

Consequences of an occasional secondary phosphorus release on enhanced biological phosphorus removal

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Abstract

Laboratory experiments were performed to determine the conditions for an occasional secondary release of phosphates (release in the absence of any exogenous carbon input), and its consequences on the enhanced biological phosphorus removal process.

Phosphorus accumulating sludge from two extended aeration waste-water plants was subjected, in an Erlenmeyer flask, to successive sequences of anaerobiosis, with or without the addition of raw water, and of aeration. Secondary release occurred between 1 and 3 h after decanting the sludge. It would appear that this phenomenon is linked to the low nitrate concentration in the aqueous phase of sludge ($\text{NO}_3\text{-N} < 0.5 \text{ mg/l}$). This release occurs at very low rates (0.2 and 0.4 mg P/g VSS-h) over an oxidation reduction potential range between +100 and +250 mV/NHE. This secondary release does not lead to any excess accumulation of phosphorus in the course of later aeration. It would not appear that the occasional secondary release affects the enhanced biological phosphorus removal process. On the one hand, the phosphorus released without COD is completely reabsorbed even after a long period of anaerobiosis (20 h), and, on the other hand, this secondary release has no effect on the further release in the presence of COD, nor on the good reabsorption of phosphorus.

Nomenclature

BOD	-	biochemical oxygen demand
COD	-	chemical oxygen demand
mV	-	millivolt
NHE	-	normal hydrogen electrode
ORP	-	oxidation reduction potential
p.e.	-	population equivalent
VSS	-	volatile suspended solids

Introduction

Enhanced biological phosphorus removal is based on the alternation of the anaerobic-aeration phases. In the presence of COD, the sludge releases phosphates in the anaerobic phase, then, in the aeration phase reabsorbs a greater quantity than was initially released to give enhanced phosphorus uptake (Marais et al., 1982; Ekama and Marais, 1985; Wentzel et al., 1985; Meganck, 1987; Meganck and Faup, 1988; Somiya, 1988; Randall, 1991). As the quantity of phosphates reabsorbed in the aeration phase is proportional to the quantity of phosphates released in the anaerobic phase (Wentzel et al., 1985; Meganck, 1987; Wouters-Wasiak, 1994), the anaerobic phosphate release must be optimised.

For this purpose, certain authors (Paepcke, 1982; Kerdachi and Roberts, 1983; Gerber and Winter, 1984; Brodisch and Joyner, 1982) recommended a long anaerobic residence time to maximise the release. Other authors (Barnard, 1984; Tracy and Flammino, 1987; Nicholls et al., 1987) have indicated that long anaerobic residence times will lead to excessive phosphate release without uptake of organic matter and that this is detrimental to the biological dephosphatation efficiency, and accordingly recommending short anaerobic residence times (Barnard, 1974, 1976; Krichen et al.,

1987; Pitman, 1991).

The phosphorus release in the presence of exogenous COD has been well documented. In contrast the secondary phosphate release (release in the absence of any exogenous carbon input), has few bibliographical references, and still remains somewhat obscure. Such a release can occur in the clarifier or in an anaerobic zone with a low input of raw water, or with very long residence times, as is often the case overnight.

The purpose of this study was to determine (from batch tests on activated sludge from two urban sewage works) the conditions which stimulate phosphorus release in the absence of exogenous COD and its consequences on the biological dephosphatation efficiency.

Material and methods

Methodology

Two types of experiments were performed :

- Monitoring of a secondary phosphorus release from sludge collected at the end of an aeration cycle and left to decant in an Erlenmeyer flask to simulate residence in the clarifier. The medium was agitated one minute prior to the collection of each sample. This was followed by monitoring the reabsorption of the phosphates during subsequent aeration of the sludge.
- Monitoring of a secondary release, then of a release with the anaerobic input of exogenous carbon, and of the final reabsorption by aeration of the sludge. Two trials were performed concomitantly with the same sludge, collected at the same time. In the first Erlenmeyer flask, the sludge was left to decant for 4 h so as to produce a "secondary" phosphorus release. The raw water was then added, and a second 3 h release period started, but in the presence of added COD. The aerator was then started. In the second Erlenmeyer flask, for the first 4 h the sludge was subjected to continuous agitation and aeration to prevent any phosphorus release. The raw water was then added, the rest of the experiment being identical to the first.

