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WASTEWATER EFFLUENT FROM A VARIETY OF TREATMENT PROCESSES

Article Type: Research Paper

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Comber

Abstract: Eutrophication of surface waters is a major issue across the planet, with diffuse (agricultural) and point sources (wastewater treatment works, WwTW) being the main inputs. In the UK WwTW effluent discharges are currently permitted for discharge based on total phosphorus concentration, whereas environmental quality standards (EQS) are set as soluble reactive phosphorus (SRP), which better reflects the bioavailable fraction of phosphorus present in water. This study reports for the first time, concentrations and relative proportions of SRP in effluent from a number of different WwTW employing aluminium and iron dosing for phosphorus removal. In the case of aluminium treatment, SRP constituted only 10 \pm 4% of the 0.75mg P/l total phosphorus in the effluent. Where iron was dosed SRP comprised 66% \pm 20% of the total phosphorus present where a single dose was applied, which dropped to 26 \pm 17% after a second dose and additional tertiary sand filtration. Phosphorus was determined using two established analytical methods after acid digestion, filtration to 0.45 μ m (on site and after return to the laboratory and refrigeration for up to 9 days) and settlement. Phosphorus speciation was shown to be stable within all effluents for up to 6 days storage at a temperature of <5°C without the need to filter on site and this was recommended for future effluent monitoring programmes and compliance assessment. Furthermore, because iron and aluminium dosing significantly reduce the SRP proportion in effluents, future monitoring programmes and policy decisions regarding meeting the phosphorus EQS derived as SRP should take this into account.

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10 August 2015

Dear Sir/Madam

**DETERMINATION OF THE FORMS AND STABILITY OF PHOSPHORUS IN
WASTEWATER EFFLUENT FROM A VARIETY OF TREATMENT PROCESSES**

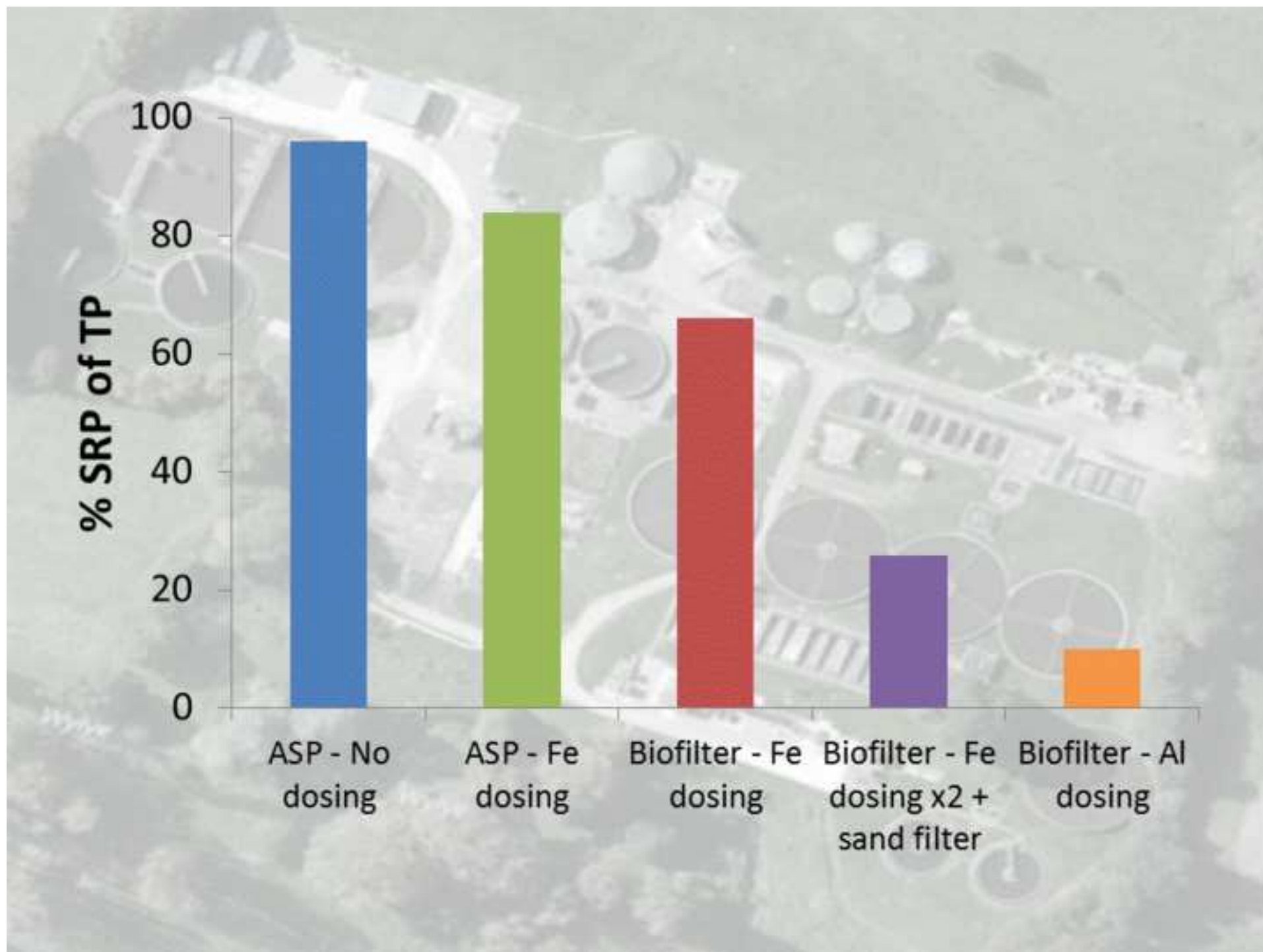
Please find attached our manuscript for consideration for publication in Journal of Environmental Chemical Engineering. The paper determines the speciation of phosphorus in effluents from a number of different sewage treatment works including those that dose iron and aluminium salts for P reduction. Our data for the first time shows that the form of the P discharged at dosed works has very little soluble reactive P compared with undosed works. The regulatory significance of this is highlighted regarding phosphorus management under the Water Framework Directive.

I look forward to hearing from you.

Yours faithfully



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Manuscript #:

Title: **DETERMINATION OF THE FORMS AND STABILITY OF
PHOSPHORUS IN WASTEWATER EFFLUENT FROM A VARIETY OF TREATMENT
PROCESSES**

Author list: Dr Sean Comber, M Gardner, J Darmovzalova, B Ellor

Your name: Dr Sean Comber

Date 10 August 2015

Ms. Ref. No.: JECE-D-15-00916

Title: DETERMINATION OF THE FORMS AND STABILITY OF PHOSPHORUS IN WASTEWATER EFFLUENT FROM A VARIETY OF TREATMENT PROCESSES Journal of Environmental Chemical Engineering

The due date for submitting your revised manuscript is Oct 03, 2015

Thank you for the useful comments provided for our manuscript. We have set out below our responses and have provided a revised manuscript with and without track changes to show the amendments.

