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Review

Conditioning of Feed Material Prior to Feeding: Approaches for a Sustainable Phosphorus Utilization

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Abstract: A circular phosphorus (P) bioeconomy is not only worthwhile for conserving limited mineral P reservoirs, but also for minimizing negative environmental impacts caused by human-made alterations. Although P is an essential nutrient, most of the P in concentrates based on cereals, legumes and oilseed byproducts is organically bound to phytate. The latter cannot be efficiently utilized by monogastric animals and is therefore diluted into the environment through the manure pathway. This review examines various strategies for improved P utilization in animals and reflects the respective limitations. The strategies considered include feeding of debranned feedstuffs, pre-germinated feed, co-feeding of phytase and feeding material with high native phytase activity. All these approaches contribute to an improved P bioavailability. However, about half of the organic P content continues to be excreted and therefore remains unused by the animals. Nevertheless, technologies for an efficient utilization of P from cereal-based feed already exist; however, these are not industrially established. Conditioning feed material prior to feeding fosters P-reduced feed; meanwhile, P bound to phytate can be recovered. Based on known techniques for P separation and solubilisation from cereal products and phytate conversion, potential designs for feed material conditioning processes are proposed and evaluated.

Keywords: phosphorus; bioavailability; phytate; phytate conversion; feed conditioning; monogastric animals; circular bioeconomy

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1. Introduction

Due to the continuous growth of the human population as well as its welfare, the worldwide food demand and thus the request for crops and livestock have drastically increased [1,2]. To cover this demand, fertilizers and especially phosphorus (P) are increasingly gaining more importance [3]. Unlike nitrogen, P cannot be captured from the atmosphere, but is almost exclusively gained by P rock mining [4]. Due to the increased fertilizer production, a depletion of mineral P reservoirs is expected to occur within a few centuries [3]. Consequently, the EU framework has identified P rocks as a critical and "non-renewable" raw material [5].

However, the increased concentration of livestock production systems and the strongly growing human consumption of livestock products continuously influence the distribution of P across the global landscape [6]. Losses that occur during the human-made P alteration

are leading to eutrophication of aquatic ecosystems, resulting in declining biodiversity [7]. Hence, valid resource management concepts within the framework of a circular bioeconomy are mandatory for the shift towards an economy based on renewable resources and recycling strategies achieved by the sustainable use of resources.

Main causes of eutrophication are P losses from agriculture due to excess fertilizing and P-rich wastewater from households and industry. In this context, P recovery from wastewater is becoming increasingly important in research, industry and the regulatory framework [8]. Nonetheless, especially in the case of intensive livestock farming, a significant P oversupply as a result of limited utilization of P in the animal and the subsequent input into natural environment through manure is becoming progressively challenging [3,9]. Here, phytic acid (inositol-hexakisdihydrogen phosphate, $InsP_6$) and its corresponding salt phytate play a crucial role. $InsP_6$ is the principal storage form of P in seeds and grains. However, monogastric species, such as swine and poultry, cannot digest phytate present in plant-based feeds due to limited activity of endogenous intestinal $InsP_6$-hydrolysing enzymes [10]. As a result, the insufficient use of phytate-bound P not only impacts agricultural productivity but also poses a threat to the water quality due to losses of excess P into water bodies [11]. Moreover, additional P sources are needed to meet the nutritional requirements, which are, in turn derived from P rock mining [12].

To counteract the human-made alteration process, some strategies to diminish environmental effects caused by $InsP_6$ have already been implemented. Major progress has recently been reinforced by law and technically achieved in P recovery from fertilizer industry wastewater [13]. However, in grain processing and livestock production systems, it is apparent that there is hidden potential for a more sustainable use of resources, particularly in the conditioning of feedstuff. Thus, this review represents existing approaches and the limitations of feed conditioning, comparing as well as discussing potential improvements and strategies. Based on established methods and those on a research scale, potential process designs for feed material conditioning are illustrated and evaluated.

2. Background

The phosphorus (P) cycle is a crucial but fragile process on earth. Since P only regenerates within geological timeframes in the form of minerals, it is a resource limited to mining. However, to safeguard the worldwide food demand, humans have been altering the P cycle by intensifying the releases of P from the lithosphere to ecosystems. The majority of the rock mined P flows into fertilizer production and is finally diluted from cropland [4,7,14,15].

The largest P pool on earth is the apatite mineral [4,7]. Since in its original state apatite is not water soluble and, therefore, unavailable as a plant P source, harsh chemical processing is necessary for its conversion into phosphoric acid (expressed as phosphoricanhydride, P_2O_5). As a side-product, gypsum ($CaSO_4$) is formed and removed by filtration [16]. Generally, four to five times more gypsum is formed compared to P_2O_5 relative to the mass [4]. Besides the intensive resource consumption (1.3 t H_2SO_4, 83 t H_2O/t P_2O_5), the value chain is coupled with heavy metal impurities, pollution in the mining region, geopolitical dependencies and monopolistic economy to name but a few [3,4].

Although the amount of fertilizers and manure applied in agriculture is high, only a small portion of the P is taken up by the plants [17,18]. Therefore, a significant amount enters freshwater systems and is transported by rivers to coastal areas, resulting in eutrophication of aquatic ecosystems [7,19,20]. Additional P input originates from domestic wastewater further aggravates eutrophication. Therefore, in many developed countries wastewater must legally be removed in wastewater treatment plants and can be recovered for use in the fertilizer industry [21,22].

2.1. P Uptake by Plants

P is an essential nutrient for all organisms and one of the most limiting in agricultural production. The total amount of P in the soil of agricultural land might be high, but is often

present in unavailable chemical-bound forms or in forms that are only available outside the rhizosphere [17]. Additionally, the high chemical fixation rate and slow diffusion in soil (10^{-12} to 10^{-15} m^2/s) makes it one of the least available nutrients for plants [23].

Most of the P acquired by plants is taken up as inorganic P (P_I) in form of ortho-P, but generally the term is used to refer to any hydrated or substituted form of the ion (e.g., HPO_4^{2-}, $H_2PO_4^-$, H_3PO_4, $CaPO_4^-$) [23,24]. The ideal pH for the P_I uptake is around 4 to 7, but more likely at lower pH, and often supported by arbuscular mycorrhiza fungi [25]. After uptake, P_I circulates through the vascular network and enables complex control mechanisms to co-ordinate the distribution in the plant [26]. A part of the P_I is used to sequentially phosphorylate inositol-phosphate (inositol-P). The biosynthesis involves several protein clusters to finally synthesize phytic acid ($InsP_6$), which serves as a significant P source during germination [27].