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Experimental procedures

The biological medium to be studied was placed in a 4 l Erlenmeyer flask, the top opening of which was capped by a plastic film during the anaerobic phase. Water maintained at the temperature of the collected sludge was recirculated in an outside jacket in which the flask was placed. The medium could be agitated (magnetic bar) and/or aerated (porous diffuser connected to a compressor). The samples placed in the flask were taken with a 50 ml syringe fitted with a tube dipped into the sludge. The sample was immediately filtered over a No. 183 ash-free 180 mm dia. filter (Durieux) and analysed. The ORP was monitored by a combined INGOLD Pt 4805 DXK platinum electrode connected to a DEMCA TR 20 A high input impedance millivoltmeter. Prior to each experiment, the platinum was polished under a water jet using Tacussel BSC 3 and then BAO 3 abrasive strips (grain of 3 and 0.3 μm). All tests were duplicated.

Origin of sludge and waste water

The activated sludge and domestic waste water used for these tests came from two extended aeration waste water plants: the Benfeld (16 000 p.e.) and the Bavilliers Works (15 000 p.e.). The Benfeld Wastewater Treatment Works was designed for carbon, nitrogen and biological phosphorus removal (mean operating F/M ratio = 0.11 kg BOD/kg VSS-d (Audic, 1992)). The treatment plant consists of five tanks: contact, anaerobic, anoxic and two aeration tanks in series. The aeration tanks are equipped with separated mixing-air diffusion systems. The Bavilliers Wastewater Treatment Works (Wouters-Wasiak et al., 1994) was designed for carbon, nitrogen and chemical phosphorus removal (mean operating F/M ratio = 0.04 kg BOD/kg VSS-d) and consists of an anoxic and an aeration tank also equipped with separated mixing-air diffusion systems. The anoxic tank was transformed in an anaerobic tank by stopping the mixed liquor recycle. Nitrification and denitrification were both performed in the aeration tank by sequencing the aeration.

Sludge and raw waste-water samples were taken concomitantly. For the experiments presented in the section **Secondary Release of Phosphorus Followed by Uptake**, the sludge was collected from the aeration basin at the end of an aeration cycle. For the experiments presented in the section **Secondary Release Followed by Release in the Presence of Carbon and of Reabsorption**, the sludge from the Bavilliers Works was collected from the aeration basin at the end of an aeration cycle and concentrated by decantation, whilst the sludge from the Benfeld Works was collected from the recycle flow.

During the experimental period, the mean biological dephosphatation efficiency obtained from the Benfeld Works was 75% for a COD/P ratio of 55 ($\text{BOD}_5/\text{P} = 32$). For the Bavilliers Works (COD/P ratio of 42), the mean phosphorus elimination efficiency was only in the order of 40% due to the dilution of the waste water.

Analytical methods

The following sludge characteristics were determined according to the AFNOR methods (1990): total suspended solids (TSS_s), volatile suspended solids (VSS_s), pH_s and temperature (T_s).

Chemical oxygen demand (COD_w), pH_w and temperature (T_w) were measured on the raw waste water (AFNOR methods, 1990). The waste-water sample was filtered over a No. 183 ash-free 180 mm dia. filter (Durieux) to determine soluble chemical oxygen demand (COD_{w,s}).

Phosphate and nitrate concentrations were measured in the supernatant. The phosphate concentration was determined by the molybdovanadate acid method and read off a DR/2000 HACH spectrophotometer at 430 nm.

The nitrates present in the sample were reduced to nitrites by metallic cadmium. In an acid medium, the nitrite reacts with the sulphanic acid to form a diazonium salt, which reacts with gentisic acid to form an amber-coloured complex. Reading is performed on a DR/2000 HACH spectrophotometer at 500 nm.

Results

Secondary release of phosphorus followed by uptake

Monitoring of the secondary release

The evolution of the phosphate concentrations in the liquid phase of the sludge subjected to a secondary release is shown in Fig. 1, for the Benfeld sludge, and in Fig. 2 for the Bavilliers sludge, for which simultaneous monitoring of the Redox potential was performed. The sludge characteristics are summarised in Tables 1 and 2.

Benfeld

Date	TSS _s g/l	VSS _s g/l	pH _s	T _s °C
19/11/92	4.2	2.7		
30/11/92	4.2	2.8	6.4	12.8
02/02/93	4.7	3.1	6.9	10.0

For the sludge from the Benfeld Works, the secondary release occurs between 1 and 2 h after the start of the decantation in the Erlenmeyer flask. The release rates are linear between 0.2 and 0.4 mg P/g VSS-h.

