 (site 13). Site 8 with aluminium dosing showed a correlation of 0.38 ($p < 0.05$) between aluminium and phosphorus, however, non statistically significant correlations between TP and TFe at iron dosed sites were observed. This is as opposed to what would be expected, since iron-bound-phosphates entering into the reed bed suggest that strong correlations between both elements should exist. In addition, there were no statistically significant correlations between phosphorus and suspended solids except at sites 7, 12 and 13, where weak correlations were observed, i.e. from 0.19 to 0.50.

Sites 7 and 9 were selected as problematic sites (from now on called sites P1 and P2) and site 11 as a reliable site (from now on called site R1).

Table 4.2 Mean, maximum values, and removal efficiencies of total suspended solids (TSS) at the 14 studied WwTP. Problematic sites (sites 7 and 9) and reliable site (site 11) are highlighted. Standard deviations in brackets. (Source: Severn Trent Water database, August 2012)

		Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10	Site 11	Site 12	Site 13	Site 14	
Total suspended solids (TSS) mg/L	Crude ¹	Sample size, n	11	40	67	74	16	53	45	32	22	-	7	123	31	33
		\bar{x}	228.6	175.6	212.8	229.2	808.0	133.4	240.6	264.6	328.3	-	256.9	317.7	374.7	238.8
		Maximum	582.0	524.0	2,720.0	644.0	6,000.0	1,290	1,860.0	1,060.0	2,080.0	-	412.0	8,520.0	2,900.0	1,810.0
	Final effluent ²	Sample size, n	79	103	106	52	67	157	26	128	39	124	97	197	162	135
		\bar{x} (sd)	5.0 (5.4)	3.7 (2.5)	7.3 (5.7)	4.1 (6.9)	4.5 (4.3)	11 (7.6)	3.0 (2.5)	2.1 (1.5)	4.7 (3.6)	2.8 (2.3)	3.2 (3.3)	9.9 (12)	7.0 (13)	5.0 (16)
		Maximum	29.0	14	32.0	47.0	30.0	40.0	11.0	10.0	21.0	15.0	18.0	137.0	110.0	196.0
	Removal efficiency, %	98%	98%	97%	98%	99%	92%	99%	99%	99%	-	99%	97%	98%	98%	

¹Data used for crude concentrations correspond to the entire period for which data is available.

²Data used for final effluent concentrations correspond to the period with iron dosing for phosphorus removal on site.

Table 4.3 Mean values, 95%iles and removal efficiencies of total phosphorus (TP) at the 14 studied WwTP. Problematic sites (sites 7 and 9) and reliable site (site 11) are highlighted. Standard deviations in brackets. (Source: Severn Trent Water database, August 2012)

		Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10	Site 11	Site 12	Site 13	Site 14	
Total phosphorus (TP), mg/L	Crude ¹	Sample size, n	9	31	59	24	-	37	7	2	6	-	17	26	12	3
		\bar{x} (sd)	3.5 (1.2)	7.0 (3.3)	7.5 (2.8)	7.0 (2.6)	-	3.4 (2.4)	9.8 (6.9)	6.7 (4.6)	5.1 (4.8)	-	7.8 (2.8)	7.3 (3.5)	13.5 (8)	12 (0.9)
		95%ile	5.7	12.1	13.6	12.7	-	6.9	24.0	10.0	12.0	-	12.2	11.5	35.0	13.3
	Final effluent ²	Sample size, n	47	29	107	17	59	45	24	104	37	97	76	148	133	113
		\bar{x} (sd)	1.2 (0.8)	0.7 (0.6)	0.6 (0.6)	0.8 (0.2)	0.7 (0.7)	0.7 (0.5)	1.7 (0.9)	0.2 (0.3)	1.3 (1.3)	1.4 (1.3)	0.6 (0.4)	1.3	1.6 (1.5)	1.7 (1.5)
		95%ile	2.3	1.1	1.1	1.4	1.8	1.7	3.6	0.7	4.0	4.2	1.5	3.9	5.5	5.0
	Removal efficiency, %	66%	90%	92%	89%	-	79%	83%	97%	75%	-	92%	82%	88%	86%	

¹Data used for crude concentrations correspond to the entire period for which data is available.

²Data used for final effluent concentrations correspond to the period with iron dosing for phosphorus removal on site.

Table 4.4 Mean, maximum values, and removal efficiencies of total iron (TFe), at the 14 studied WwTPs. Problematic sites (sites 7 and 9) and reliable site (site 11) are highlighted. Standard deviations in brackets. (Source: Severn Trent Water, August 2012)

		Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8 ³	Site 9	Site 10	Site 11	Site 12	Site 13	Site 14	
Total iron (TFe), mg/L	Crude ¹	Sample size, n	9	21	2	24	-	30	7	1	6	-	1	23	15	-
		\bar{x} (sd)	1.4 (1.5)	9.5 (7.1)	3.5 (3.8)	0.8 (0.6)	-	3.9 (6.0)	1.3 (2.4)	10.5 (0)	1.2 (1.1)	-	0.9 (0)	0.8 (1.9)	3.9 (3.0)	-
		Maximum	5.2	20.1	6.2	2.7	-	20.9	6.8	10.5	2.9	-	0.9	9.3	8.7	-
	Final effluent ²	Sample size, n	35	37	93	46	41	62	24	59	25	51	43	130	68	62
		\bar{x} (sd)	0.5 (0.4)	0.5 (0.4)	1.0 (0.9)	0.2 (0.3)	0.3 (0.4)	0.7 (0.9)	0.3 (0.5)	0.1 (0.4)	0.5 (0.8)	0.2 (0.5)	0.1 (0.1)	1.8 (1.7)	0.8 (2.0)	0.1 (0.1)
		Maximum	1.6	2.2	4.7	1.8	2.0	3.5	1.9	2.8	3.5	3.7	0.6	8.7	13.6	0.4
	Removal efficiency, %	64%	95%	71%	75%	-	82%	77%	99%	58%	-	89%	-125%	79%	-	

¹Data used for crude concentrations correspond to the entire period for which data is available.

²Data used for final effluent concentrations correspond to the period with iron dosing for phosphorus removal on site.

³Values at site 8 correspond to aluminium dosing instead of iron.

Table 4.5 Pearson correlation coefficients (r) (significance level $p < 0.05$) between total phosphorus (TP), total iron (TFe) and total suspended solids (TSS) in the final effluent at the 14 studied WwTPs. Problematic sites (sites 7 and 9) and reliable site (site 11) are highlighted (Source: Severn Trent Water, August 2012)

	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8 ¹	Site 9	Site 10	Site 11	Site 12	Site 13	Site 14
Sample size, n	31	5	92	17	41	45	24	59	25	48	43	109	65	59
Correlation (TP, TFe), r	-0.14	0.19	-0.11	-0.31	0.06	-0.13	0.14	0.38*	0.19	-0.11	0.10	0.20*	0.23	0.01
Sample size, n	47	29	97	16	59	45	24	97	36	94	76	148	132	111
Correlation (TP, TSS), r	0.14	0.33	0.06	-0.40	0.01	0.16	0.50*	0.08	0.33	0.00	0.03	0.20*	0.19*	0.08
Sample size, n	35	37	83	45	41	62	24	52	24	48	43	126	67	60
Correlation (TFe, TSS), r	0.50*	0.70*	0.57*	0.48*	0.49*	0.40*	0.45*	-0.08	0.89*	0.11	-0.06	0.70*	0.93*	0.13

¹Values at site 8 correspond to aluminium dosing instead of iron.

*Correlation coefficients are significant at $p < 0.05$ (two-tailed).

In bold strong correlations (> 0.70)

4.2. Influence of particle size over iron and phosphorus retention in reed bed

Fractionation of influent and effluent samples revealed that the majority of P by mass was associated with the suspended solids and dissolved phases in the influent compared to dissolved fraction in the effluent sample (Fig. 4.2). The dissolved fraction of phosphorus at site P1 was the highest in both influent and effluent, but increased from 44% to 60% after passing through the reed bed. Suspended solids was the highest fraction of phosphorus in the influent at site P2 at 75%, compared to the effluent where 78% was associated to dissolved phosphorus. The same occurred at site R1 where the highest percentage in the influent corresponded to suspended solids at 54% and changed to a 90% of the phosphorus being associated with the dissolved phase in the effluent. In contrast, iron fractionation showed suspended solids as the most important fraction in the influent whilst in the effluent varied from suspended solids at sites P1 and P2 and dissolved phase at site R1. Percentages corresponding to suspended solids in the influent at each site P1, P2 and R1 were 64%, 92% and 87% respectively. Effluent iron fractionation resulted in a 57% and a 55% associated to suspended solids at sites P1 and P2, and a 74% to dissolved phase at site R1.

Looking into the nature of iron compounds to differentiate between iron (III) (Fe^{3+}) and iron (II) (Fe^{2+}), it was observed that iron in both influent and effluent corresponded mainly to Fe^{3+} compounds (Figure 4.4). However, the percentage of Fe^{3+} decreased from the influent to the effluent of the reed beds in favor of an increase of Fe^{2+} species. Iron (II) percentages at sites P1, P2 and R1 increased from 16 to 31%, from 15 to 23%, and from 16 to 50% respectively, whereas iron (III) at the same sites decreased from 83 to 69%, from 85 to 77%, and from 84 to 50%. Although the increase of iron (II) in relative terms, its concentration level was still reduced through the reed beds at all three sites.

Between 70-95% of the total P in both influent and effluent corresponded to reactive phosphorus (orthophosphate, PO_4^{3-} , Figure 4.4). This percentage range was within the levels generally found in wastewater treatment plants where above 75%

and up to 95% of the phosphorus occurs as phosphate species in each stage of treatment (Tchobanoglous et al., 2003; Martin, 2010). Orthophosphates increased by passing through the reed beds in all the studied sites. Percentages increased from 80% to 93% at site P1, from 73% to 88% at site P2, and from 81% to 96% at site R1. In contrast to iron (II), orthophosphates increased in both relative and absolute values at all three sites, resulting in higher concentrations of orthophosphates in the effluent than influent of the studied reed beds.

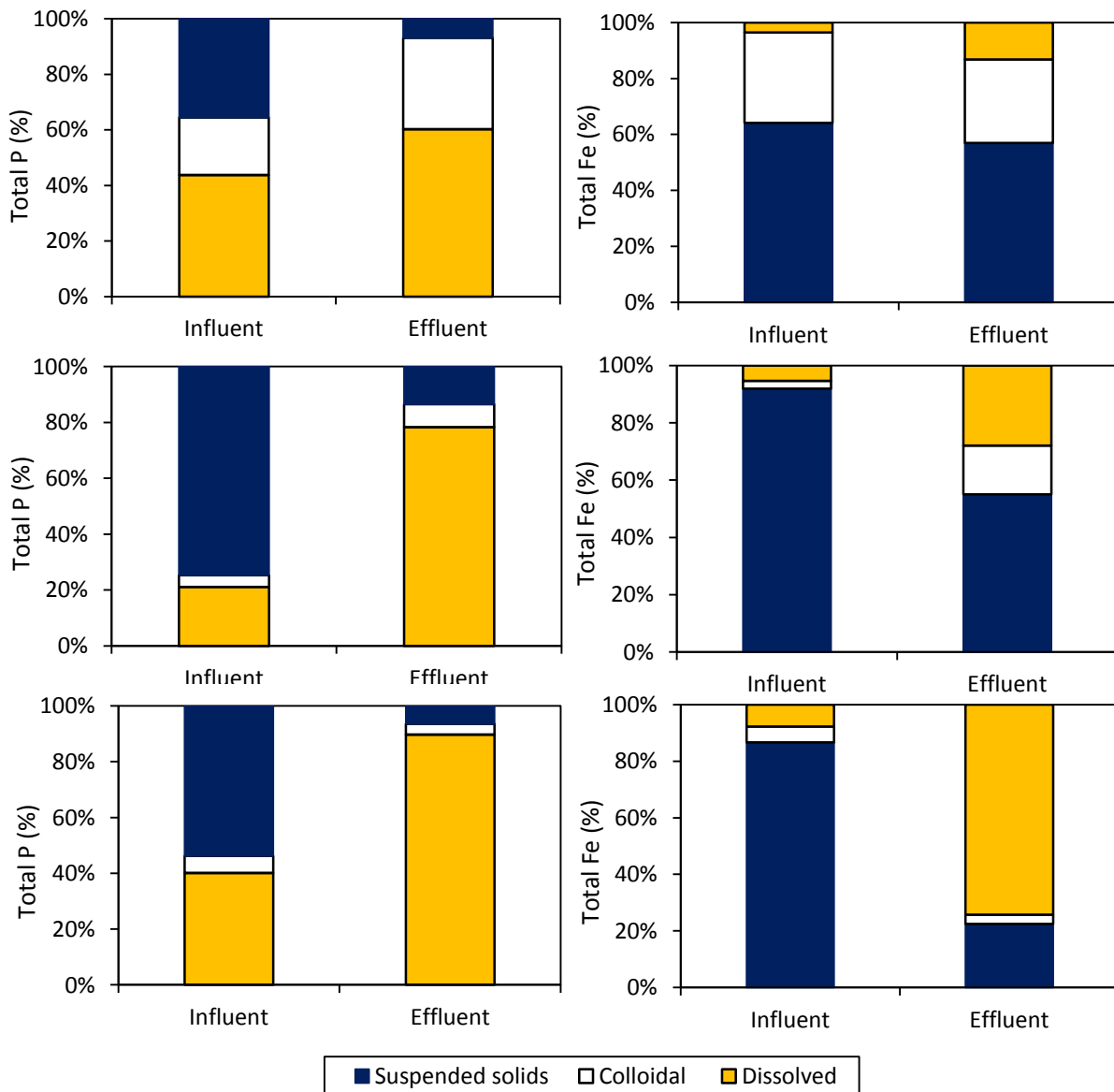


Figure 4.2 Percentages of each fraction (i.e. suspended solids, colloidal and dissolved) for total phosphorus and total iron at influent and effluent of the studied reed beds at problematic sites (P1 (top) and P2 (middle)) and reliable site (R1 (bottom)).