Reviewers' comments:

Reviewer #2:

I. Multiple errors related to formatting, editing, and technical language.

The manuscript has been carefully checked for formatting, editing and technical language.

II. Author have utilized activated sludge process (ASP), biological aerated filter (BAFF) and Biofilter for the present study but did not mentioned anything about the process parameters attained for the same.

Process data now summarised in more detail in a table.

III. Because the study was concerned to Phosphorous removal for corresponding combinations of Coagulants-Biological treatment, it is must to mention the dose of the coagulants (Ferrous or Alum) used and important parameters of biological treatment. Unfortunately, no information have been presented in the present form of manuscript.

Additional process details have been provided.

IV. The activated sludge process temperature is one of the critical process parameter for the removal, solubility and conversion of the Phosphorous in any form. The relevant temperature range and its impact over treatment yield have not been presented.

We were not assessing the performance of the works *per se*, rather the speciation and stability of the P being discharged. It was therefore assumed that the works were being run sufficiently efficiently to meet their discharge consents. This point has been made in the manuscript.

V. Do the sampling at five consecutive time (nine days) is enough as a witness to reframe the present status of the UK's pollution regulations for P-removal, as well as the prominence of study at scientific platform.

Agreed – further studies are required to confirm the data provided here. This point is made in the conclusions.

VI. The kinetics of the Phosphorous existence may be beneficial for better scientific elucidation of the trends witnessed throughout the study. It is highly recommended to include the same.

The kinetics of P stability over a period of up to 9 days is provided.

VII. Author did not mentioned in clarity about the type of wastewater utilized and its characteristics, whether sanitary (high strength, low strength) or industrial.

Good point – wastewater characteristics provided.

VIII. It is highly recommended that to compare the present study trends with a probable treatment carried out for wastewater type (may be industrial) having no phosphorous (may be as literature).

As part of the literature review, other P speciation data was sought from the literature for other WwTW with or without P removal using metal salts, but no data could be obtained, this point is now made stronger in the text.

IX. The formation of biological Phosphorous is directly influenced with the change in MCRT or SRT (sludge retention time) of the activated sludge process. No relevant information have been presented for the MCRT of system during given duration of the study.

Yes this is a fair point, however, again the objectives of the research were to determine the speciation and chemical stability of P in the final effluents post a variety of treatment processes. A full assessment of within works processes was outside the scope of this study.

X. The type and dose of coagulant promotes a particular species of bacteria and also its capability and inhibition. In relevance to the present instance, a numerous number of studies have already been published, and prominently revealed the impact of Ferrous and Aluminium salts on microbiology (ASP or BAFF) of the wastewater treatment system. It is highly recommended that to utilize the same to draw the critical justification for existence and removal of Phosphorous in the present form of manuscript.

Yes, it is agreed that metal dosing can change the microbial community with the WwTW, however, investigating the literature, we cannot find any data regarding how this may impact on P removal (may of the papers published are related to load reduction or odour control. Furthermore the main focus of this research was not to assess the efficiency of P removal and mechanisms within the sewage treatment process, but to determine the P speciation in effluent and its stability. This point has been made more clear in the text.

Reviewer #3:

The Abstract does not address key points. The abstract should attract interests of scientists in this field and wide public. The reviewer suggests the author revising the abstract to make it have the research aims, methods, main results and importance.

Abstract now revised taking account of these points

For the METHODOLOGY part, it could be clearer to make a table for 'The five WwTW processes selected for sampling'.

Table provided

In the Result part, the "Figure 1. SRP for samples filtered on site and stored (4 o329 C) over a period of 9 days" is not clear, please use different shapes for different run, so readers could read it if it is printed black and white.

Different shape markers now provided

Reviewer #4:

1. Introduction. It is quite long, but very useful.

a. Maybe Table 1 and its discussion should be removed because it is not used elsewhere in the manuscript.

Text removed as suggested.

b. Lines 195-198: Please introduce better the manuscript content.

Text amended and made more clear.

2. Methodology. About WWTPs:

a. Why do you choose small plants? Because they are the major source of UK river pollution? Please explain it.

They were selected to ensure they received predominantly domestic sewage. This point is now made in the text.

b. Please describe with more details the WWTPs (e.g. retention time of filters; dosing of Fe-Al; source of raw sewage: urban only or mixed urban-industrial?). The features are useful for better explain the results.

c. Is WWTP A without final sedimentation?

More data now provided in the table as suggested above.

3. Results and discussion.

a. Why do you split them? Please merge them. In my opinion the results should be clearer and not dispersive.

Results and discussion combined and text tidied up.

4. Discussion and Conclusions

In my opinion, there are few data to affirm that Al is better than Fe for P removal. After Fe/Al addition, a filtration stage is always needed in order to remove the Al/Fe+P particles. Plant B (Al addition) has a type of final filtration which is not present in WWTP C and D (Fe addition). Comparing WWTP B (Al addition) and E (Fe addition) with a filtration final stage, P in the effluent is comparable. Therefore, I suggest you to modify the manuscript.

Fair point, text amended accordingly.

Lines 475-478: Where are the results which support such recommendations? Please modify the manuscript.

Text amended, although we feel the data provided supports the conclusions regarding sample filtration and storage. It was the point of the work in the first place.

Minor comments:

- Lines 105-108: please check the sentences;

Text amended

- Please check the units (e.g.: "l" or "L"? "mg/l" or "mg L⁻¹");

Consistently mg P/l now.

- Line 257: ICP-MS is not explained before;

Abbreviation explained

- Lines 235-262: In my opinion, the indentation of the section is not clear. Please try to improve it;

Better explanation provided.

- Figures: please improve them (e.g. remove the title inside the graph; improve x/y-axis labels).

