

# The Enigma of Fertilizer Phosphorus Utilization

Ewald Schnug and Silvia H. Haneklaus

**Abstract** The need for a sustainable use of the limited resource phosphorus in agriculture is generally acknowledged though scarcity is no pressing topic. There is no doubt that phosphorus losses from agricultural soils to the environment are a major contributor to eutrophication of water bodies. There is also no doubt that the excessive application of farmyard manure in the vicinity of big livestock enterprises yields an undesired accumulation of P in soils, while on numerous arable farms phosphorus mining can be observed. The premise for a sustainable P use in agriculture is a balanced P fertilization where inputs equal outputs. This chapter summarizes the chemical behavior of fertilizer-derived phosphorus in soils, and it presents a novel approach to assess the fertilizer phosphorus utilization completely and reliably as a tool to quantify the genuine phosphorus demand of agricultural crops.

**Keywords** Actual phosphorus utilization • Apparent phosphorus utilization • Balanced fertilization • Immobilization • Off-take • Speciation • Utilization coefficient

## Introduction

Phosphorus (P) is an essential plant nutrient and a sufficient P supply is required in order to maintain a high level of crop productivity. Next, P has an eminent and well-known relevance as an ecological contaminant (Bai et al. 2013; Frede and Bach 2003; Perspectives Agriculture 2011). Thus it is vital for sustainable crop production to develop strategies and measures to close the agricultural P cycle (Perspectives Agriculture 2011).

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The waste of the non-renewable resource P, which is mainly consumed for fertilizer purposes, is of major concern for sustainable development. Here, P fertilization strategies request significant advancements towards sustainability. Pessimistic assessments see world P reserves last only for another 50–150 years and the term ‘peak phosphorus’ (Cordell et al. 2009) has caused audible public uproar (Schwarz and Weingärtner 2013).

In industrial countries agriculture uses more P for fertilization than it exports with agricultural products. There is an ongoing discussion about the scarcity of P reserves that will affect agricultural production within the next decades. Ulrich and Frossard (2014), however, showed that available data do not support such apprehension. Meanwhile the problem stepped from scientific to public awareness and finally has reached the political level: in the coalition agreement for the 18th legislative period of the Lower House of German Parliament the P problem is addressed in the chapter “Water bodies and marine environment protection” with the phrase: “We will end the agricultural use of sewage sludge and retrieve P and other nutrients.” (Anonymous 2014).

But retrieving P is only one part of the story, making it into suitable fertilizers, however, a complete different one. The core process of separating P from wastes is making it insoluble and undergoing precipitation. In contrast, the core process of making P-fertilizers is making it soluble and thus available for plant uptake. It had been one of the great breakthroughs in plant nutrition and fertilization when *John Bennet Lawes* showed more than 150 years ago “that bones, treated with sulfuric acid and to produce superphosphate increased the yields of turnips grown on the soils at Rothamsted” (e-RA 2014). A key in assessing the overall sustainability of P fertilization is the question to which extent soil-applied P is taken up by crops cumulatively over an infinite period of time. Common understanding is that if P is used for fertilization a certain amount of the nutrient will always be lost in the system requiring that more P needs to be fertilized than is removed by the crop plants (Djodjic et al. 2005; Finck 1979; Platzen and Munk 1975; Syers et al. 2008; Wiechmann and Werner 1976). It is intrinsic that this assumption postulates no global validity as otherwise no ecosystem would be able to survive over time without any external supply of P. Despite a number of such ecosystems (Vitousek et al. 2010) the perhaps most popular example and evidence are “ecospheres” which are materially closed ecological systems and which are self-sustaining over a period of years (Taub 1974; Sagan 1986; Wikipedia 2014).

P fertilizers are the most significant carriers of hazardous substances into agro-ecosystems. P fertilizers manufactured from rock sources are contaminated with heavy metals and radio-nuclides (Taylor et al. 2016; Schnug and Haneklaus 2015; De Kok and Schnug 2008) and those deriving from organic sources may carry significant amounts of pharmaceuticals and other organic xenobiotics (Bloem et al. 2016), both hampering the sustainability of P fertilization from the material point of view. Promising technology has been developed to destroy organic xenobiotics in sewage sludges by incineration combined with solubilization of P and heavy metal extraction which delivers recycled P fertilizer materials that are comparable to manufactured mineral P fertilizers (Adam et al. 2009). With view to

the contamination of phosphate rock with uranium (U) Haneklaus and Schnug (2016b) developed an innovative concept to employ the extracted U for energy and fertilizer production. Sustainable P fertilization not only requires a complete utilization of the nutrient itself, but also needs to limit collateral damages to soil and food quality. The primary questions to be answered in this chapter are: “What are the factors governing the utilization of fertilizer P and what are the circumstances under which a complete (100 %) utilization of fertilizer applied P can be expected”.

