Ewald Schnug · Luit J. De Kok *Editors*

Phosphorus in Agriculture: 100 % Zero

Springer

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Editors
Ewald Schnug
Institute for Crop and Soil Science
Julius Kühn Institute
Braunschweig
Germany

Luit J. De Kok
Laboratory of Plant Physiology
University of Groningen
Groningen
The Netherlands

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Ewald Schnug (* 7 September 1954)

The contributing authors have decided to dedicate this book to Ewald Schnug for various reasons. One is his 60th anniversary, yet another one is his outright devotion to fertilizer research that started almost 40 years ago. It was the work of Armi Kaila (1920–2003) on the apparent utilization of phosphorus that inspired him and triggered his ambition to deliver a benchmark on phosphorus fertilization. The outcome is a standard work, which summarizes cutting-edge knowledge on phosphorus research in different disciplines commendable for a mixed spectrum of readers including scientists, farmers, and politicians. It is the comprehension of these different perspectives into decision-making rules for fertilization, which are the core for a truly balanced use of phosphorus, which is agronomically adequate, environmentally sound, and socio-economically just.

Preface

Nutrients in phosphorus (P) fertilizer which are completely (100 %) utilized by crop plants without (Zero) contaminating the soil with environmentally relevant substances is a future concept for P fertilization in agriculture. P scarcity is one of the major challenges for agriculture in the near future. The waste of the nonrenewable resource P, which is mainly consumed for fertilization is of major concern for a sustainable development and there is no doubt that P fertilization strategies require significant advances towards sustainability. Pessimistic assessments see world P reserves last only for another 50–150 years. In industrial countries agriculture uses more P for fertilization than it exports with agricultural products. Some uncertainty in practical P fertilization derives from the fact that there are no experimental means to estimate the true long-term utilization of fertilizer P. The traditional concepts (differential and radioisotope method) suggest that on an average only 75 % of the fertilizer P applied is finally used by plants, implicating that always more P has to be fertilized than will be recovered by agricultural products. Next to P scarcity, excessive P loads on soils with intensive livestock farming and use of P sources, which are not completely available for plant result inevitably in a dissipation of this nonrenewable resource. Yet, another problem is the guidelines for site-specific P fertilizer recommendations in relation to land use systems.

The breakthrough towards an understanding for the prerequisites for a complete P utilization and thus also a complete recycling of fertilizer P came with an empirical approach published in 1965 by the Finnish scientist Armi Kaila (1920–2003), for which the term “apparent utilization” has been coined. Based on Kaila’s hypothesis, P fertilization concepts can be designed, which warrant a full utilization of fertilizer P in agriculture. This book agglomerates the basic knowledge required to target a 100 % P utilization which comprises the basic concept of “apparent utilization”, the fundamental principles of P turnover in soils and plants, the evaluation of the P nutritional status, and characteristics of fertilizers and fertilization concepts whereby the latter is addressed on national level.

Second to the goal of a 100 % utilization of fertilizer P is the objective to avoid or at least to limit the soil contamination and accumulation of hazardous inorganic and organic substances coming with the various types of P fertilizers. What seems like cutting the Gordian knot may be a challenge for future development in fertilizer manufacturing technology, energy neutral P fertilizer production using high-temperature nuclear reactors, where the energy required to make a clean fertilizer comes with the raw material.

Last but not least, this book addresses one of the first not only basic issues of sustainability of P fertilization but also its socio-economic aspects and proposed governance instruments.

Braunschweig, Germany Ewald Schnug
Groningen, The Netherlands Luit J. De Kok

“Phosphora”

A hand-sewn textile collage from cotton and silk (44 × 42 cm) by Bettina Franckenberg, Bodrum, Turkey (2016)

In search for the elusive Philosopher's stone, which turns ordinary metal into gold, Henning Brand discovered in 1669 the element phosphorus. Alchemists of that time often used light as a symbol of the spirit. Thus they were especially interested in light that seemed to be trapped in matter and their vision was coupled into the idea of a perpetual, eternally burning light. The light emanated from phosphorus inspired a few artists: in E.T.A. Hoffmann's fairy tale "The Golden Pot" (1814), the lucent, obviously male, "Phosphorus" fights with a black dragon and in Bettina Franckenberg's "Phosphora" his female sibling debuts in form of a sphere of radiating light and luminosity in all directions. The stitched threads direct the way, the soft fabric nestles to flowing vibes, and the beads symbolize notions clear as crystals. The interplay of these elements reflects Phosphora's impression as spirited light. Children and open-minded are close to her heart, she empowers the will to live and her spiritual strength promises healing.

