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A Study on the Situation and Learnings of the Precipitant Shortage in the German Wastewater Sector

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Abstract: Wastewater treatment companies are particularly confronted by the energy and supply crisis resulting from the war in the Ukraine. More specifically, production and supply problems with precipitant production have shown that today's wastewater treatment technology in Germany is not crisis-proofed and must become more resilient. The aim of this paper was to determine a required precipitant quantity for Germany with regard to chemical phosphorus elimination, as well as the expected shortfalls due to the shortage situation. Furthermore, possible solutions were identified for how the precipitant can be saved or substituted. Study surveys were conducted to gather data for a meaningful response regarding the operators (wastewater treatment plants, industry, and water suppliers), manufacturers, and the German federal states. A recommendation is given on what a path to more resilient wastewater management with a focus on phosphorus elimination could look like. Based on the data obtained, the report focused on wastewater engineering issues for wastewater treatment plants and industry. The results of the study are relevant for decision-makers, researchers, and operators in the wastewater sector in order to intervene in the market themselves if necessary, e.g., money for production or conversion to biological phosphorus elimination.

Keywords: phosphorus; precipitant shortage; resilience of WWTPs; resilience of wastewater treatment plants; Bio-P; biological phosphorus removal; chemical phosphorus removal; German wastewater sector

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1. Introduction

Although phosphorus (P) is a limited resource, a total of approx. 15,400 t of P per year is discharged into German surface waters, including all input pathways [1] (p. 109), [2]. The urban input pathways of municipal wastewater treatment plants (WWTPs) and sewer systems account for the largest shares [1,3].

Plant growth is promoted by P, and it has an eutrophic effect on water bodies and coastal waters, which can lead to odor pollution when biomass dies and temperatures are high [4,5]. Accordingly, P inputs have been regulated by annex 1 of the German Wastewater Ordinance (AbwV) for size class 4 and bigger since 1989. According to this, the following monitoring values must not be exceeded within the effluent of WWTPs:

- 2 mg/L at 10,000 population equivalent (p.e.) (size class 4);
- 1 mg/L from 100,000 p.e. (size class 5) [6].

The Baltic Sea area and the Northern Sea need extra protection [7]. According to the German Surface Water Ordinance (2016), lower monitoring values may be required on a regional and water body-specific basis. Some federal states have been implementing stricter operating mean values [8].

WWTPs, direct dischargers, and indirect dischargers favorably use precipitants for the purpose of chemical phosphorus elimination (PC), as well as "support precipitants" in biological phosphorus elimination (PBC) [9,10].

Precipitants can be used in pre-precipitation, post-precipitation, or simultaneous precipitation, for example, in the classical aeration tank. Precipitants must be used for advanced P elimination. This is mainly performed by the flocculation filtration process.

Phosphorus is listed as a critical raw material that is important in various ways, and the world's resources are finite [11,12]. Especially in Europe, there are only a few natural sources. Thus, alternative efficient strategies of gaining P must be explored [11–13]. According to the reorientation of the German Sewage Sludge Ordinance (AbfKlärV) in 2017, environmental and resource protection as goals moved further into focus with comprehensive specifications for the recovery of P as a critical raw material [12,14]. Preference is the recovery from biological phosphorus elimination (PB), since PC binds the phosphorus too strongly to the salts, and P can only be recovered with high energy input [3].

Current developments due to the war in the Ukraine and the resulting energy and supply crises have caused an emergency in wastewater treatment [15–18]. As early as autumn 2022, WWTP operators have increasingly complained about supply shortages of chemicals that are needed in particular as precipitants for PC and PBC. The use of ferric chloride as a precipitant is widespread. Unfortunately, ferric chloride is produced as a by-product in the titanium industry, which decreased the production immensely. While the situation has currently eased, the supply of precipitants can be described as fragile, and the situation of WWTPs in Germany with regard to precipitants can be described as non-resilient.

If precipitants are not available or only available to a limited extent for the WWTP operators, then it must be clarified to what extent precipitants can be saved or substituted.

The course of the occurring emergency situation made evident how dependent German WWTPs are on precipitants for P. It became apparent that too little data were available on precipitant usage in Germany in terms of type, quantity, and frequency to react sensibly to the emergency.

In order to obtain a substantiated overview, the German Environment Agency (UBA) commissioned a study for Germany-wide surveys on the part of operators and authorities, as well as Europe-wide surveys on the part of manufacturers. This study was conducted by the mentioned researchers above. The situation in the industry (direct and indirect dischargers) and in the drinking water sector was also considered in the surveys. Based on the data obtained, this article focused on wastewater engineering issues for wastewater treatment plants and the industry.

2. Materials and Methods

2.1. Survey Procedure and Statistical Analysis

Data were gathered as part of the study for the German Environment Agency (UBA). The final report of the whole study will soon be available in German via UBA Texte [19].

The study design consisted of three broad surveys, which are shortly introduced in the following. Additionally, anonymous data of volunteering WWTPs were analyzed regarding considerations on the German sampling regime.

The design of an online survey was chosen as the preferred method for data collection because of its advantages, such as a larger geographical area, quicker responses, fewer errors, and lower costs [20]. All surveys were conducted using the LimeSurvey platform with a secured server at the Technical University of Berlin. Every survey began with its purpose, the expected survey duration, and the assurance of anonymity and confidentiality. All survey designs were developed specifically for the purpose of the study.

- Survey 1: The operator survey was addressed to the municipal wastewater sector (WWTP operators) and additionally to water suppliers, as well as indirect and direct dischargers in Germany. The questions were specifically tailored based on the set of rules (WWTPs or drinking water industry) for the following recipients: municipal wastewater disposers/WWTPs, industrial dischargers, and water suppliers. The survey link was distributed through the Federal Ministry for the Environment, Nature Conservation, Nuclear Safety, and Consumer Protection (BMUV) and relevant industry associations in Germany. The survey was addressed in German and was administrated between 14 November 2022 and 1 January 2023. An overview of the questions is attached in Appendix A. The questions consisted of open, as well as semi-open, multiple-choice and grid questions. In every question, the option 'other' was included. The questionnaire was reviewed by the UBA before publication. Based on the review, some questions were modified and clarified to improve their quality. After publication, two follow-up participation requests were sent to gain higher participation in the survey.

