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Title: Changes in soil phosphorus balance and phosphorus use efficiency under longterm fertilization conducted on agriculturally-used Chernozem in Germany.

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Abstract

This study investigates changes in soil phosphorus (P) in different fertilization treatments applied since 1902 on Chernozem soil at a "Static Fertilization Experiment" in Germany. Total and plant-available soil P, and soil P balances were assessed at 0-30, 30-60, and 60-90 cm depth layers in unfertilized "Zero", mineral "NK" and "NPK", and combined mineral and organic "FYM+NK" (farmyard manure + NK) and "FYM+NPK" fertilization treatments. P use efficiencies were determined for each crop in rotation (sugar beet, spring barley, potato, and winter wheat). The 110 years of P fertilization at rates between 22 and 55 t ha⁻¹ year⁻¹ resulted in significant increase of available P contents. P stocks increased up to 60 cm depth. Total P accumulation comprised 1.4 t ha⁻¹ for NPK, 1.3 t ha⁻¹ for FYM+NK, and 3.1 t ha⁻¹ for FYM+NPK. Crops cultivation without P fertilization in Zero and NK treatments resulted in negative P balances and reduction of available P below recommended levels. Reduction of mineral P application rates after 1981, along with crop variety-dependent yield increases, resulted in an improved P use efficiency. An organic fertilization combined with mineral N and K fertilizers (FYM+NK) was found to be the most P-efficient treatment for Chernozem soils.

Introduction

Phosphorus (P) is one of the major nutrients required for plant nutrition. Although the total P content of soils may be large, only a small part of it is available for plant uptake (Syers et al. 2008; Krupenikov et al. 2011). This causes the need to apply P fertilizers on agricultural fields to fulfil plant requirements and ensure high yield production. However, due to the limited global reserves of phosphate rocks used for production of P fertilizers and due to the high costs of these fertilizers, they should be used wisely. Moreover, an excessive use of P fertilizers, which raises plant-available P content above certain levels, has little or no effect on crop yields (Syers et al. 2008). For this reason, agricultural managers and soil scientists have been searching for the best P fertilization strategy for resource efficient and high yielding crop production. In order to make recommendations for farmers, the particular soil type of a region has to be taken under consideration, as the soil type determines natural P content and P behaviour after entering the soil. When fertilizer is applied to a soil, only a small amount (10-30%) of it is available for plant uptake, while the major part (70-90%) becomes rapidly sorbed to soil particles and transformed into less available forms (Manske et al. 2000; Sarkar et al. 2014). In acid soils, P is mainly sorbed to iron (Fe) and aluminium (Al) oxides and hydroxides, and in calcareous soils to calcium (Ca) carbonates (Brady and Wile, 1999). The highest availability of soil P is found is soils with neutral pH between 6 and 7.5. The sorbed P can be gradually desorbed and used by plants, having a so-called 'residue effect', which may increase yields of subsequent crops for a number of years (Syers et al. 2008). The rates of P sorption and desorption are strongly dependent on the particular soil type, texture, pH, amounts of organic matter and freely available sorption surfaces on Ca-, Fe-, Al-compounds (Brady and Wile, 1999).

In this study we put the focus on Chernozem soil, which is known to be the most fertile soil in the world, exceptionally suitable for arable cropping (Campbell et al. 2005; Hejcman et al. 2012). A number of studies investigated changes in soils P in response to mineral fertilizer and organic manure application in agricultural used Chernozem soils worldwide (Campbell et al. 1986; O'Halloran 1993; Kashem et al. 2004; Qian and Schoenau 2004). These studies revealed that although Chernozems are

quite well-supplied with total P, they also require P fertilization to maintain available P levels for crop growth (Tiessen et al. 1983; Krupenikov et al. 2011). Inadequate P fertilization due to economic reasons has resulted in a decrease of available P to below optimum values, and consequently in crop yield losses in some Chernozem regions (Hamkalo et al. 2005; Dodocioiu et al. 2012). On the other hand, high P application rates in fertile Chernozem soils have resulted in excessive accumulation of available P (Kashem et al. 2004; Qian et al. 2004). These studies investigated either the effect of mineral fertilizer (Wagar et al. 1986; O'Halloran et al. 1987) or organic manure (Campbell et al. 1986; Qian and Schoenau 2000; Qian et al. 2004), while studies investigating different combinations of mineral and organic manure on the same site with the same crop rotation system are rare (Zhan et al. 2015). Furthermore, most of these studies lasted over a relatively short period of time ranging from a few years to a couple of decades. However, it was shown that the effect of P fertilization increases with the duration of the experiment (Qian et al. 2004). Moreover, as yields and nutrient uptake by crops vary between years at the same site due to differences in weather conditions, experiments should ideally last for many years (Rothamsted Research 2006; Syers et al. 2008).

