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Characterisation of phosphorous forms in wastewater treatment plants

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Abstract

The removal of different forms of phosphorous (namely total phosphorous, soluble phosphorous, particulate phosphorous and total phosphate) has been studied in two municipal wastewater treatment plants (WWTP) with different characteristics, but without any specific implemented strategy for phosphorous removal.

The results obtained for the different forms of phosphorous can be summarised as follows: (1) complete removal of particulate phosphorous is achieved in either primary or secondary clarifiers; (2) total phosphorous concentration in the effluent is mostly soluble phosphorous and this is mainly phosphate; (3) a small amount of soluble phosphorous is removed by biomass growth and/or biosorption; (4) both WWTPs presented a high-buffered behaviour in response to high inlet loading of phosphorous, showing a constant pattern at the outlet of the WWTP; (5) removal of total phosphorous was approximately 60–70% for both WWTPs; and (6) recirculation streams such as supernatant from centrifuge sludge dehydration operation can have a significant contribution to the inlet amount of phosphorous.

The results presented in this paper provide a basis to develop prospects for phosphorous removal, which may be adapted to the particular configurations of the WWTP studied.

Keywords: Phosphate; Phosphorous forms; Phosphorous removal; Wastewater treatment plant; Clarifier

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1. Introduction

Removal of phosphorous from municipal and industrial wastewater is a crucial aspect in limiting the water pollution problem of eutrophication, which can result in an excessive growth of photosynthesising organisms, and therefore unbalancing the natural water ecosystems [1,2].

A number of different policy initiatives have been initiated to overcome this problem. In Europe, the most important initiative is the urban wastewater treatment Directive 91/271 [3]. The limit values of phosphorous are 2 mg/l in agglomerations of between 10,000 and 100,000 population equivalent and 1 mg/l in larger agglomerations. According to this Directive, many municipal wastewater treatment plants (WWTP) are required to remove phosphorous, although the level of implementation of the measures for correction of phosphorous concentration at the output of WWTPs is significantly different in the Member States. The situation in Spain is described as 'a major effort is required in order to achieve compliance with the obligations and periods established by the urban wastewater treatment Directive' [4]. In practice, most of the WWTPs located in Spain are in an early phase of implementation of nitrogen and phosphorous control.

Phosphorous removal can be accomplished either biologically or chemically. Chemical removal is achieved through the use of common products such as alum ($Al_2(SO_4)_3\cdot 14H_2O$), ferric iron salts ($FeCl_3\cdot 6H_2O$), ferrous iron salts (e.g. $FeCl_2$, $FeSO_4\cdot 7H_2O$) or lime [5–7]. For instance, modelling of phosphorous removal from wastewater using ferric iron has been achieved using a set of 14 chemical reactions [5]. Also, spent alum has been used for the phosphate removal [6]. After chemical addition and mixing, phosphorous compounds are removed by either sedimentation or flocculation.

Biological phosphorus removal from wastewater is based on the activity of phosphorous-accumulating organisms (PAOs), which are characterised by two different metabolisms: (1) anaerobic phase: accumulation of readily biodegradable carbon substrates and the hydrolysis of intracellular polyphosphate which is released in the bulk liquid in form of orthophosphate; and (2) aerobic phase: phosphate accumulation in form of intracellular polyphosphate using readily biodegradable carbon substrates (intracellular carbon accumulated in anaerobic phase if there is no carbon available in liquid phase) as an energy source. In the aerobic phase, PAOs take up more phosphate than that released in the anaerobic phase, resulting in a net phosphorous uptake [8–10]. Recently, a metabolic modelling of full-scale biological phosphorous removing WWTPs has been published [11].

In addition, some investigations have demonstrated that biological and chemical removal of phosphorous can take place simultaneously. For example, Cloete and Oosthuizen [12] showed how the extracellular polymers found in activated sludge can act as phosphorous reservoirs whereas Witt et al. [13] and Maurer et al. [14] studied the interactions between biological and physico-chemical mechanisms in biological phosphate elimination.

This work presents the results obtained in a study of the different forms of phosphorous in two WWTPs without any specific phosphorous treatment. This is the most common situation in Spain. Our purpose was to establish a starting point in order to implement future specific phosphorous removal technologies, which will be based on chemical and/or biological processes.

