

On the trail of orthophosphate

Measurement of orthophosphate in municipal wastewater treatment plants

Dr Petra Gahr

Application specialist, Endress+Hauser Conducta GmbH+Co.KG

Phosphorus and phosphate in the environment

In chemistry, phosphorus is the second element of Group V in the periodic table of elements, with the symbol P and the atomic number 15. In nature, phosphorus is found exclusively in bound inorganic form as ore (apatite) in the Earth's crust. Apatite is a group of chemically similar phosphate minerals. A study in 2018 revealed that around 71% of worldwide rock phosphates occur in Morocco and Western Sahara [1] [2]. Germany has to import all its rock phosphates and the mineral fertilizers made from them.

As an essential nutrient, phosphorus is decisive for plant growth in most aquatic ecosystems and, even in low concentrations at the microgram level, it can have a eutrophying effect. This leads to excessive algal growth and even fish kill. Figure 1 below describes the phosphorus cycle (extract from [3]).

Phosphate is mobilized by the process of leaching out of weathered rock and sediment. Plants absorb phosphate from the soil, while humans and animals take in phosphate through food. Microorganisms convert organic wastes (plant waste, excrement) to plant-available phosphates. This natural cycle is disrupted by man. Through agriculture, phosphate is extracted from the soil and added back into the cycle elsewhere by fertilization.

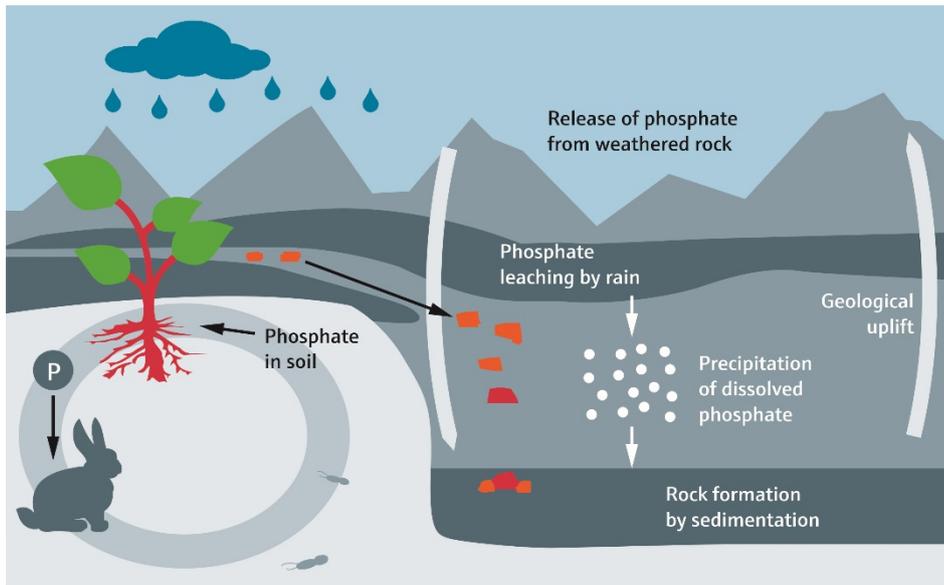


Figure 1. The phosphorus cycle. Phosphorus is present as phosphate in minerals and rocks. As a consequence of weathering or erosion, phosphate enters the soil and water. Phosphate in the soil and water can be taken up and stored by plants. Plants are digested by humans and animals as part of their food and excreted again. In this way, phosphate is returned to the cycle. [3]

Orthophosphate and total phosphorus

Table 1 shows an overview of different phosphorus fractions. They are categorized as “A” naturally occurring, “B” chemically classified and “C” of importance to measurement technology. Raw wastewater, e.g. in the influent to wastewater treatment plants, contains inorganic and organic phosphorus compounds in dissolved form. Inorganic phosphorus compounds include orthophosphate (o-PO_4 , $\text{o-PO}_4\text{-P}$), condensed phosphates and polyphosphates. Polyphosphates are – in chemical terms – condensation products of the salts of orthophosphoric acid.

Organic phosphorus compounds include phosphonates (salts of phosphonic acid), which, for example, are used in the textile industry and are poorly degradable [4]. Phosphorus can also be bound in solids. In analytical chemistry, it can be converted to orthophosphate form by oxidative decomposition techniques. In wastewater treatment, particulate phosphorus is separable from the accruing sludge and is therefore removed from the wastewater. For the operator of a wastewater treatment plant, the distinction between orthophosphate and total phosphorus (TP) is important. For the monitoring of a treatment plant's effluent, the total phosphorus value has traditionally been used, while measurements of orthophosphate are important for the automation of phosphorus removal.

This categorization and its significance for quality monitoring is still the subject of debate as it remains unclear how particulate phosphorus behaves on leaving a treatment plant for the water bodies. In a complex ecological system, chemical and physical behavior, e.g. remobilization of particulate phosphorus, depends on numerous factors. These include the pH value, redox potential and water

body temperature. As such, water chemists and aquatic ecologists are in demand. They will, in future, concentrate more intensively on the chemophysical relationships between the phosphorus inputs into the environment and their ecological impacts.

Table 1: Terminology for naturally occurring phosphorus fractions that occur naturally (A), are chemically classified (B) and are of importance to measurement technology (C).

Phosphorus fraction		Definition
A	Inorganic phosphate	In rocks and minerals, e.g. apatite-bound PO_4^{3-}
A	Organic phosphate	Phosphorus in humus, adsorbed to organic compounds
A	Dissolved phosphate	Plant-available phosphate in the form of H_2PO_4^- or HPO_4^{2-}
B	Particulate phosphorus	Phosphorus compounds bound to solids (e.g. sediments, activated sludge flocs)
B	Dissolved phosphorus	Inorganic and organic phosphorus compounds present as solutes in the aqueous phase
C	Total phosphorus, TP	Sum of all phosphorus fractions, i.e. inorganic and organic phosphorus compounds and phosphorus compounds bound to solids
C	Orthophosphate, o-PO_4 , $\text{o-PO}_4\text{-P}$	Orthophosphate is the anion of phosphoric acid; it is the simplest form of naturally occurring phosphorus and is most commonly found in a dissolved state in the wastewater. In the analysis of wastewater samples, orthophosphate is separated from the particulate phase by filtration (membrane filter with pore size $0.45\ \mu\text{m}$) [5]).