In this regard, long term studies are of a particular importance for P-related studies. Long-term studies provide a unique opportunity to detect changes not only related to the recently applied fertilizer, but also changes related to the P residue effect of previously applied fertilizer and are, therefore, of particular value for the development of optimal fertilization strategy for crop production. From this perspective, the 110 years-old "Static Fertilization Experiment" provides a perfect platform to study P balances of agricultural systems. It comprises different mineral and organic fertilization treatments, on which a crop rotation, consisting of sugar beet, spring barley, potato, and winter wheat, is cultivated. The main objective of this experiment is to examine the influences of organic and mineral fertilization on crop yields and soil fertility.

A previous study conducted at this site in 1986, demonstrated strong accumulation of total and available P in fertilized treatments (Wechsung and Pagel 1993). The P application rates has been adjusted and reduced since then, which has likely changed the P balances in the last decades. In the same study, the authors suggested that significant amount of P could be obtained by crops from soil depth below 20 cm, as the decrease of total soil P was lower than the cumulative P uptake of crops.

As most P-related studies, this study was focused only on the topsoil (0-20 cm), since this layer is recognized to be the most relevant for crop growth. Studies on the subsoil P are rare, even though P applied with fertilizer may partly be transported down the soil profile by leaching and particulate movement, where it can be used by long crop roots (Godlinski et al. 2004). According to Kautz et al. (2012) and Koch et al. (2018), subsoils can greatly contribute to P plant nutrition. Therefore, the investigation of P levels in the deeper soil layers is of great importance to estimate the total P available for crop growth and to ensure adequate application of fertilizers (Gransee and Merbach 2000; Kautz et al. 2012).

The objectives of our study were: 1) to assess the effects of different fertilization treatments on phosphorus contents in top- and subsoil layers up to 90 cm depth of Chernozem soils, and 2) to assess yield responses to fertilization, and, phosphorus use efficiencies of crops. We hypothesized that: (i) P fertilization does not only increase total and available phosphorous in the ploughed soil layer, but also, due to a vertical transport of P, in deeper Chermozem layers; (ii) vertical transport of P in the soil profile depends on P contents in the topsoil layer, P sorption capacity and P saturation of soils; (iii) breeding-related crop yield increases along with the reduction of P fertilization rates over the recent decades moderate the strong P accumulation that has been previously observed by Wechsung and Pagel (1993) for highly fertilized treatments, and consequently increase P use efficiency. The outcomes of our study would help to update recommendations for P fertilizer application at Chernozem soils in order to sustain soil fertility, and simultaneously reduce fertilizer costs and save limited resources.

Methods

Study area

The "Static Fertilization Experiment" is located at the experimental field station of the Helmholtz-Centre for Environmental Research in Bad Lauchstädt, Sachsen-Anhalt, central Germany (11°53 E; 51°24 N), with average annual precipitation of 486 mm and average annual temperature of 8.9 °C. In the last decades, a temperature increase has been recorded, with an annual average for the recent decade of 9.8 °C (Merbach and Schulz 2013). The soil is silty loam, classified as Haplic Chernozem (FAO) (Altermann et al. 2005). Soil value number is 94-98 (maximum of 100). Soil properties are presented in Table 1. Further information about the study area is given by Merbach and Körschens (2002).