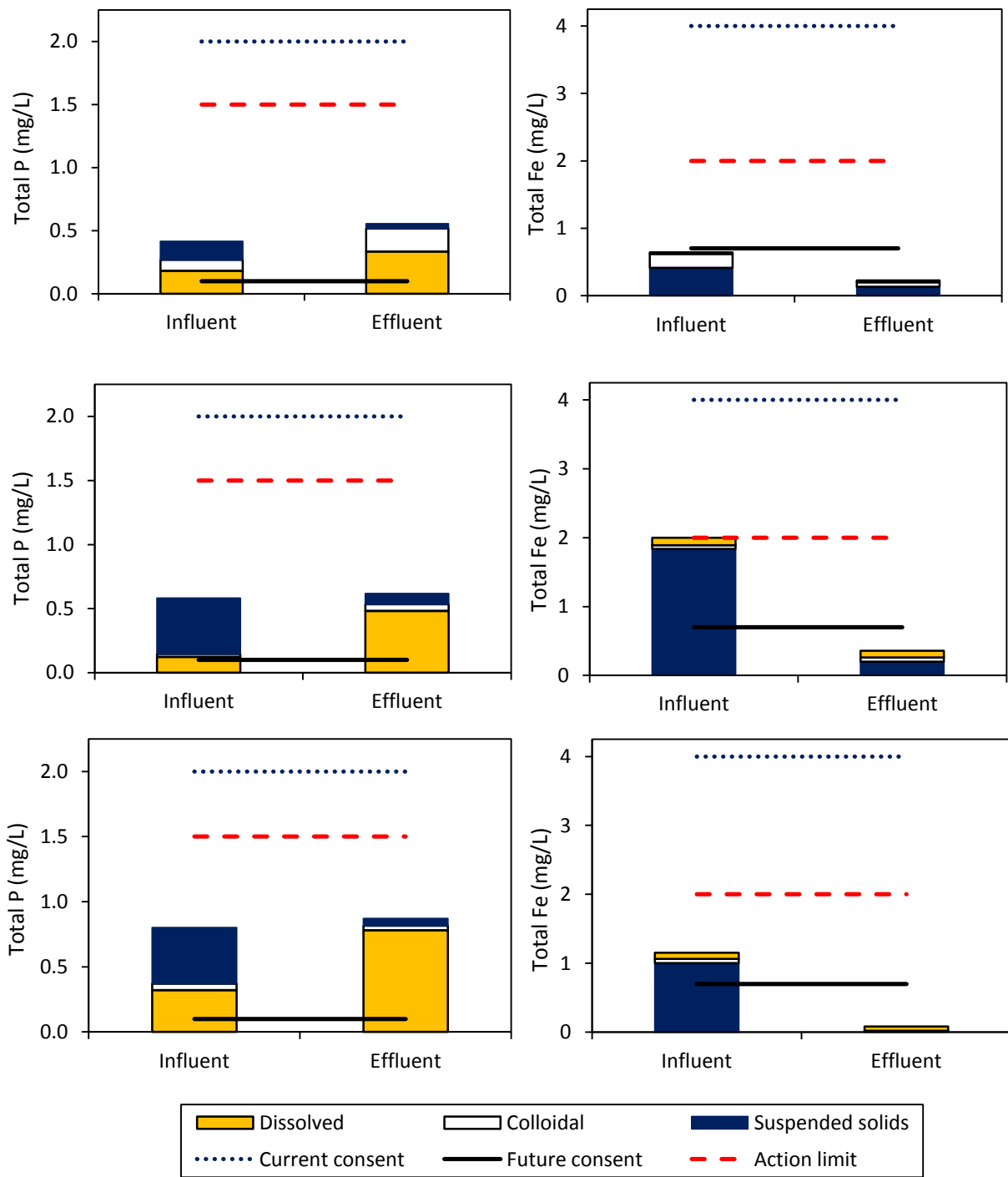


Figure 4.3 Results of the fractionation analysis of total phosphorus and total iron at influent and effluent of the studied reed beds at problematic sites (P1 (top) and P2 (middle)), and reliable site (R1 (bottom)) (mean values).

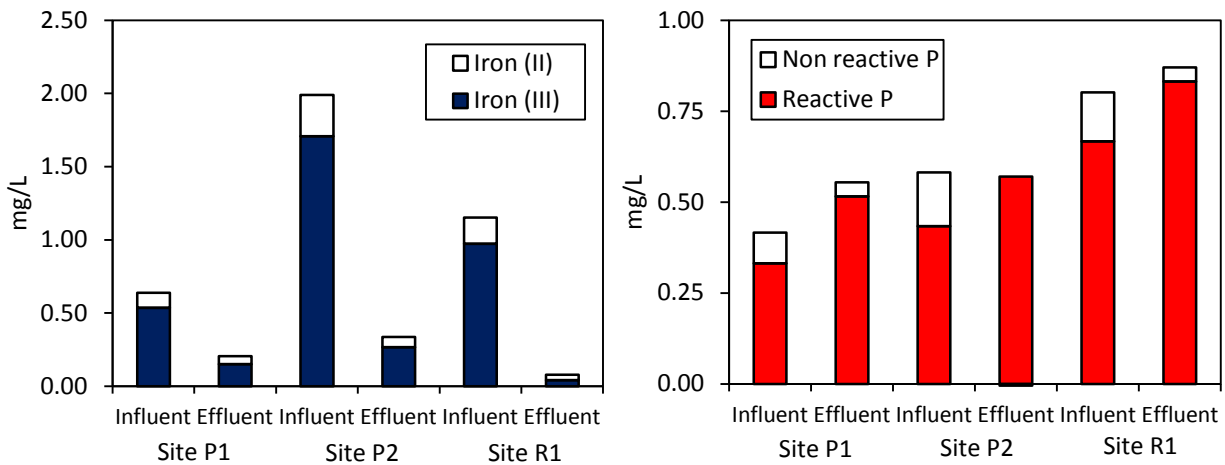


Figure 4.4 Concentrations of iron (II), iron (III) and orthophosphates at influent and effluent of the studied reed beds at problematic sites (P1 and P2) and reliable site (R1).

4.3. Phosphorus and iron accumulated within reed bed sludge

Phosphorus concentrations in the sludge accumulated above the granular media varied substantially between reed beds. Among the 14 studied reed beds P content ranged from a minimum of 5.7 g/kg dry mass (DM) (site 4) to a maximum of 55.9 g/kg DM (site 11) (Table 4.6). Results obtained are significantly higher than those reported in similar studies for other water bodies. The lower phosphorus concentrations in this study were comparable with the maximum value found in anoxic sediments from lakes reported by Lake et al. (2007) (7.4 g/kg DM). Average P concentration (26.2 ± 16.2 g/Kg DM) was about 70-fold higher than in a constructed wetland treating storm water from an urban catchment (0.33-0.35 g P/Kg DM) (Lai and Lam, 2009), about 45-fold higher than in constructed wetlands treating agricultural and farmyard waste water (0.45-0.87 g P/Kg DM) (Y. Ann et al., 2000; Dunne et al., 2005), about 14-fold higher than in natural rivers (0.23-1.92 g P/Kg DM) (House and Denison, 2002; Kim et al., 2003), and more than 100-fold higher than in natural lakes and lakes affected by mining (0.005-0.15 g P/Kg DM) (Samecka-Cymerman et al., 2001).

Iron content in the top sludge ranged from 8.2 g/kg DM to 246.6 g/kg DM. The higher concentrations were of the same magnitude than those reported by Samecka-Cymerman et al. (2004) for lakes affected by copper mining (101-158 g Fe/kg DM).

Table 4.6 Results of the analysis of sludge samples collected from reed beds across 14 chemically-dosed WwTPs. Table shows total solids and phosphorus and iron content in the sludge. (In.=Inlet zone, Mid.=Middle zone, Out.=Outlet zone of the reed bed area; \bar{x} =mean, sd=standard deviation). Data not showing standard deviation means just one sample was obtained per reed bed zone.

WwTPs	Total solids			Phosphorus			Iron		
	g/L sludge, $\bar{x} \pm sd$			g/kg dry mass, $\bar{x} \pm sd$					
	In.	Mid.	Out.	In.	Mid.	Out.	In.	Mid.	Out.
Site 1	71.4	60.2	440.8	39.9	31.3	29.1	145.8	103.7	97.5
Site 2	85.2	49.9	-	51.3	50.5	-	203.1	246.6	-
Site 3	73.1	163.4	95.1	47.5	42.8	52.4	160.6	175.5	197.4
Site 4	80.7	59.1	209.5	32.0	13.3	5.7	82.4	37.2	39.7
Site 5	96.1	111.8	122.6	23.6	23.4	16.6	88.2	81.7	59.3
Site 6	61.9 ± 2.1	53.9 ± 12.4	-	40.2 ± 5.2	41.6 ± 2.5	-	160.7 ± 16.9	197.7 ± 35.3	-
Site 7	196.4	72.7	133.3	19.8	15.4	19.8	14.9	9.3	8.2
Site 8	64.3	89.7	65.6	29.1	21.8	20.9	10.1	9.2	8.89
Site 9	72.2	55.7	78.7	18.7	22.3	17.8	25.4	42.8	36.03
Site 11	107.7 ± 12.6	-	-	55.9 ± 9.8	-	-	117.7 ± 12.7	-	-
Site 12	111.7 ± 25.8	138.2 ± 36.3	-	33.1 ± 2.4	30.5 ± 3.0	-	139.6 ± 3.7	140.6 ± 11.7	-
Site 14	111.3 ± 20.8	148.4 ± 16.9	150.3 ± 27.4	39.7 ± 2.6	37.4 ± 3.1	18.4 ± 9.0	103.7 ± 7.8	80.6 ± 9.2	49.3 ± 14.2

Sites 10 and 13 do not appear in the table above since there was no sludge above the granular media.

However, the results from this study are higher than the concentrations found in constructed wetlands for typical wastewater treatment. Vymazal and Švehla (2012) reported a much lower concentration range for a horizontal subsurface flow constructed wetland treating domestic wastewater (8,7-21,6 g/kg DM). Lower concentrations were also reported by Lesage et al. (2007) for another HSSF CW treating domestic wastewater (23.5-35.3 g Fe/kg DM). Maine et al. (2007) observed lower Fe concentrations of 19.7 g/kg DM for a free water surface constructed wetland

(FWS CW) treating wastewater in a metallurgical plant. Average Fe concentration in this study (79.9 ± 71.7 g/kg DM) was comparable with the average value found in rivers in the Thames catchment (74.9 g/kg DM) by House and Denison (2002), but much higher than those reported for natural lakes by Samecka-Cymerman et al. (2001) (0.1-0.2 g/kg DM).

If all sludge in the reed bed was accumulated as ferric phosphate, the concentrations of phosphorus and iron in the sludge would be 205.4 g P/Kg DM and 370.3 g Fe/Kg DM. As it could be expected, these values are higher than the concentrations measured in this study, indicating that also other pollutants as organic matter are trapped in the reed bed. On the other hand, all sampling points among all 14 studied reed beds had threefold higher concentrations of iron than phosphorus on average (2.7 ± 1.4 , 3.0 ± 1.6 and 2.9 ± 2.3 times at inlet, middle and outlet areas, respectively). This ratio was higher than the 1.8 that would result from a completely FePO_4 sludge. It was consistent to the iron:phosphorus molar ratio applied in chemical phosphorus removal, where it is required higher amounts of iron than the indicated by FePO_4 stoichiometry. This also suggests that iron hydroxides non bound to phosphates enter into the reed bed and are retained within the media.

The studied reed beds had higher sludge accumulation levels in the inlet zone than in the outlet. This was consistent with García and Corzo (2008) who reported that suspended solids are accumulated mainly within the first third or quarter of the total reed bed length. Sludge accumulation occurred mainly in the upper layers of gravel and on the surface. This is related to the surface-based inlet distribution system that produces an overland flow across the reed beds. It may result in a change of the flow regime from horizontal to vertical flow, facilitating the settlement of suspended solids and sludge build-up over the surface of the bed. Surface sludge layers in this study were found to be up to 210 mm thickness in the inlet (site 2) and up to 100 mm in the outlet (site 1). These values were comparable to those observed by Cooper et al. (2008) in a survey of 255 reed beds in UK which had sludge accumulations in excess of 150 mm at the inlet and 40 mm at the outlet. In general, higher sludge accumulations

in the inlet area had also higher concentrations of phosphorus and iron. Only site 2 had higher Fe concentration in the middle zone (246.6 g/kg DM) than in the inlet (203.1 g/kg DM) although sludge accumulations were 100 mm and 210 mm respectively.

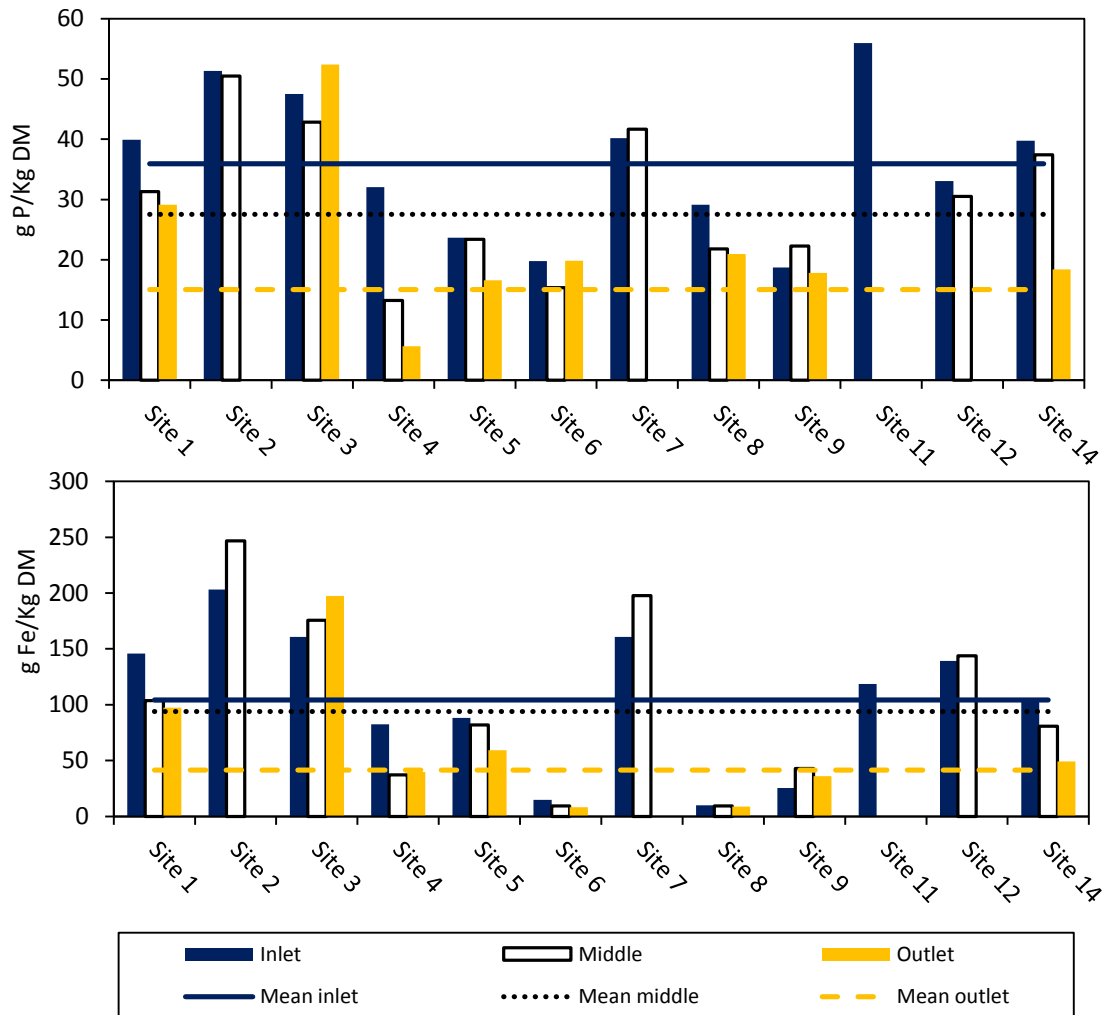


Figure 4.5 Phosphorus and iron content (g/kg dry mass) in the sludge accumulated over the surface media of the analysed reed beds at the inlet, middle and outlet zones of the bed.