## **Fate of Fertilizer P in Agro-ecosystems**

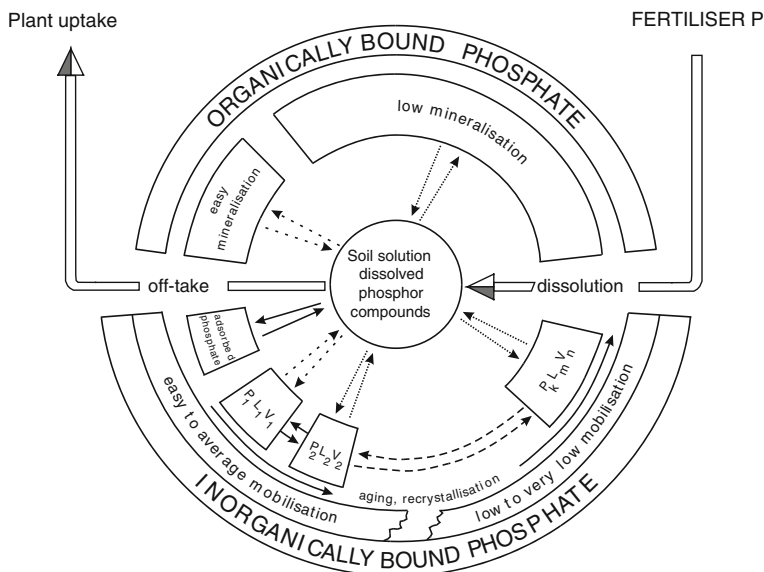
The following section summarizes the common understanding of the behavior of fertilizer-derived P in agro-ecosystems in the context of its utilization by plants.

### ***Turnover of Inorganic P in Soils***

A general overview about the turnover of P in soils is given in Fig. 1. On an average half of the total P in a soil is bound organically, the other half exists in form of inorganic compounds. A small amount of the inorganic P is to be considered as virtually inert. This implies for instance apatites in the parent material of the soil, and insoluble P-containing fertilizer materials.

Plants have access to the P resources of a soil only through P dissolved in the soil solution. This is usually orthophosphate, but also in distinctly lower amounts low molecular organic compounds, which are able to pass the *Caspary* strip in the roots (Barber 1980). The amount of P dissolved in the soil solution at any time is always only a fraction (approximately about one-tenth of a percent) of the total P content in the soil, and constitutes not more than half of the amount of P taken up by an average harvest of crops (20 kg/ha P). This implies that P in the soil solution has to be constantly replenished from soil resources. A site will become P deficient and respond to P fertilization if the P demand of the crop for optimum growth exceeds the amount of plant available P in the soil. Fertilizer P increases the P concentration in the soil solution, the amount of adsorbed P and the quantity of P precipitated as secondary minerals. The nature of the precipitates depends on the predominance of Ca, Fe or Al ions and thus the pH-value of the soil (Sample et al. 1980). The utilization coefficient of P in the year of application depends strongly on the amount and nature of available adsorption sites in the soil (Schwertmann and Taylor 1989).

The utilization coefficient of mineral P fertilizers decreases with an increasing number of adsorption sites relatively to the P concentration (Roemer 2003). Doering (1956) estimated that 30–55 % of adsorbed P is available to plants in the first year after application. The speciation of fertilizer P in secondary minerals is mainly governed by the soil pH: in acidic soils Fe- and Al-phosphates prevail, while



**Fig. 1** The soil P engine. Plants take P up as dissolved orthophosphate from the soil solution. P replaced by fertilization first dissolves in the soil solution, some of it is taken up by plants but the majority transfers into the organic and inorganic storage pools. The latter undergoing aging over time:  $P_1, P_2, \dots, P_k$  = inorganic P species;  $L_1, L_2, \dots, L_m$  = solubility of  $P_1$ – $P_k$ , decreasing from  $L_1$  to  $L_m$ ;  $V_1, V_2, \dots, V_n$  = rate of solubility of  $P_1$ – $P_k$ , decreasing from  $V_1$  to  $V_n$

in neutral to alkaline soils Ca-phosphates are predominant (Munk and Gross 1975; Werner 1969). These initial, still labile precipitation products undergo further reactions with the soil environment. They change into more stable and less soluble, and thus less plant available P compounds over time (Sample et al. 1980). These processes follow thermodynamic principles, and thus are driven by an increase in entropy. In calcareous soils the first reaction product is brushite, whereby a continuous exchange of  $\text{Ca}^{2+}$  for  $\text{H}^+$  in the crystal surface leads to the formation of hydroxyapatite. However, in temperate climates the formation of apatite has never been observed under field conditions (Werner 1970, 1971a; Lookman et al. 1995). This is highly significant as precipitation products deriving from P introduced through the soil solution by fertilization obviously never become completely inert.