At the end of August 2018, the Stuttgarter Zeitung quoted the Hessian Ministry for the Environment in this regard, stating that 65% of the phosphorus loading of water bodies originates from wastewater treatment plants [6]. The article illustrated that the origin of phosphorus loading in the aquatic environment in the individual federal states (*Länder*) is still a matter of controversial debate. However, limiting the use of phosphates in detergents has succeeded in reducing population-specific phosphorus loading to approximately 1.8 g per capita per day [7].

Phosphorus's journey through the wastewater treatment plant

Figure 2 illustrates the process flow of a wastewater treatment plant. It also identifies the measurement locations that are important to phosphorus determination for monitoring and control tasks. Explanatory details follow in the text below.

Phosphorus first enters the treatment plant with the arrival of wastewater. The phosphorus compounds that it contains originate from human excreta, food waste, the food industry (pH buffers, preservatives and acidulants) and, to a small extent, laundry and cleaning detergents, water softeners and complexing agents [8].

In the subsequent mechanical treatment stages, e.g. grease trap and grit chamber or in the primary clarifier, some of the particulate phosphorus compounds can be separated from the wastewater. The majority of phosphorus compounds are removed from the wastewater by precipitation processes, sedimentation, flotation or filtration, which typically take place in the biological treatment stages and in the secondary clarifier. As part of these processes, the phosphorus is transferred to the sludge, concentrated in the course of anaerobic sludge treatment and, in Germany and Switzerland, is to be substantially recovered in future.

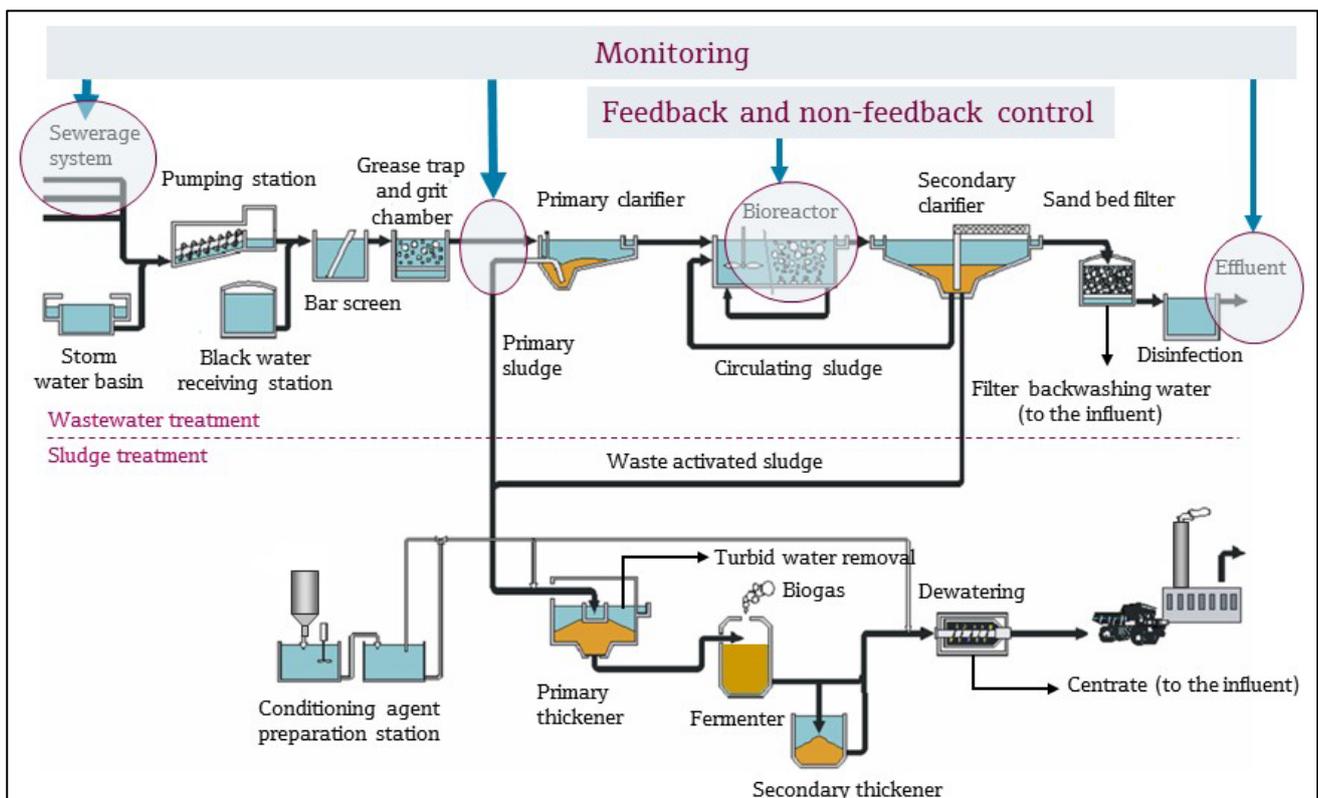


Figure 2: Schematic diagram of a wastewater treatment plant. Monitoring of the phosphorus concentration can take place in the influent, primary clarifier and effluent. In the aeration basin, the wastewater treatment is subject to feedback and non-feedback control (phosphate precipitation).

Small residual amounts of dissolved and particulate phosphorus compounds remain in the wastewater and enter the natural water cycle through the effluent. With the aim of contributing to phosphorus removal, ultimately in order to achieve “good quality water” as required by the EU, German law prescribes the monitoring of total phosphorus at the outfall of a wastewater treatment plant. The measurement of orthophosphate, however, takes place in the biological treatment stage. The results are processed for the automation of chemical phosphorus removal. In addition, German law also stipulates requirements for the quality of the sewage sludge as prescribed by the Sewage Sludge Ordinance.

Details on legislation are described in Chapter 6 “Legal bases”. The relationships between the law, control values and requirements for measurement and control technologies in a wastewater treatment plant are depicted in the schematic diagram of Figure 3.