Vymazal and Švehla (2012) reported that iron concentration in the sediment also decreased with the increasing length of operation in seven reed beds treating municipal sewage. However, in this study those sites with shortest operational length with iron dosing (three months at sites 7 and 9) had the lowest Fe concentrations (mean Fe concentrations of 10.8 g/kg DM and 34.7 g/kg DM). The highest concentrations were found at sites 2 and 3 with mean values of 149.9 g/kg DM and

177.8 g/kg DM and 5 and 3 years with chemical dosing on site. Site 14 had the longest operational time under chemical dosing (7 years) but had a lower mean Fe concentration of 103.7 g/kg DM, probably because a summer consent is applied. Therefore, as opposed to Vymazal and Švehla (2012), iron concentrations in sludge increased with increasing length of operation. These opposite trends may be related to higher Fe concentrations in the inflow of tertiary reed beds at chemically-dosed sites than in reed beds at non-chemically dosed sites.

4.4. Retention or release of phosphorus and iron in reed beds

In the problematic sites, a negative P mass balance with a loss of -156.1 g P/day at site P1 and -164.8 g P/day at site P2 was observed (Table 4.7). In contrast, the studied reed bed at the reliable site had a positive mass balance of 91.4 g P/day. The negative value found at sites P1 and P2 means that the amount of phosphorus output was greater than the input, and so the missing mass was released from the reed bed itself. Iron mass balance showed that iron was effectively retained within reed beds at all three studied reed beds. The amount of iron going into the bed was greater than that found in the effluent and so mass balances at sites P1, P2 and R1 had positive absolute values of 43.6, 132.3, and 96.8 g Fe/day.

Table 4.8 shows mass removal rates for phosphorus, iron, nitrates and suspended solids during the two weeks sampling period at each studied reed bed. Similar to the mass balance for the whole period with chemical dosing on site (Table 4.7), mass removal rates for iron during sampling were equal or higher in the two sites suspected to be problematic works (0.28 ± 0.08 and 0.37 ± 0.19 gTFe/m²day at site P1 and P2 respectively) than in the reliable site where there was almost no iron removal (0.09 ± 0.06 gTFe/m²day). Whereas iron was removed in all three sites, phosphorus removal was unreliable and showed some episodes in which the concentration in effluent was higher than in influent exhibiting phosphorus release from the reed bed. Average P concentrations in water passed from 0.42 ± 0.03 to 0.55 ± 0.07 mg/L at site P1, from 0.58 ± 0.18 to 0.57 ± 0.40 mg/L at site P2, and from 0.80 ± 0.58 to 0.87 ± 0.16 mg/L at site R1 (Figure 4.6).

Table 4.7 Phosphorus and iron mass balance at problematic sites (P1 and P2) and reliable site (R1) for the period compressed between the dosing start date and the sampling date.

WwTPs	Bed dimensions		Average daily flow	Mean flow concentration				
	m			mg/L, \bar{x}				
	L	W	m ³ /day per bed	Influent		Effluent		
			P	Fe	P	Fe		
Site P1	12.5	18	127.5	0.4*	0.6*	1.6	0.2	
Site P2	15	16	114.5	0.6*	2.0*	2.0	0.6	
Site R1	12.5	32	63.9	2.0	1.6	0.6	0.1	

WwTPs	Mass input		Mass output		Mass balance		Mass removal rate	
	g/day		g/day		g/day		g/m ² ·day	
	P	Fe	P	Fe	P	Fe	P	Fe
Site P1	53.1	82.0	209.2	30.6	-156.1	51.4	-0.7	0.2
Site P2	66.6	228.2	231.4	68.7	-164.8	159.5	-0.7	0.7
Site R1	128.5	104.8	37.1	7.7	91.4	97.2	0.2	0.2

*P and Fe influent average concentrations for Sites P1 and P2 correspond only to the sampling period.

Analysis in terms of averages does not consider the relative variation of concentrations between inlet and outlet. To complete the analysis, it is also necessary to compare maximum inlet concentrations and minimum outlet concentrations taking into account the residence time of reed beds to discuss whether actual phosphorus release occurs or not. The studied reed bed at site P1 had P release during the whole sampling period within time intervals equal to its EBCT (approximately 22 hours). The smallest difference in P concentrations was between 0.38 mg/L at inlet and 0.49 mg/L at outlet after residence time. Site P2 exhibited two different stages during the sampling period. During the first five sampling days, the reed bed was releasing phosphorus with a minimum difference between inlet and outlet P concentrations of -0.14 mg/L after a approximately 51 hours (EBCT). In the last part of sampling, phosphorus release stopped and the minimum difference between inlet and outlet P concentrations had a positive value of 0.22 mg/L. Site R1 also showed two different stages, a first period when the reed bed was removing phosphorus and a second when

Table 4.8 Mass removal rates for phosphorus, iron, nitrates and suspended solids at problematic sites (P1 and P2) and reliable site (R1) during the sampling period.

	Site P1 (n=5)	Site P2 (n=5)	Site R1 (n=7)
Mass removal rates ($\bar{x} \pm sd$, g/m ² -day)			
Total P	-0.09±0.06	-0.04±0.15	0.00±0.03
PO ₄ ³⁻ -P	-0.12±0.07	-0.10±0.15	-0.01±0.03
Total Fe	0.28±0.08	0.37±0.19	0.09±0.06
Fe ²⁺	0.03±0.01	0.03±0.01	0.01±0.01
Fe ³⁺	0.25±0.07	0.33±0.18	0.08±0.05
NO ₃ ⁻ -N	4.05±1.40	4.23±2.21	0.86±0.26
TSS	1.51±1.37	2.29±0.88	0.45±0.33

Highlighted values indicate mass release instead of removal.

	Site P1 (n=5)		Site P2 (n=5)		Site R1 (n=7)	
	$\bar{x} \pm sd$ (mg/L)					
	Influent	Effluent	Influent	Effluent	Influent	Effluent
Total P	0.42±0.03	0.55±0.07	0.58±0.18	0.57±0.40	0.80±0.58	0.87±0.16
PO ₄ ³⁻ -P	0.33±0.03	0.52±0.08	0.43±0.10	0.64±0.40	0.67±0.49	0.83±0.14
Total Fe	0.64±0.05	0.21±0.15	1.99±1.06	0.34±0.12	1.15±0.55	0.08±0.02
Fe ²⁺	0.10±0.02	0.06±0.02	0.28±0.23	0.07±0.03	0.18±0.08	0.04±0.01
Fe ³⁺	0.54±0.04	0.15±0.12	1.71±0.90	0.27±0.09	0.97±0.47	0.04±0.01
NO ₃ ⁻ -N	22.5±2.15	16.42±2.8	7.91±2.76	1.82±1.47	29.18±1.4	18.91±5.5
TSS	3.75±0.88	1.50±1.12	17.8±11.3	5.46±1.68	7.45±5.04	1.98±2.12

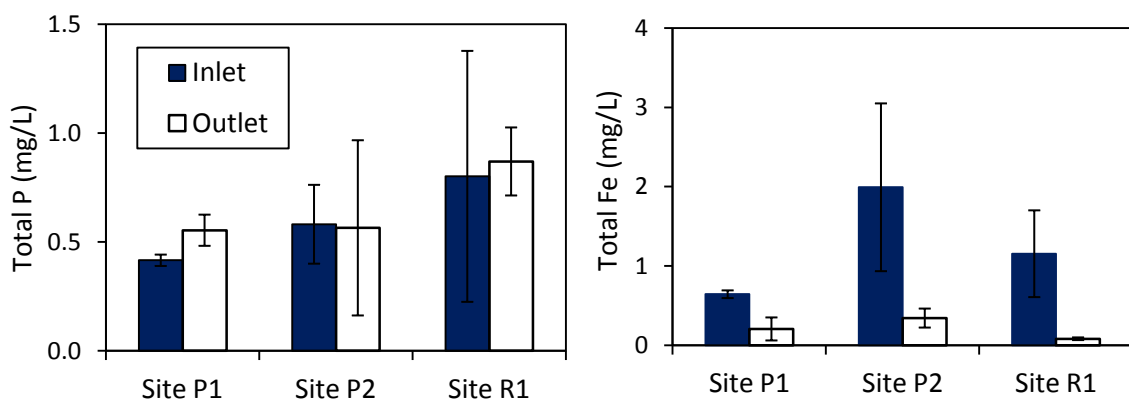


Figure 4.6 Average concentrations of total phosphorus and total iron at reed bed influent and effluent in the problematic sites (P1 and P2) and reliable site (R1) during the sampling period.

the removal changed to P release. Minimum differences between inlet and outlet P concentrations considering an EBCT of approximately 57 hours were 0.45 mg/L during the removal period and -0.30 mg/L during P releasing. As opposed to phosphorus, iron was removed in all three studied reed beds when taking into account each respective residence time.

Sites P1 and P2 also presented higher suspended solids and nitrate removal rates (Table 4.8). The latter suggested that denitrification occurred in a greater degree in the two problematic sites than in site R1.

4.5. Effect of anaerobic conditions over phosphorus and iron release

Steady releases of iron and soluble reactive phosphorus (orthophosphates) were observed under anaerobic conditions during the 24 hours incubation period batch experiment (Figure 4.7). Anaerobic conditions were defined by average dissolved oxygen of 0.09 ± 0.09 mg/L and redox potential of -211 ± 63 mV. Initial concentrations of orthophosphates and iron were 0.19 mg/L and 1.1 mg/L and increased to 1.2 mg/L and 11.6 mg/L after 24 hours of incubation period. Average PO_4^{3-} and Fe release rates were $44.6 \text{ mg/m}^2\text{day}$ and $353.7 \text{ mg/m}^2\text{day}$ (m^2 of the sediment area in the reactor). Soluble reactive phosphorus flux found in this study was higher than those reported for sediments from other water bodies. The PO_4^{3-} release rate was comparable to that reported by Lai and Lam (2008) in eutrophic marshes under anaerobic conditions ($31.7 \pm 5.8 \text{ mg/m}^2\text{day}$), and to that observed by Pant and Reddy (2003) in a constructed wetland over agricultural land ($25 \pm 9 \text{ mg/m}^2\text{day}$).

In the 6 days incubation period batch experiment, concentration of iron in the overlying water changed with time producing very different iron flux under aerobic and anaerobic conditions (Figure 4.7). In the case of the aerobic reactor the average dissolved oxygen concentration was 7.6 ± 1.2 mg/L with a redox potential of -60 ± 3 mV, compared to 0.08 ± 0.03 mg/L and -253 ± 4 mV respectively in the case of the anaerobic reactor. During the first two days of incubation the slope of the relation used to estimate average sediment Fe flux was significantly greater in the reactor under

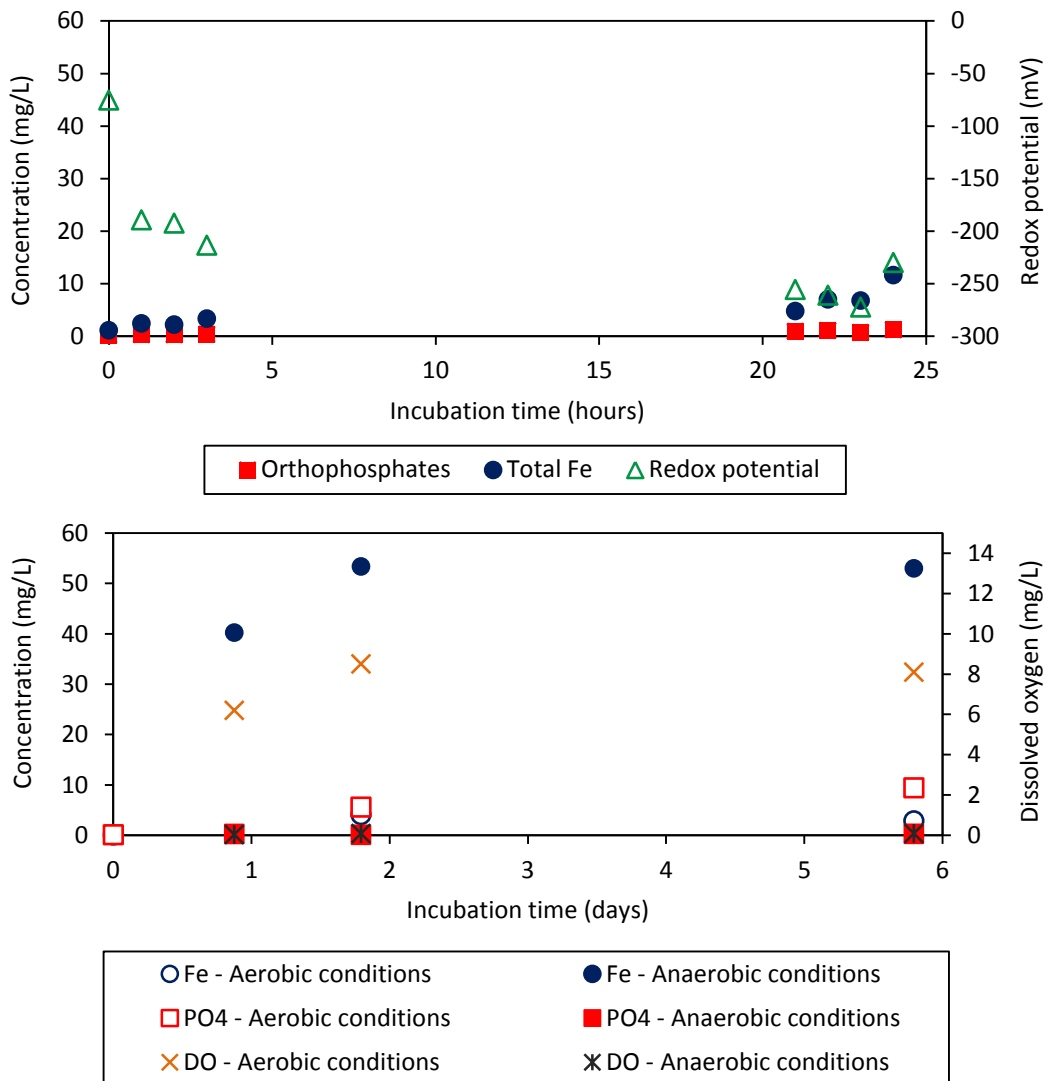


Figure 4.7 Total iron and orthophosphates concentrations in the overlying water of the anaerobic sludge from the studied reed bed at site P2. On the top, results from batch reactor under anaerobic conditions during 24 hours of incubation time. At the bottom, results from batch reactors under aerobic and anaerobic conditions during 6 days of incubation time.