Figures improved as suggested

Highlights

- Phosphorus forms in metal salt dosed sewage works effluent reported for first time
- Soluble reactive phosphorus in dosed effluents as low as 10% of total phosphorus
- Soluble reactive phosphorus stable in refrigerated samples for up to 9 days
- Future permitting of discharges should take account of phosphorus speciation

DETERMINATION OF THE FORMS AND STABILITY OF PHOSPHORUS IN WASTEWATER EFFLUENT FROM A VARIETY OF TREATMENT PROCESSES

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Abstract

Eutrophication of surface waters is a major issue across the planet, with diffuse (agricultural) and point sources (wastewater treatment works, WwTW) being the main inputs. In the UK WwTW effluent discharges are currently permitted for discharge based on total phosphorus concentration, whereas environmental quality standards (EQS) are set as soluble reactive phosphorus (SRP), which better reflects the bioavailable fraction of phosphorus present in water. This study reports for the first time, concentrations and relative proportions of SRP in effluent from a number of different WwTW employing aluminium and iron dosing for phosphorus removal. In the case of aluminium treatment, SRP constituted only 10 ±4% of the 0.75mg P/l total phosphorus in the effluent. Where iron was dosed SRP comprised 66% ±20% of the total phosphorus present where a single dose was applied, which dropped to 26 ±17% after a second dose and additional tertiary sand filtration. Phosphorus was determined using two established analytical methods after acid digestion, filtration to 0.45µm (on site and after return to the laboratory and refrigeration for up to 9 days) and settlement. Phosphorus speciation was shown to be stable within all effluents for up to 6 days storage at a temperature of <5°C without the need to filter on site and this was recommended for future effluent monitoring programmes and compliance assessment. Furthermore, because iron and aluminium dosing significantly reduce the SRP proportion in effluents, future monitoring programmes and policy decisions regarding meeting the phosphorus EQS derived as SRP should take this into account.

Key Words

Phosphorus, speciation, wastewater, effluent, soluble, reactive

1. INTRODUCTION

Inputs of phosphorus from wastewater treatment works (WwTW) and agricultural diffuse sources have led to significant contamination of much of the UK's and the planet's surface waters (Hogan, 2014). Across Europe, river basins are failing nutrient standards with typically more than half of all waterbodies not meeting the standards set as soluble reactive phosphorus (SRP), the immediately bioavailable fraction of phosphorus (EEB, 2010). For the UK for example, assessments under the Water Framework Directive (WFD) have estimated that only 53% of waterbodies are compliant with the new site specific Environmental Quality Standards (EQS) designed to provide conditions suitable to support good ecological status for diatoms and macrophytes (WFD, 2013). Phosphorus present in many forms in sewage (Houhou et al., 2009) can become bioavailable during wastewater treatment processes to the extent that the majority discharged into receiving waters is measured as SRP and considered bioavailable to aquatic plants (Millier and Hooda, 2011). Several EU Directives have set out to decrease concentrations of phosphorus in EU rivers, including the Urban Wastewater Treatment Directive (UWwTD, EU, 1991), Birds and Habitats Directive (EU, 1992) and Water Framework Directive (WFD, 2000). Diffuse agriculture sources of phosphorus have been reduced via measures funded under agricultural countryside stewardship schemes (Defra, 2015). For point source WwTW effluents, measures are available and have been implemented for reducing phosphorus loads to waterbodies through chemical dosing using iron or aluminium salts (Omoike and van Loon, 1999). Currently across the EU a population of 187 million is served by WwTW reducing phosphorus concentrations under the Urban Wastewater Treatment Directive (UWwTD, EU, 1991), approximately 37% of the entire population (EEA, 2015). In the UK there is phosphorus reduction at almost 700 WwTW treating a total population of approximately 24 million people. In the UK alone, over £10bn has been invested in wastewater treatment between 1990 and 2005 (Defra 2002), however, there is still widespread non compliance with WFD EQS and few measureable improvements in ecological status (UKWIR, 2012). The UK has now starting a new cycle of investment (2015-2020) which will include treatment at yet further WwTW, as well as investigations to achieve effluent phosphorus levels of less than 1 mg-P/l as total P, the currently accepted Best Available Technique for chemical dosing (EA, 2012). Whether or not this additional treatment is likely to result in widespread compliance is uncertain.

Interpreting the fate and compliance of phosphorus in the aquatic environment is complicated by the fact that different Directives have set differing criteria for phosphorus standards and permits, for example:

- **WFD EQS** (WFD, 2013) is set as **soluble reactive phosphorus**, samples are filtered (0.45µm) followed by molybdenum blue colorimetric determination(Murphy and Riley, 1962).
- **Habitats Directive** standards are set as **total reactive phosphorus**, on unfiltered sample determined by molybdenum blue colorimetric determination(Murphy and Riley, 1962).
- **UWWTD** permits for WwTW effluents discharged to rivers are set as **total phosphorus**, determined by Inductively Couple Plasma (ICP) on unfiltered sample using acid digestion (Jarvie et al., 2002).

There may be a number of reasons why different forms of phosphorus have been determined, ranging from application of the precautionary principle, assuming that eventually particulate bound phosphorus may become bioavailable once discharged into the aquatic environment; through to the convenience of using colorimetric analysis of unfiltered samples. However, understanding the form of phosphorus in effluents (particularly SRP) and receiving waters and using an appropriate analytical technique not only allows the application of sound science to environmental regulation, but can also avoid excessive conservatism in standard setting leading to the implementation of expensive technologies which deliver little or no environmental benefit.

The situation is further complicated by previous definitions used and analytical procedures implemented to monitor phosphorus in the aquatic environment. The forms of phosphorus considered to be of particular environmental/ecological relevance are referred to in current UK technical recommendations for the implementation of the Water Framework Directive (WFD, 2013) and UK government river basin planning guidance (Defra, 2014) as “reactive phosphorus” (RP). This was previously and more commonly in the scientific literature described using the term “soluble reactive phosphorus” (SRP). Both these authoritative

reports contain the following statements relating to the definition of relevant phosphorus species:

- a) *“Reactive phosphorus” means the concentration of phosphorus as determined using the phosphomolybdenum blue colorimetric method. Where necessary to ensure the accuracy of the method, samples are recommended to be filtered using a filter not smaller than 0.45 µm pore size to remove gross particulate matter.*
- b) *Previous UKTAG standards were referred to as soluble reactive phosphorus (SRP). Most analyses by UK agencies are of molybdate reactive phosphorus in unfiltered samples from which large particles have been allowed to settle and referred to here as “reactive phosphorus” (RP). In practice, the difference between RP and SRP is usually minor”.*

Statement (a) prompts the question *“when might it be necessary to filter to ensure the accuracy of the method”*? The answer obviously is “always”, otherwise how is it possible to decide whether or not accuracy is compromised? The truth of the first sentence of statement (b) was confirmed by a review of the existing methodology (referred to as “orthophosphate”) used by thirteen laboratories involved in the analysis of surface waters and sewage effluents. Responses to inquiries regarding methodology were in general agreement, indicating that samples were not filtered, with several respondents mentioning that “dirty” samples were allowed to settle before analysis. The statement in (b) that *“In practice, the difference between RP and SRP is usually minor”* is shown by this research to be incorrect.