2.2. P in Animal Feed Sources

In livestock nutrition P is an essential nutrient and must be supplied to the animal in adequate amounts. Plant seeds and corresponding feeds contain P mainly as $InsP_6$ and its salt, phytate [28,29].

Pig fattening in Germany is predominantly based on cereal-rich compound feeds supplemented by legumes or rapeseed or the by-products of oil and fat extraction (soybean or rapeseed cake or extraction meal) as a protein source. In both cereals and rapeseed or soybean extraction meal, P is present to a large extent as phytate bound P (phytate-P), i.e., bound to $InsP_6$. Table 1 lists the percentages of total P, phytate-P and the ratio of phytate-P to total-P as well as the intrinsic phytase activity for various compound feed ingredients.

Table 1. Total P, phytate-P and endogenous phytase activity in feed ingredients [29–31].

	Total P (%)	**Phytate-P (%)**	**(Phytate-P/ Total P) × 100**	**Phytase Activity (U/kg)**
Cereals	0.23–0.31	0.17–0.23	59–78	56–5147
Legume seeds	0.33–0.73	0.08–0.33	21–56	32–258
Oilseeds	0.6–1.05	0.34–0.76	57–72	73–295
Cereal by-products (bran)	0.83–1.16	0.68–0.88	76–82	25–7339

The animal body contains 4 to 7 g P/kg, depending on species and stage of growth [32,33]. The most efficient and simplest way to reduce P input and excretion is nutrient-adapted feeding (phase feeding), resulting in 20% reduced P excretion [34]. By changing body composition as animals grow, the amount of P in the diet can be reduced with age [34].

2.3. P-Digestion in Monogastric Animals

The P bound to $InsP_6$ is only partially available to non-ruminants because phytate-P can only be utilized after gradual cleavage from the phytate molecule by phytases or other phosphatases. With technical Ca-Mg phytate in a phytase-free compound feed, it was shown in pigs that there was no hydrolysis of the phytate neither in the stomach nor in the small intestine [35]. In the large intestine, however, hydrolysis was detectable, which was recently confirmed by Rutherfurd et al. Nevertheless, due to insufficient digestion, mineral P and phytases are often added to feed rations for non-ruminants [12].

Besides the low P accessibility, the polyanionic $InsP_6$ molecule binds multivalent cations such as calcium, iron, and zinc, resulting in a reduced bioavailability of these minerals [31,36,37]. In addition, an impairment of the utilization of other nutrients, such as proteins, starch, and fats, from the diet is also discussed [31,38]. Studies confirm that increasing the amount of phytate in the feed ration leads to lower growth rates in broilers [39–42] and pigs [43]. Thus, phytate is considered one of the most important antinutrients in animal feed [37].

Enzyme activity present in the feed enables the hydrolysis of the bound P and the release of minerals in the anterior digestive tract and subsequently the absorption of the

dissolved compounds. These phytases may also be plant-own enzymes, depending on the components used, and can contribute to P digestibility [44].

2.4. P Occurrence in Animal Manure

Animal manure is an intrinsically heterogeneous organic material containing animal feces and urine [45]. It is rich in nutrients, being excreted as metabolic by-products or from excess feeding. Especially its N and P content are exploited for use on agricultural land for fertilizing purposes [46]. The total P content in manure accounts for 0.3 wt.% to over 4.5 wt.%, strongly depending on the animal species and feeding conditions. Thereby, P is dissolved in solution, precipitated as minerals or complexed with metals and organic compounds [47]. The highest amounts of P in manure were reported for swine and poultry [48].

In general, P forms in manure are categorized into P_I and organic P (P_O), while some authors additionally subcategorize into enzymatic hydrolysable and non-hydrolysable P [46,47,49]. However, content and form of P_I and P_O in manure differ for various animal species. Ajiboye et al. studied the proportions of P_I to P_O in liquid pig manure and showed ratios of 1:1, 7:3 and 3:2 for sows, fattening pigs, and nursery pigs, respectively [50]. Considering P_I, Pagliari and Laboski reported most of P_I in manure are water soluble, indicating P_I may come from the dissolution of Mg-phosphate minerals (e.g., struvite) and/or amorphous Ca-phosphate (e.g., hydroxyapatite) [46]. Given P_O species, inositol-P content, and in particular $InsP_6$ is greater in manure of monogastric animals than that for ruminants due to indigestibility, but still accounts for the majority of P_O content in manure overall [23]. In addition, $InsP_6$ is the predominant form of hydrolysable P [46]. Although only 20% of the total annual manure application belongs to monogastric animals, it causes over 35% of total P emissions [34].

2.5. P in Soils and Run-Off

In soils, the primary form of P_I is ortho-P but also inorganic polyphosphates exist (e.g., $P_2O_7^{4-}$) [51]. However, a large part of the soil P is present as P_O, mainly found within diesters, monoesters, phosphonates, polyphosphates, and inositol-P [23,24]. All these have in common that they are either of plant or microbial origin [51]. Inositol phosphates are by far the most abundant P_O compounds [23,27,31,51]. Large quantities of P_O are adsorbed (e.g., on metal oxides) [24,52]. Nevertheless, P mobilization may occur either chemically (solubilisation in water) or physically, where P remains attached to sediment or colloidal material which is subsequently moved. Therefore, two primary pathways for P to enter surface water occur, namely surface and subsurface run-off [19,45]. Subsurface run-off was often considered negligible; however, recent research shows a significant contribution to P leaching [19]. The extent of P run-off depends on soil characteristics (e.g., P sorption capacity, redox conditions), hydrology and climate [47,51,53]. When excess P enters aquatic ecosystems, excessive growth and accumulation of algae and other aquatic plants follow in response to increased nutrient input. Impairment of water quality and loss of biodiversity are observed [7,20].

2.6. P Losses in Agriculture

Agricultural processes, combining farming and livestock breeding, have the highest P demand among all sectors, including nutritional and industrial P consumption [54]. On a European scale, P consumption by agriculture is over 19 Mt_P/a (10^6 metric tons of P annually), especially in the form of mineral and organic fertilizers, plant-based animal feed and feed additives, making up 72% of all P imports [55]. Nonetheless, about half of the applied P cannot be used, but is either excreted by animals or leached from agricultural land [54]. The amount of P lost through leaching, manure and soil accumulation was quantified to 1 Mt_P/a at European level [55].