anaerobic conditions compared with aerobic conditions. After almost two days of incubation, iron concentrations in the overlying water column were 4.1 mg/L under aerobic conditions and 53.4 mg/L under anaerobic conditions. Average Fe release rates during the first two days of incubation under aerobic and anaerobic conditions were 156.9 mg/m²day and 1,657.9 mg/m²day. After the two first days of incubation and until the batch experiment was finished concentrations of iron were stabilised and

remained constant under anaerobic conditions (53 mg/L) and decreased slightly under aerobic conditions (2.9 mg/L) (Figure 4.7). Reactive phosphorus release under the same aerobic/anaerobic conditions behaved unexpectedly. PO_4^- release in the aerobic reactor was higher than in the anaerobic reactor, reaching P concentrations in the overlying water of 9.5 mg/L and 0.3 mg/L respectively after 6 days of incubation. It seems that the high Fe release observed under strong anaerobic conditions was not accompanied by release of orthophosphates as it should have happened if breakdown of iron bound phosphates species under anaerobic conditions was the cause of such releases.

4.6. Effect of poor mixing over chemical phosphorus removal

Simulated poor mixing conditions resulted in higher concentrations of PO_4^{3-} and Fe in the supernatant after slow mixing and settlement phases. Differences on orthophosphate content in the supernatant between poor and good mixing for a same molar ratio ranged from 0.11 to 0.47 mg/L at site P1, from 0.09 to 0.37 mg/L at site P2, and from 0.06 to 0.40 mg/L at site R1. The impact of poor mixing was more significant for iron by mass than for phosphorus, and higher differences between poor and good mixing were found ranging from 0.54 to 1.74 mg/L at site P1, from 0.41 to 1.84 mg/L at site P2 and from 1.01 to 4.81 mg/L at site R1 (Figure 4.8).

Initial concentrations of orthophosphate varied significantly between wastewater samples collected in different days from the same site. Despite this variability orthophosphate removal was highly efficient with an average removal percentage of 89.9% (Figure 4.9) and achieving values below 0.9 mg/L regardless the molar ratio, mixing conditions and initial P concentration. In general, with a rapid mixing stage before slow mixing and settlement phases little improvement was achieved in doses in excess of a 1.5:1 Fe: PO_4 molar ratio. Orthophosphate removals above 90% were achieved with such ratio except in Site R1 where it was required a 2:1 ratio. With lack of rapid mixing, the molar ratio to achieve similar removal percentages was less clear but in general higher ratios were required. At site P1 a molar ratio of 3.5:1 achieved a 87% and 91% with initial PO_4^{3-} concentrations of 3.8 mg/L (sample 1) and 4.1 mg/L (sample

2). At site P2 the 3.5:1 molar ratio achieved an 89% PO_4^{3-} removal with a initial 2.9 mg/L PO_4^{3-} concentration but in a second sample with just 1.8 mg/L PO_4^{3-} (sample 2) a removal about 90% was achieved in a range of ratios from 2.5:1 to 5.5:1. Site R1 achieved a removal of 92% with a molar ratio of 2.5:1 and an initial PO_4^{3-} concentration of 3.6 mg/L (sample 1), but in a second sample with a lower initial PO_4^{3-} of 2 mg/L (sample 2) it was needed a molar ratio as high as 7.5:1 to achieve a removal of 84%.

In contrast to the orthophosphates behavior, iron content in the supernatant showed different trends with increasing molar ratios at each site. Iron concentration in samples from site P1 showed an uptrend with increasing molar ratios, achieving the lowest concentration in both good (2.7 mg/L) and poor mixing conditions (3.4 mg/L) for a molar ratio of 1.5:1. In contrast, iron concentration in the supernatant with samples from sites P2 and R1 decreased with increasing Fe: PO_4 ratios. Lowest concentrations in site P2 under good mixing were reached for molar ratios above 2.5:1 achieving Fe concentrations between 1.1 mg/L (sample 2) and 1.6 mg/L (sample 1), whereas under poor mixing the lowest concentrations were higher (2.8 mg/L in sample 1 and 1.6 mg/L in sample 2) and were achieved for a higher molar ratio, i.e. 3.5:1. At site R1 the lowest iron concentrations were also reached for the highest molar ratios tested during jar tests (4.5:1 in sample 1 and 7.5:1 in sample 2) obtaining minimum concentrations of 1.9 mg/L and 3.8 mg/L for good and poor mixing conditions.

Depending on flow and orthophosphate concentrations average molar ratios at each site varied slightly between the stoichiometric ratio (1:1) and up to 2:1 (Table 4.9). Average molar ratios were 2.1:1, 1.3:1, and 1.7:1 for site P1, P2 and R1. Doses are increased on site based on P and Fe concentrations in the effluent, targeting a 50% of the metal consent and a 70% of the phosphorus consent, and applying maximum molar ratios of 4.40:1, 2.64:1 and 2.33:1 at sites P1, P2 and R1. The molar ratios used at each of the studied sites are close to the optimal molar ratio 1.5:1 for orthophosphate removal found in this study, and so using the minimum amount of chemical dosed and achieving removal efficiencies above 80% under poor mixing conditions.

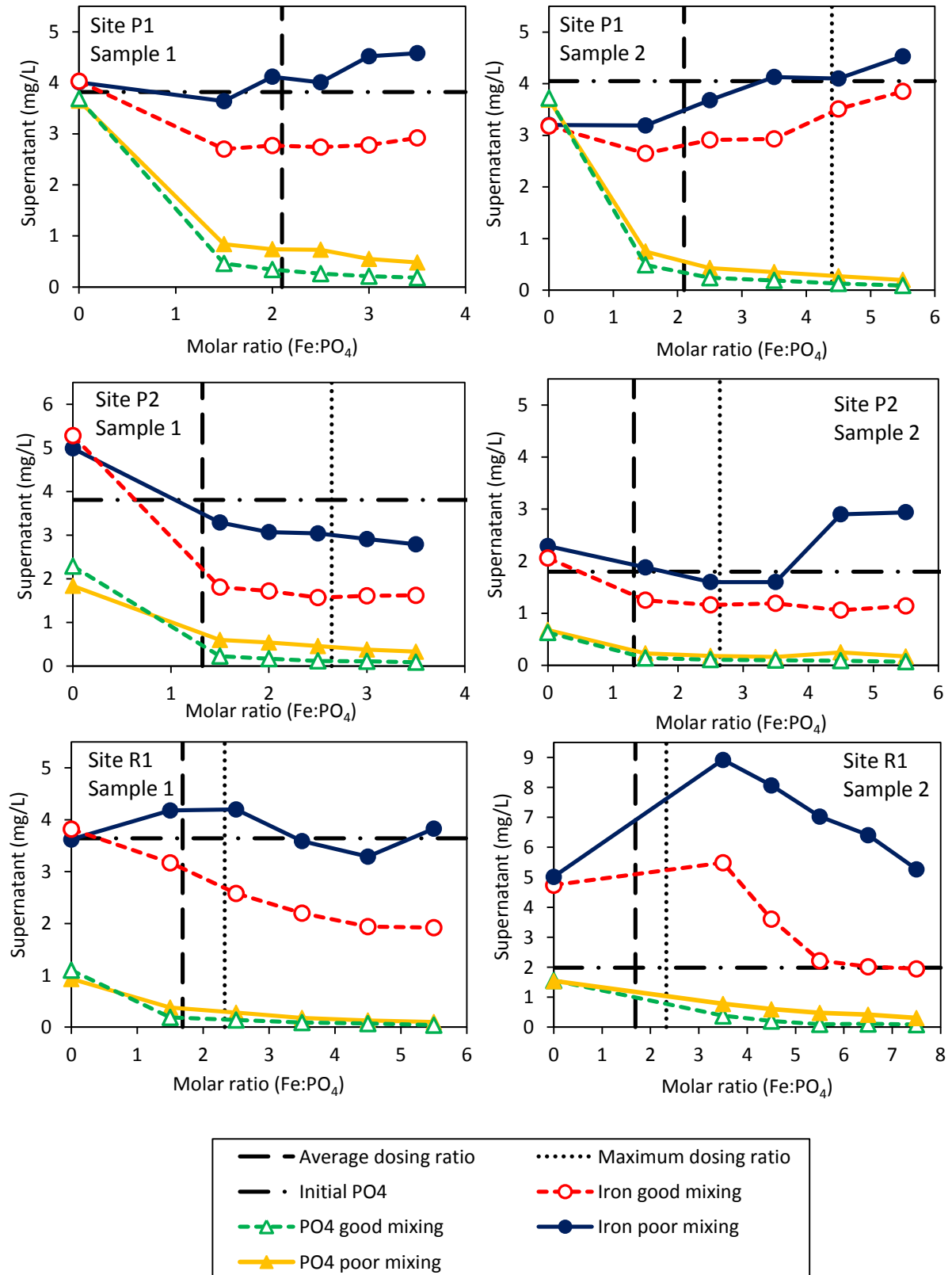


Figure 4.8 Jar tests results for site P1 (top) , site P2 (middle) and site R1 (bottom) using two wastewater samples from two different days. Vertical lines refer to the average and maximum molar ratio used at each site.

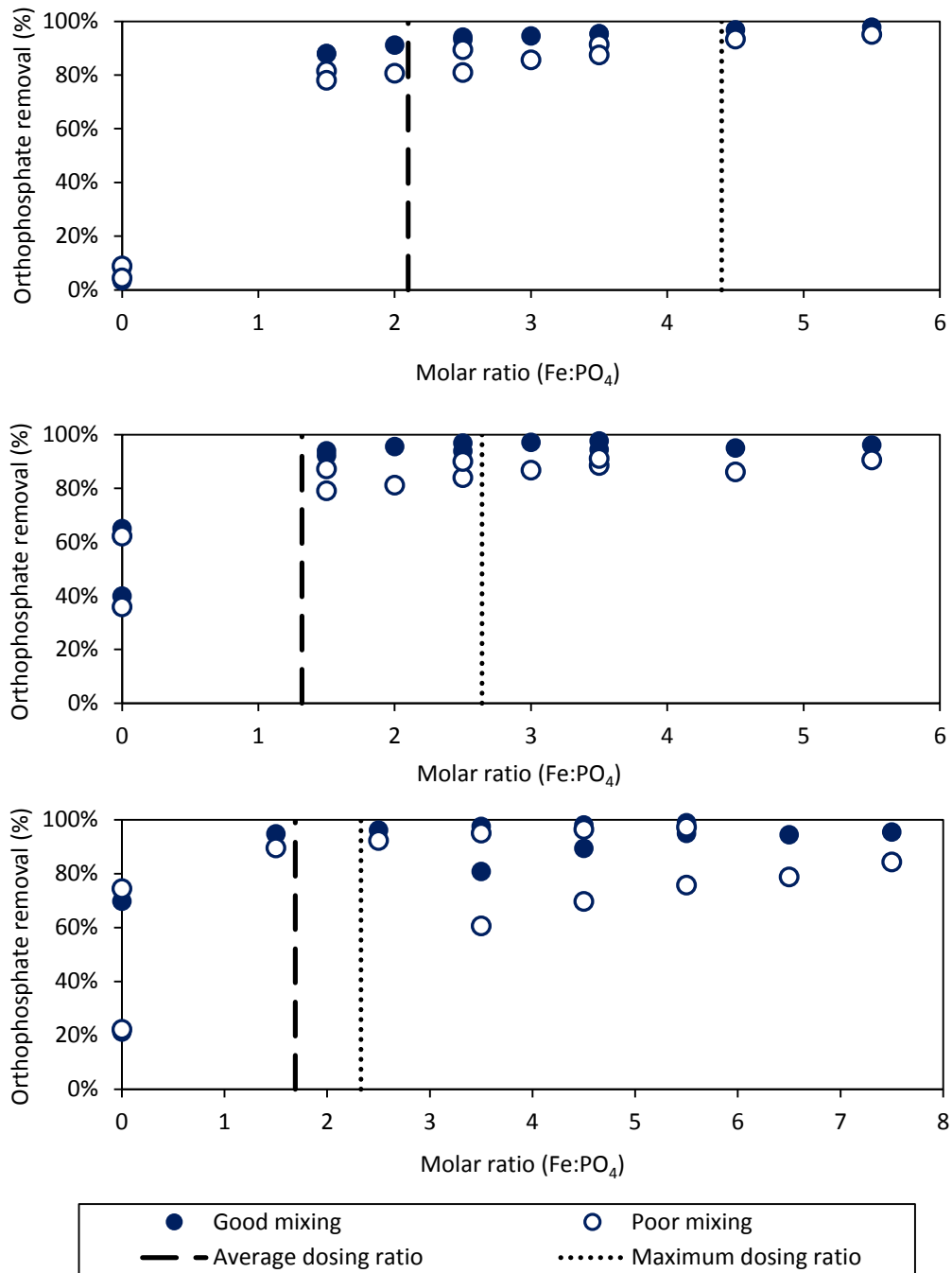


Figure 4.9 Orthophosphate removal efficiency at different doses of ferric sulphate for site P1 (top) , site P2 (middle) and site R1 (bottom). Vertical lines refer to the average and maximum molar ratio used at each site.

Table 4.9 Dosing and molar ratios used at the studied sites for chemical phosphorus removal (source: Severn Trent Water).