This raises important questions concerning inadequacies in the specification of the analytical methodology for reactive phosphorus, specifically with respect to sample pre-treatment. It is worth noting that the analytical method (based on the method of Murphy and Riley (1962), updated as a Standard Method, (SCA, 1992) for reactive phosphorus involves sulphuric acid based reagents that have the potential to extract phosphorus from particulate matter if this is present in the sample of interest. The vaguely defined procedure used in the past is therefore likely to result in the (unwelcome) inclusion of a variable proportion of particulate phosphorus in the “reactive forms”, depending on:

- the type of particulate matter present, its phosphorus content and the lability of such phosphorus forms to acid dissolution; all widely variable between say sewage effluent and river water and between different rivers (Haygarth, 1997; Hens and Mercx, 2002);
- the propensity for particles to settle (not known but variable);
- the settlement time allowed (not defined);
- the strengths of the reagents used, which are not necessarily the same in different laboratories((Jarvie *et al.*, 2002) and the different analytical techniques applied (e.g. manual, flow injection, auto- or discrete- analysers).

It may be concluded that the historic determination of reactive phosphorus might be considered imprecise and with unknown and inconsistent accuracy. Basing consenting policy and potentially substantial investment on analytical data of unknown and variable reliability is not sound or credible science.

There have been previously reported numerous studies into (i) the form and fate of phosphorus in the aquatic environment (McKelvie *et al.*, 1995; Jarvie *et al.*, 1998; Neal *et al.*, 2000; Palmer-Felgate *et al.*, 2008), (ii) catchment modelling of phosphorus concentrations (Neal *et al.*, 2010) and (iii) ecological impacts (Stutter *et al.*, 2010). Data are available that show WwTW not dosing for phosphorus reduction discharge mostly SRP (Millier and Hooda, 2011). There are, however, no readily available data for phosphorus speciation, and in particular SRP concentrations, in WwTW effluents dosing iron or aluminium salts for phosphorus reduction.

The work reported in this paper was prompted by two factors. Firstly, ecologically relevant forms of phosphorus for a number of reasons were not being determined sufficiently rigorously in UK wastewaters discharged to surface waters. Secondly, this was likely to have serious consequences to the framing of measures under the EU Water Framework Directive (WFD) (EC, 2000) to control concentrations of phosphorus in surface water. Given that such measures have the potential to prompt multi-million pound investments in the implementation of new treatment technologies, it is essential that they are based on a reliable monitoring data. The pending launch of a major series of UK investigations into phosphorus

concentrations in effluents (*The National Phosphorus Trials*) also required the identification of a robust methodology.

The aim of this study was to establish a suitable methodology for sample filtration and storage to preserve phosphorus speciation in WwTW effluents using a variety of treatment processes, including with and without aluminium or iron dosing for phosphorus reduction. At the same time, data is presented on the forms of phosphorus in effluents for the first time. It should be noted that wastewater treatment processes are complex and subject to numerous microbiological and physico-chemical factors which impact on removal rates and speciation of chemicals present, including phosphorus. The data presented here focus on the speciation and stability of phosphorus in the final effluent discharged to the receiving waters **after** a variety of treatment processes, from a regulatory point of view..

METHODOLOGY

Details of the five WwTW processes selected for sampling are provided in Table 1. Works receiving predominantly domestic wastewater were chosen to avoid complicating factors associated with any industrial effluent entering the sewerage system.

Table 1 Details of the selected WwTW treatment processes

	Works A	Works B	Works C	Works D	Works E
Estimated population	10,000	12,000	13,000	6,000	6,000
Preliminary treatment	Inlet screens & grit removal	Inlet screens & grit removal	Inlet screens & grit removal	Inlet screens & grit removal	Inlet screens & grit removal
Primary treatment	Primary settlement	Primary settlement (2 tanks)	Primary settlement	Primary settlement (4 tanks)	Primary settlement
Secondary treatment	Activated sludge	Trickling filters (4)	Activated sludge (oxidation ditch)	Trickling filters (4)	Trickling filters (4)
Final settlement	Humus tank	Humus tank (4)	Humus tank	Humus tank	Humus tank
Tertiary treatment	None	Nitrifying filter, biological aerated flooded filter (BAFF), UV treatment	None	None	Fluidised bed sand filters (3)
Dosing for P removal?	No	Polyaluminium chloride (Brenntag) into the nitrifying filter dosed at a 2:1 Al:P stoichiometry	Iron (II) sulphate added after screening at a 2:1 Fe:P stoichiometry	Iron (II) sulphate added after screening at a 2:1 Fe:P stoichiometry	Iron (II) sulphate added after screening and before sand filters at a 2:1 Fe:P stoichiometry

Samples were collected on five occasions between September and November 2014. Samples were collected using acid washed (5% hydrochloric acid) 1 litre capacity spot samples and stored in 1.5 litre acid washed (5% hydrochloric acid) polyethylene terephthalate (PET) bottles. Four replicate determinations for the different forms of phosphorus at time = 0, 1, 3, 6 and 9 days. Time =0 day samples were determined on site using the same colorimetric method, utilising a Jenway6051 portable colorimeter at a wavelength of 710nm using a 4cm pathlength cuvette. All samples were stored in a cool box on site and subsequently under refrigeration at 3-5 °C, before being brought to room temperature immediately prior to analysis. All filtration was undertaken using disposable 25mm diameter 0.45µm cellulose

acetate membranes supplied by Cole Parmer Ltd. Filter blanks used for each batch of analysis showed no significant contamination with phosphorus.

2.1 Sample pre-treatment

A number of different types of sample manipulation were carried out to establish the form of phosphorus present in the different types of WwTW effluent, to either replicate the methods currently used for compliance assessment, or to investigate sample stability over a 9 day period:

- **Soluble Reactive Phosphorus (SRP)** - used here to denote a determination made on a 0.45 µm filtered sample using the molybdenum blue colorimetric procedure based on SCA Method A(SCA, 1992) implemented in a batch-wise (15ml scale) manual process. This was designed to demonstrate adequate sample stability, consistency of results and to act as a reference point for other determinations and other phosphorus forms.
- **Unfiltered SRP(uf SRP)fully mixed sample** was determined in order to demonstrate the consequences of not filtering samples and to establish how the distribution of particulate and soluble reactive forms might change over time, for different storage periods. This is an analogue of TRP as specified under the Habitats Directive.
- **Refiltered SRP** was determined in order to make sure that once filtered there was no further precipitation of particulate phosphorus during storage, which might have consequences for the operation and usefulness of tertiary filtration processes.
- **Unfiltered settled SRP** was determined in order to illustrate that orthophosphate (historically used for monitoring water quality and WwTWUWwTD compliance) might not be relevant for either of the key regulated forms of phosphorus: total phosphorus and SRP.
- **Filtered laboratorySRP** was determined as a check on the need to filter on-site (filtration on site is an onerous requirement that it would be practically advantageous to avoid, provided there was clear evidence that it was not essential).