To maintain P in the long term as a nutrient and a valuable industrial resource and to avoid eutrophication as a result of enhanced P run-off, losses need to be prevented.

Therefore, some approaches are already aimed for, such as specific nutrient control and more sustainable and controlled farming on agricultural land; others are still under development [56]. A promising technique, especially regarding its theoretical P potential, is the supply of customized animal feedstuff with the right amount and forms of P for the respective animal. Targeted P feeding, firstly, improves P supply from a nutritional perspective and, secondly, reduces P_O amounts in animal excreta. Since only about half of the P in animal feed is currently used by animal metabolism, this leaves an extremely high potential of about 2 Mt_P/a for an efficient and sustainable additional supply of P in agriculture at a European scale [55]. Other important sources of P recovery include wastewater, sewage sludge, and slaughterhouse residues, all contain significant amounts of P that are currently diluted into the environment [57]. However, this article focuses specifically on optimal use of grain P in the feed industry and thus does not address the use of these P sources.

3. State-of-the-Art: Existing Approaches for Improved P Digestibility in Animal Feed and Their Respective Limitations

There are various techniques for improved P digestibility. Some are already applied in industry; others are still being researched. The methods considered range from purely mechanical through enzymatic to chemical approaches. While mechanical methods focus on the separation of P rich grain fractions, enzymatic and chemical methods aim at the hydrolysis of phytate. However, each method has its own advantages and disadvantages in terms of efficiency, applicability, and nutrient supply.

3.1. Mechanical P Separation from Whole Grains

All grains consist of three biological parts: endosperm, germ, and the hull with several different cell layers. From a milling perspective, all components that are not pure endosperm, and thus do not serve as white flour are summarized as bran and account for up to 27 wt.% of the whole grain. The outer layers contain the aleurone, testa and pericarp, as shown in Figure 1 [58,59].

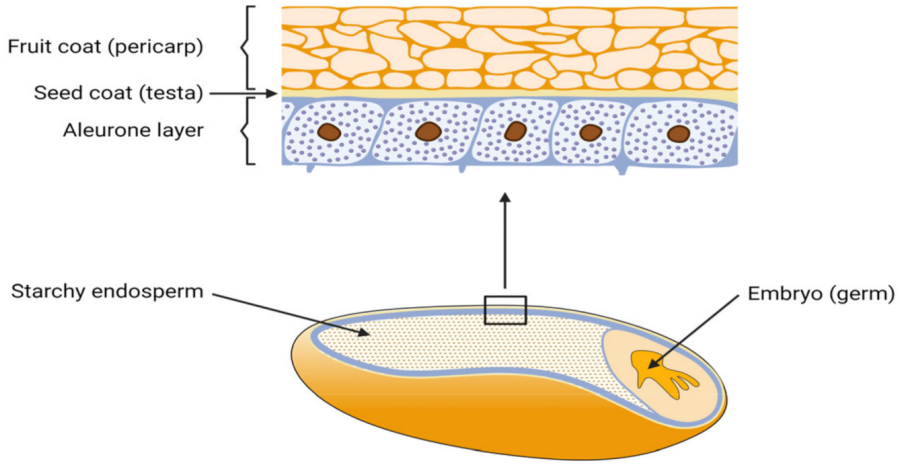

Figure 1. Composition of a grain and the outer bran layers (created with biorender.com, accessed on 20 October 2021).

In Europe, major cereal types produced and used as animal feed are wheat (32 to 45%), corn (32 to 35%) and barley (22 to 35%) [60]. P in common grains, such as wheat and barley is mostly accumulated in the aleurone, which is a layer in between the endosperm and the outer grain hull. Here, P is bound in the form of phytate within protein globoids, accounting for up to 90% of the total P content [61]. Phytate in corn, in contrast, is up to 80 to 90% accumulated within the germ, thus also in the bran fraction [62]. Therefore, two ways to separate a P-rich fraction in a purely mechanical way exist: either grains can be fully debranned which leaves endosperm flour as a P-poor fraction or specific layer

exclusion can be performed. The latter aims to separate a very small grain fraction in the region of the P-rich cell layers, which, at the same time, contains maximum P quantity.

3.1.1. Debranning

Bran, the outer part of the grain, contains many valuable nutrients, such as high amounts of dietary fiber, proteins, and minerals [62]. Among the minerals, especially P is enriched up to a three times higher content in the bran fraction than in whole grains [63]. Wheat in particular typically undergoes a milling process where the starchy endosperm is separated from all other grain components for use in food industry [58], whereas wheat bran is mostly used in animal feeding [64]. Other cereals, such as corn and barley, are specifically grown for animal feeding and used as whole grains in compound feeds [58]. However, debranning processes also exist for barley and corn. Barley is partly fed in a de-hulled form and corn is debranned for use in the starch industry [58,65].

Wheat bran accounts for 20 wt.% of the whole grain on average; for corn and barley, bran makes up approx. 30wt.%. About 72% and 76% of P is accumulated in wheat and corn bran, respectively [61,63,66,67]. Barley bran contains approximately 55 to 70% of all P [58]. Thus, debranning can significantly reduce the total cereal P content by up to 70 to 80%. Especially phytate-P can be separated to an even higher extent of up to 90% [67].

However, with the debranning of grains for animal feed, significant amounts of fiber and proteins can be lost. In the corn hull, especially heteroxylan type dietary fiber is enriched by a factor of 10, whereas proteins are evenly distributed between bran and endosperm [65,68]. Main nutrients in barley bran are the fiber components arabinoxylan and β-glucan. For humans, it was shown that both components show positive health effects, e.g., through prebiotic properties or cholesterol reduction, thus expected to be similarly positive for animal feed as well [66,69]. Likewise, 30% of lipids are accumulated in the barley bran; proteins, in turn, are mostly in the endosperm and therefore remain within a debranned feed fraction [58].

When debranned corn or barley is fed, missing components need to be replaced in the diet [31]. Also, some contaminants, such as pesticides, heavy metals and undesired microorganisms are present in the outer grain layers, so that, for example, removal of only the outer 4 wt.% was shown to reduce bacterial contamination by 87% [69]. Thus, debranning comprises both positive and negative secondary effects on nutritional quality of cereal-based animal feed to be considered in compound feeding.