WwTPs	Dosing rate		Average flow L/hour	PO ₄ ³⁻ -P concentration at dosing point \bar{x} , mg/L	Molar ratio (Fe:PO ₄)	
	L/hour				Fe:PO ₄	
	Average	Maximum			Average	Maximum
Site P1	0.49	1.03	4,506	1.15	2.1:1	4.4:1
Site P2	0.58	1.16	7,919	1.23	1.3:1	2.6:1
Site R1	2.8	3.5	10,619	3.45	1.7:1	2.3:1

Chemical: Ferric sulphate (12.5% as iron and 1.6 specific gravity).
Dosing point: Front end RBC.

Table 4.10 Jar test results applied to the dosing ratios used at the studied sites.

WwTPs		Initial orthophosphate concentration (mg/L)	Supernatant orthophosphate concentration (mg/L)			
			Average dose		Maximum dose	
			Good mixing	Poor mixing	Good mixing	Poor mixing
Site P1	Sample 1	3.82	0.34	0.73	-	-
	Sample 2	4.05	0.34	0.56	0.14	0.28
Site P2	Sample 1	3.81	0.50	0.76	0.12	0.29
	Sample 2	1.80	0.21	0.44	0.11	0.18
Site R1	Sample 1	3.64	0.18	0.63	0.15	0.55
	Sample 2	1.98	0.98	1.17	0.78	1.04

4.7. Clogging and anaerobic conditions in reed beds

Site P1 showed the highest TS content of all three sites with 11.3 kg/m² and 15.7 kg/m² at the inlet and middle zones of the reed bed (Table 4.11). Highest TS content at sites P2 and R1 were found in the inlet zone and corresponded to 6.6±2.0 kg/m² and 9.6±0.1 kg/m². Only site P2 showed a clear decreasing trend from inlet to outlet, although the values observed in the inlet and middle zones were higher than in the outlet in all cases.

Comparing TS content values between all three sites and relating it to the operational time without reed bed refurbishment, it was observed that sites P1 and P2

had the highest accumulation rates. Site P1 had similar accumulation rate (1.94 kg/m²/year) than site P2 (1.50 kg/m²/year) which is consistent to the fact that both sites started iron dosing at the same time. However the accumulation rates between the sites are significantly different at 1.08 kg/m²/day. Both reed beds were refurbished approximately at the same time but site P1 shows a much lower accumulation rate even though has been performing under chemical dosing for its whole operational time (5 years) whereas site R1 only for few months. This may be attributed to a better performance of site R1 or a higher suspended solids loading rate into the reed bed at site P1.

Solids accumulation rates found in this study were comparable to those reported by Tanner et al. (1998) for four non-chemically dosed reed beds, which ranged from 1.34 kg/m²/year to 2.95 kg/m²/year. Values in this study were also relatively lower than those observed by Caselles-Ososrio et al. (2007) in secondary and tertiary reed beds, 0.7-3.2 kg/m²/year and 0.6-2.9 kg/m²/year.

Table 4.11 Accumulated total solids, redox potential and dissolved oxygen in the upper layer of the granular media of the studied reed beds at sites P1, P2 and R1.

WwTPs	Total solids (n=2)			Redox potential (n=3)			Dissolved oxygen (n=3)		
	$\bar{x} \pm sd, \text{kg/m}^2$			$\bar{x} \pm sd, \text{mV}$			$\bar{x} \pm sd, \text{mg/L}$		
	In	Mid	Out	In	Mid	Out	In	Mid	Out
Site P1*	11.3	15.7	5.6	-	-	-	-	-	-
Site P2	6.6±2.0	2.7±0.6	2.4±1.2	-68±62	102±50	160±23	0.1±0.0	0.6±0.6	2.0±0.2
Site R1	9.6±0.1	2.6±1.6	5.8±0.8	211±15	144±42	150±35	1.7±0.5	0.4±0.3	0.7±0.3

*Only one sample could be collected at site P1 for total solids (n=1)

Measurements of oxidation reduction potential (Eh) and dissolved oxygen in the upper layer of the granular media showed different trends between site P2 and R1. The lowest Eh value at site P2 was located in the inlet (-68±62 mV) whereas site R1 had the highest value (+211±15 mV) in the same area. However, along the reed bed length both reed beds Eh were equalizing until reaching a similar value in the outlet area (160±23 mV at site P2 and 150±35 mV at site R1). Redox values in the upper layer of the whole reed bed area at site R1 were in the range of denitrifying bacteria activity

using NO_3^- as electron acceptor (i.e. between +400 mV and +100 mV). The studied reed bed at site P2 showed an increase of the redox values from the inlet to the outlet areas. Redox potential in the inlet area was clearly within the range of reduction of Fe^{3+} to Fe^{2+} (i.e. between +100 mV and -100 mV) whereas the middle area of the same reed bed showed values that varied between iron and nitrate reduction ranges, to finally reach values in the outlet area clearly above +100 mV and so suggesting use of NO_3^- as electron acceptor.

Low dissolved oxygen concentrations observed at both sites P2 and R1 indicated that anaerobic conditions were not present in the upper layer of the studied reed beds in general. Only the inlet area of the reed bed at site P2 showed dissolved oxygen concentrations typical of anaerobic environments. In this reed bed, DO concentrations passed from average values of 0.1 ± 0.0 mg/L at inlet to 2.0 ± 0.2 mg/L at outlet showing an increasing trend and moving from anaerobic to aerobic conditions. In contrast, site R1 had the highest DO concentration in the inlet area (1.7 ± 0.5 mg/L), decreasing in the middle and outlet areas to values between 0.1 and 1 mg/L. These differences may be related to higher denitrification taking place in the reed bed at site P2 than R1, as it can be suggested from the higher nitrates removal rates observed in the problematic sites. It is also likely that lower DO concentrations were present in deeper layers of the bed, away from the surface layer of water where diffusion could be responsible for higher DO values and were saturated media is liable to have lower concentrations of dissolved oxygen leading to establish an anaerobic environment in the system.

5. DISCUSSION

This study has shown that the standard solution for phosphorus removal applied in small WwTP consisting on chemical dosing of iron salts with reed beds as final filtration stage may perform satisfactorily achieving phosphorus and iron compliance. Analysis of historic performance data showed that high average removal percentages for both phosphorus (85%) and iron (79%) were achieved, and that concentrations of P and Fe well below the compliance consent levels (2 mg-TP/L and 4 mg-Fe/L) can be reached. Furthermore, this may be achieved regardless of the technology used as secondary biological treatment (RBC, trickling filters or SAF), chemical dosing point (crude, RBC's front end or humus tank feed) and initial chemical mixing conditions (whether a rapid mix system is used or not). However, some considerations must be taken concerning the use of reed beds as tertiary filters in chemically-dosed small WwWTP in order to ensure satisfactory results and compliance with current and future environmental quality standards.

5.1. Considerations for the use of tertiary reed beds in treatment plants with chemical phosphorus removal

A first concern regarding reed beds' performance is the possibility that colloidal and dissolved particles in the secondary effluent may pass through untreated the granular media of the tertiary reed bed . Fractionation analysis in this study revealed significant differences between phosphorus particle size in the influent and effluent of the reed beds. The results obtained show that the majority of total phosphorus in the influent is associated to either suspended solids or dissolved fractions, whereas in the effluent TP is mainly dissolved (above 60% (site P1) and up to 90% (site R1) of TP). On the other hand, iron is clearly associated to the suspended solid fraction in the influent, and very low concentrations can be achieved in the effluent (average concentrations ranged from 0.08 to 0.34 mg-Fe/L) as suspended, colloidal or dissolved fractions. This suggests suspended solids are mostly retained within the bed, reinforcing the idea that reed beds are robust technologies for polishing of suspended organic matter and solids, but

that iron phosphates or unbound phosphorus as colloidal and dissolved particles may not be captured within the bed. This poses a potential risk of failure if high levels of dissolved and colloidal phosphorus remain in the secondary effluent after chemical precipitation and settling. It also emphasises the importance of a good and reliable strategy for chemical dosing and effective secondary sedimentation processes, to ensure colloidal and dissolved phosphorus are trapped in the form of iron-bound-phosphorus flocs and settled within the humus or final settling tanks.

The significantly higher iron and phosphorus content found in the sludge of the studied reed beds in comparison to those reported in sediments from other water bodies highlights the impact of chemical dosing on their accumulation within tertiary reed beds. Iron and phosphorus concentrations in sludge also increase with increasing length of operation of the reed bed. The results suggest that the main removal mechanism in mature beds is settlement of suspended iron-bound-phosphorus particles. This is related to the surface-based inlet distribution system of the studied reed beds. The impact of this is a change of the flow regime from horizontal to vertical flow in the inlet area, producing sludge build-up in the upper layers of the granular media and above the bed. This may have a negative impact since gradual accumulation of sludge above the bed can result in surface clogging causing reduction of hydraulic conductivity of the media and surface ponding. In the worst case scenario, sludge accumulation may result in a change from subsurface to surface flow producing short-circuiting of part of the flow and increasing the risk of escaping untreated through the overflow pipe if sufficiently high levels of water accumulate on the top of the bed.

In addition, results from this study indicate phosphorus release from the reed bed can occasionally occur. Such episodes occurred at the same time as an increase in the mass of soluble reactive phosphorus (orthophosphates) in the effluent. It suggests that the reed beds can release SRP, which correlates to the increase being seen mainly in the dissolved fraction in the final effluent. From the literature reviewed, potential causes of phosphorus release can be related to the high reactivity of iron hydroxides in anaerobic environments. It is actually the use of iron as an electron acceptor (i.e.,

reduction of Fe^{3+} to the more soluble form Fe^{2+}) that causes the breakdown of iron-bound-phosphates with the subsequent release of dissolved phosphates and iron into the water column. Batch experiments in this study showed some phosphorus and iron release from sediments under anaerobic conditions. Also low concentrations of dissolved oxygen observed in the upper layer of the granular media suggest anaerobic conditions were likely present in the depth of the bed. It is important to highlight that these measurements were obtained during the summer, when temperature is higher and the activity of microorganisms is more intense, leading to low Eh values and the depletion of dissolved oxygen. Phosphorus release in the studied reed beds were without the subsequent release of iron, as would be expected by the breakdown of iron-bound-phosphates. Indeed, iron compounds in both influent and effluent of the studied reed beds corresponded mainly to Fe^{3+} species. A possible explanation could be that after breakdown of iron-bound-phosphates, ferrous ions migrate through the bed until they are re-precipitated as iron hydroxides due to a change of redox conditions from reducing to oxidising. Nevertheless, it seems clear that tertiary reed beds in WwTPs with chemical dosing may present the appropriate conditions for P release from breakdown of iron-bound-phosphates: saturated media liable to establish anaerobic conditions and high amounts of iron phosphates accumulated in the bed. Further research regarding strategies to avoid release episodes should be undertaken, probably focusing on the use of aerated reed beds to turn anaerobic conditions to aerobic and thus to promote the use of oxygen as electron acceptor instead of iron. Nitrate content of the wastewater could also be playing a role and more research is needed to understand how effective nitrate addition could be in keeping redox conditions above the threshold for iron transformations. Alternatively, other metal salts less sensitive to changes in redox conditions such as aluminium may be used.

Finally, another aspect that should be considered for the optimal performance of reed beds is related to the initial mixing conditions when adding iron salts. It was proposed that poor initial mixing may result in higher levels of colloidal and dissolved particles in the secondary effluent that would not be trapped in the tertiary reed bed. However, the results in this study have shown that high orthophosphate removal

efficiencies are achieved even when initial rapid mixing is discarded. This may be explained as the use of iron dose in excess of the stoichiometric requirements may minimise the effect that mixing conditions could have over the removal of phosphorus. On the other hand, high concentrations of iron in the supernatant resulted after mixing, coagulation and settlement. This indicates that iron dosing resulted in both precipitation of phosphates and colloidal iron compounds in suspension. High iron doses may encourage the formation of iron hydroxides rather than iron phosphates. Once most of phosphates have precipitated as either iron phosphates or by adsorption to iron hydroxides, the remaining iron hydroxides in excess may keep unreacted and in suspension. These may need also longer settlement times than one hour as used in the jar tests. However, this may have a positive effect in WwTPs since suspended iron compounds can keep removing orthophosphate downstream dosing point and settling tanks.

5.2. Future use of tertiary reed beds at chemically-dosed sites

Although compliance of quality discharge standards is achieved, the above commented aspects regarding reed bed performance may put at risk the use of tertiary reed beds in chemically-dosed sites with future tightening of P and Fe consents.

It is expected that current phosphorus consent of 2 mg TP/L applied in Europe and the UK will be tightened to levels approaching consents in USA (<0.07 mg TP/L; Environment Agency, 2012a). The current most lenient P concentration for good status of a water body is 0.12 mg SRP/L, but it is likely that in the future a 0.1 mg TP/L will be established (Environment Agency, 2012a). If this tighter consent is applied, the results in this study suggest that the current strategy of chemical dosing, followed by tertiary reed beds as final filtration, would not provide sufficient removal. The results show that phosphorus dissolved fraction at the reed bed influent would exceed a future consent of 0.1 mg TP/L. Since dissolved particles are not trapped within the reed bed and some soluble reactive phosphorus release may occur, it appears that the efficient removal of suspended solids in reed beds would not be enough. However, results also

show that reed beds would achieve satisfactory future iron consents (expected at about 0.7 mg Fe/L). This is clearly related to the fact that iron is strongly correlated to suspended solids, which are captured within the bed.

Therefore, unless dosing strategies and settling processes upstream of reed beds produce a reed bed influent consisting of only particulate P, additional treatment stages will be required, either by replacing the reed bed with more sophisticated filtration methodologies such as ultrafiltration or by removing the dissolved fractions with sorptive reactors. This would suppose a significant increase of the treatment costs compared to the low cost, low maintenance and low energy requirements offered by reed beds.