2. Materials and methods

2.1. Sampling

Samples (1 l) were taken from the WWTPs during the period from 3 to 16 July 2001, covering 2 weeks of operation. In the case of the Vilanova del Vallès WWTP, samples were taken daily from the influent and the effluent of the plant (except on the first weekend, days 7 and 8 of July) and on days 3, 5, 6, 10, 11 and 16 from the supernatant of sludge centrifugation recirculated to the plant inlet (days on which centrifugation was carried out). In the case of the La Llagosta WWTP, samples were taken daily from the influent and the effluent of the plant and from the outlet of the primary clarifier and on days 3, 6, 10–13 and 16 from the supernatant of sludge centrifugation recirculated to plant inlet (days on which centrifugation was carried out).

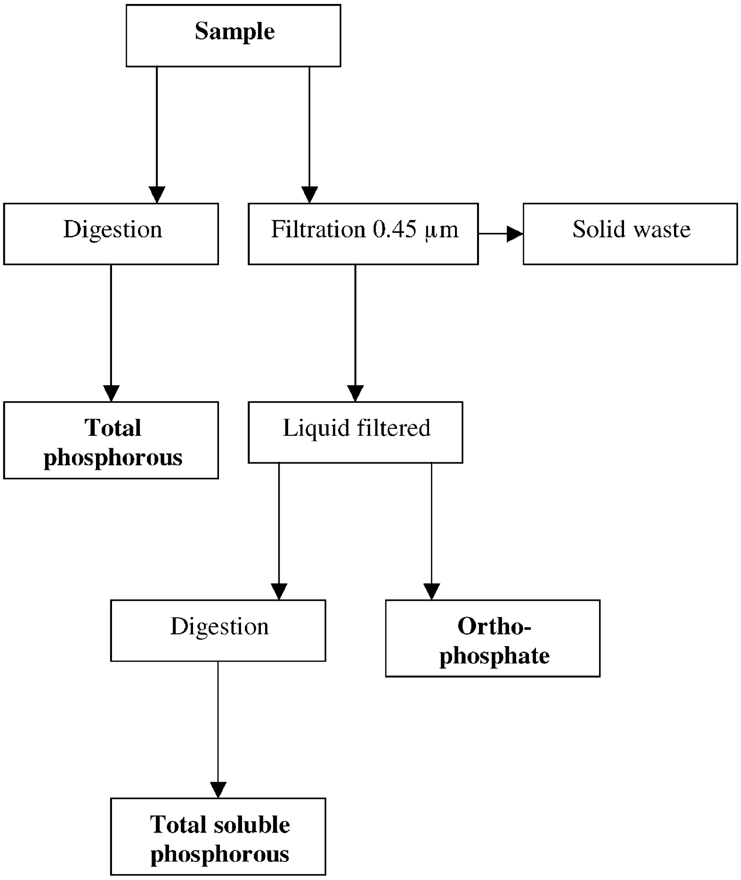

Fig. 1. Scheme of the analytical protocol used in the determination of phosphorous forms.

Table 1
Main characteristics of the two WWTPs studied

Parameter	La Llagosta	Vilanova del Vallès
Design flow (m^3 per day)	43,000	5000
Working flow (m^3 per day)	43,000	3000
BOD removal (%)	92	95
Nitrogen removal (%)	–	62
Type of biological reactor	Continuous stirred tank	Plug-flow
Hydraulic retention time (h)	8	24
Primary sedimentation	Yes	No
Anaerobic sludge digestion	Yes	No
Number of industrial wastewater discharges	Large (8000)	Reduced (90)

2.2. Phosphorous analysis

Total phosphorous, soluble phosphorous and total phosphate were determined according to Standard Methods [15], whereas particulate phosphorous concentration was calculated as the difference between total and soluble phosphorous. A scheme of the protocol used in the analytical determination of phosphorous forms can be seen in Fig. 1. All the analyses were performed in duplicate, and the results are presented as an average. Briefly, the method is