About the Artist

Bettina Franckenberg was born in February 3, 1956 in Essen, Germany. Handcraft and artistic abilities were encouraged early in her parent's house. After graduating from college in 1975 she continued with her education in the field of occupational therapy, graduated in 1979, and started to specialize in psychiatry, supplementary qualification as psychodrama assistant—at the same time initiation to "patchwork". In 1982 she discovered the Mediterranean (living the first 2 years in Greece) as well as her "textile ambitions"—1986 she opened her first exhibition in the Castle of St. Peter in Bodrum. She went back to live in Berlin for some years—between 1989 and 1992 she worked as an occupational therapist in psychiatry and organized several "textile art" exhibitions in Germany, Switzerland, Latvia, and Turkey.

Since 1992, Bettina Franckenberg has been living permanently in Bodrum, Turkey and between 1994 and 2005 she had her own Atelier-Gallery in the holiday-village Sea-Garden in Yaliçiftlik. She continues working as a freelance textile artist living in Kizilagac near Bodrum.

Her first artwork on a scientific subject was "Uranyum", a hand-sewn textile collage from velvet and silk (38 × 37 cm) which appeared on the cover of the book "Loads and Fate of Fertilizer Derived Uranium". Edited by L.J. De Kok and E. Schnug (2007), Backhuys Publishers, Leiden, The Netherlands.

The Preparation of the Fosperus, or the Astrum lunare Microcosmicum.

William Y-Worth, *Chymicus Rationalis... In which is contained, A Philosophical Description of the Astrum Lunare Microcosmicum, or Phospheros.* London, 1692.

As is before shewed, take Urine well putrefied in a Tub, exposed to the Air for seven Weeks, all one as you do when you're to make a Spirit of it; the Spirit being drawn, or rather the whole of it being evaporated to the consistance of Honey, in which lies the Fosperus; but the Art is somewhat difficult to get it from thence, in two cases, the one is in making choice of a proper Agent to be mixed therewith, and the other is the exact regiment of the Fire. Now as to the Agent, it must not (as some have said) be Sand; but one that is free from Salt, and consequently from the glass-making Faculty, or any thing that will vitrifie, for if it doth that, you shall never obtain the Fosperus; but that you may, we direct you to make use of a Fire within and without your Vessel, which is thus to be understood; take the Sap of Urine, as before 'tis said, or that of Dung and Urine putrified together, and incorporate it with Charcoal dust, and put it into a German Retort, and lute on a Receiver, that is filled half full with Water, that when the Fosperus comes over, it may immediately drop into the Water and be preserved thereby. Observe. That you are to begin with a very small Fire, but you are to increase it gradually into the highest degree that possibly can be made, and let it be in such a Furnace, that upon occasion the Bellows may be used, and that the Fire may play well about the Vessel, continuing so long at its greatest heighth, till no more comes over, and you'l see Flakes like Lightening, that will come over in the Receiver of two substances, the one like a thick muddy Water, which will sink to the bottom, the other swimming over it; separate by inclination these two substances, and keep each by it self in a Glass, the gummy Nature may be made into what form you please, by being dissolved in Spirit of Sal Armoniack or other Urinous Spirits; in B. 'tis thereby putrified.

Observations concerning it. It must always be kept in Water, for the Air sets it on fire. The thick Liquor, if rubbed upon the Hands, Cloaths, or Hair, they will appear in the dark, as if all in fire, but will not burn, and if you open the Cork of the Glass, all its vacancy will appear like the flame of Brimstone. If you put this thick Liquor, hardened by digestion into a Gum in Oyl of Cloves or of Cinnamon, and let it remain there 24 hours, and pour off the Oyl from it into a Glass, the same Oyl will as you pull out the Cork, and set it in the Air, appear so bright, that in the dark, if it's in a large and clear Viol, you may see it to read distinctly. If you write upon the Palm of your Hand, or upon Paper with the said Gum, what ever you write will appear all on fire, and the Letters may be read a long time after; but you must have a great care, that you do it softly, and to put it into Water, as soon as you have done, for if it happen to fire 'twill burn the place most dreadfully.