6. CONCLUSIONS

Seven conclusions were drawn from this study:

- Chemical dosing of iron salts in small WwTPs with reed beds as final filtration stage can perform satisfactorily, achieving phosphorus and iron compliance with current standards (85% TP and 79% TFe removal; 1.04 mg/L TP and 0.41 mg/L TFe at final effluent).
- The majority of total phosphorus in the reed bed influent is associated to either suspended solids (35.6-73.9%) or dissolved fractions (21.1-43.8%), whereas in the effluent TP is mainly dissolved (60.8-90%). Iron is clearly associated to the suspended solid fraction in the influent (60.3-89.7%), and to either suspended, colloidal or dissolved fractions in the effluent.
- Phosphorus and iron suspended solids fractions are mostly retained within the reed bed (74-87% TP and 69-98% TFe removal) whilst colloidal and dissolved P and Fe particles may pass through untreated.
- Tertiary reed beds in chemically-dosed sites present significantly higher Fe and P concentrations in sludge (5.7-55.9 g P/Kg DM and 8.2-246.6 g Fe/Kg DM) compared to those reported in sediments from other water bodies (0.005-7.4 g P/Kg DM and 0.1-158 g Fe/Kg DM). The main mechanism for trapping of Fe and P in mature beds is settlement of suspended iron-bound-phosphorus particles, being accumulated in the upper layers of the granular media and above the bed at the inlet zone.
- Phosphorus release from the reed bed can occasionally occur (average P removal rates varied from -0.09 ± 0.06 g/m²·day to 0.00 ± 0.03 g/m²·day) This may be related to anaerobic conditions within the bed causing the breakdown of iron bound phosphates. However, iron release of up to 1,658 mg/m²·day observed under anaerobic conditions in the laboratory was not accompanied by release of orthophosphates. More research is needed to clarify the mechanism responsible for the release observed in full scale reed beds.

- Poor initial mixing conditions of the coagulant have an insignificant impact over P removal. Removal efficiencies of up to 90% and supernatant concentrations lower than 0.9 mg P/L can be obtained regardless molar ratio, mixing conditions, and initial P concentration.
- The current dosing strategy is insufficient to achieve consents tighter than 0.55 mg TP/L. Additional treatment stages will be required in future unless dosing strategies and settling processes upstream of reed beds produce a reed bed influent consisting of only particulate phosphorus.

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APPENDIX

Individual site reports for the sites selected as problematic (sites P1 and P2) and reliable (site R1).

Problematic site P1

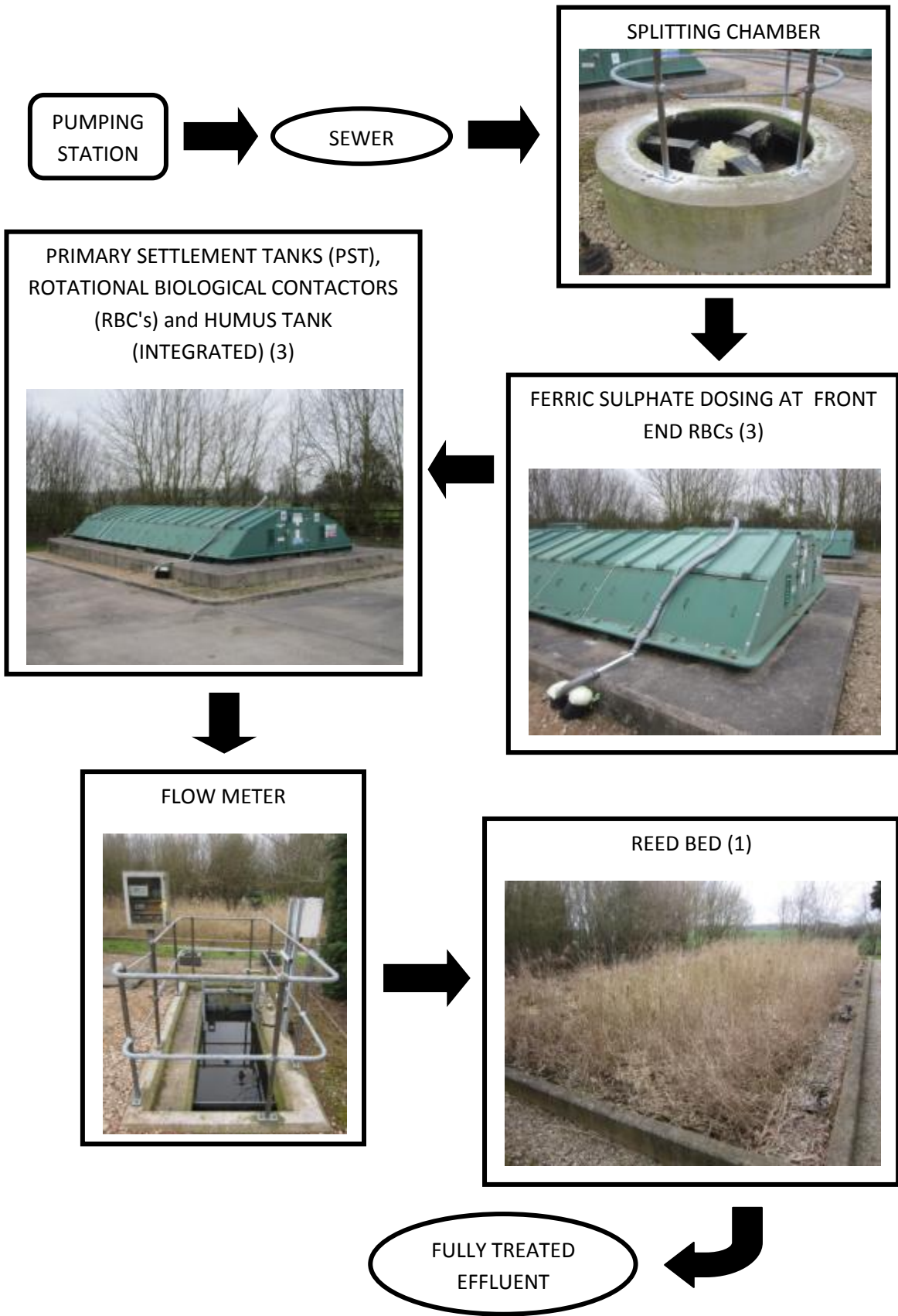
SEWAGE TREATMENT WORKS REPORT

16th March 2012

❖ Consents	
BOD	40 mg/l
Suspended solids	60 mg/l
Ammonia	No consent
Total P	2 mg/l (currently commissioning ferric sulphate)
Iron (Fe)	4 mg/l (currently commissioning ferric sulphate)
Aluminium (Al)	No consent

❖ Characteristics	
Works class	Tertiary treatment works
Primary treatment	Primary Settlement Tank (PST) (Integral at RBC Tank)
Secondary treatment	Rotation Biological Contactors (RBC) & Humus Tank (Integral at RBC Tank)
Tertiary treatment	Reed bed
Nutrient removal	No
Dry weather flow	121 m ³ /day (1.4 l/s)
Population equivalent	526 PE
Flow meter record on site	1.51 l/s (on 16/03/2012 at 10 am)
Chemical dosing	Ferric sulphate is added at the front end of the biological zone,
Dosing start date (P consent start)	Commissioning started on 14 th March 2012.

❖ Wastewater treatment process



❖ Primary treatment: Primary Settlement Tank (PST)	
Number of lines	3
Condition	Good
Comments: Not known issues.	

❖ Secondary treatment: Rotating Biological Contactors (RBC)	
Number of lines	3
Condition	Good
Comments: Not known issues.	

❖ Secondary treatment: Humus Tank	
Number of lines	3
Condition	Good
Last time de-sludged	7/02/2012
Comments: Not known issues.	

❖ Tertiary treatment: Reed bed	
Number of lines	1
Condition	Regular (old reed bed design)
Last time refurbished	Before 2007
Dimensions (length x width)	13 m x 28 m
Number of inlet points	6
Spacing between inlet points	3 m
Freeboard	40 cm (approximately)
Gravel size	-
Apparent size distribution	-
Sludge accumulation	-
Water level	15 - 20 cm above surface media (flooded)
Status of the effluent pipe	Good (old design)
Deviations from standard design	Instead of v-notches there are 6 pipes, with a distance between centres greater than 2.5 m. The effluent pipe (bellmouth) is different than the standard design L-shaped.

Comments: The reed bed is flooded from the inlet to the outlet zone, and it is not possible to appreciate neither the sludge accumulation nor the gravel size.



Image 1. Inlet zone of the reed bed.



Image 2. Outlet zone of the reed bed.



Image 3. View of the reed bed from the outlet side.

❖ Other information and issues

- Operators visit the plant less than once a week.
- There is an old humus tank non-operative anymore that nowadays it is used as a holding tank to store water from one of the three RBC tanks during RBC's desludging tasks. After desludging, the water stored in the old humus tank is pumped back to the splitting chamber, from where goes through the integrated RBCs and finally to the reed bed. During this process, the water flow to the reed bed is increased rapidly and can reach values 3 times greater than the existing flow before the pumping (on the day of the site visit the flow changed from 1.51 l/s to 4.8 l/s). This may increase the quantity of suspended solids reaching the reed bed and increase the sludge amount in the bed, producing clogging of the media. This could be the cause of the flooding state of the reed bed.



Image 4. Old humus tank.

- Just started commissioning of ferric sulphate dosing. On 14/03/2012 Service Delivery turned Ferric sulphate dosing on.



Image 5. New Ferric sulphate dosing tank.

- The WwTP is performing well at the moment, with BOD and ammonia levels at the effluent around 0 mg/l.
- New management of the site started 2 months ago.

❖ Data review

In terms of BOD and suspended solids removal, works are performing consistently well, reaching BOD and SS values far below from consents (Figure 1). There is no consent for ammonia, however ammonia levels at final effluent are mostly below 2 mg/L (Figure 2).

Figure 1. BOD & Suspended solids (fully treated effluent)

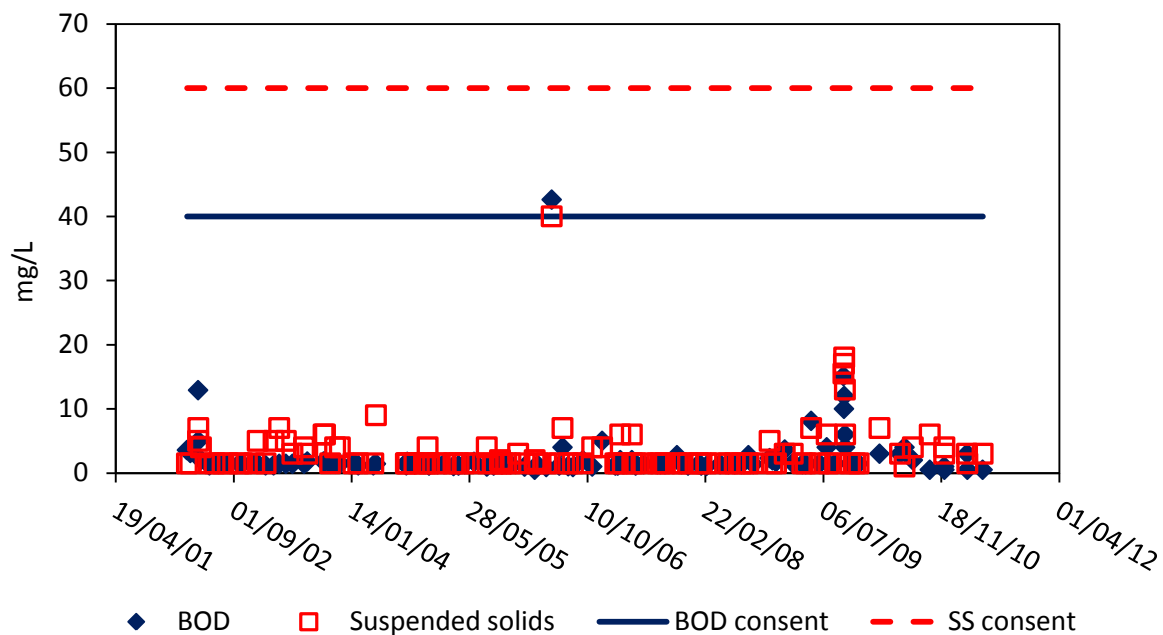
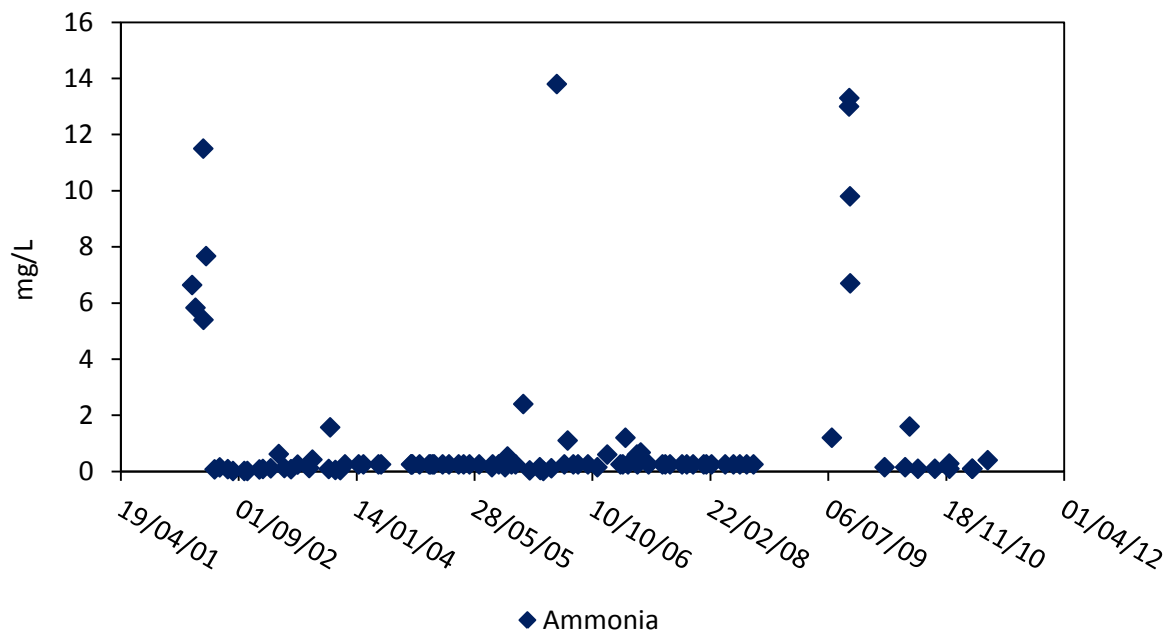


Figure 2. Ammoniacal nitrogen as N (fully treated effluent)