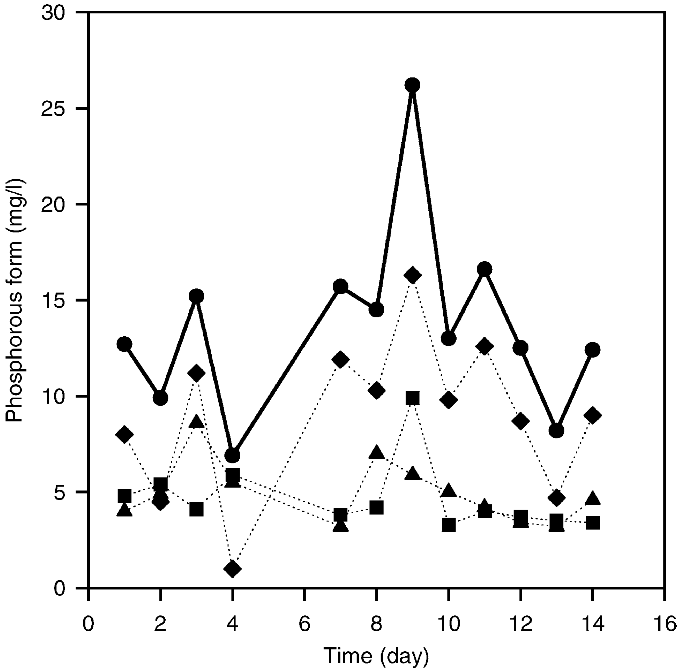

Fig. 2. Different forms of phosphorous in the influent of the Vilanova del Vallès WWTP ((●): total phosphorous; (■): soluble phosphorous; (▲): phosphate; (◆): particulate phosphorous).

based on the determination of orthophosphates in samples (digested or not according to the form of phosphorous determined) by reaction with a solution of 4 g/l of potassium tartare, 4 g/l of antimony tartare (3-hydrated) and 40 g/l of ammonium molybdate (4-hydrated), producing a complex antimonyl-orthophosphomolybdate. After 30 min of reaction in the dark, absorbance is measured at 710 nm. Calibration is carried out by means of hydrated potassium phosphate from 0 to 1.5 mg/l of total phosphorous.

In some cases, soluble phosphorous concentration was higher than total phosphorous, which implied that there was some interference to the analytical procedure, which could not be determined.

2.3. WWTP studied

WWTPs studied are located near Barcelona (Spain) in an industrial zone and a very populated area. They are on the river Besòs basin and serve to the municipalities of Vilanova del Vallès and La Llagosta.

The Vilanova del Vallès WWTP is designed to treat a flow of 5000 m^3 per day, which comes from several municipalities and approximately 90 industries. The plant has: bar screens, grit chambers and fat removal equipment, a biological reactor, secondary sedimentation with sludge recirculation and purge and dehydration of sludge by centrifugation with recirculation of supernatant.

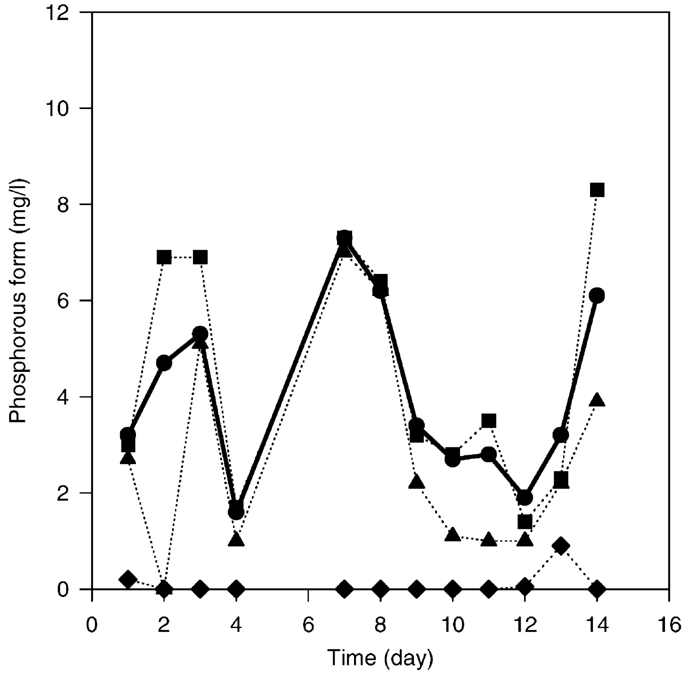

Fig. 3. Different forms of phosphorous in the effluent of the Vilanova del Vallès WWTP ((●): total phosphorous; (■): soluble phosphorous; (▲): phosphate; (◆): particulate phosphorous).