The 'Static Fertilization Experiment' was established in 1902. The 4 ha experimental area is divided into eight strips (SH 1 - SH 8, Fig. 1). We conducted our study on SH 2, SH 3, SH 6, and SH 7 strips. The crop rotation consists of sugar beet (B. vulgaris), spring barley (H. vulgare), potato (S. tuberosum) and winter wheat (T. aestivum), whereby crop varieties changed over the course of the experiment, and high-yielding and disease-resistant cultivars were used over the last decades. Each year, the four crops of the crop rotation are grown in parallel, i.e. each crop on one of the four strips of the experiment. The crop strips are divided into plots of 10 x 26.5 m = 265 m² size, where different fertilizer treatments are applied. We conducted our study at the following treatments: no fertilizer (Zero), mineral NK and NPK fertilizer, and combined farmyard manure and mineral fertilizer FYM+NK and FYM+NPK. As the fertilizers were applied at each of four sampled strips, each treatment had four replica plots. Although the design of the study has no clear randomization, the soil properties (in particular the amounts of clay, Ca carbonates, and Fe- & Al- oxides and hydroxides, which play the most important role in P sorption), are homogeneous between different treatments. Therefore the observed trends in P accumulation in different treatments should be attributed to the fertilization effect. FYM was applied at a rate of 30 t ha⁻¹ to potato and sugar beet. The amounts of nutrients applied with fertilizers are presented in Table 2. Mineral P fertilization was reduced after 1981, while nitrogen (N) and potassium (K) fertilization were adjusted after 1970.

Fig.1

Tables 1&2

Soil sampling and analyses

Soil samples were collected in October 2013 before the fertilizers had been applied and crops had been sown. At each replica plot (Fig. 1), 20 soil cores were taken with a Pürckhauer sampler (12 mm

diameter) from 0-30, 30-60 and 60-90 cm soil depth layers. As the Chernozem soil at the sampling site has very thick A horizon of about 50-60 cm (Altermann et al. 2005), the upper two layers (ploughed 0-30 cm and unploughed 30-60 cm) can be defined as topsoil, and the lowest layer (60-90 cm) as subsoil. The samples for a particular soil depth for each plot were pooled, air-dried and sieved to < 2 mm. Samples were analysed for total P by aqua regia digestion method with concentrated HCl and concentrated HNO₃ in the ratio 3:1 (DIN EN ISO 11885 E22 09.09), and for available P by the double-lactate method, which is commonly used in Germany for estimating available P (Egner et al. 1960). Soil bulk density was determined according to ISO 17892-2 (2014) using soil cores (5 cm diameter) collected from 0-30, 30-60 and 60-90 cm soil depth layers. Values for total and available P contents were compared with the values of 1986 obtained by Wechsung and Pagel (1993). Crop yields were assessed annually. In each plot, 4 replica plots were sampled for crop yields.

To characterize soil properties for the studied site presented in Table 1, samples collected at Zero, NPK, and FYM+NPK treatments from strips SH2, SH6, and SH7 were analysed for soil texture by pipette method (Day 1965), pH (1:2.5 soil:water) (Rhoades 1982), total carbon by dry combustion (Vario El CNS Elemental Analyser, Hanau, Germany), inorganic carbon with 10% HCl using Scheibler device (DIN ISO 10693 2007), organic carbon (OC) was calculated as a difference between total and inorganic carbon, total Ca, Fe and Al by pressure digestion in HNO₃ (65%), followed by inductively coupled plasma atomic emission spectrometry (ICP-AES) (Heinrichs et al. 1986), dithionite-citrate-extractable iron (Fe_d) and aluminium (Al_d) (Mehra and Jackson 1960), ammonium-oxalate-extractable iron (Fe_{ox}), aluminium (Al_{ox}) and phosphorus (P_{ox}) (McKeague and Day 1966).

Calculation and statistical analyses of soil P balance, crop yields and crop P use efficiencies

P balance for each treatment was calculated as difference between P input with fertilizer and P removal with crops for 10-year intervals over the experimental period. For the calculation, mean annual values for all replica plots within each treatment were summed. Annual yield values for each crop in each treatment were obtained from the database of the Helmholtz-Centre for Environmental Research. For mean crop yield calculation of each year, yield values for the four replica plots within

each plot were averaged. P removal with crops was calculated by multiplying mean annual crop yields and crop P contents (0.08 kg dt⁻¹ for sugar beet, 0.44 kg dt⁻¹ for spring barley, 0.06 kg dt⁻¹ for potato, 0.47 kg dt⁻¹ for winter wheat) according to Roschke et al. (2000). P stocks in soil were calculated by multiplying the mean total P concentrations at the particular soil layer of the treatment, soil bulk density, and thickness of soil layer (30 cm). Degree of phosphorus saturation (DPS) was calculated according to Beauchemin and Simard (1999) from the ratio of oxalate extractable P_{ox} to the sum of oxalate extractable Fe and Al:

$$DPS = P_{ox} / (Fe_{ox} + Al_{ox}) * 100\%$$
(1)

Phosphorus use efficiencies were determined for different crops and treatments according to Syers et al. (2008) by removal-to-input ratio:

$$P_{ue} = U_P / F_P * 100\%$$
(2),

where P_{ue} – represents P use efficiency, U_P the amount of P removed by crops in fertilized treatment, and F_P the amount of P applied with fertilizer (calculated from mean values for 1902-1981 and 1982-2013 periods).

