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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 $10 \pm 4\%$ of the 0.75 mg 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 μm (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.

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 [1]. 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 [2]. For the UK for example, assessments under the Water Framework Directive (WFD) [3] 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 [4]. Phosphorus present in many forms in sewage [5] 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 [6]. Several EU Directives have set out to decrease concentrations of phosphorus in EU rivers, including the Urban Wastewater Treatment Directive (UWwTD, [7], Birds and Habitats Directive [8] and Water Framework Directive WFD, 2000. Diffuse agriculture sources of phosphorus have been reduced via measures funded under agricultural countryside stewardship schemes [9]. 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 [10]. Currently across the EU a population of 187 million is served by WwTW reducing phosphorus concentrations under the Urban Wastewater Treatment Directive (UWwTD, [7], approximately 37% of the entire population [11]. 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 [12], however, there is still widespread non compliance with WFD EQS and few measurable improvements in ecological status [13]. The UK has now starting a

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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 [14]. 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 [4] is set as **soluble reactive phosphorus**, samples are filtered (0.45 μm) followed by molybdenum blue colorimetric determination [15].
- **Habitats Directive** standards are set as **total reactive phosphorus**, on unfiltered sample determined by molybdenum blue colorimetric determination [15].
- **UWwTD** permits for WwTW effluents discharged to rivers are set as **total phosphorus**, determined by Inductively Couple Plasma (ICP) d on unfiltered sample using acid digestion [16].

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 [4] and UK government river basin planning guidance [17] 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 [15], updated as a Standard Method, [18] 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 [19,20];
- 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 ([21] 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 [22–25], (ii) catchment modelling of phosphorus concentrations [26] and (iii) ecological impacts [27]. Data are available that show WwTW not dosing for phosphorus reduction discharge mostly SRP [6]. 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