- Survey 2: The manufacturer survey was distributed through LimeSurvey in the European Inorganic Coagulants Producers Association (INCOPA) and focused on the 30 biggest European manufacturers and manufacturers' association with a possible sales market for precipitants in Germany. The goal was to determine the produced quantities for Germany before the precipitant shortage, the actual situation, and the predicted future. The survey was administrated in English between 25 November 2022 and 1 January 2023. An overview of the questions is attached in Appendix B. The questions consisted of open, as well as semi-open, multiple-choice and grid questions. The questionnaire of survey 2 also included the option 'other'. The survey link was distributed through the INCOPA network, and the questionnaire was reviewed by the UBA before publication, too. Based on the review, some questions were modified and clarified to improve their quality. One follow-up participation request was sent after publication.
- Survey 3: An orienting survey of the water law decisions at the federal state offices or ministries of the environment was carried out regarding P thresholds and sensible water bodies in Germany. The survey addressed all federal states in Germany (survey area), and the survey link was distributed through the BMUV like survey 1. It was administrated in German between 30 November 2022 and 31 March 2023. The questions in the survey are attached in Appendix C. The questions consisted of open, as well as semi-open, multiple-choice or grid questions and included the option 'other'. As before, the questionnaire was reviewed before publication. Based on the review, some questions were modified and clarified to improve their quality. Three follow-up participation requests were sent.

The responses to each survey were collected and exported to a Microsoft Excel spreadsheet (version Office16). The software is obtained via a license from the Technical University of Berlin. The quantitative data of the whole study were analyzed after a plausibility check using descriptive statistics (percentages) to show the respondents' choices. Double responses and extreme outliers were removed best as possible. Due to temporary server overloads, duplicates and incomplete submissions may have occurred. Accordingly, only complete submissions were considered for the evaluation. Graphical methods on the data were employed.

2.2. Further Background Information

Furthermore, background information was collected to support the analysis and will be listed in the following:

1. Destatis: The German Federal Statistical Office (Destatis) provides open access to the wastewater treatment and the disposal database, which was used for validating the total achievable quantity of WWTP in p.e. in Germany in survey 1 [21].
2. Background information of the German Association for Water, Wastewater, and Waste (DWA), which is a politically and economically independent association, was also used. The DWA works in expert groups designing and further developing the set of rules for WWTP in Germany, which are not open access. For the decision of common precipitants, the DWA-A 202 was especially used in survey 1 and 2. DWA-A 202

describes the set of rules for the chemical-physical processes for the elimination of phosphorus from wastewater [22].

3. For the set of rules for drinking water facilities, a list of treatment substances and disinfection in accordance with §11 of the German Drinking Water Ordinance (TrinkwV) version of the 24th amendment (November 2022) was used in survey 1 and 2 [23].

Detailed information on the dataset and outcomes from the web-based surveys are accessible upon request.

3. Results

3.1. Operator Survey Regarding Use of Precipitants

The results of the operator survey with a focus on precipitant usage at WWTPs and the industry are briefly presented. During the survey period, 2775 complete surveys of operators were collected. Of these, some consisted of summaries of associations of wastewater, depending on which level the survey was completed. A total of 72% of the recipients were WWTPs, 14% were direct and indirect dischargers, and another 14% were from drinking water facilities. The data show that especially federal states with a lot of smaller WWTPs like Bavaria or Baden-Wuerttemberg submitted a lot of surveys (49%), which demonstrates that a lot of plant operators participated in the survey themselves.

In total, Germany has an estimated 152,000,000 p.e. for all size classes of WWTPs. Size classes of German WWTPs are defined in the AbwV in annex 1, part C [6]. The survey reached 136,460,601 p.e., including WWTPs and indirect dischargers, which is 89% of the total p.e. in Germany. The data regarding the size class of the German WWTPs showed that 66% were in size class 4 (38,200,265 p.e.) or size class 5 (94,213,156 p.e.). The high participation (95%) of these size classes makes sense in terms of P-elimination, since, for size class 4 + 5 in the AbwV, P-elimination is obligatory and so is the particular concern of the shortage of precipitants. Additionally, in size class 3 (16% in survey 1), thresholds may exist with regard to P. Destatis lists in the open data base for wastewater treatment and disposal in size class 4 + 5 of WWTPs a sum of 138,000,000 p.e. [21]. Accordingly, around 90% has been collected.

Regarding the industry (365 total choice), 49% are direct and 51% are indirect dischargers. Furthermore, the branches of industry were queried, which could be affected by the precipitant shortage. The collection of branches was based on annex 2–57 from the AbwV and the Pollutant Release and Transfer Register (PRTR) [24]. Some industries chose more than one option; therefore, in total, 368 answers were given. Branches like chemical industry, chemical parks (summarized 19.6%), paper and pulp industry (11%), meat and slaughter processing plants (6.25%), and milk processing (5.5%) were chosen regularly. The most common choice of precipitants was selected on the basis of DWA A 202 and depended on the local wastewater composition. Due to the precipitant shortage, 63% of the WWTPs and industries switched to alternative precipitants listed in the DWA A 202, as long as the precipitant were still available. Only 1% considered the use of alternative precipitants not listed in the DWA A 202. The following alternatives were listed most often:

- PrecaPhos
- VTA Aluferol 91
- VTA Ferrodual
- FerroSorb

Additionally, it was asked whether there is a fear of impairment of the WWTP by alternative precipitants. A total of 47% (1132 answers) of the operators said ‘yes’. The main concerns most frequently cited were the risk of filamentous bacteria and bulking sludge and an increase in hydrogen sulfide (H_2S) from switching to alternative products.