Cut a little piece of the said Gum, and lay it upon Paper, and rub it on with the point of a Knife, and 'twill set the Paper on fire. Put a little piece of the said Gum to steep 24 hours in Spirit of Wine, then taking it out again, if you pour this Spirit of Wine by drops upon a Bason of Water, you will see Flashes like Lightening, somewhat like the flame of Brimstone, and somewhat of a purplish colour. Rx. Of the aforesaid Gum one drachm, and in a white earthen Vessel expose it to the Air, and the Air will set it on fire, and when it hath done burning, you will have four drachms of Spirit of Salt, which it attracts out of the Air. If the Privy Parts be therewith rubb'd, they will be inflamed and burning for a good while after.

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Urgent Need for Action in the Baltic Sea Area

Leena-Marja Kauranne and Marjatta Kemppainen

Abstract Phosphorus has a central role in eutrophication of the Baltic Sea. Severe algal bloomings are the visible sign of the excess of nutrients for all living around the sea. Agriculture is responsible for more than a half of the waterborne nutrient loads in the Baltic Sea. It is also the most difficult sector to tackle in curbing the nutrient emissions. Since 1974 the Helsinki Commission (HELCOM) has taken a major role in joint efforts to improve the state of the Baltic Sea. The HELCOM (Helsinki Commission) Baltic Sea Action Plan aims at reaching a good environmental status of the Baltic Sea before 2021.

Keywords Baltic sea action plan · Diffuse source · EU strategy for the Baltic Sea region · Eutrophication · Helsinki commission · Manure · Nutrient load · Point source · Water framework directive

Introduction

The Baltic Sea is an extraordinary and unique, almost land-locked, shallow water basin with brackish water and an average depth of only 54 m. Very specific hydrographic, chemical and physical conditions make the Baltic Sea extremely sensitive to environmental impacts. Its catchment area covers 1,720,000 km^2 with a population of 85 million people. The state of the Baltic Sea has drastically changed over the recent decades. Human activities both at sea and throughout its catchment area are placing rapidly increasing pressures on the marine ecosystem. Of the many

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Retired from the Ministry of Agriculture and Forestry of Finland in 2013.

L.-M. Kauranne (✉)
Ministry of the Environment, P.O. Box 35, 00023 Helsinki, Finland
e-mail: leena-marja.kauranne@ymparisto.fi

M. Kemppainen
Ministry of Agriculture and Forestry of Finland, Helsinki, Finland

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environmental challenges, eutrophication is one of the major problems for the sea, for the lakes and the rivers in the catchment area, especially in the southern and eastern parts of the Baltic Sea. It is caused by excessive nitrogen and phosphorus inputs. This leads to problems like increased algal blooms, murky waters, oxygen depletion and lifeless sea bottom (HELCOM 2009).

Nutrients enter the Baltic Sea via rivers, through atmospheric deposition and in direct discharges from pollution sources located along the coastline. Phosphorus enters the sea mainly as waterborne input; only about 1–5 % of the total input is airborne. The riverine discharges originate both from point sources, such as industrial or municipal wastewater plants, and from diffuse sources, such as agriculture and forestry, scattered dwellings, traffic and atmospheric deposition within river basins. The Baltic Sea is connected to the North Sea and the Atlantic Ocean through the narrow Danish Straits and Sound areas. Inflows of fresh seawater occur rarely and poor oxygen conditions release phosphorus accumulated in the bottom sediments.

Agriculture is the main source of phosphorus and nitrogen inputs to the Baltic Sea accounting about 50 % of the total diffuse loads. Managing emissions from agricultural land and livestock operations is critical to restore the ecological balance of the Baltic Sea.

Putting an end to further destruction and avoiding an irreversible disaster of the Baltic Sea marine environment calls for immediate wide-scale coordinated action in all sectors. Failure to react now would undermine both the prospects for the future recovery of the sea and its capability to react to the projected stress by the climate change with the risk of increasing precipitation and thereby intensified run-off from agriculture as well as changes in water temperature and salinity. Furthermore, inaction will affect vital resources for the future economic prosperity of the whole region and would cost much more than the cost of action. Efforts to combat eutrophication have already been and are taken on many different fora at different levels but it is a complicated and long-term task to curb loads from diffuse sources.