Particularly for wheat, debranning is already carried out to separate the food from the feed fraction [58]. Thus, the P-poor endosperm is not available as a feed component. Here, a specific layer exclusion is the only mechanical separation technique potentially feasible.

3.1.2. Specific Layer Exclusion

In contrast to a whole debranning step, a specific separation of the P-rich grain part can prevent the loss of valuable nutrients in the bran and a higher total mass for animal feed is retained. The separated grain mass should be limited to a minimum, while the P content of the separated fraction is maximized [70]. Considering a complete and pure removal of the P-rich grain components, aleurone and germ, a similar amount of P is expected to be removed compared to debranning, but a significantly higher share of the grain remains for feeding [63,71]. The aleurone of wheat and barley accounts for 5 to 6 wt.% and contains 95% of P_O [58,71]. For corn, the germ with 7.5 wt.% of the whole grain contains around 90% of all P_O [61,72]. Therefore, theoretically, 90 to 95% of P_O (equaling 50 to 76% of the total P) can be separated from wheat, barley, and corn, while over 90% of the mass remains available for feeding. In comparison to whole debranning (removal of 20 to 30 wt.% of the grain), 35 to 45 Mt/a additional P-modified feedstuff from wheat, barley and corn can be provided in Europe [73].

Since the germ is located at the outside of the corn grain and differs in certain mechanical properties, its removal is comparably unchallenging. Therefore, various processes have already been established for corn degermination, usually comprising moistening

to around 20 wt.% water content, a milling step and subsequent separation by density difference. Degermed corn is used in corn starch production and the germ—being rich in fat—is currently widely fed or extracted to oils [74]. An exact separation of the aleurone layer, in turn, is hardly industrially feasible. The fact that the aleurone is a difficult to access single- to three-cell layer within the grain makes the process less favorable to be implemented than common debranning [71]. A few patents were filed for an industrial separation of aleurone. The processes are all based on various grinding and separation steps, as known from classical milling, although the type of separation significantly differs. Here, the aleurone is separated by electrostatic forces, as aleurone cells contain specific structural sugar compounds and are therefore charged differently than other cell wall components. This is the only yet known technique for a larger scale aleurone removal from a bran mixture which reached purities of 60–90% aleurone cells [71]. Thus, a significant amount of P_O can be separated by this process.

3.2. Enzymatic Feed Treatment

In contrast to mechanical separation techniques, a reduction in inositol-P, while the total amount of P and other valuable nutrients remain in the feed ration, can be achieved by enzymatic hydrolysis. Enzymatic approaches aim for improved bioavailability through hydrolysation of inositol-P present in the feed. This can be either achieved by feed rations with high native phytase activity, therefore simulating the natural hydrolysis during germination, or by supplementation of commercially produced phytases.

3.2.1. Feeding of Phytase-Rich Feed

When using feed components with elevated plant phytase activity, P digestibility can be increased [75,76]. Under standardized conditions and using a low P ration, the P digestibility in pigs was determined several times using different raw materials (various varying native phytase activities). P digestibility was shown to be highest in feeds with high native phytase activity (wheat and rye), followed by feeds with medium phytase activity (barley) and feed components with low phytase activity (maize or oilseed meals) [77–79]. The native phytase activity in feeds is subject to large natural variations (depending on genotype and environmental conditions), resulting in the different digestibility of P [78,80]. In grain-rich rations for monogastrics, it is therefore important whether the native phytase activity has been preserved during the production process (e.g., at storage or drying conditions) [80]. High temperatures ($\geq$70 °C) and humidity often occur during pelleting, significantly reducing the native phytase activity [37,80,81].

With increasing phytase doses, P digestibility can be increased until a certain plateau is reached. Degradation of phytic acid beyond this level is not achieved due to limited solubility and the retention time in the stomach [82].

Schlemmer et al. found in the stomach contents of pigs only 10% of the phytase activity of the feed with high plant phytase activity, and therefore conclude that there is a strong deactivation of phytases during digestive processes within the stomach [83]. According to this, there is only low activity of intrinsic feed phytases in the small intestinal chyme, whereas added microbial phytases show higher activity in the small intestine. This is in line with subsequent research by Schlemmer et al. where microbial phytases are reported to be more stable than intrinsic plant feed phytases to digestive processes in the stomach and small intestine in pigs [84].

3.2.2. Germination of Phytate-Rich Feed

Germination is the first stage of ontogenesis in seeds as well as sprouting and begins with the uptake of water by dry mature seeds. It is a mechanism in which metabolic processes are activated, resulting in morphological and physiological changes [45]. During germination, phytate is hydrolyzed by endogenous phytase and other phosphatases to release P, inositol and micronutrients for plant development [70]. Inositol-P and its deriva-

tives are implicated in RNA export, DNA repair, ATP synthesis, signaling, endocytosis, cell vesicular trafficking, and cell wall formation [31,70].

Soaking in water reduces phytate content in cereal seeds by the action of endogenous enzymes. It remains unclear whether the increase in phytase activity is the result of the activation of pre-existing enzymes or based on de novo synthesis of the protein [31]. However, phytate hydrolysis during soaking has been shown to be influenced by temperature and pH. Thus, soaking can effectively reduce phytate under maximum conditions for enzymatic activity [85]. In addition, the reduction is also favored by mass transfer, as phytate is water soluble, but loss of minerals, water-extractable proteins, and vitamins also occur [31,70].

The effectiveness of phytate reduction is a species-dependent phenomenon, which is connected to endogenous enzyme activity (Table 1). For lentil, a phytate reduction of up to 60% after 12 h pre-steeping and germination under a wet muslin cloth for 48 h was shown [86]. Greiner et al. showed over 50% reduction in rye grains during two days. After 10 days, phytate content was reduced by over 80% [87]. Pakfetrat et al. investigated the reduction of certain substances in wheat grain during germination, among them phytate. After 14 days, phytate content was reduced by 63% [88]. Reddy et al. summarized phytate degradation rates for various cereal types. Within this study, rye showed complete reduction after five days, followed by barley and corn with 66% and wheat with 52% [89].

3.2.3. Phytase as Feed Additive

Microbial produced phytases are routinely used in monogastric diets, representing the largest market for phytase application. Especially fungal phytases with remarkably high temperature maxima ranging from 45 to 77 °C are well suited to withstand pelleting of animal feed [90]. First commercialized phytases were derived from the fungal *Aspergillus niger* [91,92], *Peniophora lycii* and *Penicillium funiculosum* [93] which were launched in 1991 as feed additive.