Plants developed a number of mechanisms to revise the process of P immobilization in the soil through organic acids excreted by the root, i.e. citric, oxalic and galacturonic acid which form stable complexes with metals, and thus are able to exchange and utilize even strongly bound P (Haneklaus and Schnug 2016a; Nagarajah et al. 1970; Oburger et al. 2013; Rovira 1965).

In acidic soils the aging of fertilizer P is characterized by a change from amorphous to more crystalline phosphate minerals, whereby orthophosphate displaces  $\text{OH}^-$  from coordination positions at the surface of the Fe- and Al-oxides (Werner 1971a; Werner and Wiechmann 1972). Although the initial reactions of

P fertilizers in the soil are rapid and result quickly in equilibrium between reaction products and soil solution, aging is a continuous process that yields the formation of more stable and less available P forms (Werner and Wiechmann 1972; Scharafat and Finck 1973; Sample et al. 1980).

In addition, thermodynamic processes of energy releasing phosphate transformations are accompanied by energy consuming microbiological processes that have a solubilizing effect on phosphate minerals (Sharma and Singh 1971; Mosse et al. 1976; Frossard et al. 2000).

Half or more of the total P in soils may be present in organic forms (Harrison 1987). Organically bound P originates from residues of crops grown on a site, or from organic fertilizers charging soils with additional P in organic form. Despite low molecular P containing organic compounds such as ATP organic P is less readily available for absorption by the plant than the inorganic P pool. More than 50 % of P in organic matter occurs as high molecular weight molecules such as esters of the phosphoric acid or inositol phosphates (Baeumer 1971; Schachtschabel 1960; Anderson 1980; Noack et al. 2013). Inositol phosphates form a number of insoluble salts and also form strong complexes with proteins and some metal ions, which cannot be utilized by the plant without prior mineralization by micro-organisms. Ivanov and Sauerbeck (1972) estimated an annual utilization efficiency of about 1.0–1.5 % for these P species. The rest of the organic P species occurs in form of easily soluble nucleic acids and phospholipids. The annual utilization efficiency is estimated to be 15–20 % (Ivanov and Sauerbeck 1971, 1972).

### ***Turnover of Organic P in Soils***

The release of organic P into the soil solution, where it is translocated before being adsorbed by the root, is controlled by the mineralization rate of organic matter (Turner et al. 2013). Generally, tillage of the soil promotes the decomposition of organic matter by stimulating the activity of the soil micro-flora (Harrison 1987). As with N, a high ratio of soil organic matter to organically bound P may result in P deficiency in the soil system. This so-called biological P-lock has been reported for soils with a C/P<sub>org</sub> ratio >150 (Baeumer 1971; Finck 1976; Kaila 1949). In this process the fixation kinetics of the different organic P species follow the same principles as the aging of the inorganic P fraction. Thus in the first year of application, the utilization efficiency of P applied as organic fertilizers does not differ from those reported for P in inorganic fertilizers (Diekmann 1966; Debruk and Voemel 1970; Asmus et al. 1973; Isermann 1978; Latkiewicz 1977; Sanderson and Jones 1997; Ibrieki et al. 1999; Anderson et al. 2001; Whalen and Chang 2001). Crop type and associated land management practices influence decomposition processes in the long run, and each management system will stabilize around a steady organic P level.

## ***P-Losses from Agro-ecosystems***

P is a macro-nutrient with no chemical or physical interferences with the atmosphere so that P will not evade from a soil through gaseous losses. For most agricultural systems P losses from soils by leaching or surface run-off are considered low with an average of 0.5 kg/ha year P except when extraordinary conditions favoring preferential flow occur (Boysen 1977; Hoffmann 1978; Svanbaeck et al. 2014). This amount seems like a ubiquitous background level which is little affected by agronomical or environmental factors. A much more significant factor for P losses from agro-ecosystems is erosion (Catt et al. 1997; Fuchs et al. 2009; Sharpley et al. 2000; Schroetter et al. 2016) which, based on averaging data provided by UBA (2015) would account to a mean value of 7–8 kg/ha year P in Germany. In contrast to leaching, losses through erosion can be controlled and kept on low levels by implementing codes of good agricultural practices (GAP) (Al-Kaisi 2015; BMVEL 2002). The expressed spatial persistence of P in soils was recognized long ago by European geographers and since then used in archaeology to trace back ancient settlements (Arrhenius 1931; Broadbendt 1981; Proudfoot 1976).