Total phosphorus using ICP-MS

- **Total Phosphorus (TP)** is the benchmark for all phosphorus forms and offers a total concentration.

- **Total soluble phosphorus (TSP)** was determined by digesting and determining by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) on filtered samples. This provided a check on the extent to which SRP determines all soluble forms.

2.2 Analytical methodology

2.2.1 Molybdenum blue colorimetric method

The method based on the established Murphy and Riley (1962) approach used the following reagents which were of analytical laboratory grade or higher: Sulphuric acid (25% of concentrated acid in high purity water, $>18\text{ M}\Omega/\text{cm}$), ascorbic acid (10g dissolved in 50ml high purity water plus 50ml 25% sulphuric acid solution). This was stored in an amber lab glass bottle in refrigerator and was stable for at least a week and can be used as long as it remains colourless.

A mixed reagent was prepared as follows: 12.5g ammonium heptamolybdate tetrahydrate, was dissolved in 125ml high purity water. 0.5g potassium antimony tartrate, was dissolved in 20ml high purity water. The molybdate solution was added to 350ml 25% sulphuric acid solution, stirring continuously, followed by the tartrate solution and mixed well. Stored in a borosilicate glass bottle the reagent was stable for several months.

For phosphorus determination, 0.25 ml ascorbic acid was added to 12.5ml sample in HCl washed (5%) 15ml centrifuge tubes (Fisher Scientific, UK) followed by 0.25ml mixed reagent to the solution. Colour was allowed to develop for 10 minutes, followed by measurement within 30 minutes at 710nm in a 1cm acrylic disposable cuvette, using a Cecil 2021 colorimeter.

Limit of detection (LOD) was estimated from 6 replicates of blank determinations and calculated as 3 times the standard deviation of the blank using a 1cm cell. To ensure data quality the following procedures were carried out:

- 1) Blanks for each batch of analysis
- 2) Filter blanks for each batch of filtrations
- 3) External reference material to be included in each batch of analysis: EnviroMAT EP-L-3 drinking water, low level concentrate (QMX Ltd).
- 4) Control chart constructed for duration of the studies.

2.2.2 Total P

Total phosphorus was determined by adding concentrated hydrochloric acid (to a concentration of 10% (e.g. 1.25ml concentrated HCl –Romil-Spa super purity acid, Fisher, Scientific, UK + 12.5ml sample) into acid washed (5% HCl) 15ml centrifuge tubes (Fisher Scientific UK) and heated to 90°C for 3 hours until all particulates were digested. Total phosphorus determinations were made using a Thermo Scientific X Series 2 Inductively Coupled Plasma-Mass Spectrometer in collision cell mode.

Overall analytical performance data are provided in Table 2.

Table 2. SRP and total soluble phosphorus analytical performance data

	Unit (mgP/l)			
	Within batch sd ¹	Between batch sd ¹	Total sd ¹	Limit of detection
Molybdenum Blue method (SRP)				
Sd¹	0.021	0.014	0.025	0.03
DoF²	12	12	38	12
rsd%	4.2	2.7	5.0	
ICP-MS (TP)				
Sd¹	0.023	0.033	0.040	0.01
DoF²	12	12	15	12
rsd%	4.6	6.6	8.0	

¹sd = standard deviation; ²DoF = degrees of freedom

3. RESULTS AND DISCUSSION

Data for the different processes are shown separately. The five different sampling occasions at each works are termed “runs”. It should be noted that for different runs the effluent concentrations were different (they were different samples) so these differences do not show anything other than acting as indications of the variability of phosphorus concentrations at the works concerned at the time of sampling. Figure 1 shows the stability of SRP in solution, after filtering the sample on site and then refrigerating for up to a period of 9 days. No statistical differences in measured concentrations were observed across the storage period.