Thenceforth, varieties of phytases have been discovered in the last 25 years. Enzymes from the Enterobacteriaceae family, e.g., *E. coli* or *Y. mollaretii* [94–96] with specific activities above 1000 U/mg [97] lead to commercial bacterial phytase products. Thereby, *E. coli* phytase AppA is one of the most studied and used enzymes due to its high specific activity. In production, expression hosts are often fungal, even for bacterial phytases, to take advantage of post-translational modifications and high titers [98,99]. Glycosylation is reported to be beneficial for improved thermo-stability [100].

Phytases with outstanding performances have been optimized by rational and semi-rational design or by directed evolution approaches [101–105]. New thermostable phytases were discovered by functional metagenomics [106–108]. Furthermore, chimeric enzymes are a future trend and highlight the great potential of DNA recombination strategies to combine improved properties and generate new enzymes. A hybrid 6-phytase based on the genes of the enterobacteria *Hafnia* sp., *Yersinia mollaretii* and *Buttiauxella gaviniae* was released in a commercial product (Natuphos®E) [109]. Recently, a phytase chimera of *Citrobacter braakii*, *Hafnia alvei* and *Yersinia mollaretii* was reported, which exhibit sequence identities of $\leq$80% to their parental enzymes [110].

Genetic engineering tailors phytases for their application in the feed market. The aim is to increase the enzyme stability in vivo, i.e., in the intestinal transit (specific activity, pH stability and protease resistance) and/or its thermostability to withstand feed pelleting [9,101].

3.2.4. Enzymatic Hydrolysis

Phytases catalyze the release of P from phytate in a stepwise hydrolysis reaction [111,112]. The sequential hydrolysis of $InsP_6$ proved an accumulation of inositol-triphosphate ($InsP_3$). A full hydrolysis to *myo*-inositol is not achieved, due to the structural conformation of these phytases. Even if some phytases are able to further hydrolyze to inositol-monophosphate ($InsP_1$), an accumulation of $InsP_3$ was observed [37]. Thereby the hydrolysis pattern is influenced by the enzyme dose and the substrate concentration. In vivo, phytases are

able to further hydrolyze inositol-tetraphosphate ($InsP_4$) [113]. Reports show that in the small intestine of piglets [114], $InsP_3$ was detectable; meanwhile, hydrolysis in vitro ended with $InsP_4$ [115]. Such studies can be performed with an in vitro system mimicking the digestive track in monogastric animals and allow for valuable insights into the phytate degradation pattern. Indeed, a remaining challenge is that only up to 50% of phytate is degraded in the animal intestinal tract [85], releasing considerable amounts of lower inositol-P (< $InsP_4$). A challenge in enzyme engineering is the further hydrolysis of $InsP_4$ and $InsP_3$ to $InsP_1$, thereby accessing complete and fast degradation of the available phytate without compromising the thermostability and specific activity. Although phytase from metagenomics analysis like for example rPhyXT52 [106] and phytase blends of a 3- and a 6-phytase (different stereospecificities) [116] were reported in vitro to degrade $InsP_6$ to $InsP_1$, an accumulation of $InsP_4$ in vivo was measured [117–119].

Noureddini et al. studied the enzymatic hydrolysis of a side stream in ethanol distillation. Light steep water, a side stream from wet milling of corn prior to fermentation, is a phytate-rich stream with a total P content of approx. 5 mg/g. After 7 h treatment of the substrate with PhyA phytase extracted from *Aspergillus niger*, it was shown that more than 75% of phytate was degraded, releasing significant amounts of P_I [120]. Herrmann et al. established a process using a side product of food oil manufacturing. They reported the hydrolysis of phytate from rapeseed meal and several other deviled seeds by *Escherichia coli* AppA phytase. An advancement of the process by using a blend of 3-phytase and a 6-phytase (rPhyXT52/Dc phyt) reached 78 to 90% reduction in inositol-P in rape, sunflower, or soya meal. Thereby, the P recovery by enzymatic treatment was increased by 40%, releasing up to 26 g P_I/kg of deoiled seed. The hydrolysis took place in a reaction buffer at pH 5 and 37 °C during 6 to 16 h incubation time [116].

The "Value-PP process" (research project) which is still not industrially established, enables the mobilizing of phytate-P from deoiled seeds, nuts and bran. An enzymatic hydrolysis with subsequent biotransformation recovers phytate–P from food manufacturing side products which is accumulated in the yeast *S. cerevisiae* to polyphosphate (37 mg PO_4^{3-}/g bran, 38.1 g polyP/L). Biotechnological production of polyphosphate-rich yeast extracts is a valuable food additive (preservative, texture improvement, and flavor) which can be produced from rape meal, rice barn, wheat, soya meal, among others. The emerging value chain leads to the valorization of the biomass as well as to P-reduced feed components. The total P content of the meals after enzymatic treatment is reduced by up to 90% without compromising feed quality or ingredients [121].

3.3. Chemical Feed Treatment

Similar to the application of enzymes, chemical methods aim for a cleavage of ester bonds between the inositol ring and the P groups. Common carbon esters can be hydrolyzed by catalytic use of acids (e.g., sulphuric acid) or bases (e.g., sodium hydroxide), while carbonic acid (in the case of a basic hydrolysis as the corresponding salt) and alcohol are produced [122]. Also, hydrothermal decomposition is a widely used technique in biomass utilization. Various compounds were shown to be degraded and therefore better available for further processing, among them mainly ether bonds [123,124]. However, also simple esters can partly be degraded via hydrothermal treatment [125]. Phosphomonoesters, in particular, are hydrolyzed by use of acid, water and/or other nucleophiles via either a dissociative or associative mechanism, as shown in Figure 2. Nonetheless, the reaction rate is low, although thermo-dynamically favorable, and therefore needs to be catalyzed [126].

3.3.1. Hydrothermal Treatment

A treatment of cereal products using water and elevated temperature has several effects:

- Since phytate is water-soluble, a certain proportion is dissolved into the liquid phase and, therefore, eliminated from the substrate [31].
- At moderately elevated temperature, intrinsic enzymes are activated and therefore contribute to phytate hydrolysis [58,127].

- Higher temperatures enhance thermal phytate degradation [128,129].