Action Already Taken

The Baltic Sea is a target of actions at several different levels. Many tools to protect and restore the Baltic Sea have been and are currently taken to improve its state: the EU Water Framework Directive (WFD), the Marine Strategy Framework Directive (MSFD) as well as the EU Strategy for the Baltic Sea Region (EUSBSR) at the European level, the HELCOM Baltic Sea Action Plan (BSAP) at the regional level and numerous projects and programmes at national and local levels. The impact of the EU Common Agricultural Policy on the state of the Baltic Sea is also significant. Moreover, the EU Nitrates Directive sets a frame for prevention of nitrate pollution from agricultural sources but no equivalent legislation exists for phosphorus at the EU level.

HELCOM Shows Way for Baltic Sea Protection

The Baltic Marine Environment Protection Commission, more usually referred to as the Helsinki Commission or HELCOM, is an international organisation made up of the nine Baltic Sea coastal countries and the European Community, working to protect the marine environment of the Baltic Sea. HELCOM is the governing body of the "Convention on the Protection of the Marine Environment of the Baltic Sea Area"—also known as the Helsinki Convention, which was signed by all the Baltic Sea countries in 1974 and it came into force in 1980. A new updated convention was signed in 1992 by all the states bordering on the Baltic Sea and the European Community, and the Convention entered into force in 2000. The Convention covers not only the Baltic Sea, but also the surrounding catchment area within the coastal countries.

The Baltic Sea Action Plan Sets the Protection Targets

Since the establishment of the Helsinki Convention, HELCOM has, with the help of several programmes, been working to reduce the nutrient loads to the sea. The latest HELCOM programme with new nutrient reduction targets is the Baltic Sea Action Plan (BSAP), which was adopted by all nine Contracting Parties (eight EU Member Countries and Russia) and the European Community at the Ministerial Meeting on 15 November 2007 in Krakow, Poland (HELCOM 2007).

HELCOM follows the progress towards reaching politically agreed goals by collecting and reporting load data. The latest Baltic Sea Pollution Load Compilation (PLC-5) was published in late 2011 whereas the first one (PLC-1) in 1987. A project called PLC-5.5 provided updated and corrected data and more complete information on pollution loads including data for 2009 and 2010 for the HELCOM Ministerial Meeting in 2013 (HELCOM 2011).

The ambitious target of the BSAP is to restore the good ecological status of the Baltic marine environment by 2021. The cross-sectoral Plan identifies the specific actions needed to achieve the agreed targets within a given timeframe for the main environmental priorities: (1) combatting eutrophication, (2) curbing inputs of hazardous substances, (3) ensuring maritime safety and response capacity to accidents at sea, and (4) halting habitat destruction and the ongoing decline in biodiversity. The HELCOM Member States have developed their own national implementation plans. The BSAP has strong links to global legislative frameworks and is also seen, for those Parties being also EU Member States, as a contribution to the implementation of key EU directives, in particular, the Marine Strategy Framework Directive and the Water Framework Directive.

The objectives of the Baltic Sea Action Plan to combat eutrophication include: no excessive nutrient concentrations; clear water; no excessive algal blooms; natural oxygen levels; and natural distributions and abundance of plants and animals.

Actions are needed both for point and for diffuse sources in the following areas: (i) waste waters: municipalities, scattered settlements and single-family homes; (ii) agriculture; (iii) transboundary air- and waterborne pollution (HELCOM 2007).

HELCOM has estimated that for good environmental status to be achieved by the year 2021, the maximum total allowable annual nutrient inputs into the Baltic Sea would be 21,000 tonnes of phosphorus and about 600,000 tonnes of nitrogen. Over the period 1997–2003, average annual inputs amounted to 36,000 tonnes of phosphorus and 737,000 tonnes of nitrogen. Therefore, annual reductions of some 15,000 tonnes of phosphorus and 135,000 tonnes of nitrogen would be required to achieve the crucial ‘clear water’ objective set in the Baltic Sea Action Plan. The 2013 HELCOM Ministerial Meeting adopted the revised HELCOM nutrient reduction scheme. To decrease nutrient inputs into the Baltic Sea to the maximum allowable levels, the HELCOM countries have agreed to take actions not later than in 2016 to reduce nutrient loads in waterborne and airborne inputs, aiming to reach good environmental status of the Baltic Sea by 2021. Also the country-wise provisional nutrient reduction targets were agreed upon (Table 1). To reach these targets each Member Country is encouraged to choose the most appropriate and cost-effective measures for its special needs.

