

PRACTICE REPORT

LABORATORY ANALYSIS & PROCESS ANALYSIS

NUTRIENTS

PHOSPHATE



Elimination and determination of phosphates

Increased algal growth, which in the worst case can cause eutrophication of surface waters, is a **consequence of high phosphate concentrations**. Legal limit values for $\text{PO}_4\text{-P}$ in wastewater discharges should prevent scenes such as the above. Sewage treatment plants therefore carry out **targeted phosphorus elimination** in association with nitrification/denitrification, and/or chemically, with appropriate precipitants. **Reliable $\text{PO}_4\text{-P}$ analysis** is indispensable, not only for the purpose of monitoring compliance with limit values but also for the most efficient and cost effective **control of phosphorus elimination**.



Author:
Petra Pütz
- "Dipl.-Ing. Chemie"
- Application Lab. Products
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Phosphate in water – origin and elimination



Fig. 1: DR 3800 sc spectrophotometer with 230 preprogrammed HACH LANGE methods, e.g. for the determination of COD, $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, $\text{NO}_2\text{-N}$, TN, ortho $\text{PO}_4\text{-P}$ and P_{tot}

Effects of phosphate on surface waters

Phosphorus compounds are plant nutrients and cause algal growth in surface waters. Depending on the phosphate concentration in the water, eutrophication may occur. Just 1 g of phosphate phosphorus ($\text{PO}_4\text{-P}$) promotes the growth of up to 100 g algae. When these algae die, decomposition processes result in an oxygen demand of about 150 g. The critical concentrations for incipient eutrophication are about 0.1-0.2 mg/l $\text{PO}_4\text{-P}$ in running water and 0.005-0.01 mg/l $\text{PO}_4\text{-P}$ in still water. In view of the potential hazard to surface waters, EU Directive 91/271/EEC specifies limit values for the discharge of phosphate compounds into receiving waters. Depending on the size of the sewage treatment plant, these values are 2 mg/l P_{tot} (10,000 - 100,000 PE) or 1 mg/l P_{tot} (> 100,000 PE).

Where does the phosphate come from?

The phosphate compounds that are found in wastewater or are discharged directly into surface waters come from:

- Fertiliser washed out of the soil
- Human and animal excretions
- Detergents and cleaning agents

The total phosphate load is composed of orthophosphate + polyphosphate + organic phosphorus compounds, with orthophosphate usually accounting for the greatest proportion.

The phosphates are present in dissolved, colloidal or solid form. Before carrying out an analysis, it is important to consider which type of phosphates should be determined. If only orthophosphate is to be determined (e.g. for the purpose of controlling phosphorus precipitation), the sample must only be filtered before it is analysed. If, however, the total phosphate concentration is to be determined (e.g. for monitoring limit values), the sample must first be homogenised and then hydrolysed (digested).

Table 1: Composition of the phosphorus load and its determination

P compounds	Formula	Sample preparation	Cuvette tests	Process instrument	Result display + field of use
Orthophosphate	PO_4^{3-}	Filtrate	LCK049* LCK349* LCK348* LCK350*	PHOSPHAX sc (vanadate-molybdate method)	- Ortho $\text{PO}_4\text{-P}$ (e.g. wastewater: control of P precipitation) - Ortho PO_4 (e.g. drinking and boiler water)
Polyphosphates	$\text{PO}_4\text{-PO}_4\text{-PO}_4\text{-}$	Homogenisation, digestion			
Organic phosphorus compounds	R- PO_4	Homogenisation, digestion			
Total load (orthophosphate + polyphosphates + organic P compounds)	Total PO_4	Homogenisation, digestion	LCK349* LCK348* LCK350*	PHOSPHAX sigma (phosphomolybdenum blue method in accordance with EN 1189)	- P_{tot} = Total $\text{PO}_4\text{-P}$ (e.g. wastewater: limit value monitoring) - Total PO_4 (e.g. drinking and boiler water)

Important: In wastewater analysis, the PO_4 concentration is always expressed in terms of the phosphorus content of the phosphate! Eg, the result is shown as $\text{PO}_4\text{-P}$ (conversion factor: $\text{PO}_4\text{-P} \times 3.07 = \text{PO}_4$). The limit values defined in the applicable legislation, e.g. the limit value in a sewage treatment plant outflow, are expressed in the unit P_{tot} = total $\text{PO}_4\text{-P}$.

*) LCK348, 349 and 350: phosphomolybdenum blue method in accordance with EN 1189; LCK049: vanadate-molybdate method

Phosphate elimination

Nowadays the average concentration in the inflow of a municipal sewage treatment plant can be assumed to be $9\text{ mg P}_{\text{tot}}$. This must be reduced by the wastewater treatment processes to the legally specified outflow limit value. There are two ways of doing this: **biological phosphorus elimination** or **chemical phosphate precipitation** (see text boxes on the right). The disadvantages associated with all precipitation methods are the increased salinity of the wastewater (and therefore also of the receiving water) and the steadily rising prices of precipitants. Moreover, the precipitated phosphate salts cause higher volumes of sludge to be generated. In practice, a combination of biological and chemical phosphorus elimination is used in order to minimise the consumption of precipitant.

Phosphate analysis

Regular analyses at a number of measurement points in the wastewater treatment process are necessary for the control and monitoring of phosphorus elimination and ultimately for monitoring limit values. The selective addition of precipitants on the basis of the phosphorus load can result in considerable cost savings.