The La Llagosta WWTP is designed to treat a flow of 43000 m^3 per day, which come from several surrounding municipalities and a large number of industries (about 8000). It has: bar screens, grit chambers and fat removal equipment, primary sedimentation, a biological reactor (only for BOD removal), secondary sedimentation with sludge recirculation and purge, anaerobic digestion of secondary and primary sludge and dehydration of anaerobic sludge by centrifugation with recirculation of supernatant.

A summary of the characteristics of the two WWTPs studied is presented in Table 1. It is important to note that the two WWTPs studied are characteristic of facilities very common in Spain.

3. Results and discussion

3.1. Phosphorous removal at the Vilanova del Vallès WWTP

Results obtained for the different forms of phosphorous found in the three sampled points of the Vilanova del Vallès WWTP are presented in Fig. 2 (influent), Fig. 3 (effluent) and Fig. 4 (centrifuge supernatant), whereas in Fig. 5 the percentage of removal of total phosphorous is shown. A summary of the average results of Figs. 2–5 is presented in Table 2.

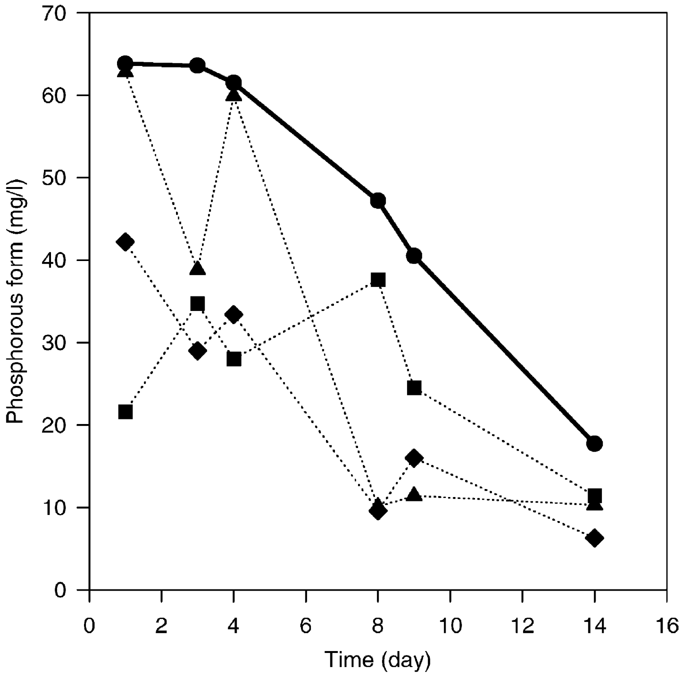

Fig. 4. Different forms of phosphorous in the centrifuge supernatant of the Vilanova del Vallès WWTP ((●): total phosphorous; (■): soluble phosphorous; (▲): phosphate; (◆): particulate phosphorous).