Furthermore, the survey asked the type of P elimination. A total of 62,443,645 p.e. of the WWTPs use only precipitants for eliminating P (PC), while 4,050,450 p.e. perform PB without any precipitants and 57,690,832 p.e. PBC with precipitants as support. This classification uses the high use of precipitants for PC or as a support.

For the inlet and outlet P concentrations in mg/L of the German WWTPs, including indirect discharger 2004, answers were collected and are presented in the box and whisker plots of Figure 1. Inlet and outlet concentrations varied regarding the mix of wastewater, also regarding the indirect dischargers.

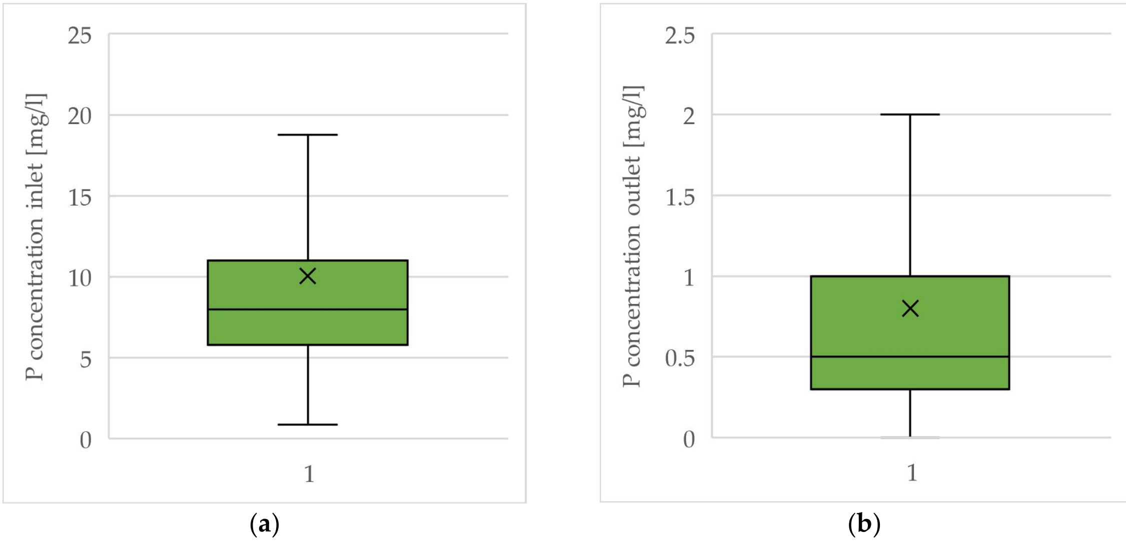


Figure 1. (**a**) Box and whisker plot P inlet concentrations in mg/L of German WWTPs. (**b**) Box and whisker plot P outlet concentrations in mg/L of German WWTPs. Cross shows the average, and the line in the box shows the median.

The median inlet concentration for P is 8 mg/L and for the outlet is 0.5 mg/L. At maximum, according to the data of the respondents, an effluent value of 17 mg/L was determined. This may be possible for small plants without a requirement for P elimination. Basically, it can be stated that P elimination in Germany is very efficient. In relation to the monitoring values, these results demonstrate a potential for precipitant savings.

In addition to the possibility of alternative precipitants, the operator survey analyzed the use of different precipitants and their percentage distribution in terms of number. Precipitants, such as ferric-chloride, aluminum ferric chloride, and ferric chloride sulphate, were used particularly frequently by the respondents before the precipitant shortage. These are precipitants that, in addition to PC, also counteract bulking sludge and help to reduce hydrogen sulfide (H_2S) formation.

In addition to the choice of precipitants, WWTPs and direct and indirect dischargers were asked about the average monthly quantity in tones (t) required per precipitant in order to obtain an estimate of the quantities required per precipitant for all of Germany. The monthly amounts were scaled up for a year and are shown in Table 1.

Germany has a high precipitant usage of ferric chloride, aluminum ferric chloride, and ferric chloride sulphate. The yearly quantity in total regarding WWTP, including the industry, for all precipitant is 1,103,743 t. Outliers were eliminated through a plausibility check. The industry (direct and indirect dischargers) needs in total only 84,941 t per year. The quantity of precipitants for WWTPs is approximately 1,015,000 t per year.

Based on the monthly quantity of necessary precipitants in t/month, the level of precipitants in stock in t and possible new delivery (yes or no, if yes: when is the delivery incoming and how much in t) was the shortage of precipitant calculated and scaled up to March 2023, June 2023, and the end of 2023 in t for the worst case regarding the WWTP and the industry. Until:

- 1 March 2023 a shortage of −91,412 t;
- 1 June 2023 a shortage of −186,226 t;
- The end of 2023 a shortage of −426,994 t.

Table 1. Estimated quantities in t required per precipitant for WWTP, including industry, in Germany per year.

Precipitant	Estimated Quantities of Precipitant per Year in t
Aluminum chloride	16,170
Aluminum ferric chloride	111,242
Aluminum sulphate	17,553
Aluminum ferric sulphate	4659
Ferrous chloride	61,172
Ferric chloride	667,109
Ferric chloride sulphate	74,974
Ferrous sulphate	50,125
Ferric sulphate	9418
Calcium hydroxide, white hydrated lime (slaked lime), stabilized milk of lime	24,355
Sodium aluminate	41,602
Polyaluminum (hydroxide) chloride (PAC)	23,672
Polyaluminum (hydroxide) chloride sulphate	910
Other precipitants	767
Total for all precipitants	1,103,743

Based on the situation in January 2023.

The worst case in total for all precipitants was determined.