$\text{PO}_4\text{-P}$ can be determined in the laboratory or online. Usually time-course curves are plotted, i.e. measurements of the $\text{PO}_4\text{-P}$ concentration at regular intervals (e.g. over 24 hours) at one and the same measurement point, in order to obtain an exact overview of the magnitude of the PO_4 load. The necessary precipitant dosage can then be regulated on the basis of the curve (see Fig. 2). Continuous measurement of the $\text{PO}_4\text{-P}$ concentration in combination with a direct link to the precipitant dispensing system is even more effective.



Fig. 3: LANGE cuvette test LCK349 for the determination of orthophosphate and total phosphate (measuring range 0.05–1.5 mg/l $\text{PO}_4\text{-P}$)

Biological phosphorus elimination

Storage of more phosphate than is normally required in the flocculated activated sludge. This occurs when the sludge is in an alternately aerobic and anaerobic environment (oxygen input on/off). Efficient biological elimination of phosphorus depends on the presence of sufficient readily biodegradable organic materials (BOD_5).

A P/BOD_5 relationship of < 0.03 and a N/BOD_5 relationship of < 0.25 in the inflow to the aeration tank favour increased biological phosphorus degradation.

Chemical phosphate precipitation

Orthophosphate compounds are precipitated as poorly soluble metal phosphates with the help of chemicals (iron or aluminium salts, milk of lime). The salts settle out and remain in the sewage sludge. The precipitant can be added during primary treatment (pre-precipitation), or in the aeration tank (simultaneous precipitation), or in an additional reaction tank downstream of the aeration tank (post precipitation). The most widely used method is simultaneous precipitation, as this is the most cost-effective variant.

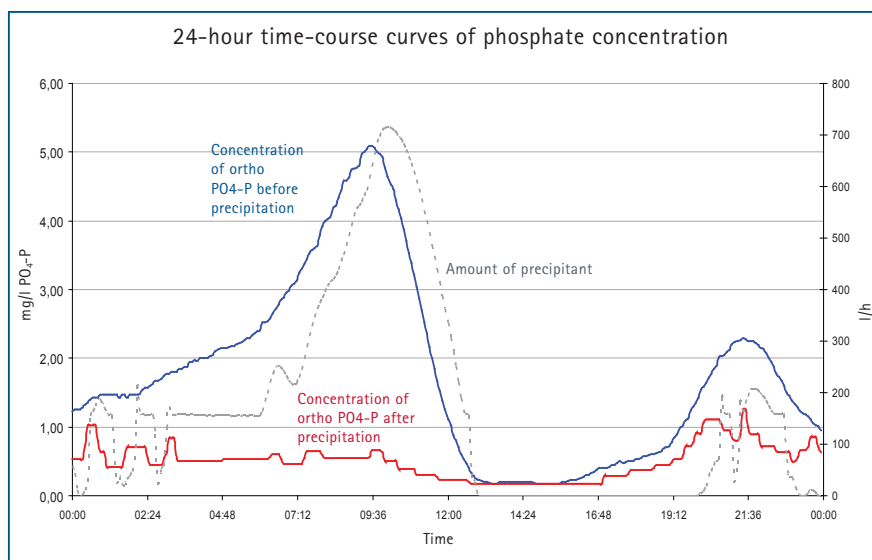


Fig. 2: 24-hour time course curves of the phosphate load at a large German sewage treatment plant

Causes and reduction of high $\text{PO}_4\text{-P}$ concentrations

High $\text{PO}_4\text{-P}$ values in the outflow

If the P_{tot} values in a sewage plant are higher than they should be, the difference between P_{tot} and ortho $\text{PO}_4\text{-P}$ should first be determined. If the difference is small, the ortho $\text{PO}_4\text{-P}$ concentration is too high.

Possible causes and responses:

1. Too little precipitant is being added, or the precipitant is being added at an unfavourable location
 - Check the precipitant dosage
 - If necessary, increase the dosage or add the precipitant at a different location
2. Phosphorus is redissolving in the secondary settlement tank
 - The ortho $\text{PO}_4\text{-P}$ concentration in the outflow of the secondary settlement tank is appreciably higher than in the nitrification stage
 - Increase the oxygen content in the nitrification stage phase or increase the returned sludge ratio

If there is a big difference between P_{tot} and ortho $\text{PO}_4\text{-P}$, a high proportion of undissolved phosphorus compounds is present.

Possible causes and responses:

1. Too high a proportion of solids, caused by sludge loss
 - Too light, small or filamentous activated sludge flocs or structure in combination with hydraulic overloads (rain, thaw)
 - Monitor the acid capacity in the aeration tank or take action to combat bulking sludge
2. Poorly degradable polyphosphonates are present, possibly from industrial cleaning agents
 - This situation can only be improved by elimination at the site point where it happens, as precipitants do not react with such compounds.

Literature

- HACH LANGE Practice Report "Die richtige Prozess-Messtechnik für den N- und P-Abbau", February 2008.
- HACH LANGE Practice Report "Optimale Nährstoffverhältnisse für die Abwasserreinigung", March 2008
- Kirsten Sölter, Norbert Weber, Bundesverband der Deutschen Kalkindustrie: Anwendungsbericht Ch. No. 76 "Optimierte P-Elimination", March 2000

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Fig. 4: PHOSPHAX sc for continuous determination of orthophosphate for the best possible control of phosphorus elimination



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