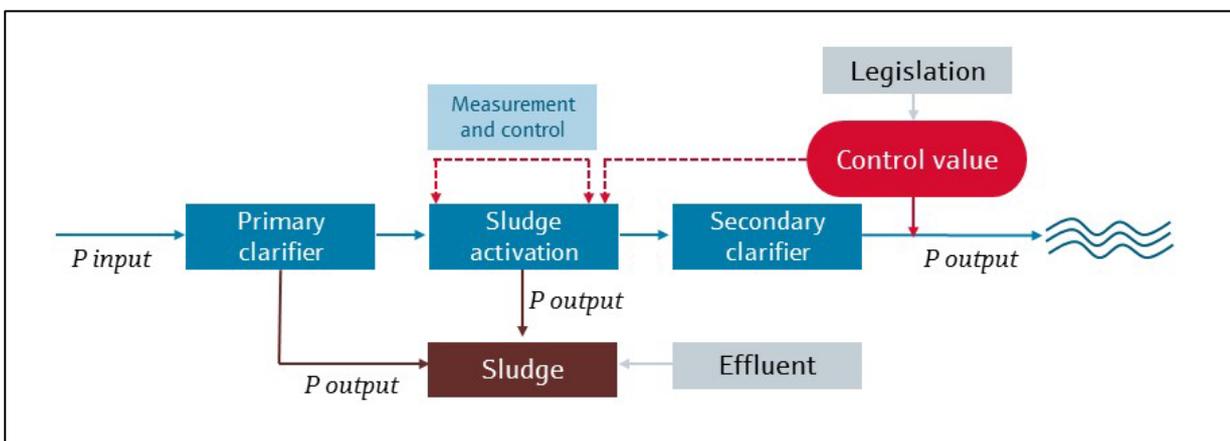


Figure 3: Schematic diagram of a wastewater treatment plant and its interaction with regulatory requirements. Phosphorus enters the wastewater treatment plant as part of the polluting load. The concentration of phosphorus leaving the wastewater treatment plant is subject to monitoring. The control value defined by the responsible authority under consideration of the minimum requirements and local water body situation also influences the way in which a treatment plant is automated.

Sludge treatment

Provided specific prerequisites are fulfilled, phosphorus can be recovered from the sludge [9]. The sludge from primary and secondary clarification, which typically has a water content of over 98%, is reduced to half its volume by means of thickeners. In the digester tank, the organic substance of the sludge is further decomposed by anaerobic bacteria and biogas forms (around 66% methane, 34% carbon dioxide). In this step, biologically bound phosphorus is partly dissolved again and can then be recovered by, for example, MAP precipitation (MAP: magnesium ammonium phosphate). Phosphorus that is bound chemically in the sludge cannot be reclaimed until it can be extracted from the ash following monocombustion (combustion of a material without mixing with other fuels). From this extract, it is possible to manufacture fertilizer or phosphoric acid.

Phosphorus balance

Phosphorus's journey through the wastewater treatment plant can be tracked in numbers: Assuming a daily wastewater quantity of 150 liters per capita per day (pcpd), it is calculated that this will result in a concentration of 1.8 g TP pcpd, which corresponds to an influent concentration of 12 mg/L. By the end of mechanical treatment, the phosphorus content is reduced by 0.2 g pcpd. A major contribution to phosphorus reduction is achieved after biological treatment: 0.4 g pcpd phosphorus is bound to waste activated sludge. With the appropriate process control, a further 0.8 g is eliminated by biological phosphorus removal (EBPR). For chemical precipitation, a small residual amount of phosphorus is left over (0.2 g pcp) with a well-functioning EBPR. Without EBPR, the greatest phosphorus concentration is chemically bound in the sludge (1.0 g pcpd).

For compliance with the control values, EBPR alone is not sufficient. In most wastewater treatment plants, EBPR is used in combination with chemical precipitation. The individual concentrations realized by biological and chemical phosphorus removal may vary widely with time. Figure 4 shows how the total phosphorus content is reduced in municipal wastewater across the various stages of a treatment plant.

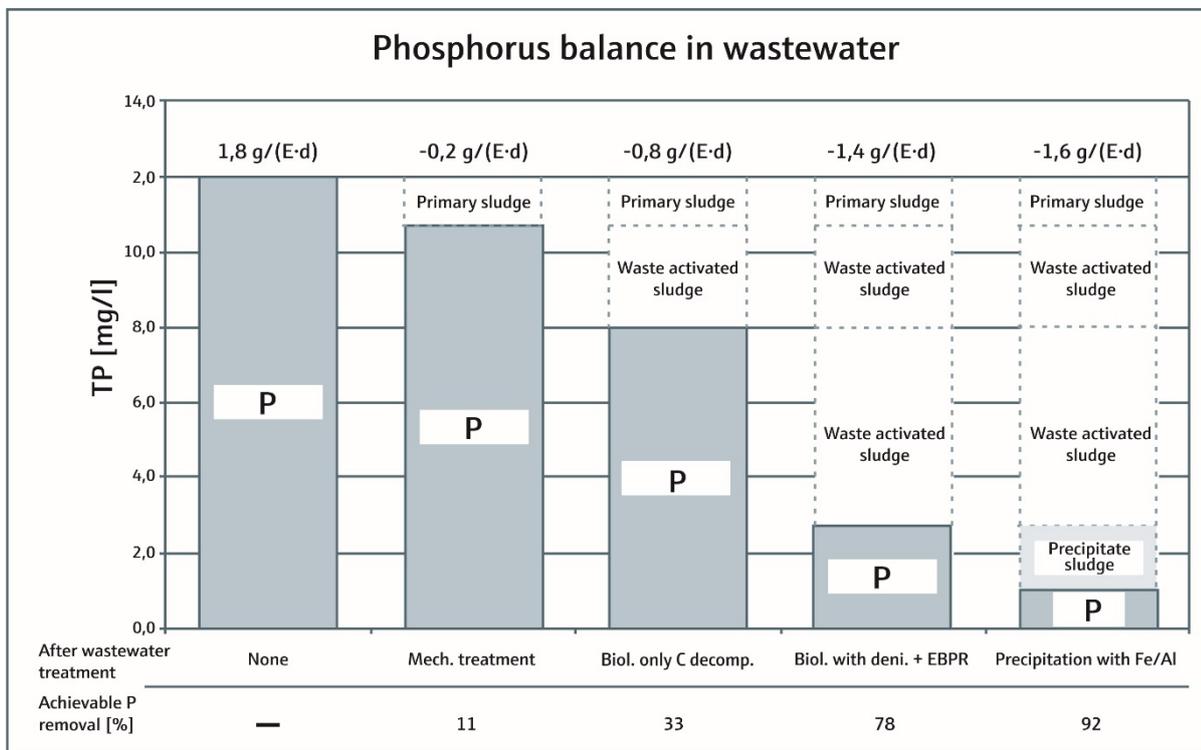


Figure 4: Reduction in the total phosphorus content of wastewater on the way through a treatment plant with EBPR [8].