## **The Utilization Coefficient of P in Fertilizers and Its Significance for Fertilization**

Phosphorus taken up by plants from soils originates either from native soil reserves or from P not taken up by previous crops. These residuals from former fertilizer applications complement the pool of native soil P reserves. Both P sources will never be utilized completely by crop plants so that a ‘utilization coefficient’ can be calculated for each nutrient source, which is required in order to determine the plant available amount of P. A defined amount of crop yield corresponds to an assigned amount of P removed from the soil. Assuming that P is yield limiting, the difference between the amount of P available from the soil pool and the amount of P removed with the targeted crop yield needs to be supplied by fertilization. In addition, it needs to be taken into account that P in a fertilizer product is not completely taken up by plants so that a utilization coefficient for this P source is necessary in order to determine the fertilizer rate. The previously mentioned parameters are summarized in the following equation:

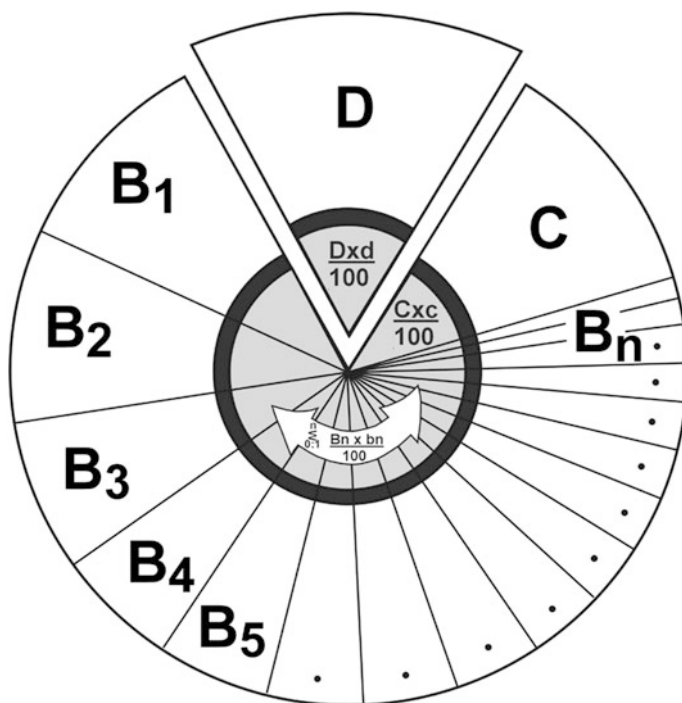
$$D = \frac{E - \left( \frac{B \times b}{100} + \frac{C \times c}{100} \right)}{d} \times 100 \quad (1)$$

B P content in the ploughed soil layer originating from previous fertilizer applications in (kg/ha)

C Native P content in the ploughed soil layer in (kg/ha)

- E P off-take by harvest products in (kg/ha) for target yield
- b Utilization coefficient of accumulated P, fertilizer-derived in (%)
- c Utilization coefficient of native P in (%)
- d Utilization coefficient of fertilizer-derived P in the year of application in (%)
- D Fertilizer rate expressed as amount of P in (kg/ha).

Equation 1 describes the factors, which determine the P utilization of the current crop. As mentioned before plants utilize fertilizer-derived P only partly in the year of application so that the residual amount restocks soil reserves. Figure 2 provides a graphical approach for a better understanding of the processes involved: the inner circle in the Fig. depicts the amount of nutrient found in the harvest products and its origins: native soil reserves (C), secondary soil reserves (B) and fertilizer (D). From the entity of each source only a fraction is utilized by the plants and removed with harvest products, which implies that a time factor needs to be considered, too. Fertilizer P not taken up in the year of application is attributed to the pool of



**Fig. 2** Origin of P taken up by a crop. ● P off-take for target yield; D = P fertilizer rate; B = residual P in the soil from former fertilizer applications; C = native P content of the soil; E = P off-take; b = utilization efficiency of residual P; c = utilization efficiency of native P; d = utilization efficiency of P in fertilizers in year of application

secondary soil reserves in the P balance of the following crop. This process reiterates within each vegetation period whereby the residual amount of fertilizer-derived P declines over time. The remaining quantity of residual P is a fraction that has aged one more year and adds to the secondary soil reserves. This implies that the total amount of P taken up by plants constitutes of fractions from previous fertilizations which contribution decrease over time.

During the year of application plants utilize only a fraction from the total amount of P applied by fertilization. The amount of fertilizer that is not taken up by plants during the growth period will remain in the soil and is potentially plant available within the next vegetation period apart from losses by soil erosion.