Up to 100 °C, phytate is reported to be chemically stable [84]. However, soaking in water at lower temperatures can already show significant phytate reduction in cereals. Incubation at about 15 °C for over 30 h is performed during the malting process to promote germination of the grains (Section 3.2.2). Larsson et al. report a maximum phytate reduction of 50% by malting barley. This results from an activation of intrinsic enzymes during the natural process of germination. Other cereal types also show phytate reduction under these conditions, albeit to a lesser extent [130]. With rising temperature above 100 °C and treatment in water only, studies with brown beans showed increasing phytate reduction. A maximum reduction of 65% $InsP_6$ could be obtained by hydrothermal treatment at 140 °C during 1.5 h [84]. Here, a purely thermal effect applies in addition to phytate solubilisation [131].

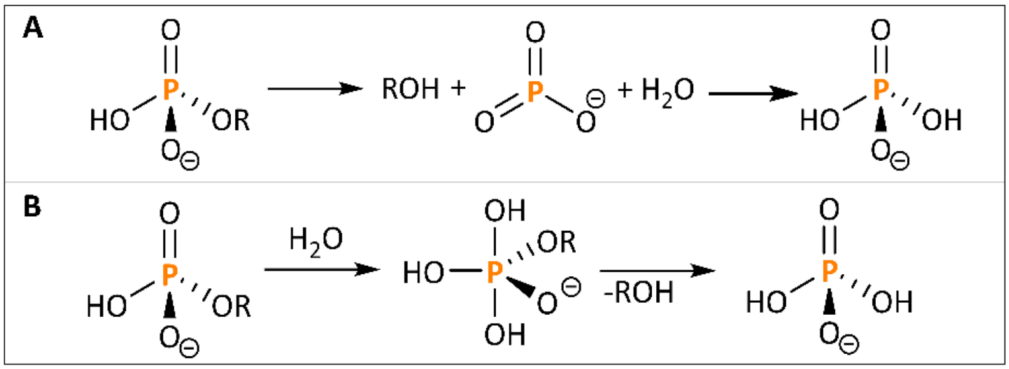

Figure 2. Dissociative (**A**) and associative (**B**) mechanism for phosphate ester hydrolysis.

3.3.2. Acid Hydrolysis

Since hydrothermal treatment has a limited effect, harsher conditions for phytate degradation might be necessary. Considering the mechanism of phosphate ester hydrolysis (Figure 2), inositol-P esters are particularly stable under basic conditions, and the presence of the anion is favorable for the reaction [126,132]. Therefore, further studies were conducted only on acidic treatment, while there are no approaches for a basic phytate degradation described in literature so far. In fact, a reduction in the pH during extraction was shown to support phytate degradation with an optimum at pH 4–4.5 [132]. Degradation usually comprises two steps: solubilisation of phytate from the substrate into the liquid phase and subsequent cleavage of the ester bonds. Solubilisation of phytate is feasible under mild conditions by incubation of cereal substrate with low concentrated HCl at room temperature [3]. A phytate degradation for a release of free P-groups, in contrast, proves to be more challenging. For a cleavage of the phosphomonoester bonds, elevated temperature is combined with low pH, this being particularly achieved in the literature through utilization of HCl and lactic acid [131].

Lemmens et al. showed a 54% phytate degradation in wheat after 8 h by a single step 60 °C thermal treatment at pH 4. The extraction solution consisted of 100 mM HCl in sodium acetate buffer [131]. Even higher degradation of up to 96% in barley was achieved through a multi-step treatment with 0.8% lactic acid. Bergman et al. examined a two-step acid soaking, with each step followed by a drying step. Best results were reached by soaking barley with 3.2 times the volume of lactic acid at 48 °C for 1 h followed by 5 h drying at 48 °C. The treatment was repeated at 50 °C and followed by additional drying of the substrate at 50 °C for 18 h and at 80 °C for 8 h [133]. Comparably high phytate degradation was also shown in 0.44 M HCl when using microwave radiation. Here, six stages each of 2 min microwave treatment at 650 W were executed, however with a model solution of dissolved pure phytic acid. Likewise, over 99% of initial phytic acid was cleaved for a liberation of free P [134]. Microwave treatment of sorghum seeds alone, i.e., without addition of acid medium, also showed phytate degradation, but with only a few

percent and thus nowhere near as effective as presented by March et al. [135]. Therefore, a combined method of acid hydrolysis with energy input by microwave radiation shows the most promising approach for phytate degradation in cereals. Table 2 provides an overview of all the methods discussed.

Table 2. Summary of the most promising methods for a P conditioning of cereal-based animal feed.

Treatment	Process	Substrate	Phytate Reduction	Process/Conditions
Mechanical	debranning	cereal grains	up to 90%	removal of outer hull (debranning) [58]
	layer exclusion	cereal grains	up to 90%	stepwise debranning/specific electrostatic separation; degermination [71,74]
Enzymatic	co-feeding of phytase	cereal grains	30–50%	phytase supplementation [85]
	germination	cereal grains	up to 100% (rye)	2 days pre-steeping, incubation in H_2O, 25 °C, 5 days [89]
	biotechnological processing	deoiled seeds, bran	up to 90%	200 to 400 U phytase, 7 volumes H_2O, 37 °C, pH 4.5–6 [3]
Chemical	hydrothermal treatment	brown beans	up to 65%	140 °C, 90 min, H_2O [84]
	acidic hydrolysis	barley	up to 96%	0.1 M lactic acid soaking, two-step heating at 48 and 50 °C for 5 h and 1 h, respectively [133]
		phytic acid solution	up to 99%	0.44 M HCl, 6 × 2 min microwave heating at 650 W [134]

4. Conceptual Design of a Feed Material Conditioning Process

This chapter provides an overview of potential designs for feed material conditioning processes based on the yet known techniques for P separation and solubilisation from cereal products and phytate conversion (Section 3). Thereby, the combined processes are expected to provide several advantages in terms of P utilization and reduced P run-off, thus contributing to the stabilization of the human-made P cycle. The processes are combined in different ways to identify the most suitable process option for a potential establishment (Figure 3). A qualitative evaluation of the general process parameters reflects the advantages and disadvantages of the depicted process options (Table 3).

Table 3. Qualitative evaluation of the process options for a feed material conditioning process (− negatively ranked, o neutrally ranked, + positively ranked). Advantageous properties are rated with + and disadvantageous with −.