Measurement and control engineering

Requirements for measurement technology

The requirements for measurement technology are strict. On the one hand, it should make the wastewater composition and the subprocesses of wastewater treatment transparent. It is expected to make the basic data needed for further studies available and to monitor treatment performance. On the other hand, there is a demand for measured values that are reliable and quickly reported. The measurement technology should work precisely and require little effort to keep up and running. Only online measurement technology satisfies this requirements profile. Possible solutions include sensors (in situ measurement) and analyzers (sample transported to the measuring instrument). A comparison of these measuring systems is described in guideline DWA-M 269 of the German Association for Water, Wastewater and Waste (DWA) [10]. The technique of continuous phosphate measurement is detailed below.

Measuring point and sample transport

The orthophosphate concentration can be determined at various places in the wastewater treatment plant. Figure 2 points out the possible monitoring locations: Influent, primary clarifier, bioreactor and wastewater treatment plant outfall. The choice of measurement location should take into consideration good access and the requirements of the measuring system. Where the measuring system is situated outside the basin, the sample is transported to the analyzer via an upstream sample preparation station.

Feedback control engineering

The fundamentals of operating bioreactors with targeted phosphorus removal are described in a dedicated publication issued by the DWA [11]. The prerequisites for wastewater treatment plants with chemical precipitation are that a controller unit be present or retrofitted and that it be possible for the dosing pumps to be controlled automatically. It should be possible for precipitant dosing to be gradually increased in line with loading on the basis of plotted time curves. With appropriate feedback control engineering, various targets are pursued, chiefly: Complying with control values, optimizing precipitant consumption and dosing, and minimizing sludge spikes. Although reducing energy consumption can also be a target for control systems, this is as good as irrelevant when it comes to phosphorus removal. As Figure 2 shows, a measuring point in the biological treatment stage is suitable for controlling purposes. More information on the automation of phosphorus removal, covering both feedback and non-feedback control, is detailed in DWA technical paper 268 [12].

Analytical methods

Continuous measurement of orthophosphate can be realized by two different photometric methods. Depending on the purpose of application, requirements for high accuracy, DIN conformity or economical performance will take priority. The appropriate measurement method should be chosen accordingly.

The measuring instruments for determining the solute content of wastewater generally display the reading as PO₄-P. The molar concentration of orthophosphate (expressed in mg/L) relates to elemental phosphorus. The following relationship applies:

$$1 \text{ mg/L PO}_4\text{-P} \cong 3.07 \text{ mg/L PO}_4^{3-}$$

Phosphate determination by the blue method: Molybdenum blue technique

With the molybdenum blue method (DIN EN ISO 6878), orthophosphate ions are converted to complex phosphomolybdic acid in the acid medium of ammonium molybdate. Reducing agents are then used to convert this product to phosphomolybdenum blue. The intensity of the blue-colored substance is measured photometrically at approximately 810 nm [5].

This technique covers the range of concentration from 0.005 to 15 mg/L PO₄-P, making it especially suitable for low concentrations. The shelf life of a reagent is dependent on ambient temperature. Particularly where room temperatures are high, shelf life should be prolonged by cooling equipment.

Phosphate determination by the yellow method: Vanadate-molybdate technique

With the vanadate-molybdate method, orthophosphate ions in an acid medium of ammonium molybdate and ammonium vanadate react to form the yellow vanadomolybdophosphoric acid. The color intensity of this acid is measured photometrically at approximately 430 nm. This technique incrementally covers a concentration range from 0.05 to 50 mg/L PO₄-P.

For a long time, the yellow method was the preferred option because the reagents are easy to handle and they have a relatively long shelf life without the need for cooling. However, the measurement reading is affected by any yellow-colored substances in the water. To a great extent, it is possible to compensate for this effect using calibration techniques.

Both phosphate determination methods are used in online analytics. Various manufacturers offer analyzers that detect orthophosphate by the yellow or blue method. A market overview was recently published on this topic [13].

Phosphate precipitation

For chemical phosphorus removal, the recognized and generally accepted good engineering practices are described in technical paper DWA-A 202 [7]. Precipitants are used to convert orthophosphate to insoluble form, it precipitates and is then separated [14]. The objective of precipitation is the elimination of phosphorus from the wastewater and, in future, the subsequent recovery of orthophosphate from the accruing sludge. Depending on where the dosing of a precipitant takes place, different methods of phosphorus removal can be identified: Pre-precipitation, simultaneous precipitation and post-precipitation. The success of precipitation is crucially influenced by the pH value and precipitant quantity. Figure 5 shows a schematic diagram of the different options for phosphate precipitation.

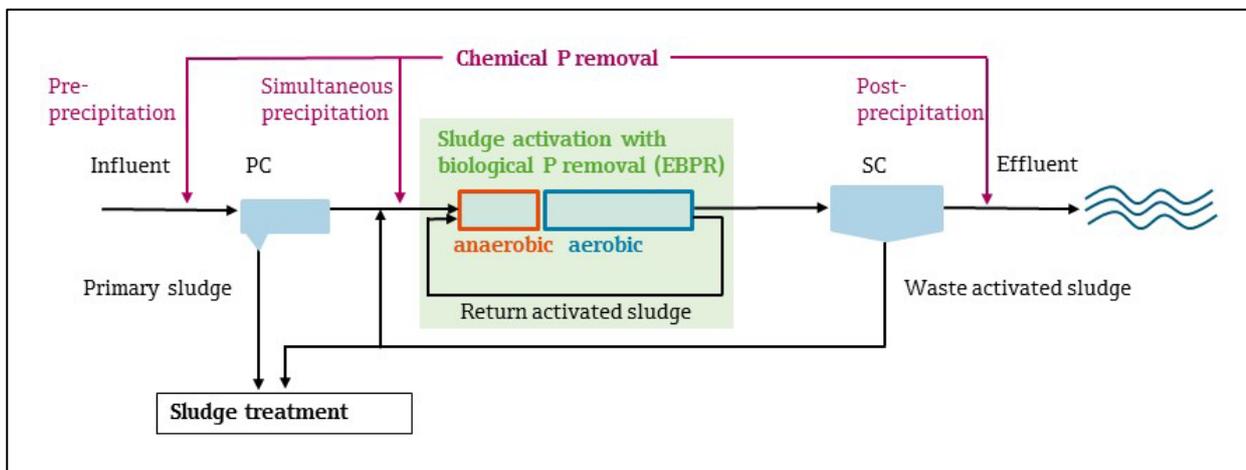


Figure 5: Process integration of chemical and biological phosphorus removal from wastewater (simplified diagram, extract from [15]). Abbreviations: VK/PC = primary clarification, NK/SC = secondary clarification.