Bavilliers

Date	TSS _s g/l	VSS _s g/l	pH _s	T _s °C
19/10/93	3.8	2.7	6.7	15
20/10/93	3.9	2.7	7.4	15.1
27/10/93	3.3	2.3	6.8	14.8

In the case of the Bavilliers sludge, the release occurs approximately 3 h from the start of decanting in the Erlenmeyer flask. The steepest slopes correspond to the most highly concentrated sludge, the specific release rates remaining between 0.2 and 0.4 mg P/g VSS-h. In all experiments, the nitrate concentrations decreased regularly from 2 to 0.5 mg N/l during the first 3 h of anoxia. The phosphate

Date	TSS _s g/l	VSS _s g/l	pH _s	T _s °C
30/11/92	4.2	2.8	6.4	12.8
02/02/93	4.7	3.1	6.9	10.0
20/10/93	3.9	2.3	7.4	15.1

release commenced at ORPs of between 100 and 250 mV/NHE and at an NO₃-N concentration of less than 0.5 mg/l.

Secondary phosphorus release followed by uptake

The evolution of the phosphate concentrations in the liquid phase of the sludge subjected to a secondary release followed by a reabsorption of phosphorus in an aerated medium is shown in Fig. 3. Sludge characteristics are reported in Table 3.

Figure 1
Evolution of the PO₄-P concentration in the aqueous phase of sludge taken from the aeration basin and maintained in anaerobiosis - Benfeld Works

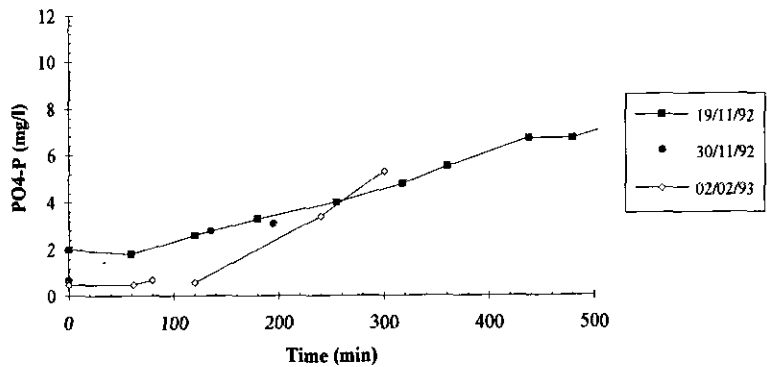
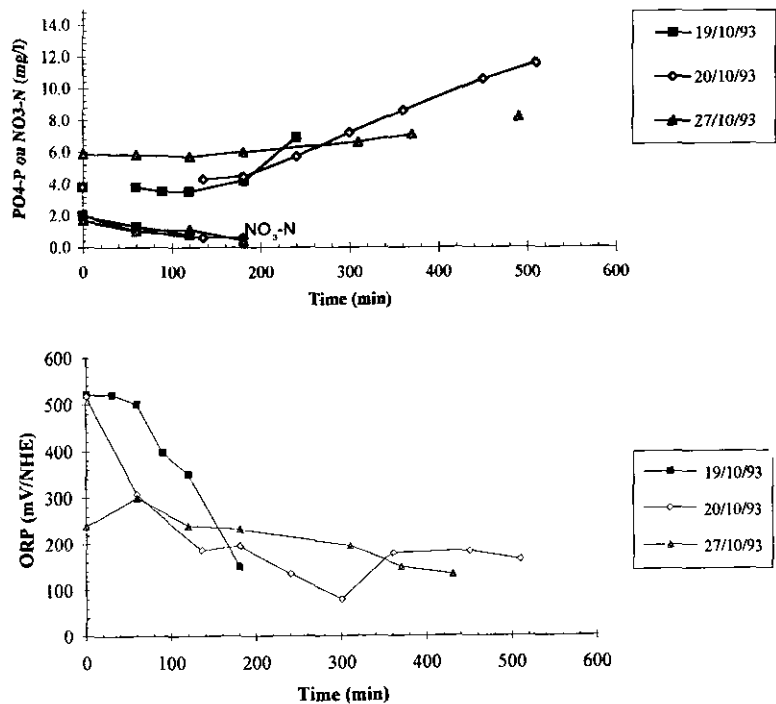


Figure 2
Evolution of the PO₄-P and NO₃-N concentration and of the ORP in sludge taken from aeration basin and maintained in anaerobiosis - Bavilliers Works



The reabsorption of the phosphorus released is all but complete, even after a very long anaerobic sequence (20 h). These results are contradicting to the conclusion of Barnard (1984) that not all the secondary released phosphates can be taken up, but confirm the findings of Wells (1969) and those of Grange and Rollin (1988) according to which it would appear that the phosphorus recovery rates drop only for anaerobic periods of more than 24 h.