	Mechanical & Enzymatic (Option i)	Enzymatic (Option ii)	Mechanical & Chemical (Option iii)	Chemical (Option iv)
Process complexity	−	+	−	o
Estimated energy demand	+	o	+	−
Harm of regents	+	+	−	−
Process maturity	−	o	−	o
Free P provision	−	o	−	+

4.1. Process Options for Feed Material Conditioning

Previous strategies for an improved P nutrient management in animal feed are based on phytase supplementation and matching specific P contents in compound feeds [136]. Although there are guide values for dietary P, the amount fed is often significantly above the actual demand. A "safety surplus" of P is fed due to limited accessibility of P [127], though various studies showed no negative effects when dietary P was reduced by up to 66% of the recommended value [34]. However, phytate-P remains unavailable to a

large extent. Therefore, conditioning prior to feeding fosters P-reduced feed. Meanwhile, phytate-P can be recovered and thereby enables an autarkic P-cycle.

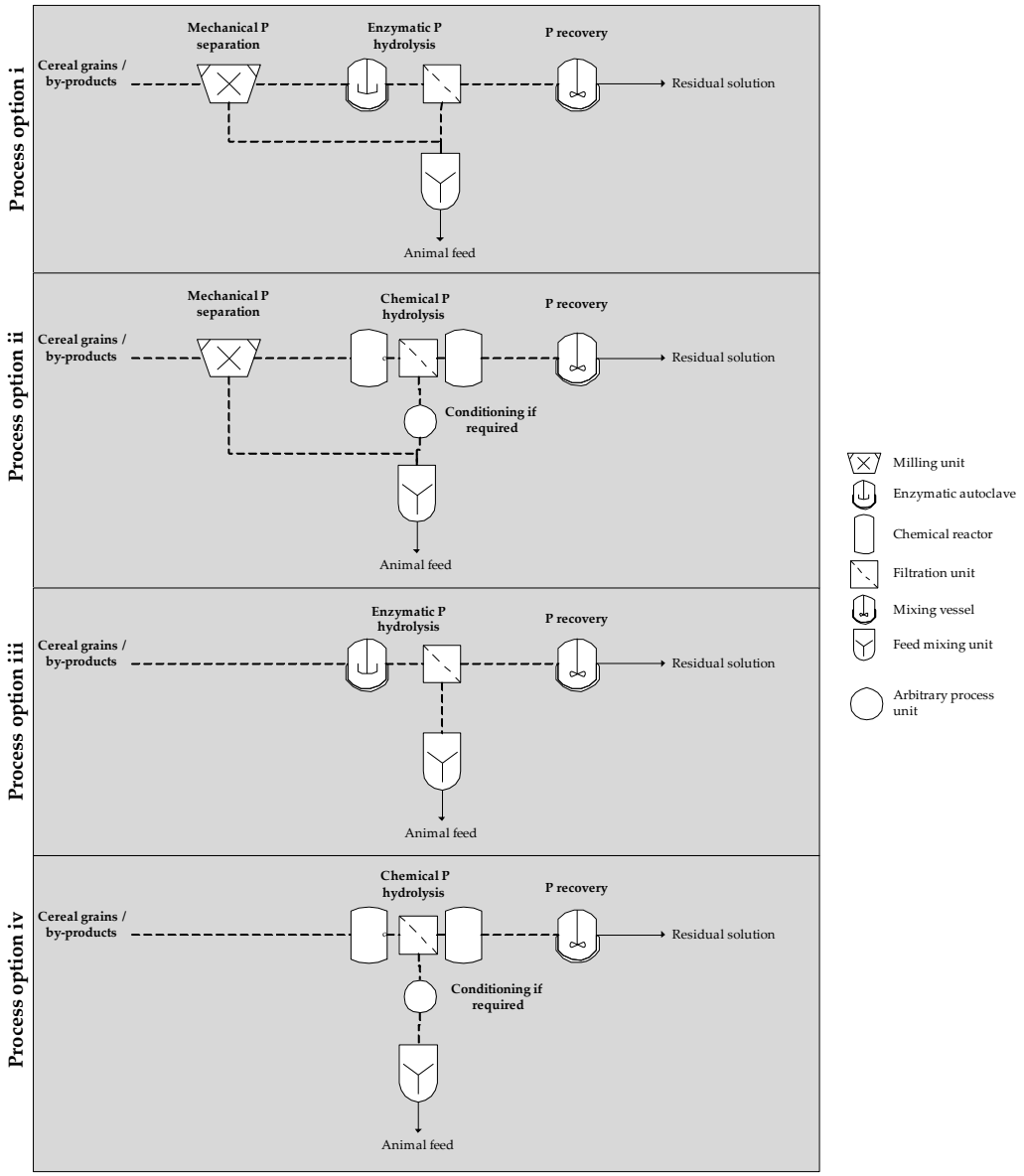

Figure 3. Schematic representation of the potential process designs for a feed material conditioning. Process option i and ii combine a mechanical pre-separation with subsequent hydrolysation by either enzymatic or chemical methods, respectively. The feed portion is directly enzymatically treated in process option iii and directly chemically treated in process option iv. At the end of each process option, a P recovery of the liberated P is performed.

A combination of mechanical pre-separation followed by hydrolysis leads to a potential design for a feed material conditioning process. The mechanical methods reduce the total mass and thus minimize the effort for subsequent operations (e.g., energy demand for heating, stirring, filtration, and drying). The resulting P-poor material stream can directly be used as feed; the P-rich material faction undergoes a further hydrolysis step by either enzymatic or chemical approaches. A combination of the aforementioned methods for reduced phytate content in feeds (Section 3) leads to four feasible process options:

- **Option i:** → Mechanical pre-separation & enzymatic hydrolysis
- **Option ii:** → Mechanical pre-separation & chemical hydrolysis

- **Option iii:** → Enzymatic hydrolysis
- **Option iv:** → Chemical hydrolysis

Although a mechanical pre-separation reduces the effort for subsequent operations, the separation itself forces additional requirements, which must be considered in the overall assessment. Thus, the process options are considered including the pre-separation (options i/ii) or the feed portion is treated directly by either enzymatic (option iii) or chemical (option iv) methods. The final process step involves the recovery of the liberated P to be used in food, feed, or the fertilizer industry. However, P recovery, e.g., through precipitation [137], is an already well established procedure and therefore not further discussed. In Figure 3, the four different process options are illustrated in a simplified process scheme.