The potential availability of P in following years depends on immobilization processes in the soil (see above). As this is a continuous process the term  $\frac{B * b}{100}$  in Eq. 1 is actually a cumulative quantity:

$$\frac{B * b}{100} = \frac{B_1 * b_1}{100} + \dots + \frac{B_n * b_n}{100} \quad (2)$$

with:

$B, B_1, \dots, B_n$  residual P from fertilization

1 of previous year

2 of year the last but two years

n of n years ago

$b_1, b_2, \dots, b_n$  corresponding utilization efficiencies of  $B_1, B_2, \dots, B_n$ .

On agricultural fields with regular P fertilizer applications it is necessary to consider the total efficacy of applied P. Besides the potential supply from native resources,

$$\left( \frac{C * c}{100} \right)$$

the utilization of P by fertilizers in the year of application

$$\left( \frac{D * d}{100} \right)$$

and their potential residual effect

$$\left( \frac{B * b}{100} \right)$$



need to be determined for calculating the required P fertilizer input. Due to the accumulation of residual P from fertilizers over time the term

$$E - \left( \frac{B * b}{100} + \frac{C * c}{100} \right) = 0 \quad (3)$$

equals zero if the utilization efficiency is calculated for the year of application in dependence on P off-take and supply by residual P so that it is sufficient to replace losses by off-take, leaching, erosion and fixation (Fig. 2). To do so the utilization in the first year of application and following years needs to be considered. Fertilizer rates, which maintain this *status quo* are economically optimum and ecologically balanced.

The utilization efficiency in the year of application represents the actual utilization, while the utilization over long periods of time with its cumulative efficacy expresses the effective (Karlovsy 1962), or apparent (Kaila 1965; Finck 1979) utilization efficiency (s). Actual utilization rate and the utilization rate from previous fertilizer applications are required for the calculation of the apparent utilization efficiency:

$$\frac{D * s}{100} = \frac{D * d}{100} + \frac{B * b}{100} \quad (4)$$

whereby the apparent utilization efficiency can be determined as follows

$$s = \frac{\frac{D * d}{100} + \frac{B * b}{100}}{D} * 100 \quad (5)$$

The turnover of P supplied by fertilization can be balanced as follows

$$D = E + V + F \quad (6)$$

with:

D Fertilizer rate

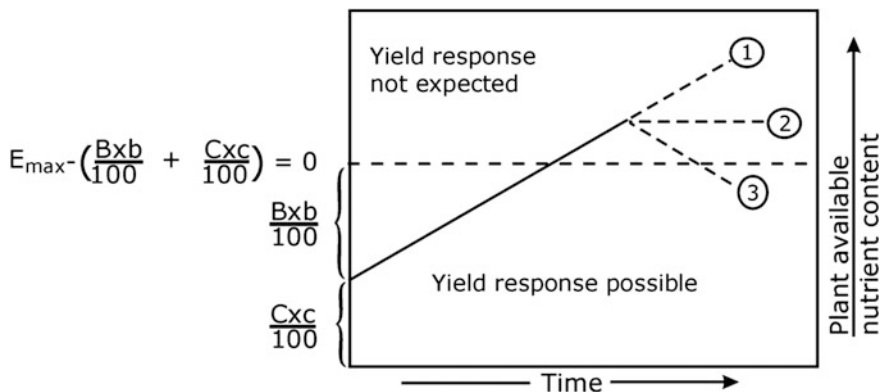
E P off-take by harvest products for target yield

V P losses by leaching and erosion

F Losses by P fixation.

and after considering a potential supply from native resources the following equation can be set up

$$\frac{E + V + F - \frac{C * c}{100}}{D} = 1 \quad (7)$$



**Fig. 3** Changes in soil nutrient concentration after reaching the optimum soil fertility level (based on fertilization considering the utilization efficiency of the fertilizer in the year of application (1), fertilization considering the effective or apparent utilization efficiency of the fertilizer (2), without fertilization (3) (Engelstad and Parks 1976, modified)

As a result of long-term P fertilization a level of residual P in the soil will adjust which is sufficiently large enough to replenish P in the soil solution required for the entire crop without adding supplementary fertilizer P after a given time (Fig. 3). At this point it would be sufficient in the future to replace only the amount of P which has been removed with the harvest products and in the form the plants have taken up this P from the soil solution which is water-soluble orthophosphate.