Problematic site P2

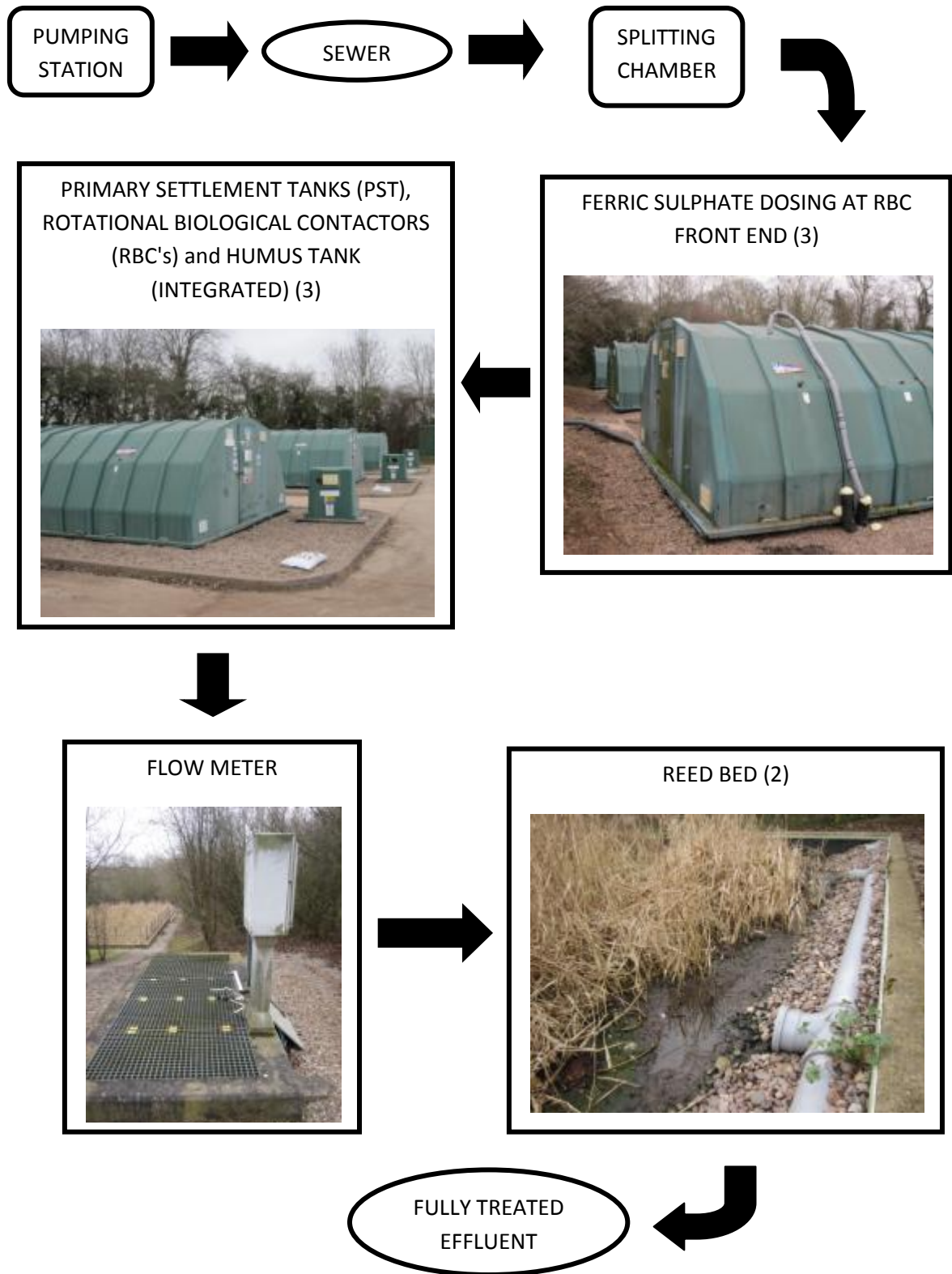
SEWAGE TREATMENT WORKS REPORT

16th March 2012

❖ Consents	
BOD	30 mg/l
Suspended solids	50 mg/l
Ammonia	No consent
Total P	2 mg/l (currently commissioning ferric sulphate)
Iron (Fe)	4 mg/l (currently commissioning ferric sulphate)
Aluminium (Al)	No consent

❖ Characteristics	
Works class	Tertiary treatment works
Primary treatment	Primary Settlement Tank (PST) (Integral at RBC Tank)
Secondary treatment	Rotation Biological Contactors (RBC) & Humus Tank (Integral at RBC Tank)
Tertiary treatment	Reed bed
Nutrient removal	No
Dry weather flow	113 m ³ /day (1.3 l/s)
Population equivalent	795 PE
Flow meter record on site	0.95 l/s (on 16/03/2012 at 10 am)
Chemical dosing	Ferric sulphate is added at the beginning of the biological zone, in the primary settlement tank.
Dosing start date (P consent start)	Commissioning started on 14 th March 2012.

❖ Waste water treatment process



❖ Primary treatment: Primary Settlement Tank (PST)	
Number of lines	3
Condition	Good
Comments: Not known issues.	

❖ Secondary treatment: Rotating Biological Contactors (RBC)	
Number of lines	3
Condition	Good
Comments: Not known issues.	

❖ Secondary treatment: Humus Tank	
Number of lines	3
Condition	Good
Last time de-sludged	13/03/2012
Comments: Not known issues.	

❖ Tertiary treatment: Reed bed	
Number of lines	2
Condition	Regular (old reed bed design)
Last time refurbished	2009-10
Dimensions (length x width)	15 m x 16 m (same size for both reed beds)
Number of inlet points	6
Spacing between inlet points	2.3 m
Freeboard	40 cm
Gravel size	15 mm
Apparent size distribution	Similarly sized gravel
Sludge accumulation	No sludge in the outlet zone of one of the reed beds. No appreciable in the flooded reed bed
Water level	15 - 20 cm
Status of the effluent pipe	Good (but old design)
Deviations from standard design	The length of the reed beds is different than the standard (12.5 m) and the area is almost square shaped. Instead of v-notches there are 6 pipes (old design).

Comments: Reed bed plants look good and are upright standing. There are some areas with no plants. Splitting chamber does not perform properly since one reed bed

receives more water than the other. Thus, one of the reed beds is flooded in the whole area (10-15 cm water level), whilst in the other reed bed the water level is above the ground level just in the inlet area (10-15 cm). Therefore, it is just possible to appreciate the gravel at the outlet zone of one of the reed beds, where there is no sludge. The splitting chamber does not look bad (although it seems to be blocked in one trough), so maybe the strange splitting flow is due to the old design of the inlet pipe.



Image 1. Inlet pipe



Image 2. View of the flooded reed beds



Image 3. Outlet zone of one reed bed



Image 4. Flooded outlet zone of the reed bed



Image 5. Gravel size compared with a 10p coin (25 mm diameter)



Image 6. Splitting chamber

❖ Other information and issues

- Operators visit the plant less than once a week.
- There are old storm tanks non-operative anymore.



Image 7. Old storm tanks used as holding tank

- Just started commissioning Ferric sulphate. On 14/03/2012 Service Delivery turned Ferric sulphate dosing on. (Ortho P = 7.5 mg/l; Tot P = 9 mg/l; Fe = 0.2 mg/l).



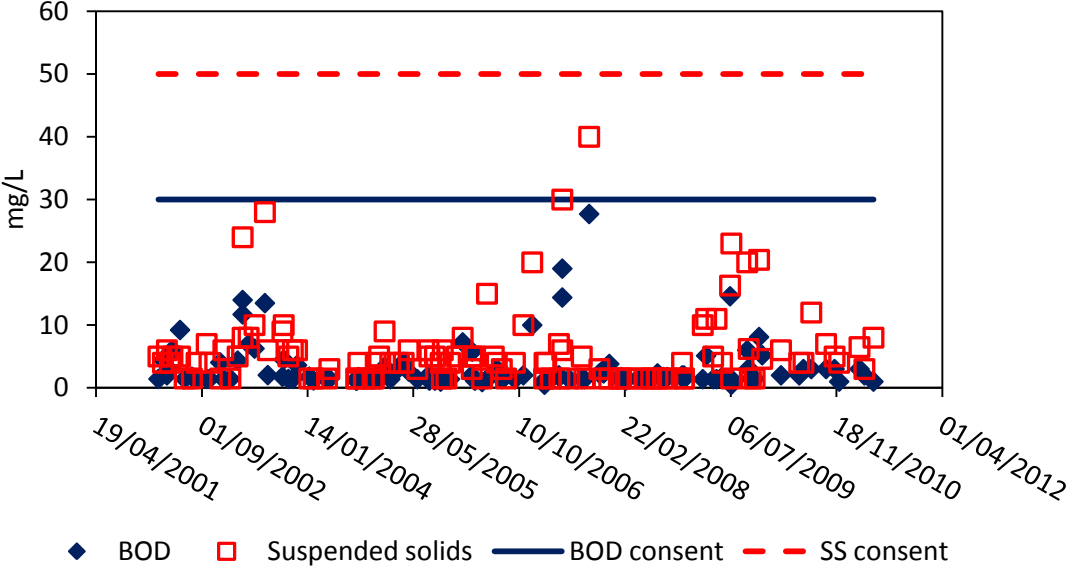
Image 8. New ferric sulphate dosing tank.

- The works are performing well at the moment.
- New management of the site started two months ago.

❖ **Data review**

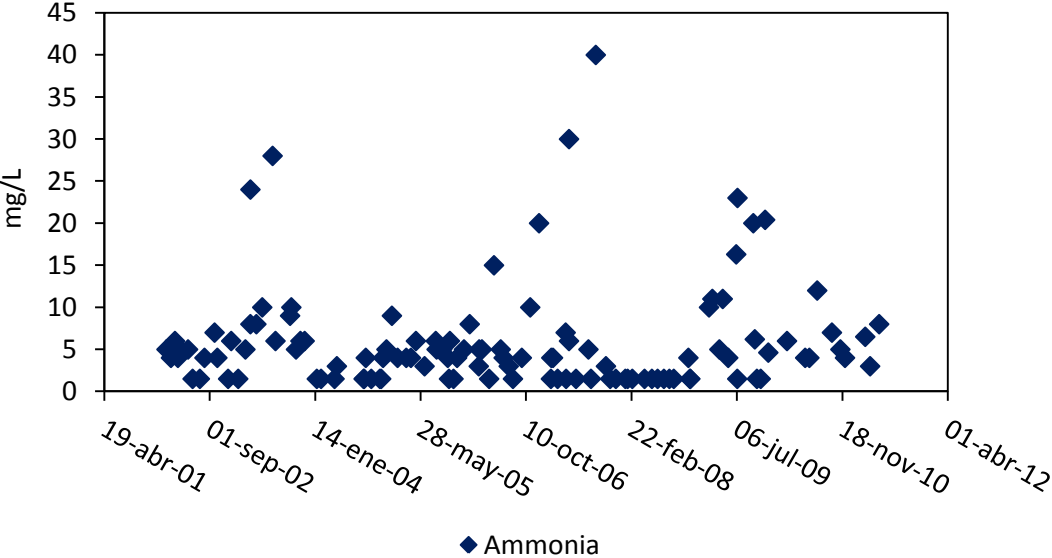
In terms of BOD and suspended solids removal, works are performing consistently well. Figure 1 shows the data available of BOD and SS concentrations at the fully treated effluent, and it can be seen that during the last 10 years the sewage works have never failed neither BOD nor SS consent.

Figure 1. BOD & Suspended solids (fully treated effluent)



This WwTP does not have an ammonia consent, but majority of ammoniacal nitrogen values at the final effluent are around 5 mg/l, which is the consent used in most of the chemically-dosed sites (Figure 2).

Figure 2. Ammoniacal nitrogen as N (fully treated effluent)



Reliable site R1

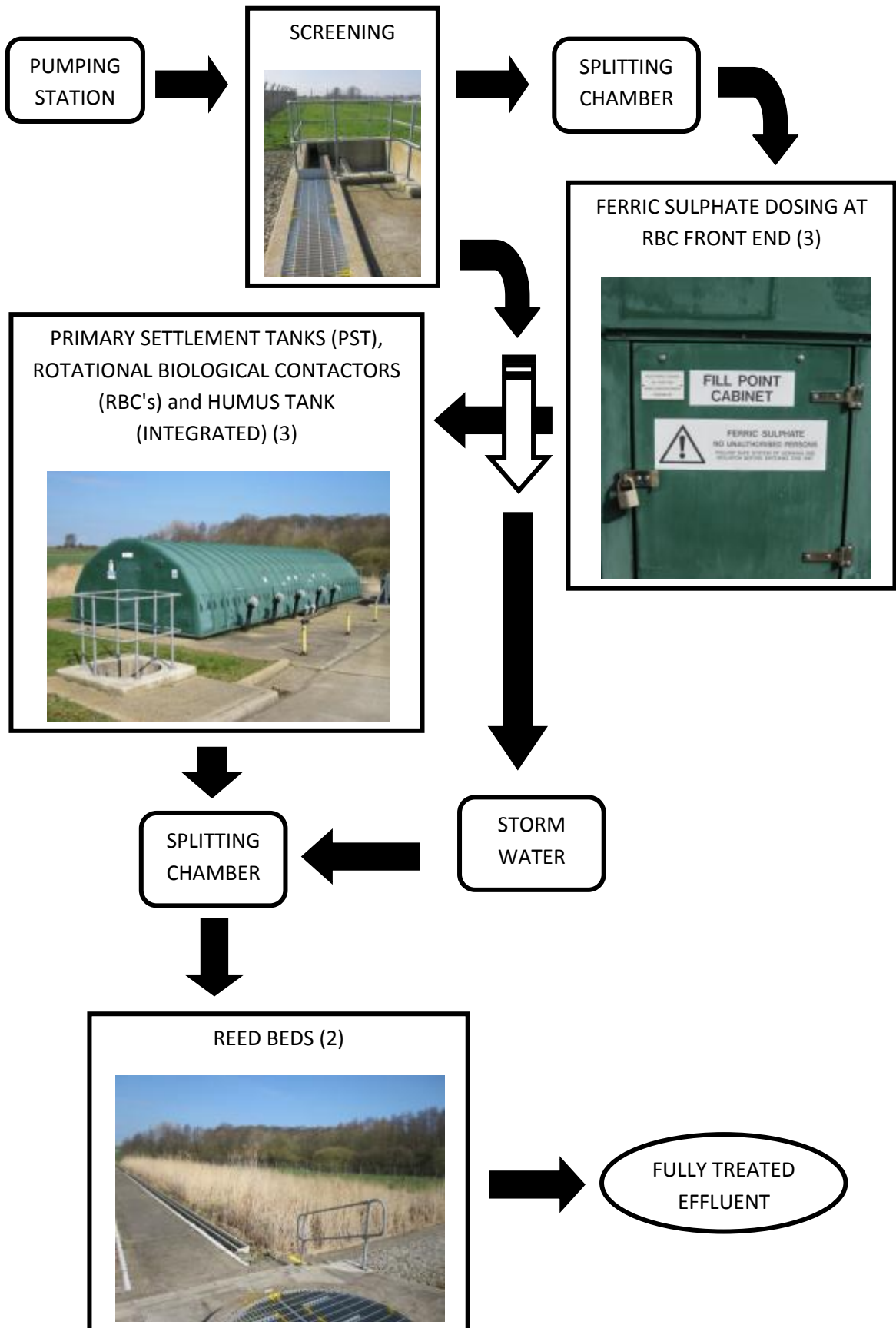
SEWAGE TREATMENT WORKS REPORT

21st March 2012

❖ Consents (95%ile)	
BOD	25 mg/l
Suspended solids	40 mg/l
Ammonia	10 mg/l
Total P	2 mg/l
Iron (Fe)	4 mg/l
Aluminium (Al)	1 mg/l

❖ Characteristics	
Works class	Tertiary treatment works
Primary treatment	Primary Settlement Tank (PST) (Integral at RBC Tank)
Secondary treatment	Rotation Biological Contactors (RBC) & Humus Tank (Integral at RBC Tank)
Tertiary treatment	Reed bed
Nutrient removal	Yes
Dry weather flow	341 m ³ /day (3.9 l/s)
Population equivalent	1297 PE
Flow meter record on site	-
Chemical dosing	Ferric sulphate is added at the beginning of the biological zone in the RBC's. (Dosing all the year)
Dosing start date (P consent start)	31 st March 2006

❖ **Waste water treatment process**



❖ Primary treatment: Primary Settlement Tank (PST)	
Number of lines	3
Condition	Good
Comments: Not known issues.	