Statistical analyses were conducted with SigmaPlot 12.0. Data were analyzed for normality by Shapiro-Wilk Test. One-way ANOVA with Tukey post hoc test was used to assess differences in total P, available P, P stocks, and soil properties between the fertilization treatments at each soil depth layer. One-way repeated measures ANOVA and Tukey post hoc test were used to assess differences in yields and P balances between the treatments. The differences were considered significant at p < 0.05.

Results

Total and available soil P

The long-term application of mineral P fertilizer and organic manure has resulted in significant increase of total and available soil P contents in soils (Table 3). After 110 years of fertilization, total P

contents were up two times higher (ranging between 692 and 969 mg kg⁻¹), and available P contents were up to six times higher (110 to 347 mg kg⁻¹) in fertilized treatments compared to Zero (474 and 42 mg kg⁻¹, respectively) and NK treatment (448 and 31 mg kg⁻¹, respectively). The increase in P content was the highest in FYM+NPK, followed by FYM+NK, and NPK. Among all treatments, NK had the lowest contents of total and available P. After 1986, the contents of total and available P decreased in all the treatments (except available P in FYM+NK). The relative decrease was higher in Zero and NK than in the P fertilized treatments.

As a result of P accumulation, P stocks significantly increased in the topsoil (0-30 and 30-60 cm layers) of P fertilized treatments (Table 4). For the 0-30 cm layer, the total P stock was significantly higher in FYM+NPK (4.1 t ha⁻¹) compared to FYM+NK (3.0 t ha⁻¹) and NPK (2.9 t ha⁻¹). All P fertilized treatments showed significantly higher P stocks compared to Zero (2.0 t ha⁻¹) and NK (1.9 t ha⁻¹). Similar trend was observed for the 30-60 cm layer, with significantly higher P stocks in FYM+NPK (2.5 t ha⁻¹) compared to FYM+NK (1.9 t ha⁻¹) and NPK (2.0 t ha⁻¹), and significantly lower stocks in Zero (1.6 t ha⁻¹) and NK (1.5 t ha⁻¹) compared to P fertilized treatments. For the subsoil (60-90 cm layer), NK (1.2 t ha⁻¹) had significantly lower P stocks than NPK (1.4 t ha⁻¹) and FYM+NPK (1.4 t ha⁻¹), while P stocks in FYM+NK (1.3 t ha⁻¹) and Zero (1.3 t ha⁻¹) were not significantly different from other treatments. The total P accumulation for the 0-90 cm soil layer comprised 1.4 t ha⁻¹ for NPK, 1.3 t ha⁻¹ for FYM+NK, and 3.1 t ha⁻¹ for FYM+NPK, compared to the Zero treatment.

Tables 3&4

Differences in yields, P use efficiencies and P balances between the treatments

Fertilization has resulted in significant yield increases, which followed the order: Zero < NK < NPK \leq FYM+NK = FYM+NPK (Fig. 2). The differences between the treatments were significant, except for FYM+NK and FYM+NPK. The application of NK fertilizer has resulted in crop dependent yield increases of 37 to 104%, compared to the Zero treatment. Potato showed the highest yield increase (+ 104%) in response to NK fertilization, followed by the spring barley (+ 89%), winter wheat (+ 69%) and sugar beet (+ 37%). Phosphorus application in NPK resulted in further yield increases of 12 to

63% compared to the NK treatment. The highest increase in response to P application was observed for sugar beet (+ 63%), followed by potato (+ 38%), spring barley (+ 25%), and winter wheat (+ 12%). NPK had 11% lower yields for the sugar beet and potato, and 8% lower yields for spring barley compared to FYM+NK and FYM+NPK, and these differences were significant. For winter wheat, there were no significant yield differences between NPK, FYM+NK and FYM+NPK.