All data were based on the status as of 1 January 2023, and the calculation assumed that no new sources (than mentioned) of supply are incoming. Thus, the calculation only shows a snapshot and considers the worst-case scenario for 2023.

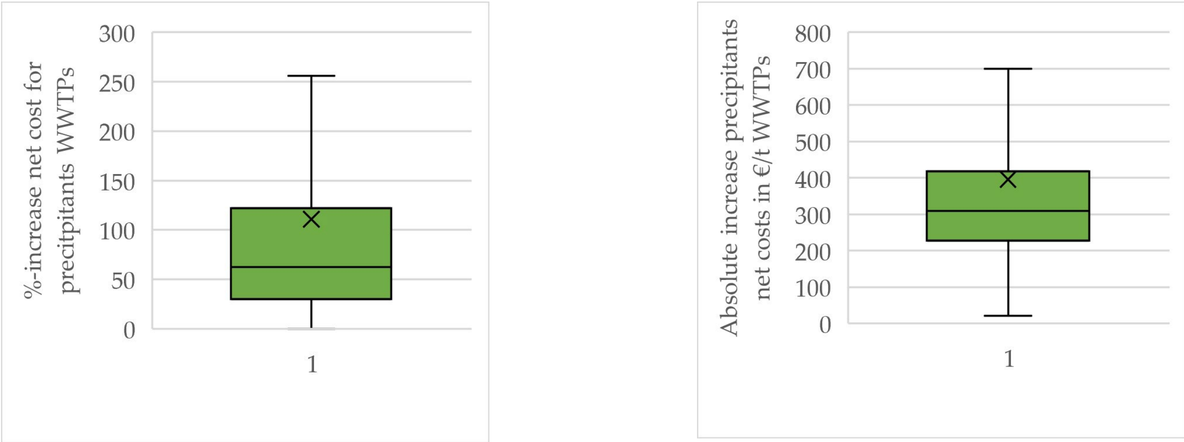
With no restart of production until the end of 2023, the shortage for precipitants in the WWTP and industry sector would have been 426,994 t. The included share of industry here was 59,430 t until the end of 2023. Consequently, without independent countermeasures taken by operators, it would mean a considerable load of P on the water bodies. The federal authorities under the leadership of the BMUV have regularly monitored and assessed the situation in order to be able to intervene further if necessary.

The shortages of aluminum ferric chloride (26,930 t), ferric chloride (14,678 t), ferric chloride sulphate (11,537 t), and ferrous sulphate (12,258 t) were most affected as of March 2023.

Due to the restart of production, the worst case did not occur, although a very fragile supply situation developed. In April 2023, the BMUV asked for an assessment of the situation in the federal states. Most federal states reported no or no further (minority) exceedances of the water limit values for P. However, the situation was described tense and was not foreseeable in the long term.

As a logical consequence, an increase in costs for precipitants happened due to the precipitant shortage. According to the survey data, 60% (1636 answers) of operators were affected by cost increases for precipitants due to the shortage. The operators had to accept higher prices and were unable to conclude long-term contracts. Supplies were difficult to plan for. Respondents were asked to indicate the percentage of price increase and the precipitant prices in 2022 compared to 2021. In some cases, the raw data included additional transport costs and energy surcharges. In addition to the desired answer format of EUR/t, EUR/kg and even EUR/g were given. Additionally, net prices were sometimes given instead of gross prices. Predominantly, ferric chloride was referred to. The prices were initially scaled to net prices and related to EUR/t. Outliers were removed via plausibility check.

In Figure 2, precipitant costs for the WWTPs are considered. The query of these questions was voluntary, and 978 respondents gave an answer. After pre-processing, the data were transferred into a box and whisker plot.



(**a**) (**b**)

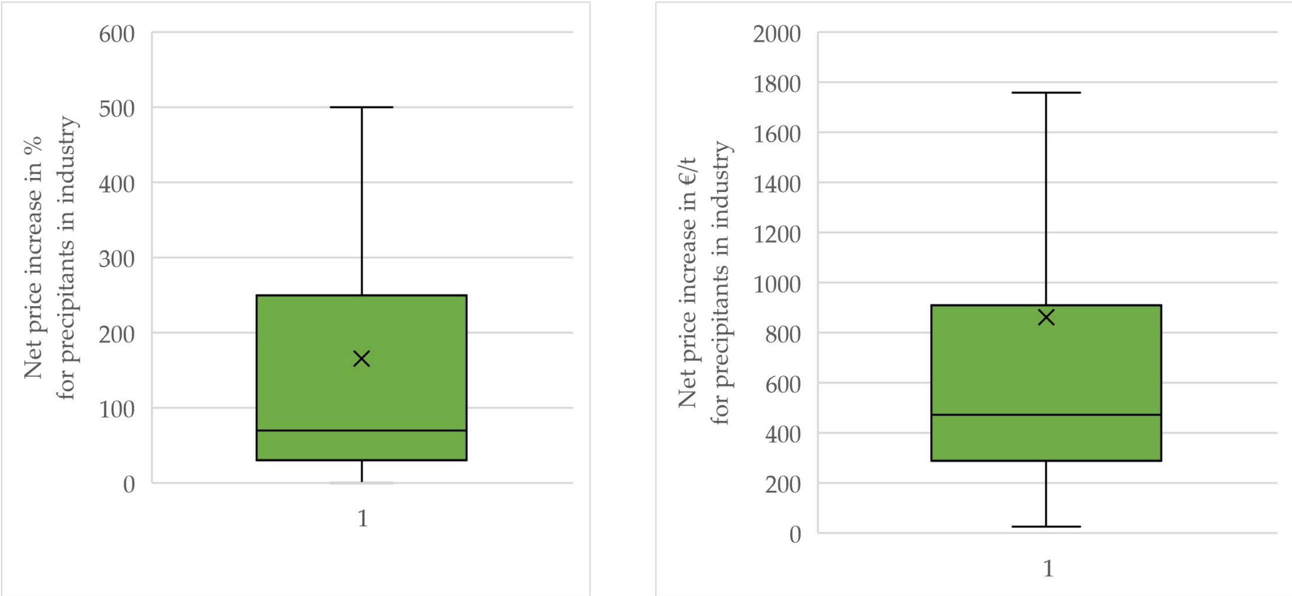
Figure 2. (**a**) Percentual net cost increase of precipitants for WWTPs from 2021 to 2022. (**b**) Absolute cost-increase in EUR/t of precipitants for WWTPs in net from 2021 to 2022. The cross shows the average, and the line in the box demonstrates the median.