❖ Secondary treatment: Rotating Biological Contactors (RBC)	
Number of lines	3
Condition	Good
Comments: Not known issues	

❖ Secondary treatment: Humus Tank	
Number of lines	3
Condition	Good
Last time de-sludged	Not known.
Comments: Not known issues	

❖ Tertiary treatment: Reed bed	
Number of lines	2
Condition	Very good
Last time refurbished	Before 2007 (at least)
Dimensions (length x width)	12.5 m x 65 m (both are equally sized)
Number of inlet points	25
Spacing between v-notches	1.25 m
Freeboard	About 50 cm
Gravel size	About 14 mm
Apparent size distribution	Similarly sized gravel
Sludge accumulation	No sludge (just remains of dead plants).
Water level	5 cm max (just at the inlet zone)
Status of the effluent pipe	Good
Deviations from standard design	Reed beds are according to the standard design.

Comments: Reed beds look very good. Reeds are upright standing and look according to the current winter weather, are spread in the whole bed, with no empty areas and high density. Due to the length of the reed beds, each one has 2 inlet distribution channels, according to the standard design that indicates that the maximum length of the distribution channel shall be 40m. Beds are not flooded, having just some ponding at the inlet zone, as usual in this type of reed beds.



Image 1. Inlet channels of the reed beds



Image 2. V-notches of the inlet channel.



Image 3. Inlet channel



Image 4. View of the reed bed from the outlet zone



Image 5. View of the gravel (outlet zone) compared with a 10p coin.



Image 6. View of the gravel (middle zone)

❖ Other information and issues

- Operators visit the plant every 2-3 days.
- As far as delivery service knows, the works are consistently performing well and they are not aware of any process compliance concerns.
- Storm water is leaded from the inlet channel straight to the distribution chamber for the reed beds. Previously, storm water is screened using a copaSac system.



Image 7. Copa sac screening system for storm water.

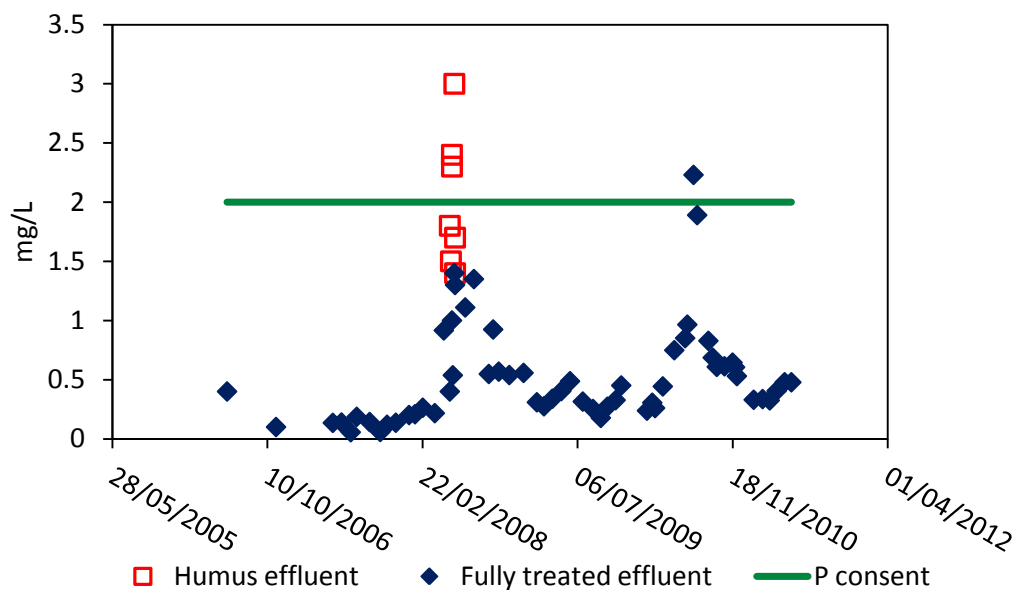
❖ Data review

Ferric sulphate commissioning in this WwTP was started on the 1st of March 2006. Since then, data regarding phosphorus and iron content at the fully treated effluent has been collected periodically every month approximately, whereas data from the humus effluent was collected only during May and June 2008.

During all that period, data shows that the WwTP have been performing correctly, complying with the phosphorus consent (2 mg/l) and achieving P concentrations at the final effluent under 1 mg/l mostly (Figure 1).

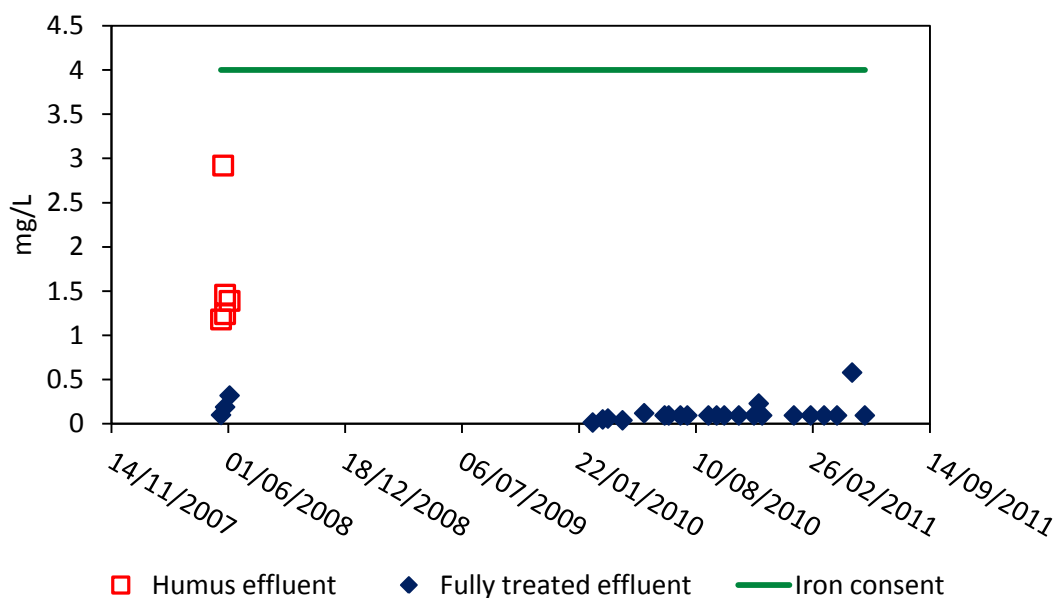
A comparison between the values at humus effluent and final effluent is not possible due to a lack of information. The two months period with data available from the humus effluent corresponds to an increase of the P concentration at the final effluent.

Figure 1. Total - P



Regarding iron removal, very low iron concentration are achieved in the fully treated effluent with values around 0.1 mg/l, well below from the iron consent (4 mg/l) (Figure 2).

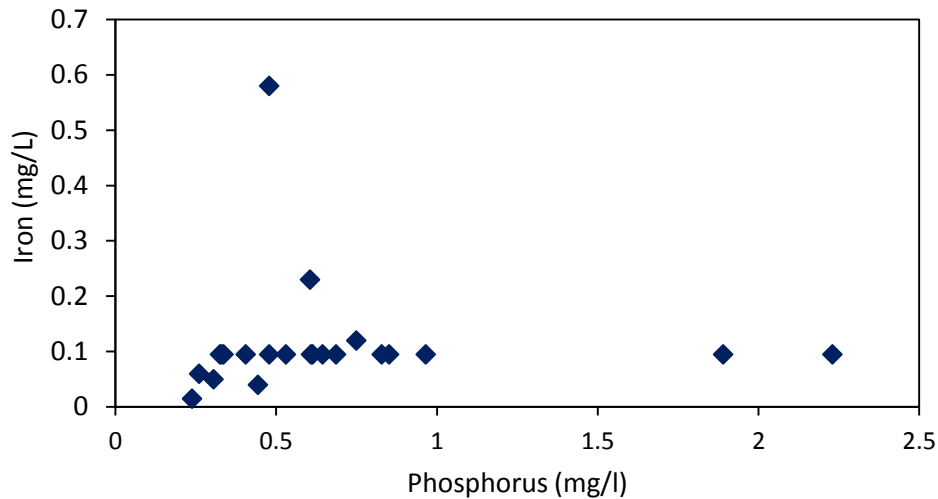
Figure 2. Total - Fe



This fact is in accordance with Figure 3, which provides a comparison between the residual iron and the phosphorus content at the fully treated effluent. Majority of

points plotted are within a same area, indicating that the ferric sulphate dose used during 2010-11 reacts with phosphates resulting in a very low P content along with a low residual Fe. This is an evidence that there is a specific chemical dose for phosphorus removal that leads to a constantly good performance in long term basis.

Figure 3. Fe vs P (14/02/2010 - 26/05/2011)
Fully treated effluent



Figures 4 and 5 show the performance of the works in terms of BOD, suspended solids and ammonia removal. It can be seen that at least since 2005 the BOD, suspended solids and ammonia content at the fully treated effluent have been below consents, and therefore no evidence of bad performance is found.

Figure 4. BOD & Suspended solids (Fully treated effluent)

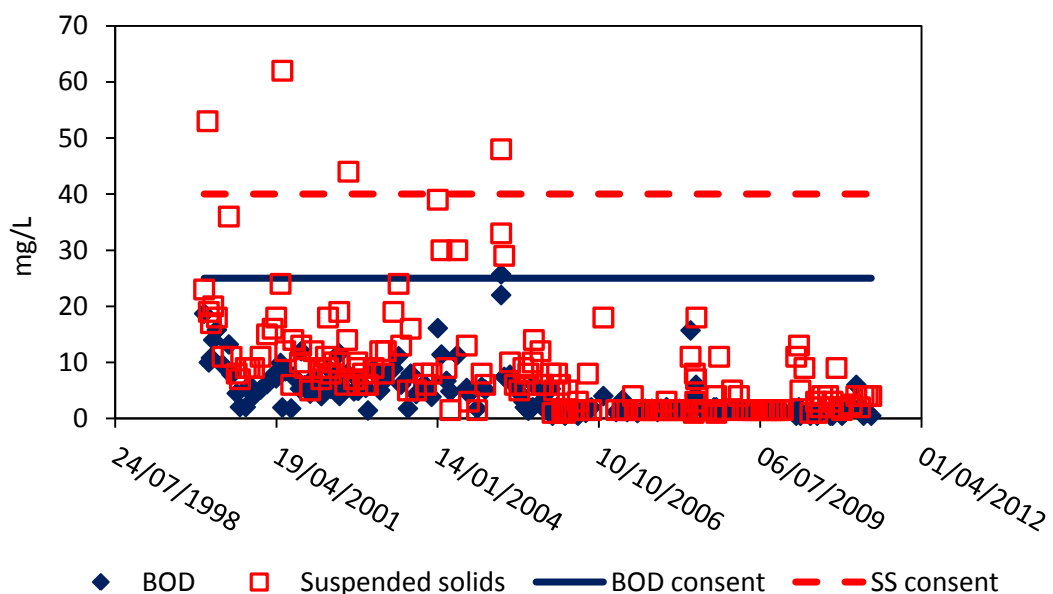
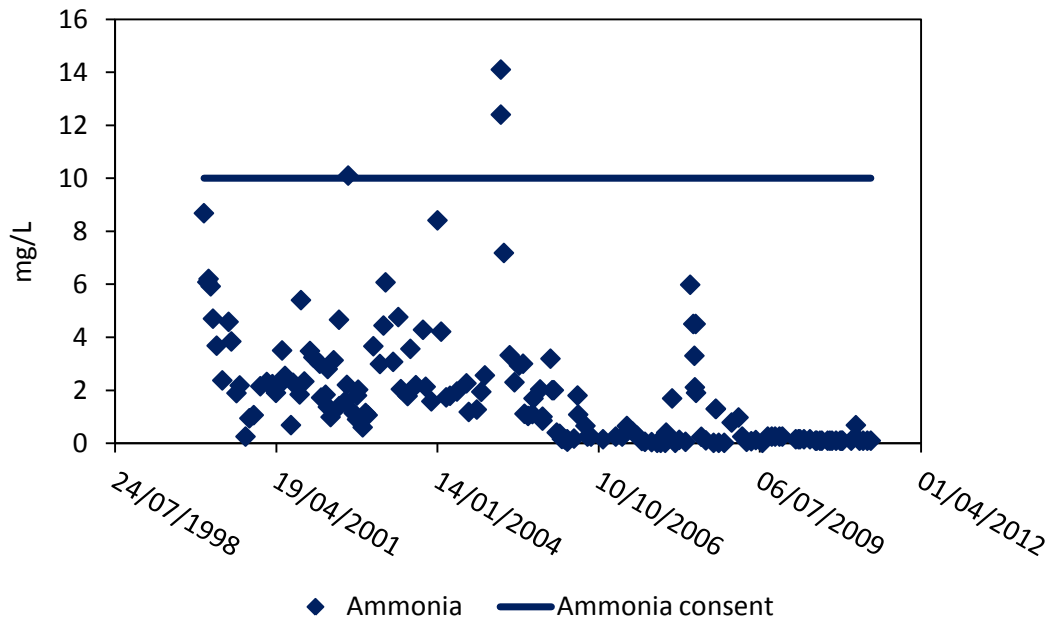


Figure 5. Ammoniacal nitrogen as N (Fully treated effluent)



In conclusion, this site is not having any kind of issue and is a good example of standard small WwTP performing consistently well.