For addressing the problems of the large agro-industrial clusters, contracting states also agreed to identify individual hotspots such as major facilities of intensive rearing of cattle, poultry and pigs, where actions should be prioritised in order to comply with revised requirements for prevention of pollution from agriculture (Annex III of the 1992 Helsinki Convention).

Environmentally sound manure management has to be assured by construction of sufficiently large and watertight manure storages, proper agri-environmental

Table 1 Updated country-wise reduction targets for nitrogen (N) and phosphorus (P) (HELCOM 2013a)

	Phosphorus		Nitrogen	
	2007	2013	2007	2013
Denmark	16	38	17,210	2.890
Estonia	220	320	900	1800
Finland	150	330 (+26[a])	1200	2.430 (+600[a])
Germany	240	110 (+60[a])	5.620	7.170 (+500[a])
Latvia	300	220	2560	1.670
Lithuania	880	1470	11,750	8970
Poland	8760	7480	62,400	43,610
Russia	2500	3790	6970	10,380
Sweden	290	530	20,780	9240

2007: as in the HELCOM Baltic Sea Action Plan

2013: as adopted by the HELCOM Ministerial Meeting on 3 October 2013

[a] Loads originating from the country but being discharged to the Sea via another country; additional specific footnotes to the above table can be found in the text of the Ministerial Declaration

measures and advisory services and by identification of agricultural areas that are critical for nutrient pollution of the Baltic Sea. This implies designation of relevant parts of agricultural land as nitrate vulnerable zones and performing risk assessments of nutrient leaching from agricultural areas. The 2013 HELCOM Copenhagen Ministerial Meeting agreed (HELCOM 2013b) that measures such as annual nutrient accounting at farm level and environmentally sound utilization of nutrients in manure should be implemented in Member Countries by specific timeframes.

PLC-5 Shows Some Positive Signs

According to the data presented on total nutrient loads into the Baltic Sea until year 2008 in the Fifth Pollution Load Compilation (PLC-5) in 2011, it seems that there has been some progress in reduction of nutrients losses from agriculture within the Baltic Sea catchment area since 2000. In fact, losses from agriculture appear to have increased in some Contracting Countries although load figures for diffuse sources are uncertain due to the impact of climatic factors and different methodologies applied, making comparisons of loads between years difficult. The total input of phosphorus and nitrogen to the Baltic Sea in 2008 was 29,000 and 859,000 tonnes, respectively (HELCOM 2011).

Comparison of the flow normalized load during 1997–2003, which is the reference period for setting provisional reduction targets in the BSAP, with flow normalized input during 2006–2008 indicates a reduction with less than 1900 tonnes of nitrogen (2 %) and more than 3300 tonnes of phosphorus (10 %). The decrease since the inception of the Action Plan was 9 % for nitrogen and 10 % for phosphorus from figures of the BSAP baseline years (1997–2003). In the longer perspective, since 1994, the reductions have been even larger inputs of N and P to the Baltic Sea have been cut by 18 and 16 %, respectively (HELCOM 2013a).

Reductions in nutrient inputs have primarily been achieved through improvements at major point sources, such as municipal sewage treatment plants and industrial wastewater outlets. Achieving further reductions is a more difficult task. Reducing nutrient losses from agriculture is much more complicated than curbing loads from point sources and will involve several measures. Due to retention in soils, groundwater and inland surface waters, a reduction of nitrogen or phosphorus in the local emissions will result in less reduction to the Baltic Sea. Besides, there is a considerable time-lag between the implementation of agricultural water protection measures and any observed impacts on lakes and rivers, and even more so for marine water bodies. This means that reductions in the loads into marine water bodies will not be observable for years or even decades.