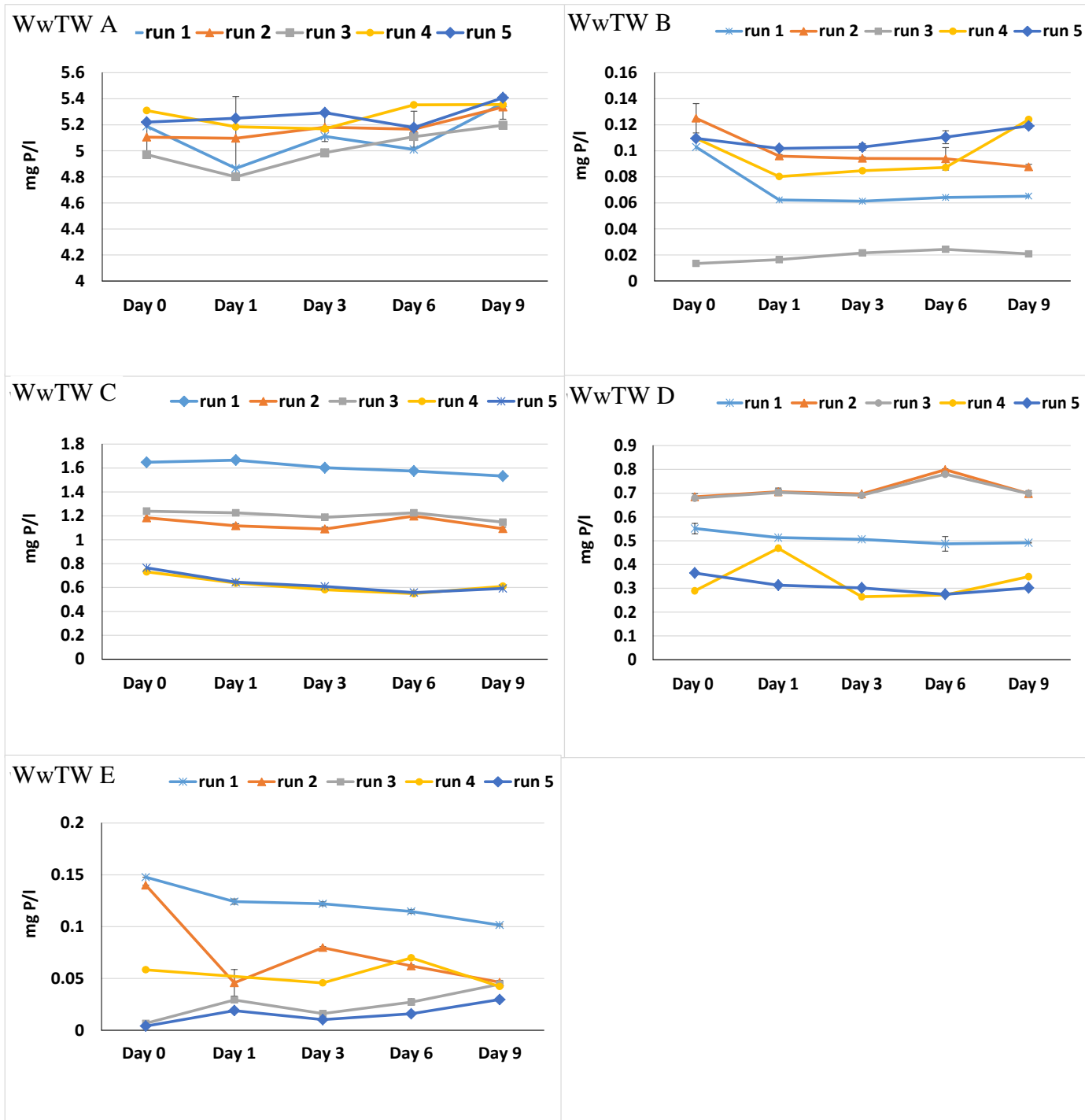


Figure 1. SRP for samples filtered on site then stored (4 °C) over a period of 9 days

Figure 2 shows the mean sample stability over the course of 9 days for samples collected from the WwTW unfiltered then refrigerated at 4 °C for 1, 3, 6 and 9 days before filtration followed by SRP determination. The data show that SRP is sufficiently stable not to require filtration on site; any observed changes in SRP concentration were statistically

insignificant based on the techniques used ($<0.03\text{mg P/l}$ at concentrations less than 0.5mg P/l or $<5\text{-}10\%$ variance at higher observed concentrations).

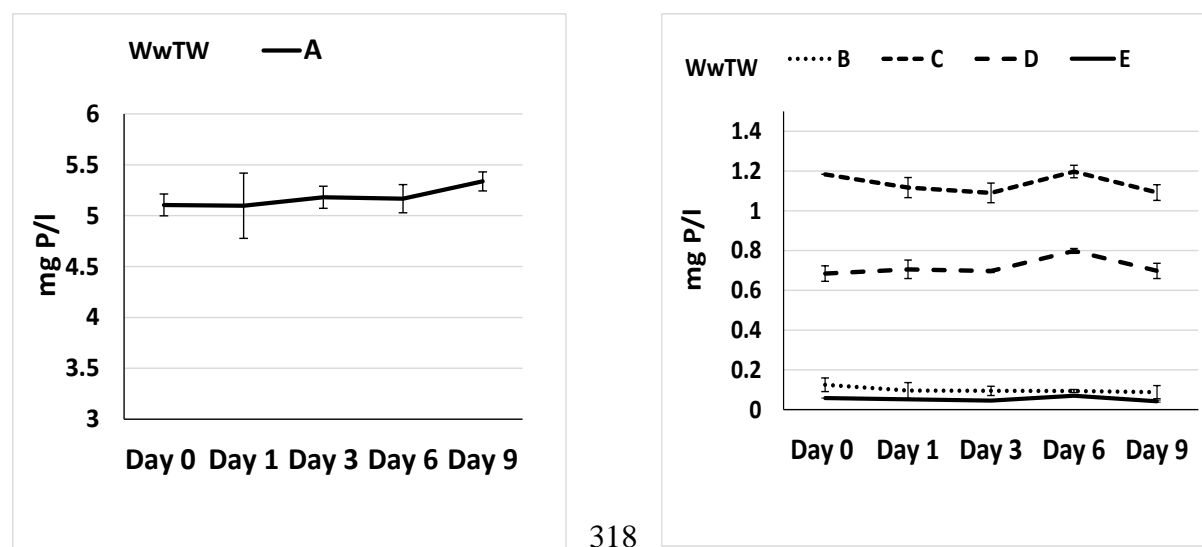


Figure 2. SRP concentrations for samples collected unfiltered then refrigerated for up to 9 days prior to filtration and analysis

Table 3 provides a comparison of proportion of phosphorus present in the effluents in the different forms. WwTW A, the undosed works unsurprisingly has the highest total phosphorus concentration of over 5mgP/l , with 96% present as SRP. The aluminium dosed WwTW B had a mean TP of 0.81mgP/l significantly below its 2mgP/l permit value, with only 10% of the phosphorus present as SRP. Total soluble phosphorus (TSP), i.e. phosphorus filtered through $0.45\text{ }\mu\text{m}$ and determined via acid digestion ICP-MS comprised 34% of the TP, suggesting filterable colloidal material is detectable by ICP-MS but not molybdenum blue 'reactive'. The iron dosed effluents lie somewhere between these extreme values. WwTW C where Fe was dosed prior to primary treatment with secondary oxidation ditch treatment had low concentrations of TP (1.2mgP/l) but 84% was present as SRP (which was not statistically significantly different from TP) and therefore accounted for all of the filterable phosphorus.

WwTW D which was a biofiltration plant receiving iron dosing prior to primary settlement had slightly lower TP concentrations of 0.79mgP/l , 66% of which was SRP, which again

comprised all of the filterable P. WwTW E was another biofiltration plant, but received 2
doses of iron, once before primary treatment and once again prior to filtration through a
fluidised bed sand filter. TP concentrations in the effluent were very low (0.22mgP/l) and
SRP was only 26% of the TP concentration. Similar to the Al dosing works TSP was higher
at 49% suggesting that there is filterable phosphorus present in the effluent that is not
reactive.

Table 3. SRP and total soluble phosphorus (TSP) versus total phosphorus

WwTW	TP (mg P/l)	% of TP			
		SRP (%)	±%	TSP (%)	±%
A	5.5	96	2	94	1
B	0.81	10	4	34	13
C	1.2	84	26	90	6
D	0.79	66	20	67	12
E	0.22	26	17	49	16

± Values are confidence intervals (p=0.1) on between day average estimates

Figure 3 shows the P speciation graphically and highlights the loss of SRP in the aluminium dosed and iron ‘double dosed’ effluent with associated error bars representing variation about the mean for the sample replicates.