Pre-precipitation

With pre-precipitation, the precipitant is added before primary clarification. The precipitated phosphates are then extracted with the primary sludge.

Simultaneous precipitation

If the precipitant is added to the aeration basin, this is known as simultaneous precipitation. The phosphates are bound to the waste activated sludge and thereby removed from the wastewater. A combination of pre- and simultaneous precipitation is called two-step precipitation.

Post-precipitation

Post-precipitation is where dosing of precipitation chemicals takes place in a separate stage after secondary clarification.

Biological phosphorus removal

In some wastewater treatment plants, an increase in phosphorus removal is achieved by supplementing precipitation with the use of special bacteria under alternating anaerobic and aerobic conditions [16]. These microorganisms accumulate phosphate in their cells, thereby extracting it from the wastewater. This process is known as enhanced biological phosphorus removal or EBPR. EBPR requires an anaerobic zone and highly decomposable organic acids in the wastewater.

Overview of precipitants

- Aluminum sulphate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$),
- Sodium aluminate ($\text{NaAl}(\text{OH})_4$)
- Iron(III) chloride ($\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$)
 $\text{pH} > 7$: $\text{Fe}^{3+} + \text{HPO}_4^{2-} \rightarrow \text{FePO}_4 + \text{H}^+$;
 $\text{pH} < 7$: $\text{Fe}^{3+} + \text{H}_2\text{PO}_4^- \rightarrow \text{FePO}_4 + 2 \text{H}^+$
- Iron(II) sulphate ($\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$; in the aeration basin)
 $\text{pH} > 7$: $4 \text{Fe}^{2+} + 4 \text{HPO}_4^{2-} + \text{O}_2 \rightarrow 4 \text{FePO}_4 + 2 \text{H}_2\text{O}$;
 $\text{pH} < 7$: $4 \text{Fe}^{2+} + 4 \text{H}_2\text{PO}_4^- + \text{O}_2 \rightarrow 4 \text{FePO}_4 + 2 \text{H}_2\text{O} + 4 \text{H}^+$
- Calcium (calcium carbonate; calcium hydrate or milk of lime $\text{Ca}(\text{OH})_2$)

Aluminum and iron salts react to form acids, while calcium is a base precipitant. Precipitation produces hydroxyphosphate complexes. Fe(III), Fe(II), Al(III) and Ca(II) all form insoluble compounds in the presence of orthophosphate in aqueous solution and these can be separated from the liquid phase by sedimentation, flotation or filtration [7].

Legal bases

Legislation specifies requirements for both the quality of water bodies and the quality of water discharged from municipal wastewater treatment plants. The benchmark for immission requirements is the EU Water Framework Directive. In Germany, national legislation governs the protection of water bodies, which is enacted at federal level primarily by the Waste Water Ordinance. This ordinance specifies the “minimum requirements”, e.g. for the total phosphorus parameter. Self-monitoring is defined by *Länder*-specific regulations, while official controls are not. The concentrations to be met in the wastewater treatment plant effluent are stated in the respective water right permit, the minimum requirements being enforced by federal law. Table 2 below shows the legal bases for the imposition of control values [17].

Table 2: Legal bases for the imposition of control values in the effluent of municipal wastewater treatment plants

EU	Federal level	Länder level	Other
Directive 2000/60/EC (Water Framework Directive, WFD)	Federal Water Act (WHG)	Water acts of the <i>Länder</i>	Statutes of cities, municipalities and wastewater associations
Directive 2008/105/EC (Environmental Quality Standards Directive, EQSD)	Ordinance on the Protection of Surface Waters (OGewV)	Implementing and administrative provisions	
Directive 91/271/EC Urban Waste Water Treatment Directive	Waste Water Ordinance (AbwV) Waste Water Charges Act (AbwAG)		
	Sewage Sludge Ordinance (AbfklärV)		

EU Water Framework Directive

The European Water Framework Directive (WFD 2000/60/EC) reformed European water policy and came into force in 2000 [18]). This defines, among other objectives, targets for good water body quality – the environmental quality standards EQSD – and, accordingly, limit values for the chemical composition of the water body. For phosphorus, the limit for bodies of water is 0.1 mg/L total phosphorus. It is intended that all bodies of water throughout Europe will have achieved good ecological status by 2027.

Federal Water Act

In the Federal Republic of Germany, the Federal Water Act (WHG) is the main instrument of German water law. The WHG contains provisions, for example, on the protection and use of surface waters and groundwater. The laws of individual German *Länder* may vary from these regulations [19].

Ordinance on the Protection of Surface Waters

The Ordinance on the Protection of Surface Waters (OGewV) transposes the requirements of the EU Water Framework Directive into German federal law. It contains, for example, limit values for pollutants and nutrients in different types of water. Some German *Länder* are promoting this transposition rigorously. In Baden-Württemberg, Bavaria, Berlin, Hesse, North Rhine-Westphalia and Schleswig-Holstein, measures are being implemented in which the control values for the effluent of wastewater treatment plants are dependent on the size and sensitivity of the water bodies.