Assuming that P losses by leaching, erosion and fixation can be neglected the long-term cumulative utilization efficiency of P or 'apparent' utilization coefficient (s) is then simply deduced by balancing plant removal and supply by of fertilization:

$$s = \frac{E}{D} * 100 \quad (8)$$

with:

s apparent utilization coefficient for P fertilizer (%)

E P off-take by crop (kg/ha P)

D amount P fertilized (kg/ha P).

The validity of this approach demonstrates the experimentation of Engelstad and Parks (1976). On soils which are sufficiently supplied with P, P rates which equal the off-take by harvest products proved to be adequate in order to maintain the level of P supply. In contrast, P rates based on the actual P utilization rate resulted in a continuous increase of the plant available P pool (Fig. 3).

## Empirical Methods to Determine the Fertilizer Nutrient Utilization Efficiency

It is one of the basic questions in fertilizer research: how much of a nutrient applied will be taken up by plants and removed by harvest products. The classic empirical approach to determine the utilization coefficient is the so-called differential method. Employing this approach the amount of nutrients taken up by plants from an unfertilized plot is subtracted from the amount of nutrients taken up from a fertilized plot, divided by the amount of fertilized nutrient:

$$(U_f - U_0)/D * 100 = d \quad (9)$$

with

$U_f$  net nutrient off-take by harvest products in (kg/ha) from the fertilized plot

$U_0$  net nutrient off-take by harvest products in (kg/ha) from the unfertilized plot (control)

$D$  fertilizer rate expressed as amount of nutrient (kg/ha)

$d$  utilization coefficient of fertilizer-derived nutrient in the year of application in (%).

A major drawback of the differential method is that it is not feasible to distinguish between nutrients originating from the soil and fertilizer-derived nutrients. The method simply assumes that all nutrients taken up from an unfertilized plot must be soil-borne. Yet, another shortcoming of this approach can be attributed to so-called priming effect, which describes increasing plant vigor by fertilization associated with a higher nutrient uptake from soil resources if the nutrient has been a minimum factor (Lehne 1968; Rauhe and Bornhak 1968; Jacob et al. 1949). Here, the differential method tends to overestimate the utilization efficiency of a fertilized nutrient (Nethsinghe 1977; Michael and Machold 1957; Behrens 1954). Vice versa the method tends to underestimate the utilization efficiency if the initial soil supply is close to optimum and additional fertilization will only yield small increases in nutrient uptake (Nethsinghe 1977; Michael and Machold 1957; Behrens 1954).

The most important fault of the differential method is its inability to estimate the valid utilization over an infinite period of time. By means of the differential method it is impossible to verify whether a fertilized nutrient can be utilized completely or not. The reason is that although the amount might be marginal, plant biomass, even when little is produced on a control plot so that the denominator in Eq. 8 will always be higher than the numerator. At the end of the day from a basically faulty experimental design the myth of occluded or fixed soil P accrued which justified among other reasons strong over-fertilization with P during the second half of the 20th century.

The experimental attempt to assess the utilization efficiency of residual fertilizer P by means of exhaustion trials was not successful as it was not possible to assess the potential amount of P that can be utilized by plants. In such experiments crops

are grown consecutively on a soil subjected afore to long-term fertilization, however, without additional supplements of fresh fertilizers (Werner 1971b; Werner and Wiechmann 1972). The reason for the ineptness of the method is that the viability and thus the ability of plants to take up nutrients is negatively affected when the crop nutritional P level declines to the deficiency range. The common fallacy made on the basis of these experiments was to interpret the physiological disability of the plants to take up nutrients as a nutrient fixation in the soil. Consistent with the old view on an always incomplete utilization of fertilizer P Werner and Wiechmann (1972) reported an average, effective utilization efficiency of 48 % for residual fertilizer P in soils. They evaluated this low efficiency as an indication of P fixation in soils (Platzen and Munk 1975; Wiechmann and Werner 1976). Finally, a total P utilization efficiency of only 60 % has been calculated by adding the previously made estimations for the utilization efficiency of residual P and the reported initial utilization efficiency of fertilizer P in the application year of 15 % (Arbeitskreis Phosphat 1978).

Quite from the beginning of research in fertilizer nutrient utilization isotopes of the nutritive elements in question have been used for labeling and tracking (Hevesy 1923; Larsen 1952). Isotopes are any of two or more forms of a chemical element, having the same number of protons in the nucleus, or the same atomic number, but having different numbers of neutrons in the nucleus, or different atomic weights. Because all isotopes of an element have the same atomic shell they show all the same chemical characteristics. Fertilizer nutrients with altered isotope composition have the same physiological features than those with natural isotope composition. Depending on availability, modifying the isotope composition can be practiced either with stable or radioactive isotopes of the particular element. In the first case, the altered isotope composition is detected by an altered atomic weight of the element or by the radiation signature of the instable isotope.