The experiment performed with the Bavilliers sludge, where the phosphate saturation was verified by an aeration phase prior to decanting, revealed that a release of phosphates in the absence of exogenous carbon does not lead to any excess accumulation of phosphorus during a later aeration phase.

Secondary release followed by release in the presence of carbon and of reabsorption

The evolution of the phosphate concentrations in the liquid phase of the sludge subjected in turn either to a secondary release followed by a release in the presence of COD and an aeration phase, or to a release in the presence of COD and an aeration phase, and the monitoring of the ORP, are shown in Fig. 4 (Benfeld Works) and Fig. 5 (Bavilliers Works). Waste-water and sludge characteristics are reported in Tables 4 and 5.

Benfeld

TABLE 4 WASTE-WATER AND SLUDGE CHARACTERISTICS								
COD _w mg/l	COD _{w,s} mg/l	pH _w	T _w °C	pH _s	T _s °C	TSS _s g/l	VSS _s g/l	N-NO _{3,s} mg/l
620	228	6.7	13.9	7.3	11.8	8.9	5.5	0.1

Bavilliers

TABLE 5 WASTE-WATER AND SLUDGE CHARACTERISTICS								
COD _w mg/l	COD _{w,s} mg/l	pH _w	T _w °C	pH _s	T _s °C	TSS _s g/l	VSS _s g/l	N-NO _{3,s} mg/l
500	285	7.8	16.5	7.4	15.1	6.2	4.3	2.0

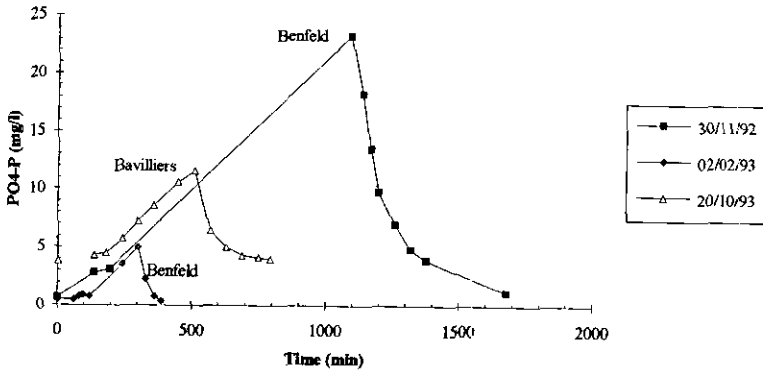


Figure 3
Secondary release of P followed by uptake: Evolution of the PO₄-P concentration in the aqueous phase of sludge from the Benfeld and Bavilliers Works