In contrast to the statutory control values, where official controls are authoritative (qualified random sample), the fulfillment of OGewV targets in Baden-Württemberg and also, in individual cases, in Hesse, is increasingly based on values to be met as part of self-monitoring by the wastewater treatment plants themselves. These take the form of an annual average or – as in Hesse – a 24-hour composite sample. The requirements are, however, very demanding. After all, these measures are intended to achieve, as far as possible, the required 0.1 mg/L total phosphorus in the affected water bodies. In Baden-Württemberg, it is therefore planned to impose an annual average of 0.16 mg/L orthophosphate (o-PO₄-P) for treatment plants from size category 3 in deficit regions. In Hesse, a limit of 0.2 mg/L orthophosphate (o-PO₄-P), for example, has to be achieved in the 24-hour composite sample (size category 4 without special requirements). In Berlin, even lower values of 0.1 mg/L orthophosphate (o-PO₄-P) are required to be maintained in individual cases due to the special lake-like nature of its water bodies.

Waste Water Ordinance

The Waste Water Ordinance (AbwV) determines the minimum requirements for the discharging of wastewater into the aquatic environment [20]. It transposes EU law into German law. In many of its annexes, the AbwV prescribes a limit value of 50 mg/L for total phosphorus for discharges from various industries. For a municipal wastewater treatment plant (AbwV Annex 1), this is a control value of 1 mg/L total phosphorus for plants with a capacity greater than 100,000 residents and 2 mg/l for greater than 10,000 residents in the qualified random sample or 2-hour composite sample. For municipal plants with a capacity of less than 10,000 residents, no phosphorus removal target has been imposed as a minimum requirement to date. The measurement method is specified in DIN EN ISO 6878 [5].

Waste Water Charges Act

Under the Waste Water Charges Act (AbwAG), pollutants and pollutant groups are required to be evaluated. These wastewater charges are intended to create financial incentives to improve the performance of wastewater treatment plants and apply only to direct discharging into a water body. For the phosphorus parameter, a wastewater charge shall be paid [21].

Other legal provisions

At *Länder* level (cf. Figure 7, column 3), further legal provisions apply. These include the respective water acts along with implementing and administrative provisions. These ordinances transpose the provisions enacted at federal level. Lastly, additional administrative provisions apply in cities and municipalities [22].

Sewage Sludge Ordinance

In October 2017, the revised Sewage Sludge Ordinance (AbfKlärV) entered into force [23]. This stipulates that, as of 2029, no sewage sludge from wastewater treatment plants of size category 5 may be used as fertilizer. At the same time, it lays down the requirement to, in future, recover the phosphorus contained in sewage sludge [24].

Application examples

Monitoring of orthophosphate in the effluent from the biological treatment stage

A municipal wastewater treatment plant is connected to the administrative district of Darmstadt and sized for 25,000 residents. The wastewater treatment plant receives ordinary municipal wastewater. The composition of this wastewater fluctuates considerably due to the presence of a health spa frequented by day visitors. The primary clarifier is constantly dosed with iron(III) salts. Whenever the orthophosphate control value of 0.2 mg/L PO₄-P is exceeded, the plant currently adds aluminum salts to the bioreactor. Compliance with the control value is monitored at the point of discharge from the biological stage. Before the clarified water is discharged, the customer takes a 24-hour composite sample. Figure 6 below shows the temporal evolution of the orthophosphate measurement in the effluent of the bioreactor.

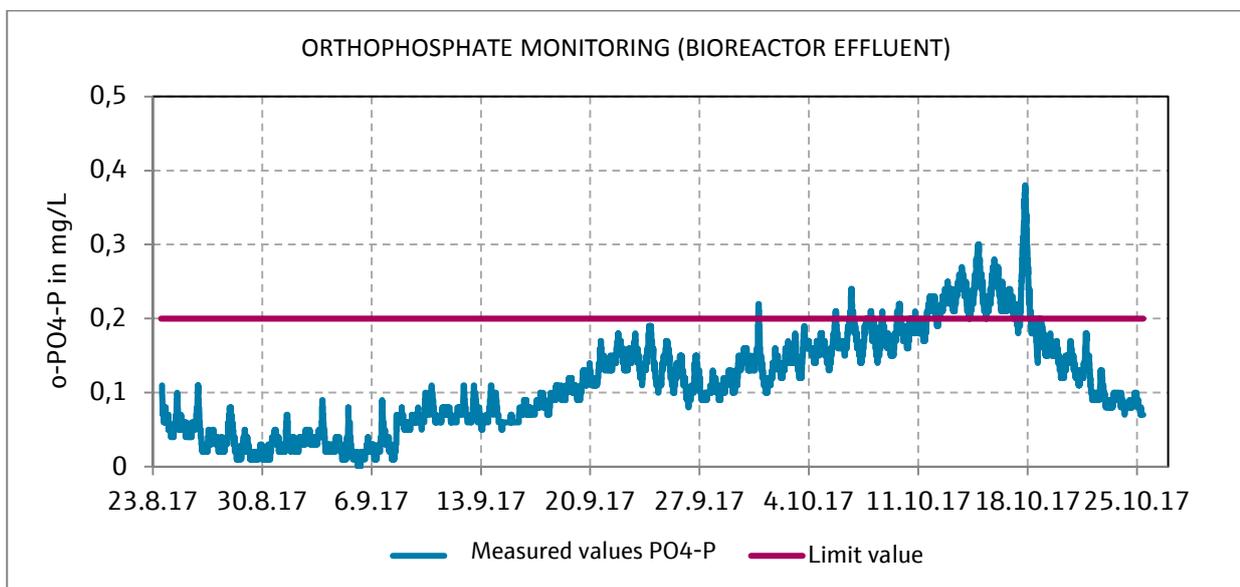


Figure 6: Time chart. In a municipal wastewater treatment plant in Hesse, compliance with an orthophosphate value was monitored in the effluent from the bioreactor over a period of approximately two months. Aluminum salts are added whenever 0.2 mg/L PO₄-P is exceeded.

This is a typical example of how a small- to medium-sized wastewater treatment plant is trying to meet the new, strict control values – here 0.2 mg/L PO₄-P – and to maintain this with an online measurement. First of all, the use of an analyzer with the blue method enabled a reliable measurement of the low orthophosphate concentrations < 0.1 mg/L (o-PO₄-P) by comparison with other standard instruments that work with the yellow method. The trend of the curve in Figure 6 makes it clear that, to begin with, the static dosing quantities led to the desired, very low discharge values. In this respect, the initial recordings reveal the maximum possible removal capability of the plant's process engineering. It is beyond question that such “overdosing” can be used to comply reliably with the exacting requirements. In the subsequent operating phase, the dosage was gradually reduced, which can be seen on the graph as a “nudging” towards the control value and even to the occasional exceedance. After an emphatic spike, the dosage was increased and the concentration returned safely below the target value. The dynamic behavior of the orthophosphate concentration at this measuring point is an impressive demonstration of how, in a plant's day-to-day running, compliance with strict legal requirements can be reliably monitored with the use of an online analyzer supporting the blue method.