The utilization coefficient is then calculated according to:

$$\left( \frac{A * \frac{B-C}{D}}{E} \right) * 100 = \text{Utilization rate (\%)} \text{ of fertilizer-derived nutrient} \quad (10)$$

- A total uptake of element by plants
- B isotopic abundance (or specific activity in case of radioactive isotopes) in plants from fertilized plots
- C isotopic abundance (or specific activity in case of radioactive isotopes) in plants from unfertilized plots
- D isotopic abundance (or specific activity in case of radioactive isotopes) in fertilizer
- E amount of fertilizer.

Stable isotopes of macro-nutrients are available only for nitrogen ( $^{15}\text{N}$ ), sulfur ( $^{33}\text{S}$ ), potassium ( $^{41}\text{K}$ ), calcium ( $^{43}\text{Ca}$ ) and magnesium ( $^{25}\text{Mg}$ ). Expensive  $^{15}\text{N}$  (which costs approximately 100 times more than the price for the element in natural

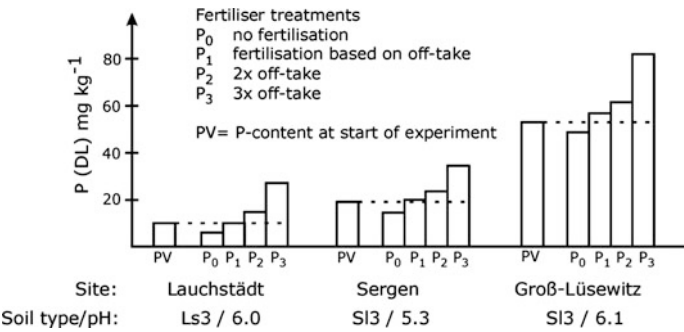
isotope configuration) still is the most affordable of all stable isotopes as all other nutrients yield prices that are several thousand times higher. Radioactive isotopes are available for studies on phosphorus ( $^{32}\text{P}$ ), sulfur ( $^{35}\text{S}$ ), potassium ( $^{42}\text{K}$ ) and calcium ( $^{45}\text{Ca}$ ). Radioactive isotopes are distinctly cheaper than stable ones, but in case of P and S only applicable for short-term studies because of their short half-life time ( $^{32}\text{P}$ : 14.3 days;  $^{35}\text{S}$ : 87.5 days).

There are only a few trials, which are able to proof the hypothesis that water-soluble fertilizer P can be utilized completely over infinite times. Shortcomings of traditional experimental designs such as the differential method and exhaustion trials have been outlined before.

Unlike C and N, which can be added to the soil systems from the atmosphere, the P status of natural systems is essentially controlled by the occurrence of primary apatite minerals (Walker and Syers 1976; Bowman et al. 1998). While this is true for most tropical soils, in temperate soils the importance of primary minerals is negligible and subsequently the aging of applied fertilizer essentially controls the P cycle. Thus, in temperate agro-ecosystems the utilization efficiency of fertilizers can be expressed as a percentage of the plant uptake (Koehnlein and Knauer 1965). Karlovsky (1962) introduced the so-called balance method, whereby under the condition of constant yield and fertilizer application rates the effective utilization efficiency can be calculated by balancing fertilizer input and plant uptake.

The non-equilibrium behavior of phosphate sorption reactions, known as hysteresis, whereby the desorption reaction usually does not take place as fast as the sorption reaction (Uehara and Gillman 1981), led to the prevailing opinion that P immobilization is higher than the dissolution of adsorbed fertilizer P and thus justifies a fertilizer rate higher than plant uptake (Arbeitskreis Phosphat 1978; Johnston 1976). However, in a seven years field trial Schachtschabel (1976) demonstrated that an application rate of water-soluble P fertilizer equivalent to plant uptake did not change the soil P level of the soils. As the natural supply of P by the soil did not have an effect on the results he concluded that a fertilization rate higher than the uptake was not economically sound. An application rate higher than the uptake will result in an increase of the soil P level which equals an accumulation of P, whereby a rate lower than the uptake would result in a decrease of the soil P level, thus in mining of P (Fig. 3). Bergmann and Witter (1965) obtained similar results (Fig. 4). Both field trials clearly demonstrate that the dissolution of initial fertilizer reaction products during the cropping season was sufficient to keep the concentration of P in the soil solution at the level of the plant requirement. Thus in these trials the apparent utilization efficiency of fertilizer P was 100 %.