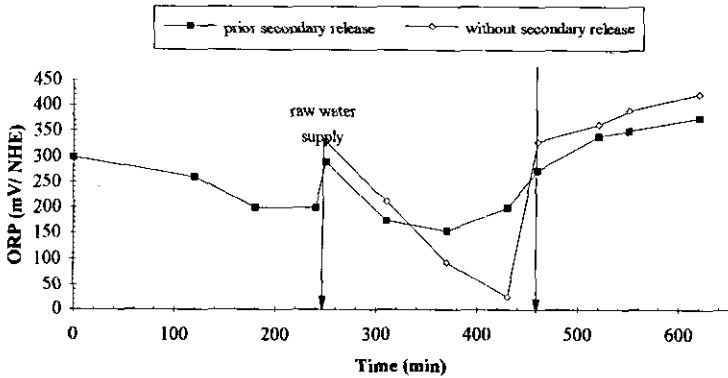
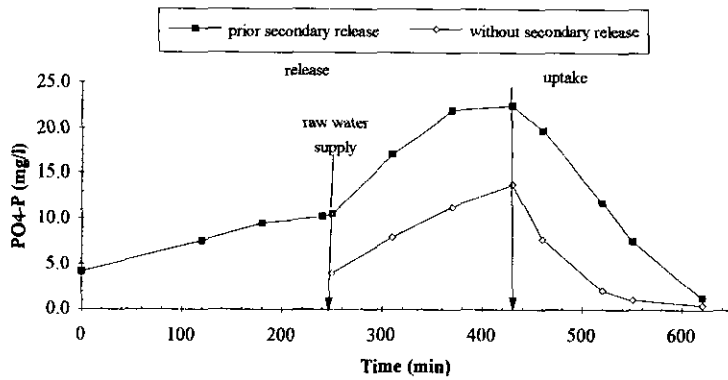
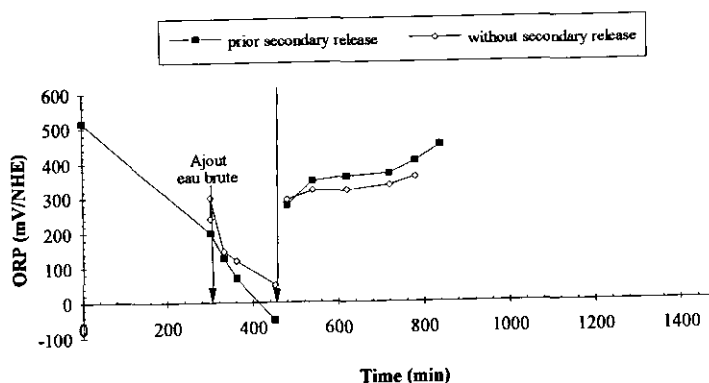
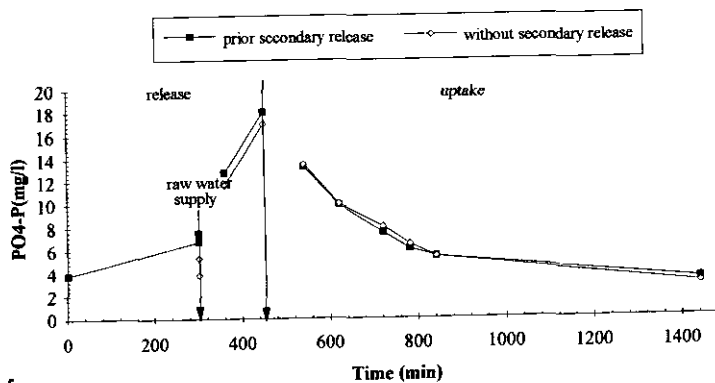


Figure 4
Evolution of the PO₄-P concentration and of the ORP of sludge subjected in turn to an anaerobic phase and an aeration phase (Benfeld Works)

Figure 5
Evolution of the $PO_4\text{-P}$ concentration and of the ORP of sludge subjected in turn to an anaerobic phase and to an aeration phase (Bavilliers Works)



These graphs show that :

- The secondary release rates (0.2 to 0.4 mg P/g VSS-h) are lower than those obtained in the presence of COD (over 1 mg P/g VSS-h).
- The initial release without the presence of COD (for 4 to 5 h) does not prevent the later release in the presence of COD.
- An initial anaerobic secondary release (up to 5 h) has no negative influence on the later absorption of phosphorus. It does not appear likely, therefore, that such a release in the anaerobic reactor, if occasional, affects the phosphorus elimination efficiency.
- The secondary release occurs at potentials in the order of 200 mV/NHE. The addition of raw water initially leads to an increase (input of dissolved oxygen) and then a drop in the potential which, in 3 cases out of 4, is within the range of -50 to +50 mV/NHE at the end of the release period. Aeration leads to an increase in the potential which exceeds +350 mV/NHE.
- The phosphorus released without COD is completely reabsorbed, even after a long period of anaerobiosis (20 h). Nevertheless, the secondary release does not cause any excess accumulation of phosphorus in a later aeration phase.
- The occasional secondary release (for 4 to 5 h) does not prevent either a later release in the presence of COD or a good later reabsorption of the phosphorus.

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Conclusion

The batch laboratory experiments performed with phosphorus accumulating sludge from two extended aeration waste-water treatment plants have made it possible to clarify the conditions of the appearance of an occasional release of phosphates in the absence of exogenous COD and its consequences on the biological dephosphatation efficiency.

In this study phosphate release occurs between 1 and 3 h after the start of decanting the sludge. It appears to be inhibited by the presence of low residual nitrate concentrations. Secondary release occurs in an ORP zone of between +100 and +250 mV/NHE (polished platinum electrode).

The occasional secondary release does not appear to affect the biological dephosphatation process:

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