The median price increase for WWTPs was 63%. There was a minimum of 0%, which was related to a long-term contract, and a maximum of 1100%, which was classified as an outlier and eliminated from the data while pre-processing. The mean value considering the acceptable outliers resulted in a price increase from 2021 to 2022 of 111%. In absolute values, this means a median price in 2022 of 310 EUR/t. The mean value indicated a price of 396 EUR/t. The upper whisker shows a range of up to 700 EUR/t without taking the outliers into account.

For industry (see Figure 3), the median price increase was 70%, and the average was 166% (for comparison, WWTP was 63% in the median and 111% in the average). According to the data, there was a minimum price increase of 0% and a maximum of 2246%, which was classified as an outlier and eliminated in the plausibility check. Accordingly, the upper whisker indicated a range of price increase up to 500%. Translated into absolute values, this means a median price in 2022 of 472 EUR/t and an average price of 897 EUR/t (cf. WWTP 310 EUR/t median and 396 EUR/t average). Since the industry usually buys smaller quantities from the manufacturer than large WWTPs, the higher prices for the industry were plausible for the time being. The upper whisker shows an absolute price range of up to 1750 EUR/t.

Furthermore, all recipients (WWTPs, industry, and drinking water facilities) were asked for procedural adjustments to reduce precipitants at their plants. The section was mandatory, and a total of 21% of all respondents performed procedural adjustments. Regarding the 2159 answers saying ‘no’, 1436 belonged to WWTPs in size class 4. It was assumed that most plants operated PC and could not switch to other measures at short notice due to the size of the WWTP. A total of 425 respondents from WWTPs gave additional information regarding possibilities for procedural adjustments and an estimation for the reduction of precipitants in percentages (most relevant listed in Table 2). Multiple responses were possible.

The avoidance of overdosing was indicated as a particularly common measure. A percentage precipitant reduction of 5–75% was estimated depending on the plant. The approximation with the threshold was often mentioned with the same goal and the same estimation for the precipitant reduction. Furthermore, switching to PB was listed as a process engineering adjustment. Here, a savings effect of 3–90% was estimated depending on the performance of the WWTP so far. Many adjustments could also aim to optimize and automate dosing, as well as online P measurement.



(a) (b)

Figure 3. (**a**) Percentual net cost increase of precipitants for the industry from 2021 to 2022. (**b**) Absolute cost increase in EUR/t of precipitants for the industry in net from 2021 to 2022. The cross shows the average, and the line in the box shows the median.

Table 2. Possibilities of process engineering adjustments for precipitant reduction and an estimated reduction in precipitants in percentages for WWTPs (n = 435).

Possibilities of Process Engineering Adjustments	Number of WWTPs	% Reduction Precipitants		
		Average	Min	Max
Avoidance of overdosing	109	25	5	75
Approximation with threshold value	55	54	5	75
PB	52	26	3	90
Online P measurement	46	19	5	40
Stretch mode operation for precipitants	45	29	5	75
Automation	33	18	5	45
Optimization PB	25	20	3	60
Optimization precipitant addition	25	16	2	30
Change of the dosing point	9	13	2	30
Load-related regulation	9	16	10	25
2-point precipitation	7	16	10	25
Optimization aeration	7	36	10	70
Manual operation of the dosing, minimum dosing	6	13	5	30
Alternative precipitant	5	43	80	20
Additional C-Source	2	40	30	50

In the industry sector, 32 respondents answered this question. Table 3 shows the possibilities of process engineering adjustments on the part of the industry. Multiple responses were possible. Again, avoidance of overdosing and automation were frequently selected as adaptation strategies. In general, a distinction must be made between short-, medium-, and long-term measures for adaptation strategies, irrespective of the query area. In the area of the WWTPs, as well as in the industry, some measures were named in each case.

Table 3. Possibilities of process engineering adjustments for precipitant reduction and the estimated reduction in precipitants in percentages for the industrial sector (relevant n = 31).

Possibilities of Process Engineering Adjustments	Number of Industry Plants	% Reduction Precipitants		
		Average	Min	Max
Avoidance of overdosing	7	22	7	75
Automation	6	18	6	25
Stretch mode operation for precipitants	4	14	4	20
Usage of alternative processes	4	28	3	100
Blending with other water streans	3	18	3	40
Alternative precipitant	3	31	3	100
PB	2	18	2	33
Optimization of process	2	24	2	50

3.2. Manufacturing Survey Regarding Production of Precipitants for the German Market

During the manufacturing survey, 11 of 30 possible survey submissions from manufacturers within the INCOPA were made. These 11 participants had, altogether, 25 production sites in European countries. Those sites delivered precipitants to Germany as well. Seven production sites were directly in Germany, and three sites were in France. Two production sites were in Norway. Otherwise, there was one production site each in Belgium, Czech Republic, Denmark, Estonia, Finland Greece, Italy, Poland, Portugal, Slovakia, Slovenia, Spain, and Sweden.

Regarding the question whether the manufacturers produce precipitants for wastewater treatment for Germany, 82% answered 'yes'. Furthermore, 45% produced precipitants for drinking water treatment in Germany. Since not all members of the INCOPA network answered, it cannot be conclusively answered whether the other members also produced precipitants for Germany in the drinking water or wastewater sector.