These results not only demonstrate that plants are capable of utilizing aging P fertilizer products despite their decreasing solubility, but also that immobilization and mobilization processes are in an equilibrium. In the light of the above discourse the intrinsic hypothesis is derived that in soils where P fertilization does not result in a surplus in crop yield (Fig. 2) as the P supply is already optimum, the fertilizer rate should be equivalent to the plant uptake, as a utilization efficiency of 100 % can be assumed. For the validation of this hypothesis it is important to note that the assumption of 100 % utilization efficiency together with a balanced fertilizer



**Fig. 4** Changes in the concentration of double-lactate-soluble P in the surface soil during a 9-year field trial with increasing P fertilization using super-phosphate (extracted from Bergmann and Witter 1965)

strategy is only feasible for P species, which will undergo total dissolution within one cropping season. For the majority of agricultural soils this effective percentage of P fertilizers corresponds to their water-soluble P concentration on soils with a pH between 5.6 and 7.5, and the citrate-soluble P concentration on soils with a pH < 5.8, respectively. For organic fertilizers it is fair to assume that in the long run all P undergoes mineralization and will be converted into orthophosphate. Thus, the effective percentage of organic fertilizers corresponds with the total P concentration.

Following the concept of balanced fertilization as it is proposed by environmentalists (Sharpley and Withers 1994; Higgs et al. 2000), in particular by a variety of conventions for the protection of marine bodies (Vermeulen et al. 1998; Schnug et al. 2001), it is sufficient for agricultural production to replenish the soil P withdrawal by crops by the equivalent amount of water-soluble P.

Summarizing the significance of the information given in this section about the premises for a complete P utilization by plants, Table 1 shows the results of a meta data analysis of references on experiments determining P utilization.

According to the data presented in Table 1 utilization rates for fertilizer P in the year of application are higher when based on pot trials and employing the differential method. Empirical assessments are based consistently on differential trials

**Table 1** Utilization rates (%) of fertilizer P determined by different methods (results from a meta data analysis provided by Schnug (1978))

Time scale	Year of application				Long-term differential	
Method	Differential	Differential	Isotope	Isotope		
	Field	Pot	Field	Pot	Field	Pot
Mean	17.5	19.9	7.9	12.7	66	70
Median	11.8	14.0	8.0	11.8	70	75
Minimum	8.0	11.3	3.5	5.0	32	36
Maximum	37.0	45.5	10.5	21.5	83	89

because of the lack of stable isotopes other than the natural isotope  $^{31}\text{P}$ , or alternatively radioactive isotopes with a long half-life time. The experiments indicate constantly that about a quarter of the fertilized P has not been used by the plants.

It is widely accepted that more than 80 % of the applied P is immobilized in the soil due to precipitation and sorption processes, whereby the limiting step to furnish crop requirements is the dissolution of initial reaction products during the cropping season (Frossard et al. 2000). However, it has been demonstrated conclusively in this section that there is virtually no experimental set-up available to assess the amount of P finally used by crops.

In this context it appears more than doubtful to draw conclusions on the effectiveness of a P fertilizer from any growth experiment. There was a lot of speculation in literature on stocking up soil P reserves with non-water soluble P forms. The greatest efforts in this context were done by the fertilizer industry marketing partially acidulated rock phosphates in order to save costs for sulfuric acid in P fertilizer production (Hagin and Katz 1984; Zapata and Roy 2004). Recently, the effectiveness of new P fertilizer products derived from recycling processes is compared by means of growth experiments in pot and field for one vegetation period and year, respectively (Roemer 2003, 2013; Cabeza et al. 2011; Siebers and Leinweber 2013; Severin et al. 2013). However, differences in efficiency in such trials reflect only the initial speed of dissolution of the product and are no measure for the long-term utilization rate.

## Conclusions

The compilation of data since the 1920s elucidated some long-known, however, generally ignored facts about the utilization of fertilizer-derived P. Firstly, water-soluble and citrate-soluble inorganic P fully contribute on a long-term basis to the plant available P pool on agricultural soils in temperate climates, while less soluble P forms need to be discarded as their contribution to the P supply of crops is strictly limited. This aspect is of prime relevance for mineral P fertilizers and recycled, secondary P fertilizers. Secondly, the determination of the actual P utilization conceals the long-term effectiveness of fertilization and fertilizer product, and is no suitable indicator for assessing the optimum fertilizer rate. Thirdly, for a truly balanced P fertilization where input equals output, it is important to determine the apparent P utilization, which is not feasible with common experimental set-ups. However, limited proper data show that regular P fertilization yields a level of residual P in the soil, which is sufficiently high to replenish P in the soil solution which is required for optimum crop growth (Fig. 4). At this point it is sufficient to replace only the amount of P, which has been removed with the harvest products in water-soluble orthophosphate form.

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