During enzymatic treatment, phytate is solubilized into the aqueous phase and simultaneously hydrolyzed (One-Pot-System). After the treatment, a separation of the solid phase (conditioned feed material) and the liquid phase for further recovery of the liberated P is required, this being achieved by a filtration unit. Considering chemical hydrolysis, solubilisation and phytate degradation are performed in separate process steps, since harsher conditions are applied. Therefore, phytate is solubilized into the aqueous phase, directly followed by a filtration unit. The phytate containing supernatant is chemically treated in a subsequent process step. In all cases, after P recovery, the residual solution can be further valorized by the recovery of soluble organic compounds.

All filtration residues as well as the P-poor fraction from mechanical separation are brought together in a mixing unit, which provides P-reduced animal feed. While enzymatically treated feed is directly suitable in the feed industry [3], chemical hydrolysis might be followed by neutralization or decontamination, thus intensifying the process.

4.2. Qualitative Evaluation of the Process Options

The process options for a potential feed material conditioning process are combined by different methods (Figure 3). Thus, various conditions prevail, resulting in certain advantages and disadvantages. Therefore, a qualitative evaluation according to the following individual assessment criteria is provided:

- The **process complexity** refers to the number of individual process steps and therefore the requirement for, for example, additional tanks, pumps, and process peripherals.
- For **energy demand**, only a rough estimation considering temperature, electricity, and energy input for drying of the conditioned feed material is provided. However, energy demand is one of the primary economic factors and thus taken into account.
- The **harm of reagents** is evaluated in terms of impact on human health and the environment. It comprises toxicity as well as acidic and basic effects, among other types of contamination.
- The **maturity** of the process indicates how far the process is from industrial application in view of a potential feed material conditioning process. The current state of research and already established methods are taken into account.
- The rate of **free P provision** refers to the amount of recovered P and the conversion into industrial relevant compounds (e.g., feed, food or fertilizer). Here, the estimation is based on results derived from ongoing research (Section 3).

A combination of mechanical pre-separation with subsequent hydrolysis results in higher efforts in plant build-up and operation, thus in an increased process complexity. In addition, the mechanical separation requires electrical energy; however, this reduces the effort for subsequent operations. Hence, a mechanical pre-separation appears to be more suitable in terms of energy demand. The techniques are well researched and already performed industrially [71], making them more likely to be implemented. Nevertheless, a combination of mechanical separation and subsequent hydrolysation is hardly described, resulting in low maturity of the designs. The rate of free P provision is reduced since mechanical methods are not fully accurate. Therefore, a certain P_O amount remains within the feed [71].

Chemical hydrolysation s more complex compared to enzymatic treatment, as additional process steps are required to ensure feed quality. Likewise, energy demand for chemical hydrolysation is higher due to higher applied temperatures [134]. Chemical hydrolysis requires strong acids which are known to be hazardous and corrosive towards certain material. In contrast, reports on enzymatic hydrolysis prove an accumulation of $InsP_3$ and $InsP_4$ [117,118]. Therefore, enzymatic hydrolysis is less effective in terms of the yield. Concerning the establishment of a feed material conditioning process, both methods are currently being investigated and therefore estimated on a comparable maturity level. The results of the qualitative evaluation of the respective process options are summarized in Table 3.

5. Conclusions

With the proceeding growth of the world's population and thus intensification of agriculture, the P demand for fertilizer and feed supplementation has drastically increased over the last decades [138]. Mineral P mining has been multiplied and the P reservoirs are nearly depleted [139]. P management strategies contribute to a circular P bioeconomy and resource stewardship. Emerging value chains enable biotechnological P recovery from renewable resources, which engender an independency from P imports [140]. A potential solution reviewed and evaluated hereby is the exploitation of P in animal feedstuff before feeding. Although P is an essential nutrient, large portions of P, especially in cereal-based feeds, are in the form of phytate and therefore excreted through the digestive tract without absorption; i.e., P is used inefficiently [31].

The reviewed methods for improved P utilization from feed material comprise mechanical P separation as well as enzymatic and chemical phytate degradation. Removing either the whole cereal bran or specific layers can lead to significant phytate reduction, though it is associated with loss of other nutrients [58]. Feeding phytase-rich feed material, e.g., rye, and the use of microbial produced phytases are currently well established in livestock nutrition to enhance phytate digestibility, albeit only to a certain extent [34,75]. However, enzymatic and chemical pre-processing of feed material experienced free P provision of over 90% [3,133,134]. Conditioning the feed grains prior to feeding fosters P-reduced feed. Meanwhile, phytate-P recovered from biomass can be used to produce fertilizer or food and feed supplements, thus enabling a step towards an autarkic P cycle.

Different designs of a potential feed material conditioning process are presented (Figure 3). The process designs are qualitatively evaluated in terms of industrial applicability and on the basis of different assessment criteria (Table 3). A mechanical pre-separation thereby reduces the material stream and thus lowers the effort for subsequent operations (e.g., drying of conditioned feed material). Nevertheless, mechanical methods are less accurate [58]. Therefore, the overall yield is lower compared to direct hydrolysis. In literature, the highest yield of 96% phytate conversion is reported for chemical processing [134]. However, enzymatic processing without any mechanical pre-processing appears to be superior, since the process design is less complex and the process conditions are milder [3,9]. This particularly refers to lower process temperature and the reagents used are less harmful. Thus, with regard to the parameters and process options considered, the direct enzymatic treatment of feed material shows the most promising properties. Nevertheless, each individual process design is expected to recover high amounts of P initially bound to phytate. The liberated P is finally converted into fertilizer, feed, and/or food ingredient. Therefore, the approach of animal feed material conditioning can significantly contribute to sustainable P management.

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Abbreviations

ATP	Adenosine triphosphate
DNA_1	Deoxyribonucleic acid
inositol-P	inositol-phosphate
$InsP_1$	inositol-monophosphate
$InsP_3$	inositol-triphosphate
$InsP_4$	inositol-tetraphosphate
$InsP_6$	inositol-hexaphosphate
Mt_P/a	10^6 metric tons phosphorus per year
P	phosphorus/ phosphate
phytate-P	phytate-bound phosphorus
P_I	inorganic phosphate
P_O	organic phosphate
polyP	polyphosphate
RNA	Ribonucleic acid
U	Unit [µmol/min]

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