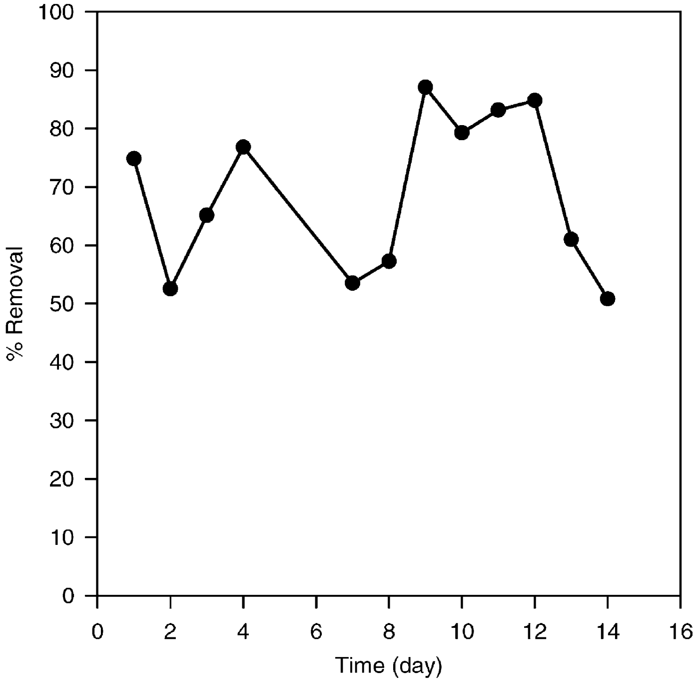

Fig. 5. Percentage of removal for total phosphorous at the Vilanova del Vallès WWTP.

From the results presented in Table 2, it can be concluded that particulate phosphorous is completely eliminated at the Vilanova WWTP. Given the configuration of this WWTP, this form of phosphorous must be preferably removed in the secondary clarifier. At the same time, a small fraction of phosphate is removed by incorporation into new biomass, resulting in an average elimination of nearly the 70% of total phosphorous in the WWTP studied.

On the other hand, the influent concentrations of the different forms of phosphorous remain practically constant in the sampling period, except for day 9 (Fig. 2), which might be due to an industrial discharge. Simultaneously, the contribution of the recirculation of centrifuge supernatant can play an important role in future phosphorous removal strategies, since the concentration of different forms of phosphorous is significantly higher than those observed at the influent of the WWTP.

Table 2
Summary of the results for the Vilanova del Vallès WWTP

Point	Average total phosphorous (mg/l)	Average soluble phosphorous (mg/l)	Average phosphate (mg/l)	Average particulate phosphorous (mg/l)
Influent	13 ± 3	5 ± 2	5 ± 2	9 ± 4
Effluent	4 ± 2	5 ± 2	4 ± 2	0 ± 0.3
Centrifuge supernatant	50 ± 20	26 ± 10	32 ± 25	17 ± 14
Total removal (%)	70	0	20	100

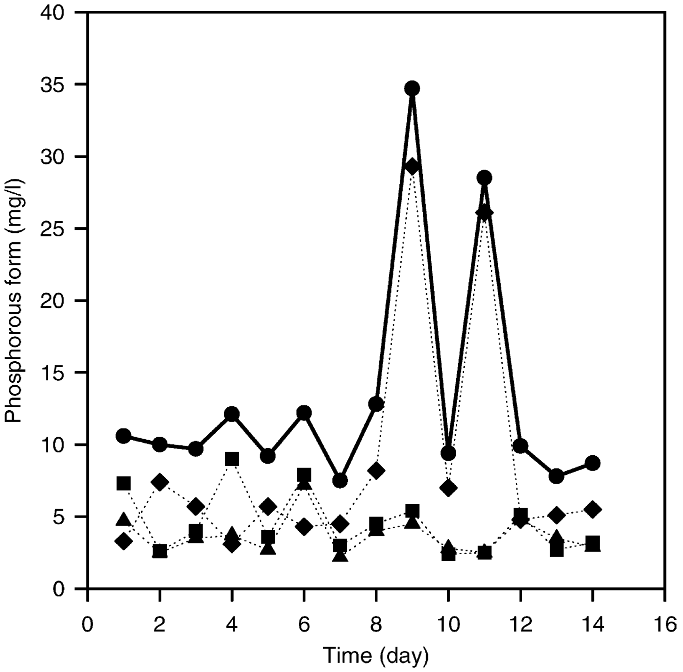

Fig. 6. Different forms of phosphorous in the influent of the La Llagosta WWTP ((●): total phosphorous; (■): soluble phosphorous; (▲): phosphate; (◆): particulate phosphorous).

3.2. Phosphorous removal at the La Llagosta WWTP

Results obtained for the different forms of phosphorous found in the four points sampled at the La Llagosta WWTP are presented in Fig. 6 (influent), Fig. 7 (effluent), Fig. 8 (primary clarifier) and Fig. 9 (centrifuge supernatant). The percentage of removal for total phosphorous is shown in Fig. 10. A summary of the average results of Figs. 6–10 is presented in Table 3.