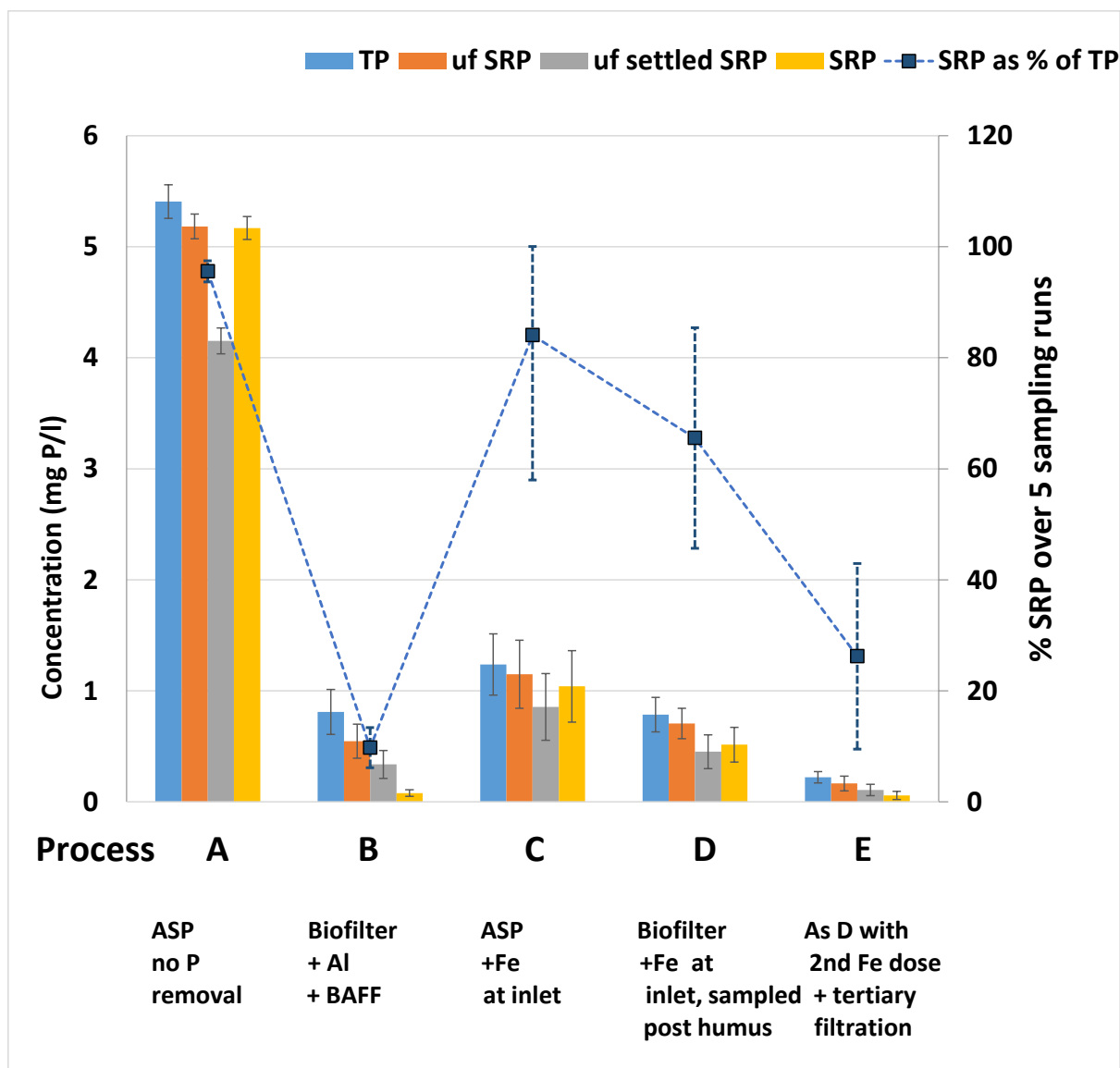


Figure 3. Overall summary of concentrations and species for the different treatment processes (with 90 percentile error bars)

The influence of chemical dosing is shown to be potentially important to the form of phosphorus discharged and its likely environmental impact in the receiving water. Without chemical dosing, the total phosphorus concentration in the effluent tested was of the order of 5mg P/l. This is consistent with previous values obtained for WwTW effluents (e.g. Gardner et al., 2012). Phosphorus discharged consisted almost entirely (85-95%) of SRP. Other undosed WwTWs might have different discharge concentrations, but there is no reason to believe that the proportion present as SRP should differ greatly, unless there are non-domestic sources or other significant contaminants present. At the works employing aluminium dosing the effluent SRP concentration, determined over several days, was between 0.02 and 0.12mg P/l (though overall nearer to the upper part of this range). Total

phosphorus concentrations were in the range 0.3 to 0.6mg P/l. Apportionment of forms as a percentage of this total value were: of SRP 65-75%, of settled SRP 45-55% and SRP 9-12%.

A clear conclusion can be drawn here showing that dosing with iron or aluminium at WwTW employing a number of post-secondary treatments (nitrifying filters and BAFF in the case of WwTW B and tertiary sand filters in the case of WwTW E) reduces the total phosphorus concentration by a factor of 10 to 20, compared with an undosed works, which is not unexpected based on the chemistry involved (Galarneau and Gehr, 1997). Furthermore, dosing significantly reduces the proportion of SRP in the effluent, even as a fraction of the much diminished total, by 80-90% (assuming a non-dosed concentration of approximately 5mgP/l). Both these conclusions are subject to the caveat that these findings relate only to this one WwTW (and therefore will need to be confirmed).

The overall proportion of the key P species present in the effluent from an ecological impact point of view, namely SRP is provided in Figure 4.