In addition, the manufacturers were asked how much they normally produce on average per precipitant in the wastewater sector (based on DWA A 202), how much they currently produce, and what production volume is expected within the next 6 months. Based on these data, the annual production volume for Germany per precipitant was estimated, and the percentage output of production at present and in the future was calculated. In summary, in Table 4, the annual production volume for the wastewater sector of the six most produced precipitants is shown. In addition, with regard to the current and expected performance, a trend was estimated in each case on the basis of the annual average production quantity and was additionally visualized using arrows. The trend shows a rising (green, ascending arrow) or falling (red, falling arrow) trend.

For many precipitants, and especially for the iron-based precipitants, a decreasing production was investigated regarding the survey. For aluminum chloride and aluminum sulfate, however, an increasing production was observed. It can be seen that some producers switched to the production of other precipitants, and some precipitants produced more. With regard to aluminum sulfate, production was even expected to continue to increase within the next 6 months. For ferrous chloride and ferric chloride, an easing and renewed increase in production was expected within the next 6 months at the time of the survey. Related to the wastewater sector, an annual total volume of all precipitants of 583,740 t/a could be provided according to the survey. This represents approximately 50% of the precipitants required per year (1,103,734 t/a) for WWTPs and the industry (see Survey 1).

As reasons for limited production (wastewater and drinking water sector answered combined) the manufacturers mentioned most often the lack of raw materials (e.g., hydrochloride acid) and the dependence of the titan production.

Table 4. Annual production volume of the 6 most produced precipitants in tones for Germany, and the current and expected volume with trends for the next 6 months regarding the shortage.

Precipitants Wastewater Treatment	Average Quantity per Month	Yearly Average Quantity	Current Quantity per Month	Capacity Current Situation	Trend Current Situation	Medium-Term (within 6 Months) Quantity per Month	Forecast Amount for 6 Months	Percentage Forecast of Yearly Amount	Expected Trend
	[t/Month]	[t/Year]	[t/Month]	[%]	[-]	[t/Month]	[t/(6 Month]	[%]	[-]
Aluminum sulphate	4225	50,700	8925	211%	↗	7250	43,500	86%	↗
Ferrous chloride	6550	78,600	3970	61%	↘	15,950	95,700	122%	↗
Ferric chloride	9440	113,280	9200	97%	↘	10,100	60,600	53%	↗
Ferric chloride sulphate	8000	96,000	2040	26%	↘	40	240	0%	↘
Ferrous sulphate	3500	42,000	1870	53%	↘	0	0	0%	↘
Polyaluminum (hydroxide) chloride (PAC)	11,120	133,440	9120	82%	↘	10,220	61,320	46%	↘

Based on the shortage situation in January 2023. Data for aluminum chloride, aluminum ferric chloride, aluminum ferric sulphate, ferric sulphate, sodium aluminate, and polyaluminum (hydroxide) chloride sulphate were also gathered. Calcium hydroxide, white hydrated lime and stabilized milk of lime were investigated as well, but no data could be collected.

Furthermore, respondents were asked whether transport costs for manufacturers increased in the current situation. A total of 91% of the respondents stated that they had been affected by higher costs. The increase varied between 15 and 35% regarding 2021, i.e., within one year (query status at the end of 2022).

In summary, precipitant manufacturers were affected differently by the production bottlenecks. Some industries had or have no bottlenecks at all, while others switched to the production of alternative precipitants. The main problem identified was the non-availability of raw materials and auxiliary materials. Currently, some major precipitant manufacturers started producing again but at stockpiles and still very high prices for the consumer (WWTPs and indirect and direct dischargers).

3.3. Orienting Survey of the Water-Law Allowances

The orienting survey of the water-law allowances regarding P thresholds with the federal state offices and/or environmental ministries ran until 31 March 2023. Using the LimeSurvey platform, seven complete submissions were received, including Baden-Wurttemberg (BW), Saarland (SL), Saxony-Anhalt (ST), Saxony (SN), Schleswig-Holstein (SH), Hamburg (H), and Thuringia (TH). In addition, outside of the survey, five states submitted information by mail to the question 'How many WWTPs have lower limiting values than those specified in the Wastewater Ordinance?', which are Lower Saxony (NI), Berlin (B), North Rhine-Westphalia (NW), Bavaria (BY), and Rhineland-Palatinate (RP). In total, 12 of 16 federal states were covered through the survey with regard to P limits. Accordingly, the remaining survey questions could only be evaluated for the seven federal states in LimeSurvey.

Concerning the question whether inquiries/requests for help of the operator had already been received at the time queried, all federal states said 'yes'. Operators reached out to the authorities. To the further question of whether transgressions with regard to the water law allowance were indicated, 57% (four federal states) answered 'yes', and 43% answered 'no' (three federal states).

Based on the situation at the end of March, no actions to set the allowance up to the monitoring value had been taken.

The explanations for no actions were, in general:

- Tolerance of non-compliance with the values of the notice was pronounced based on the presentation of appropriate justifications.
- Despite scarcity, the monitoring value was complied with so far.

Alternative actions have been mentioned in this context:

- Stretching operation (by the operators).
- Deviation from target values at wastewater treatment plants with further measures. (by the operators).
- Exchange between operators and authorities.
- Information on documentation and notification obligations in the event of precipitant shortages (by the authorities).
- Coordination of saving options (by the authorities).
- Use of alternative precipitants (by the operators).

One federal state could imagine adjusting the permit over the winter period due to the expected lower algae growth.

Furthermore, the wish to establish a central information platform on the supply situation and opportunities for substitutes was mentioned.

Federal states with sufficient and comparable raw data were compared in Table 5. It considers the federal states with regard to lower monitoring values than in the Wastewater Ordinance. The focus was on sensitive water bodies.