Table 3
Summary of the results for the La Llagosta WWTP

Point	Average total phosphorous (mg/l)	Average soluble phosphorous (mg/l)	Average phosphate (mg/l)	Average particulate phosphorous (mg/l)
Influent	10 ± 2	5 ± 2	4 ± 2	9 ± 8
Effluent	4 ± 1	4 ± 1	4 ± 1	0 ± 0.8
Primary clarifier	7 ± 2	5 ± 1	4 ± 1	2 ± 2
Centrifuge supernatant	25 ± 8	16 ± 9	13 ± 4	9 ± 5
Removal primary clarifier (%)	30	0	0	78
Total removal (%)	60	20	0	100

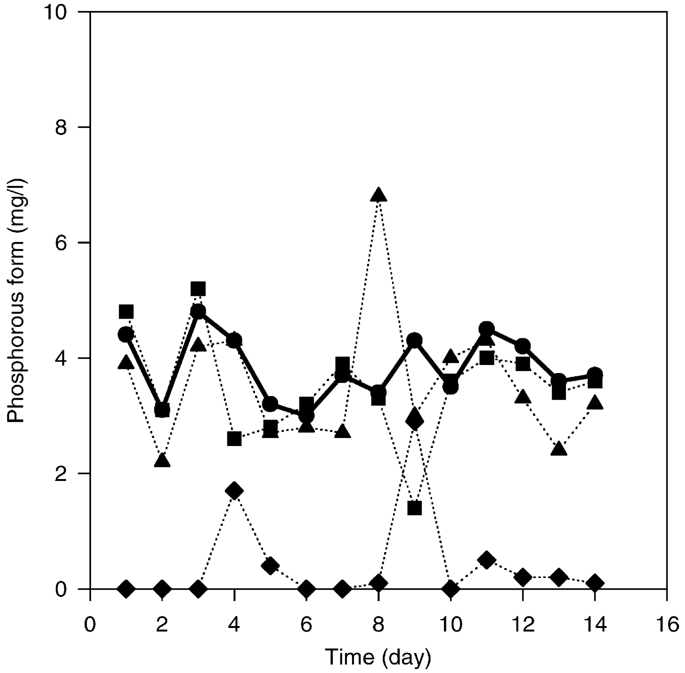

Fig. 7. Different forms of phosphorous in the effluent of the La Llagosta WWTP ((●): total phosphorous; (■): soluble phosphorous; (▲): phosphate; (◆): particulate phosphorous).

The results of the La Llagosta WWTP are very similar to those obtained at the Vilanova del Vallès WWTP. Soluble phosphorous is incorporated to new biomass in a short extent, whereas particulate phosphorous is almost entirely removed in both the primary clarifier (30% of total phosphorous and 78% of particulate phosphorous removed, Table 3), resulting in a total phosphorous elimination of about 60%.

On the other hand, the La Llagosta WWTP also presents a buffered response to high phosphorous inputs found in days 9 and 11. These high inlet phosphorous loads could be due to the higher industrial flows, which are treated in this WWTP (Table 1). Additionally, the supernatant centrifuge shows a high concentration of phosphorous in the different analysed forms, and the recirculation of this stream to the influent of the plant should be carefully considered, since the La Llagosta WWTP is working at full capacity (Table 1).

3.3. Comparison between the two WWTPs studied

In both WWTPs, it is evident that there is a high correlation between influent soluble phosphorous and total phosphorous (Figs. 2 and 6). Thus, high peaks of total inlet phosphorous correspond to high peaks of soluble phosphorous and, to a minor extent, to phosphate. This result is probably due to the fact that these sporadic high concentrations of phosphorous come from industrial effluents, which are mainly composed of phosphates. In the effluent,