Comparative determination of orthophosphate with CA80PH and DIN method

In deficit regions of Hesse, phosphorus removal is pursued even for small wastewater treatment plants in order to meet the immission-based effluent concentrations of 0.07 mg/L orthophosphate (o-PO₄-P) and 0.1 mg/L total phosphorus stipulated by the EU WFD and the German Ordinance on the Protection of Surface Waters. As an example of this kind of application, a long-term measurement was conducted in a trial treatment plant of TU Darmstadt (measuring point: Bioreactor output) and orthophosphate concentrations ≤ 0.2 mg/L (o-PO₄-P) were monitored by means of a CA80PH online analyzer. As a reference measurement, the molybdenum blue method was carried out to DIN EN ISO 6878 in the laboratory. For the appraisal of the long-term study, the measured data were evaluated statistically and the key indicators determined [25]. The results are illustrated in Figure 7.

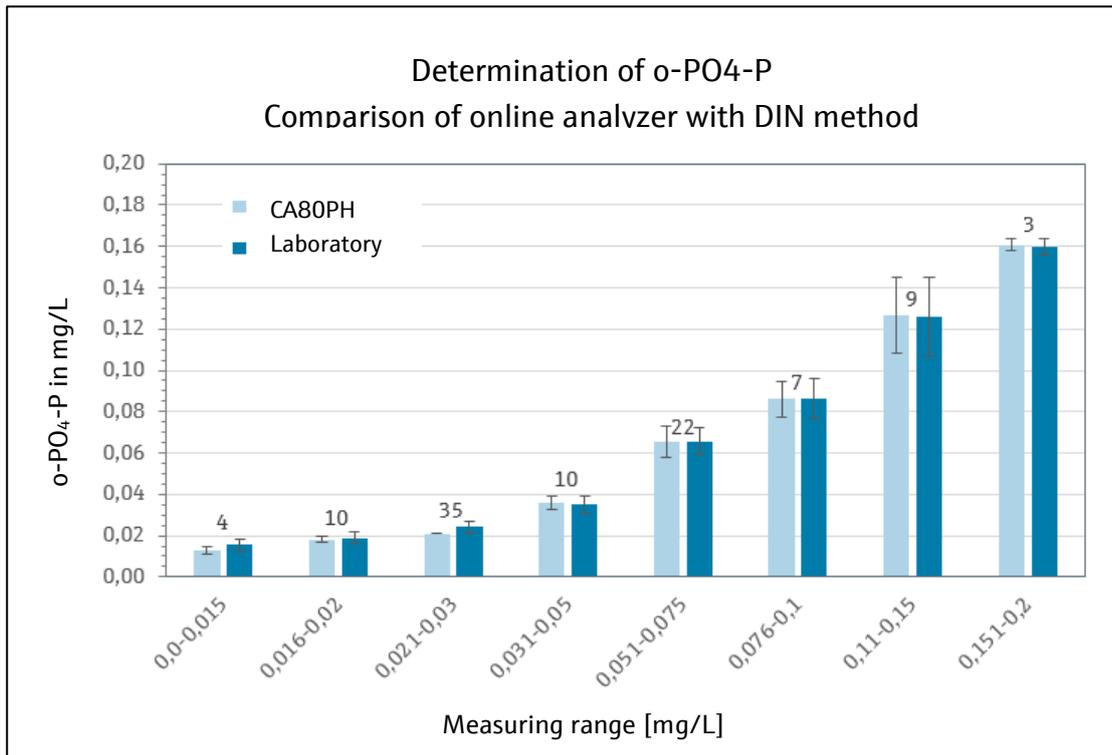


Figure 7: Bar chart. Orthophosphate concentrations are determined both by DIN method in the laboratory and by online analyzer and the measurements are compared. For each measuring range, the mean values of the online and laboratory measurements are represented. The error bars correspond to one standard deviation (1 s), the figures above the bars indicate the respective quantity of measurements.

Over a period of four months, samples were taken at regular intervals from a container (Figure 7 “Laboratory”) and measured in the lab in accordance with the DIN blue method. At the same location, a ceramic membrane filter took samples for an online analyzer (Figure 7 “CA80PH”). The values measured by the analyzer were sorted in ascending order. The laboratory results were assigned to the sorted values measured by the analyzer based on the time-stamp. Then, eight measuring ranges were defined. The measurement results of the analyzer and those from the laboratory were allocated to these ranges and a statement on the precision of the measurement methods was given by computation of the mean and calculation of the confidence interval.

It was possible to show that the results of the online analyzer tally with the results of the laboratory measurements. While measured value fluctuations were observed with the CA80PH and in the laboratory tests, the differences in the respective means were not significant. The range 0.151–0.2 mg/L orthophosphate (o-PO₄-P) is based on only three measured values and is not, therefore, statistically representative.

Summary

This white paper describes the relationships between the legal requirements for limit and control values for total phosphate at the outfall of wastewater treatment plants and the options for wastewater treatment plant operators to react with appropriate measurement and control engineering. Prominence is given to the journey of phosphorus in its various fractions through the municipal wastewater treatment plant with an illustration of the techniques for phosphorus removal. An overview of the legal bases completes the work.

With two selected examples, it was possible to show that an online analyzer that determines orthophosphate using the blue method in accordance with the DIN standard is capable of identifying events and dynamic changes in phosphate removal swiftly and precisely. As a result, it is virtually predestined to provide the operator with the exact data needed to monitor compliance with legal requirements and to be able in future to record even lower orthophosphate concentrations with high precision.

Acknowledgment

I thank Prof. Dr.-Ing. P. Baumann, Stuttgart Technology University of Applied Sciences, for his valuable suggestions, particularly with regard to the legal bases relevant to this white paper.