Table 5. Federal states regarding lower monitoring values than in the Wastewater Ordinance, with a focus on sensitive water bodies.

Size Class of WWTP	Adjusted Limit Value of the Plant Permit [mg/L]	BY	NI	NW	RP	SL	SN	ST	SH	TH	WWTPs per Size Class and Interval
5	<1–2	-	-	-	-	-	-	-	-	1	1
	<0.5–1	-	8	17	8	-	-	-	6	1	40
	<0.5	-	-	117	-	-	-	-	-	-	117
4	≥2	-	-	-	-	-	-	-	-	11	11
	<1–2	-	114	194	143	2	9	16	15	6	499
	<0.5–1	-	4	9	-	-	1	1	34	1	50
	<0.5	-	1	4	-	-	-	-	1	-	6
3 + 2 + 1	≥2	851	110	145	192	8	17	-	-	57	1380
	<1–2	11	16	82	183	4	2	-	-	60	358
	<0.5–1	1	1	8	-	-	-	-	-	4	14
	<0.5	-	-	4	-	-	-	-	-	-	4
WWTPs per federal state		863	254	580	526	14	29	17	56	141	-

Since, in some responses, the smaller size classes were summarized differently, these are summed up here for size class 3 + 2 + 1. It can be seen that, even for WWTPs of this size, 376 plants already had to comply with P limits smaller than 2 mg/L in the effluent due to sensitive water bodies. Most plants were affected by stricter discharge limits in BY. In NW, the majority of plants (117) in size class 5 were classified with discharge limits smaller than 0.5 mg/L. Overall, a very diverse picture emerged for the participating federal states. A classification according to minimum and maximum values was not possible in a way due to the different data transmission.

Furthermore, the number of sensitive waters of participating federal states is summarized in Table 6. Since not all federal states submitted data, or submitted incomplete data, this does not correspond to the total number of P-sensitive waters for Germany.

Table 6. Number of P-sensitive water bodies in federal states with sufficient data submitted in the survey.

	BY	NI	NW	SL	SN	TH
Number of sensitive water bodies	470	198	301	8	14	75

3.4. Consideration of Sampling Regime (Qualified Random Sample to 24-h Composite Sample)

For possible precipitant savings, this subchapter takes a closer look at the sampling regime in Germany. According to the EU Urban Wastewater Directive, the 24 h composite sample (24 h-MP) is compliant. However, Germany opted for the qualified random sample (qSP) or 2 h composite sample (2 h-MP) in the national wastewater directive (AbwV) and thus for more stringent regulations.

In the following, analyses regarding the effect of different sampling regimes, as well as the effect of precipitant savings, were investigated using the online data of anonymized WWTPs. In total, data of five plants could be examined. The following time periods and form of P were provided:

- WWTP 1: Orthophosphate (PO_4-P) and total phosphorus (P_{tot}) from 18 November until 17 December 2021 (PBC);
- WWTP 2: P_{tot} from 5 August until 14 August 2022 (PBC);
- WWTP 3: PO_4-P and P_{tot} from 19 December 2022 until 8 January 2023 (PBC);
- WWTP 4: PO_4-P and P_{tot} from 1 December 2022 until 18 January 2023 (PC);
- WWTP 5: PO_4-P and P_{tot} from 19 December 2022 until 7 January 2023 (PBC).

The provided data for PO_4-P and P_{tot} were firstly analyzed per day for the 24 h MP, 2 h MP, and qSP. Then, the percent deviation was put into a ratio for either qSP/24 h MP or 2 h MP/24 h MP. From the deviations per day for the data series, the average value, median, maximum value, and other statistical means were determined for each plant.

In the following, Table 7 compares all plants studied. In summary, it was noticeable that, especially for the WWTPs with PBC, changing the monitoring values to a 24 h MP is a very good possibility to save precipitants without affecting the water quality (median up to 31%). WWTPs with PC can also be optimized by changing monitoring practices.

Table 7. Comparison of analysis of all plants for qSP to 24 h MP (all size class 5).

WWTP Analyzed	1	2	3	4	5
Kind of P-elimination	PBC	PBC	PBC	PC	PBC
Median deviation P_{tot} [%]	14.39	13.48	31.48	13.91	17.5
Variance σ^2 [%]	0.06	0.05	0.68	0.14	0.05
Comments operation	-	-	-	-	Very stable

Changing the monitoring practice to the EU Wastewater Directive compliant 24 h MP would be a very good way to save precipitants without affecting the water quality.

4. Discussion and Conclusions

The results showed that German WWTPs must become more resilient. The energy and supply crisis resulting from the war in the Ukraine caused great difficulties for wastewater treatment companies. Above all, the production and supply problems with precipitant production, but also with other additives such as flocculants, etc., have shown that today's wastewater treatment technology in Germany is not crisis-proof. Additionally, the challenges of the upcoming EU wastewater directive emphasize the necessary change to resilient WWTPs.

The supply of precipitants for P elimination was particularly affected. P favors plant growth and has an eutrophic effect on the water body and on the marginal seas, which has a negative impact on the ecological household of the affected water bodies. Germany has a lot of sensitive water bodies and coastal waters, which need specific protection.

Based on the operator survey, a considerable shortfall of precipitant was calculated for the beginning of the year 2023 throughout Germany for the WWTPs and the industry. This shortfall would have led or would lead to a significant impairment of the water quality. This worst-case scenario has not yet occurred because precipitant manufacturers resumed production at their own risk at significantly increased prices and ultimately uncertain conditions. On the other hand, operators did everything in their power to save precipitants under the current local conditions. However, regarding the dependence of most WWTPs of these precipitants, the situation can worsen and occur again at any time.

A limitation of this study is that the recording of shortfalls is only a snapshot. It is recommended that the study be repeated in a similar form in order to better position the operators. Another limitation is that the Europe-wide manufacturer surveys were not answered sufficiently by all manufacturers. The alternative precipitant capacities could not be recorded in the operator survey.