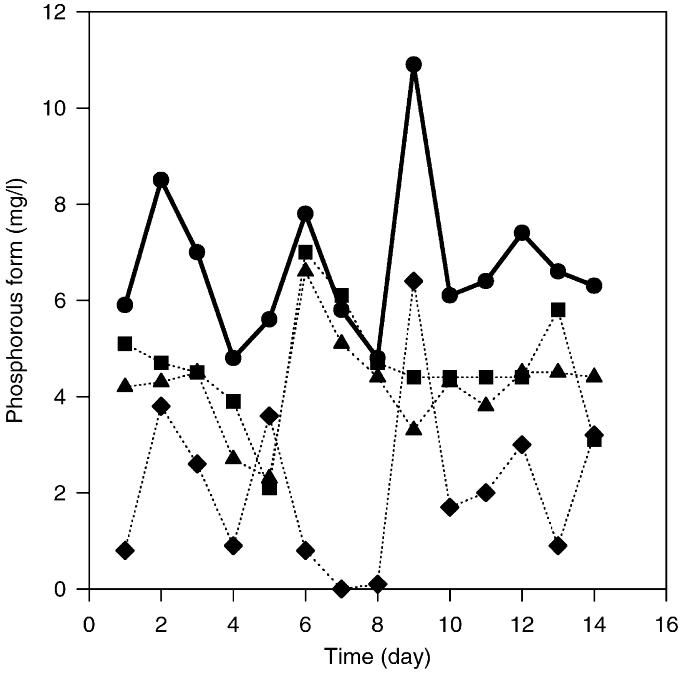

Fig. 8. Different forms of phosphorous in the primary clarifier of the La Llagosta WWTP ((●): total phosphorous; (■): soluble phosphorous; (▲): phosphate; (◆): particulate phosphorous).

given that particulate phosphorous is completely removed (Figs. 3 and 7) this correlation between influent soluble phosphorous and total phosphorous is also present, although is more evident at the Vilanova del Vallès WWTP, in which the composition of phosphorous is less variable. This result may be due to the presence of a reduced number of industrial wastewaters.

In the La Llagosta WWTP, our study of the primary clarifier effluent is especially relevant, because a complete elimination of particulate phosphorous does not occur (78%, Table 3). However, the concentration of particulate phosphorous in the effluent (Fig. 7) is practically negligible on most days, indicating that the secondary clarifier can remove the rest of this form of phosphorous. This finding is of interest because it confirms that with a proper dimensioning of the clarifiers, particulate phosphorous can be totally removed.

In both WWTPs, centrifuge supernatant contains high amounts of all forms of phosphorous, with peaks over 60 mg/l of total phosphorous at Vilanova del Vallès (Fig. 4) and peaks over 35 mg/l of total phosphorous at La Llagosta (Fig. 9). Although the contribution of these streams to the total inlet flow is low (<10% in both WWTPs) the recirculation flow to the plant inlet has to be carefully considered when a future phosphorous removal techniques are implemented, since the phosphorous forms in the supernatant do not appear to be predictable and can produce a momentary accumulation of phosphorous.

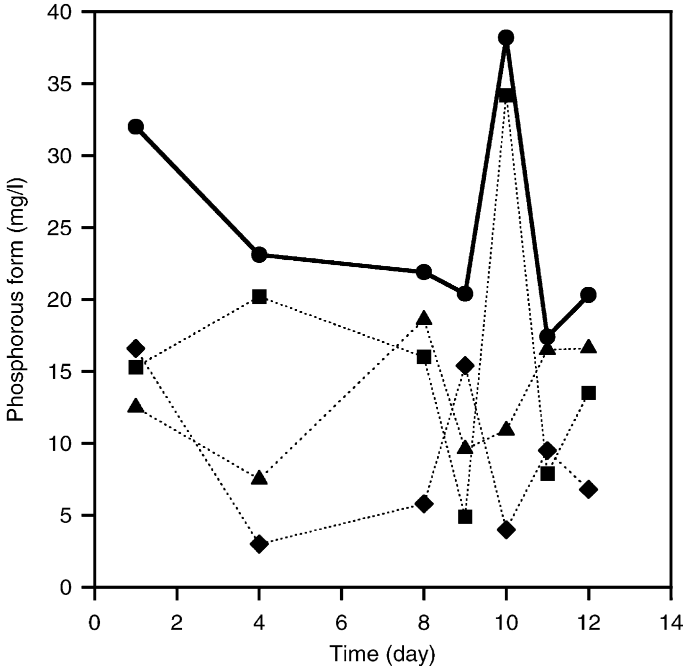

Fig. 9. Different forms of phosphorous in the centrifuge supernatant of the La Llagosta WWTP ((●): total phosphorous; (■): soluble phosphorous; (▲): phosphate; (◆): particulate phosphorous).