Around the Baltic Sea, the rise in the living standards of the eastern EU member countries and of Russia and Belarus will probably increase the proportion of animal-sourced food in people’s diets. The increasing animal production may require an expansion of the cultivated area, increasing the leaching of nutrients.

Pressures should be progressively reduced since only significant reductions of phosphorus and nitrogen will result in improved ecosystem health of the Baltic Sea. To reduce phosphorus and nitrogen losses from countless individual field plots and animal production units is a huge task that calls for identification of high-risk areas and implementation of cost-efficient agri-environmental measures. Such measures could e.g. be catch crops, buffer zones, restored and constructed wetlands, reduced mechanical treatment of soils, lime application, application of more environmentally friendly cultivation and manure handling technology, higher storage capacity for manure and application of less than yield-optimal fertilizer amounts. Enlarged animal farms and their clustered locations require more effective methods in manure handling practices and in recycling of nutrients. Slurry could e.g. be processed chemically or mechanically in order to separate nitrogen and phosphorus rich components (liquid/fibre part) and be further used for energy production. To this end, there is a need for interdisciplinary research and advice and recognition of economic, social and political constraints.

For more information about the Baltic Sea, see http://www.helcom.fi and the HELCOM Fifth Baltic Sea Pollution Load Compilation 2011.

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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).

E. Schnug (✉) · S.H. Haneklaus
Federal Research Centre for Cultivated Plants, Institute for Crop and Soil Science,
Julius Kühn-Institut (JKI), Bundesallee 50, 38116 Brunswick, Germany
e-mail: ewald.schnug@julius-kuehn.de

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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

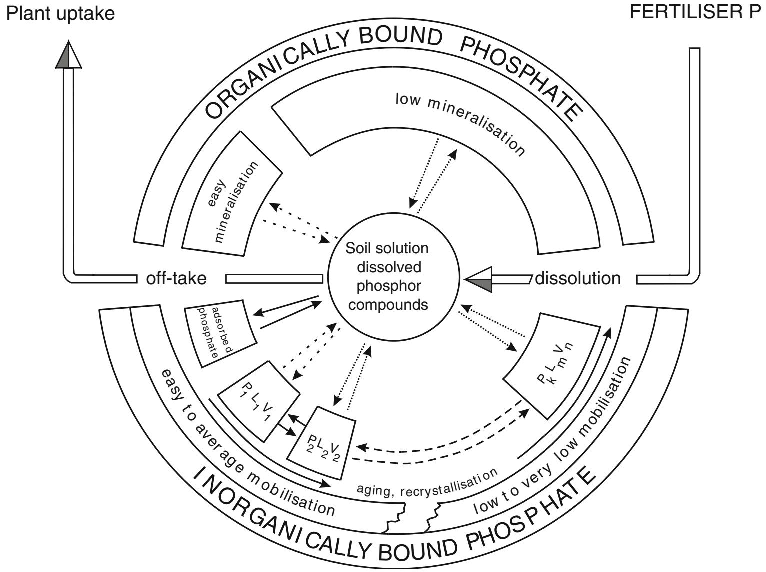

Fig. 1 The soil P engine. Plants take P up as dissolved orthophosphate from the soil solution. P replaced by fertilization first dissolves in the soil solution, some of it is taken up by plants but the majority transfers into the organic and inorganic storage pools. The latter undergoing aging over time: P_1, P_2, …, P_k = inorganic P species; L_1, L_2, …, L_m = solubility of P_1–P_k, decreasing from L_1 to L_m; V_1, V_2, …, 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 Ca^{2+} for 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 stabile 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 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_{org} 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; Latkowicz 1977; Sanderson and Jones 1997; Ibrikei 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:

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

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 faction 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