In order to make WWTPs more independent of products from various supply chains (national and international) and thus more resilient, an increased proportion of existing WWTPs could first be adapted to PB or PBC. The adaptation can be implemented in a timely manner through practice-oriented research. Additionally, this would be favorable since PC strongly bounds P in the sludge and makes it difficult under high energy usage to recycle P. Moreover, the establishment of a central information platform on supply chains and opportunities for substitutes could be one part of the solution. Another option would be a higher automation at the WWTPs and the industry for more efficient dosing of the precipitants.

Furthermore, it would make sense to change the sampling regime for Germany to the EU-compliant 24 h composite sample.

In the long term, new alternative P elimination processes should also be researched and developed to practical maturity, and regarding the indirect and direct dischargers.

Overall, however, the situation in P removal remains very fragile; thus, the above approaches should be urgently pursued.

The results of this study are relevant for decision-makers, researchers, and operators in the wastewater sector in order to intervene in the market themselves if necessary, e.g., money for production or conversion to biological phosphorus elimination.

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Appendix A

Questions of the operator survey: municipal wastewater disposers/wastewater treatment plants (KA), industrial dischargers (I), and water suppliers (W):

1. Are you a direct or indirect discharger? (I)
2. Which industrial sector do you belong to? (I)
3. How do you eliminate phosphorus? (KA)
4. What is your capacity size? Please indicate the population equivalent (p.e.) to be treated. (KA + I)
5. What volume of drinking water do you discharge? (W)
6. Which federal state do you belong to? (KA + I + W)
7. What is your average phosphorus concentration (influent and effluent) in mg/L? (KA)
8. Which precipitants, according to DWA A 202, are used for chemical phosphorus elimination under normal operating conditions? (In case of biological P elimination, please specify support precipitant) (KA + I).
9. Which precipitant, according to §11 list, is used under normal operating conditions for chemical phosphorus elimination in drinking water treatment? (W)
10. What other substances for treatment are affected by the shortage? (KA + I + W)
11. Which quantities of the precipitants, according to DWA A 202 (question 3), are used on a monthly average? What is the stock level and the promised delivery quantity? For which period? (Please specify in tons). (KA + I)
12. What quantities of each of the precipitants are used in the drinking water sector (question 3) on a monthly average? What is the stock level, as well as the committed delivery quantity? For which period of time? (Please specify in tons) (W).
13. Until when is it possible, considering stock levels and delivery commitments, to operate the wastewater treatment plants in compliance with the limit values? (KA + I)
14. Until when, considering stock levels and delivery commitments, is it possible to operate the waterworks in compliance with the limit values? (W)
15. Do you already use alternative precipitants (according to DWA A 202 or others) due to the current shortage situation? (KA + I)
16. Which alternative precipitants, according to DWA A 202, are concerned? (KA + I)
17. Which alternative precipitants, not according to DWA A 202, are used? (KA + I)
18. Do you already use alternative precipitants (according to §11 list or others) due to the current shortage situation? (W)
19. Do you plan to use alternative precipitants, according to DWA A 202, due to the current shortage situation? (KA + I)
20. Due to the current shortage situation, do you plan to use alternative precipitants that are not listed, according to DWA A 202? (KA + I)
21. Which alternative precipitants, according to DWA A 202, do you plan to use? (KA + I)
22. Which alternative precipitants not listed, according to DWA A 202, do you plan to use? (KA + I)
23. Do you fear impairments of the plant function due to the use of alternative precipitants? (KA + I)
24. Are there any potential process engineering adjustments (e.g., automation/reduction of potential overdosing/Bio-P/intermixing) that you could implement at your plant to reduce the need for precipitants while complying with regulatory requirements? (KA + I + W)
25. If yes, what percentage reduction in your precipitant requirements would you expect to achieve? (KA + I + W)
26. Can you give us an overview of price increases related to precipitants current to 2021? (KA + I + W)

27. Do you see drinking water supplies at risk in the coming months? (W)
28. Do you have any suggestions for solutions to reduce the use of precipitants? (KA + I + W)
29. Do you have any other comments/advice/requests for the federal government or your state regarding the precipitant emergency issue? (KA + I + W)

Appendix B

Questions of manufacturer survey:

1. In which countries is your company producing?
2. Do you usually produce precipitants for wastewater treatment in Germany?
3. Do you usually produce precipitants for drinking water treatment in Germany?
4. Which precipitants are produced for the wastewater treatment in Germany? How much in tons?
5. Which precipitants are produced for the drinking water treatment in Germany? How much in tons?
6. What are the reasons for the limited production?
7. Can you estimate a time frame when the production can be fully (100%) resumed?
8. What is needed to restart the production of precipitants?
9. Due to the reasons mentioned above, is a deterioration in quality to be expected with renewed production?
10. Due to the current situation: Have your transport costs increased?
11. Do you have any further comments/advice/requests regarding the issue of the precipitant emergency?

Appendix C

Questions of authority survey:

1. Which federal state are you assigned to?
2. How many facilities have lower monitoring values than those in the Wastewater Ordinance? What values do they have? Please note summary of plants in the comments.
3. Have you received any inquiries/requests for assistance regarding shortages of precipitants?
4. Have violations of the monitoring value been reported?
5. Have you already acted to assist wastewater treatment plants?
6. Do you think an adjustment to the allowance for the winter period (low algae growth expected) would be possible?
7. How long could you risk adjusting the limits over the winter period? You can select one or more months or leave an alternative answer under Other.
8. Would you like to see more support/education on the precipitant shortage?
9. In what form would you like to see more support/education on the topic of precipitant emergency?
10. Do you have any other suggestions for solutions to reduce the use of precipitants?
11. Do you have any other comments/advice/requests for the federal government or your state regarding the precipitant emergency issue?

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