Bibliography

- [1] U.S. Geological Survey, „Mineral Commodity Summaries 2018,“ [Online]. Available: <https://minerals.usgs.gov/minerals/pubs/mcs/>. [Zugriff am 01.11.2018].
- [2] K. Hoppenhaus, „Das unersetzliche Element. Ohne Phosphor kann der Mensch nicht leben. In Teilen Afrikas ist der Stoff knapp geworden. Was nun?,“ *Die Zeit*, Nr. 48, S. 34-35, 22.11.2018.
- [3] A. Müller, „Natürliche ökologische Energie- und Stoffkreisläufe,“ Bundesministerium für Verbraucherschutz, Ernährung und Landwirtschaft, 2003, S. 15.
- [4] R. Schneider, „Stickstoff- und Phosphorverbindungen im Abwasser – Herkunft und Auswirkungen. Kap. 1,“ in *Grundlagen für den Betrieb von Belebungsanlagen mit gezielter Stickstoff- und Phosphorelimination*, DWA-Landesverband Baden-Württemberg, 2016, S. 13-51 (ISBN 978-3-88721-372-5).
- [5] DIN EN ISO 6878, „Wasserbeschaffenheit – Bestimmung von Phosphor – Photometrisches Verfahren mittels Ammoniummolybdat,“ 2004.
- [6] A. Müller, „Land soll Kurs gegen Phosphor korrigieren,“ *Stuttgarter Zeitung*, 30.08.2018.
- [7] DWA-Arbeitsblatt 202, „Chemisch-physikalische Verfahren zur Elimination von Phosphor aus Abwasser,“ Verlag DWA, 2011 (ISBN 978-3-941897-87-8).
- [8] DWA Leitfaden Nr. 2-13, „Betrieb von Abwasseranlagen; Die Phosphorbilanz im kommunalen Abwasser,“ DWA Landesverband Bayern, Stand 2/2011.
- [9] A. Roskosch, P. Heidecke, „Phosphorrückgewinnung,“ in *Klärschlamm Entsorgung in der Bundesrepublik Deutschland*, Umweltbundesamt, 2018, S. 46-55, ISSN (online) 2363-832X. Kurzlink: [Bit.ly/2dowYYi](https://bit.ly/2dowYYi).
- [10] DWA-Merkblatt 269, „Prozessmessgeräte für Stickstoff, Phosphor und Kohlenstoff in Abwasserbehandlungsanlagen,“ Verlag DWA, ISBN 978-88721-651-1, 2018.
- [11] P. Baumann, „Grundlagen der Phosphat-Elimination. Kap. 6,“ in *Grundlagen für den Betrieb von Belebungsanlagen mit gezielter Stickstoff- und Phosphorelimination*, DWA-Landesverband Baden-Württemberg, ISBN 978 3 88721 372 5, 2016, S. 163-197.
- [12] DWA-Arbeitsblatt 268, „Automatisierung von einstufigen Belebungsanlagen,“ Verlag DWA, ISBN 978-3-88721-363-3, 2016.

- [13] P. Baumann, „Neues zur Phosphorelimination in Kläranlagen,“ DWA, Hennef, 05.06.2018.
- [14] M. Huber et. al., „Analyse einer möglichst weitestgehenden Phosphorelimination bei kommunalen Kläranlagen in Deutschland,“ *Korrespondenz Abwasser, Abfall*, Bd. 65, Nr. 4, S. 298ff, 2018.
- [15] Leibniz Universität Hannover, „Potential und Grenzen der Phosphorrückgewinnung für Kläranlagen mit biologischer Phosphorelimination in Niedersachsen,“ Institut für Siedlungswasserwirtschaft und Abfalltechnik (ISAH), S. 4, Hannover, 2016.
- [16] P. Baumann, Kh. Krauth, W. Maier, M. Roth, „Reinigungsziel: Chemische und biologische Phosphatelimination,“ in *Funktionsstörungen auf Kläranlagen. Praxisleitfaden. Handbuch für den Betrieb von Kläranlagen*, DWA, 2008 (ISBN 978-3-940173-46-1), S. 78-87.
- [17] „Wasserrecht,“ [Online]. Available: <https://www.umweltbundesamt.de/themen/wasser/wasserrecht#textpart-1>. [Zugriff am 07.11.2018].
- [18] Umweltbundesamt. Umweltpolitik, „Die Wasserrahmenrichtlinie – neues Fundament für den Gewässerschutz in Europa (Langfassung),“ 2004.
- [19] WHG, „Gesetz zur Ordnung des Wasserhaushalts (Wasserhaushaltsgesetz WHG),“ 2009. [Online]. Available: http://www.gesetze-im-internet.de/whg_2009/WHG.pdf. [Zugriff am 05.11.2018].
- [20] AbwV, „BGBI. I - Verordnung über Anforderungen an das Einleiten von Abwasser in Gewässer (Abwasserverordnung),“ Bundesamt für Justiz, 2016.
- [21] DWA Landesverband Bayern, „Das Abwasserabgabengesetz und seine Auswirkungen in der Praxis - Eine Arbeitshilfe für Städte und Gemeinden,“ F. Hirthammer Verlag, 2003.
- [22] Europäische Union, „Richtlinie 91/271/EWG über die Behandlung von kommunalem Abwasser (Kommunale Abwasserrichtlinie),“ Amtsblatt der EG, Nr. L 135/40 ff., Aktualisierung 22.10.2008.
- [23] Bundesrat, „Verordnung zur Neuordnung der Klärschlammverwertung,“ Bundesgesetzblatt Teil 1 (65), S. 3465-3512, 2017.
- [24] C. Schaum, V. Demmelbauer, „Ressource Klärschlamm: Zukunftsfähige Nutzungstrategien,“ [Online]. Available: <https://www.wwt-online.de/sites/default/files/fachartikel/wwt1017-sp-schaum.pdf>. [Zugriff am 16.10.2018].

[25] S. Lackner, „Nachhaltiger Gewässerschutz als Herausforderung für die Abwassertechnik,“
Vortrag im Rahmen des „Fachforum Phosphor – Nährstoff, Schadstoff und Ressource“, Mainz,
14.11.2018.

The Endress+Hauser Group

Endress+Hauser is a global leader in measurement instrumentation, services and solutions for industrial process engineering. The Group employs approximately 14,000 personnel across the globe, generating net sales of over 2.4 billion euros in 2018.

WP01112C/07/EN/01.19