3.4. Future phosphorous removal strategies

Given that particulate phosphorous is completely removed from both WWTPs in the sedimentation basins, only soluble phosphorous need to be removed from the influent. The fact that almost all soluble phosphorous is in its phosphate form, implies that any phosphorous removal strategy should have that form as a target compound. Nevertheless, the different characteristics of the WWTPs suggest that different treatment process for phosphorous removal seems more appropriate for both WWTPs. The La Llagosta WWTP is working at full capacity using a continuous stirred tank reactor for BOD removal due to a space limitations; according to this, a physico-chemical pre- or post-treatment process based on phosphate precipitation would be more suitable to achieve phosphorous removal. Otherwise, the Vilanova del Vallès WWTP has more flexibility to incorporate a biological phosphorous removal, since the biological reactor is treating only the 60% of its design flow. The fact that the reactor is designed as a plug-flow reactor permits one to create an anaerobic zone, that jointly with the existing anoxic and aerobic zones thus permitting simultaneous removal of BOD, nitrogen and phosphorous.

In addition, in both WWTPs, an extensive study on the recycle of sludge centrifuge streams to the entrance of the plant has to be carried out in order to determine the impact of this practice on the biological stability of the reactors and the economics of a separated treatment system.

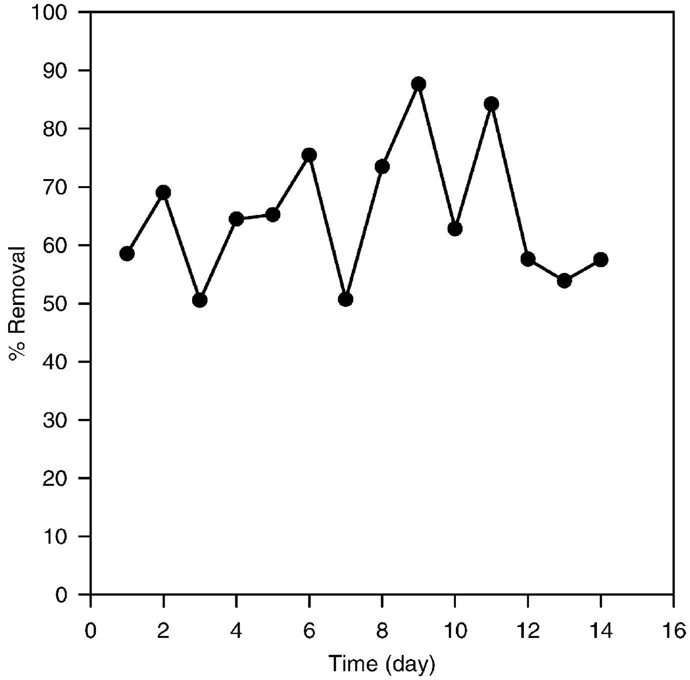

Fig. 10. Percentage of removal for total phosphorous at the La Llagosta WWTP.

4. Conclusions

From the data here presented, we can conclude that:

(1) The forms of phosphorous found in wastewater are the same in the two WWTP studied. Particulate phosphorous is completely removed in clarification equipment (either primary or secondary clarifiers), whereas soluble phosphorous (almost exclusively composed of phosphate) is incorporated only slightly into new biomass.
(2) The WWTPs studied show a buffered behaviour when high loads of phosphorous were present in the influent of the plant; this finding is of special relevance for the operators in charge of the process.
(3) Biological or physico-chemical phosphorous removal that will be regulated in the future in most of the Spanish WWTP should be focused on soluble phosphate removal and hence this requirement must be taken into account in the design of the new processes.
(4) Recirculation of some streams such as centrifuge supernatant that have considerable amounts of several phosphorous forms to the beginning of the plant can have an adverse and unpredictable effects on the long-term WWTP operation; consequently, specific treatment for these streams should be considered.
(5) Although neither of the two WWTPs studied is within the range of phosphorous defined by the urban wastewater treatment Directive 91/271 (2 mg/l for both WWTPs), a

significant reduction of phosphorous is already produced without any specific phosphorus removal strategy.

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