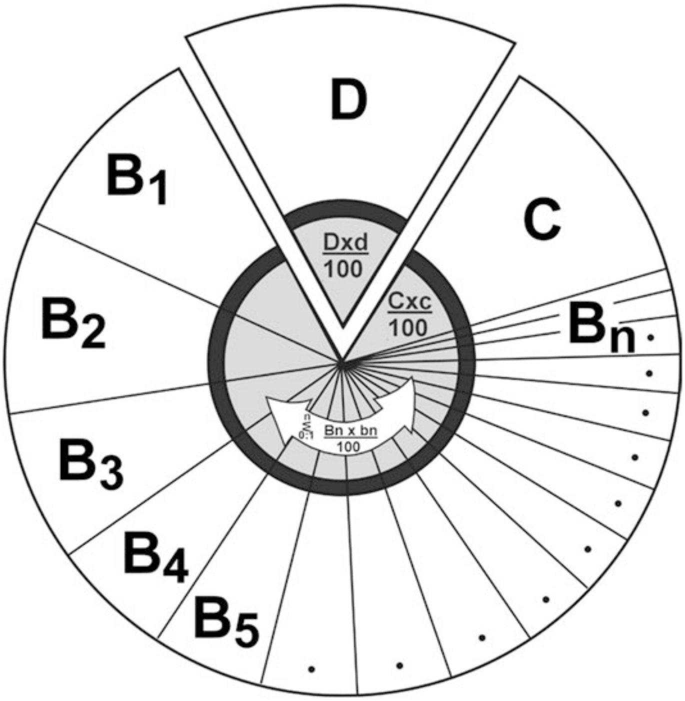

Fig. 2 Origin of P taken up by a crop. ○ P off-take for target yield; D = P fertilizer rate; B = residual P in the soil from former fertilizer applications; C = native P content of the soil; E = P off-take; b = utilization efficiency of residual P; c = utilization efficiency of native P; d = utilization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

$$\frac{B*b}{100} = \frac{B_1*b_1}{100} + \cdots + \frac{B_n*b_n}{100} \tag{2}$$

with:

$B, B_1, \ldots, B_n$	residual P from fertilization
1	of previous year
2	of year the last but two years
n	of n years ago
$b_1, b_2, \ldots, b_n$	corresponding utilization efficiencies of $B_1, B_2, \ldots, B_n$.

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,

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

the utilization of P by fertilizers in the year of application

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

and their potential residual effect

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

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

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

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 (Karlovsky 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:

$$\frac{D * s}{100} = \frac{D * d}{100} + \frac{B * b}{100} \tag{4}$$

whereby the apparent utilization efficiency can be determined as follows

$$s = \frac{\frac{D*d}{100} + \frac{B*b}{100}}{D} * 100 \tag{5}$$

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

$$D = E + V + F \tag{6}$$

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

$$\frac{E + V + F - \frac{C \times c}{100}}{D} = 1 \tag{7}$$

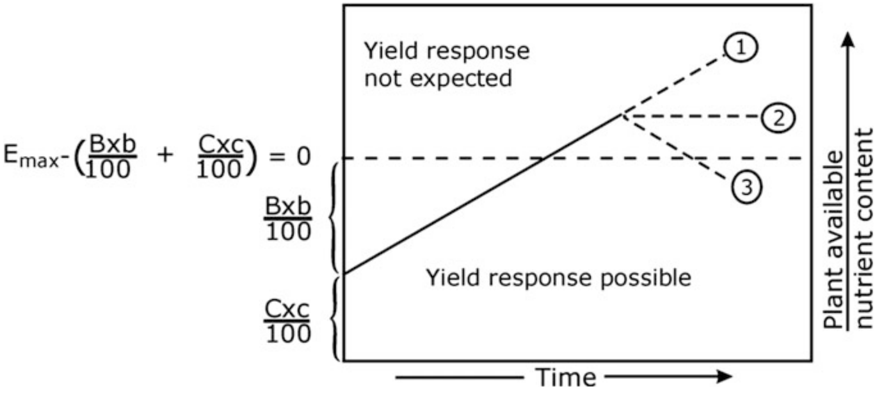

Fig. 3 Changes in soil nutrient concentration after reaching the optimum soil fertility level (based on fertilization considering the utilization efficiency of the fertilizer in the year of application (*1*), fertilization considering the effective or apparent utilization efficiency of the fertilizer (*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:

$$s=\frac{E}{D}*100 \tag{8}$$

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:

$$(U_f - U_0)/D * 100 = d \tag{9}$$

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 enumerator. 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:

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

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}N), sulfur (^{33}S), potassium (^{41}K), calcium (^{43}Ca) and magnesium (^{25}Mg). Expensive ^{15}N (which costs approximately 100 times more than the price for the element in natural