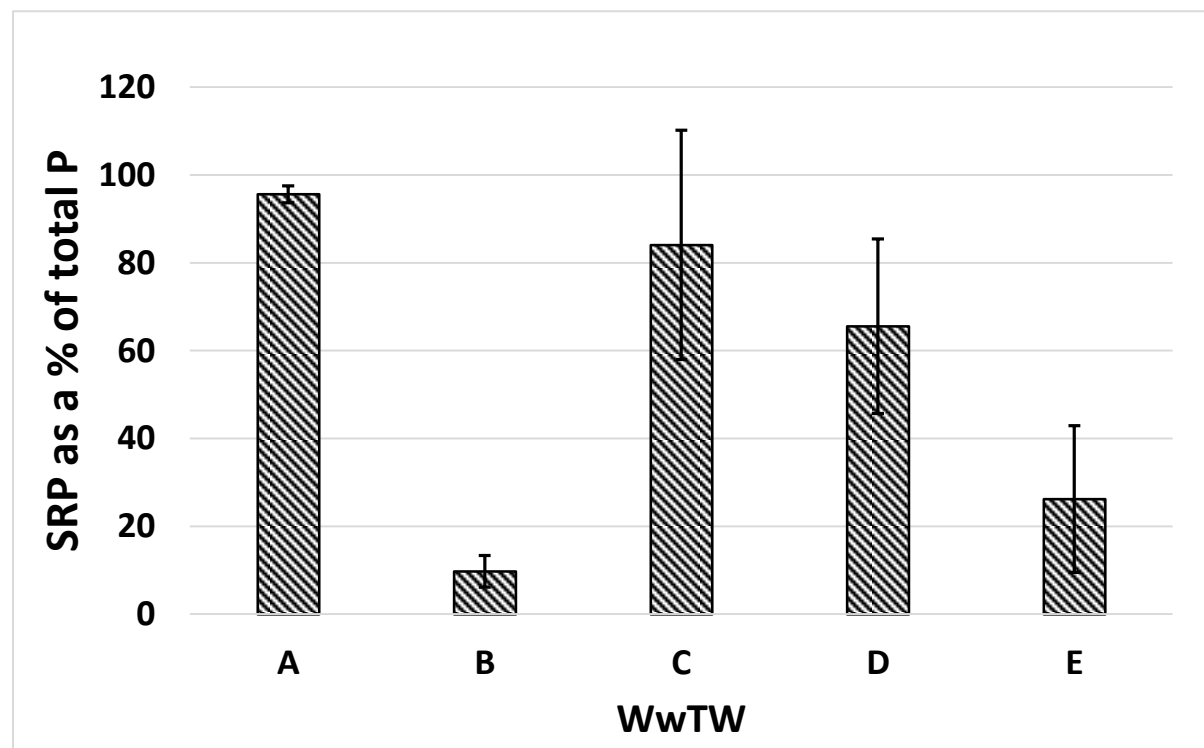


Figure 4. Mean percentage present as SRP (error bars show 90% confidence interval on the mean value)

Results from the iron dosed treatment processes (WwTW C, D and E) suggest that whilst iron does indeed reduce the concentrations of total phosphorus and SRP from a notional 5-6 mg P/l to approximately 1 mg P/l or lower, the fraction of total phosphorus present as SRP in the final effluent is not definitively lower. For the ASP process (WwTWC) there was no significant difference between average SRP and TP concentrations; for the iron dosed biofilter the difference was larger but barely significant. However, for the double iron dosed tertiary filtered biofilter effluent the reduction in SRP was significant (SRP $26 \pm 17\%$ of TP) but not as dramatic as that achieved by aluminium dosing. WwTW E did, however, exhibit the lowest TP and SRP concentrations of all of the WwTW sampled. The within WwTW processes impacting on phosphorus solubility, across primary, secondary and tertiary treatment will all effect final effluent quality and require further investigation. However, the focus of this research was on the effluent phosphorus speciation and how it relates to sample treatment and regulation.

It is interesting to note that the tertiary filtration stage for WwTW E achieved a reduction from 0.7 to 0.2mg P/l, a reduction in SRP of a similar amount and a reduction in the proportion as SRP from $66 \pm 20\%$ to $26 \pm 17\%$. It appears therefore that the effect of the further dosing and filtration stage is to remove a further 0.5mgP/l of SRP from the effluent. Hence further precipitation of SRP (and concurrent removal) appears to be occurring during tertiary sand filtration. This tertiary treatment stage therefore serves two purposes; it allows sufficient time for the dosed iron to react with residual SRP and then it removes the resulting particulate phosphorus. This is a potentially important observation. Tertiary filters appear not only allow more time for chemical reaction in the liquid phase, it is likely that under certain conditions chemical dosing can change the surface properties of the media, promoting further chemical adsorption of SRP. The degree of this mechanism may be influenced by the surface composition and properties of the media as well as properties of coagulant intermediate products as they reach the filter bed. The latter will be affected by dosing point, mixing and chemical property of the wastewater such as alkalinity and pH value (Xu et al., 2015). As noted above in relation to aluminium these findings require further confirmation before they can be accepted as more general phenomena.

Previous findings for phosphorus removal mechanisms during wastewater treatment (Wu et al., 2015) have shown that for iron dosing, the split between the reaction to form mineral iron phosphate and coprecipitation onto iron oxyhydroxide minerals was about 50:50 and

accounted for 90% of the phosphorus speciation in material collected from a membrane bioreactor. There are little data available to compare the fraction of SRP in WwTW effluents. Previous unpublished Environment Agency monitoring data at a limited number of sites have suggested that the percentage of phosphorus present as SRP in iron dosed WwTW was also low at around 16% (Comber et al., 2009) and the US Water Environment Research Foundation (WERF) have reported low SRP ($\mu\text{gP/l}$ range) concentrations in dosed effluent (WERF, 2014).

With respect to historical methodology, the practical value of unfiltered / settled unfiltered SRP is therefore highly questionable since it is not a reliable estimate of the two measures (TP, SRP) of phosphorus concentrations that form the basis of current regulation. It can only be assumed that at an earlier time when metal dosing of wastewaters was not widespread (and when in effluents SRP and TP were close in concentration) unfiltered so-called orthophosphate was a sufficiently accurate measure to meet monitoring requirements. This is emphatically no longer the case and the convenience of not filtering a sample is no longer an acceptable compromise.

Consequently for future planning of measures to improve ecological quality within river systems, it is essential to take account of the speciation of phosphorus present in the water column, and in particular the most readily bioavailable form namely, SRP. Furthermore when modelling the possible outcome of applying iron or aluminium dosing for phosphorus reduction during the wastewater treatment process, SRP should be the phosphorus form used to ensure consistency with the water quality objectives set for receiving waters (Bowes et al., 2010). Regulators across the developed world need to plan effective policy for phosphorus management, which will require monitoring and modelling in order to assess the consistency between striking the correct balance between point and diffuse sources of phosphorus to ensure compliance and adherence to the 'polluter pays' principle (Neal et al., 2005, 2008; Jarvie et al., 2006).

5. CONCLUSIONS

The data generated from this research leads to a number of key conclusions regarding the monitoring, compliance assessment and possible future consenting of phosphorus discharged from WwTW:

- 1) In order to generate data that are consistent and comparable between different sources, determination of SRP should always involve sample filtration to 0.45 µm. The results presented here provide confidence that the phosphorus speciation within an effluent sample is stable for up to 6 days storage at a temperature of <5°C.
- 2) Data for phosphorus in effluents described as “orthophosphate” should be treated with caution because they may or may not reflect the phosphorus forms of interest. The difference between orthophosphate concentration and SRP might be as large as 80% of the value of the former. Orthophosphate, whilst still being of potential value in operational monitoring (e.g. examining trends or changes in operational performance), is therefore not considered a reliable metric in any regulatory context.
- 3) Dosing with aluminium or iron was found to reduce the total phosphorus concentration in effluents by a factor of 5 to 10 fold, with additional tertiary treatment such as nitrifying filters, BAFFs and sand filtration serving to further reduce concentrations of TP and SRP in WwTW effluents (to less than 10% of TP), compared with straightforward secondary biological treatment coupled with metal salt dosing. Further trials are required to support these preliminary data, however, if confirmed, these marked differences between the forms of phosphorus present in effluents applying different treatment processes need to be taken into account when planning future effluent permitting policy.

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