Crop yields increased in all the treatments over the duration of the experiment (1903 to 2013), and showed particular high values over the last three decades (Fig. 3). The differences between fertilized and Zero treatments were small in the first two-three decades of experiment, but strongly increased with time. The increase in yield differences between P-fertilized and unfertilized treatments started earlier (in the third decade of experiment) and to a larger extent for potato and sugar beet compared to winter wheat and spring barley (Fig. 3).

Figs. 2&3

Until 1981, phosphorus balances, calculated as the difference between P input with fertilizers and P removal with crops, were positive for NPK and FYM+NPK, near-neutral for FYM+NK, and negative for Zero and NK (Fig. 4). After the reduction of P application rates in 1982, P balances slightly decreased also in NPK, FYM+NK and FYM+NPK. On contrast, phosphorus use efficiencies increased after 1982 in all P fertilized treatments (Table 5). The highest P use efficiencies of all the crops were obtained with FYM+NK fertilization. Among the crop species, sugar beet had the highest P use efficiency between 1902 and 1981, while winter wheat showed the highest P use efficiency after 1982.

Fig. 4

Discussion

Fertilization-dependent soil P availability and P balance of Chernozem soil

It is estimated that only about 20% of the applied P is taken up by plants in the first year, while the remaining P becomes quickly immobilized and retained by soil minerals, which results in building up soil P reserves (Sakar et al. 2014). This estimation is supported by our study, as long-term application of P-containing fertilizer has resulted in an accumulation of total and available soil P. Similar trend was observed in other long-term fertilization experiments conducted on Chernozem soils (Schliephake et al. 1997; Zhan et al. 2015). According to fertilization recommendations, optimal concentrations for available P in silty-loam soil determined by the double lactate method range between 56 and 80 mg kg⁻¹ (Roschke et al. 2000). However, in our study in P fertilized treatments, available P contents were above the recommended values, indicating an excessive application of fertilizer.

The reduction of mineral P application rates since 1982 in NPK and FYM+NPK, along with yield increases and consequently higher P removal from soil, have resulted in a decrease of total and available P in the P fertilized treatments (Table 3). The stronger decrease of available P in FYM+NPK compared to NPK is related to a higher reduction in P fertilization since 1982 (Table 2). Despite the total amount of P applied with fertilizer in FYM+NPK was reduced to similar amount as in the NPK treatment since 1982, total soil P concentrations were still much higher in FYM+NPK in 2013, which was caused by the application of P at much higher rates in the first 80 years of the experiment.

Despite the lower P application rates, FYM+NK had the higher available P contents compared to NPK. This finding was in line with Schliephake et al. (1997), who observed higher available P contents in an arable soil (Haplic Phaeozem, Germany) fertilized with organic manure compared to a soil fertilized with mineral NPK. P applied in FYM+NK was in manure form, which presents a mixture of organic and inorganic P-complexes. Organic acids released from manure may compete with phosphates for Al- and Fe-sorption surfaces, which consequently may increase P availability (Reddy et al. 2005; Von

Wandruszka 2006). Furthermore, available P in this treatment may increase over the years due to the continuous mineralization of organic P and conversion into inorganic, plant-available forms. In contrast, in the treatments with application of mineral P fertilizer, the available P contents may increase immediately after application of mineral fertilizer, but then rapidly decrease due to plant uptake and sorption to soil minerals.

In the Zero treatment, the content of available P was above the recommended level in 1986, 84 years after intensive crop production without fertilization. A similar observation has been made by Kunzova and Hejcman (2009) for black earths (syn. Chernozem) in the Czech Republic, where the control treatment which did not receive any fertilizer over 50 years had optimal available soil P contents for crop production. This demonstrates the high fertility of Chernozem soils, and their potential to maintain P availability due to large P reserves. As reported by Krupenikov et al. (2011) substantial P reserves have been built up by biological transformation of P to organic forms after mineral weathering. P released via weathering of primary minerals is used by crops, and after decomposition and mineralisation of crop residue supplies phosphate to the plant-available pool. The high P availability in Chernozem soils could also be related to near neutral pH, as P availability is soil is highest at pH of 6-7 due to the reduced formation of Al-, and Fe-phosphates and high dissolution of Ca-phosphates (Lindsay 1979). Chernozem soils may have lower P sorption strength and higher P desorption compared to acidic or calcareous soils, were P becomes strongly bound by Fe- and Aloxides and Ca-compounds. As reported by Melo et al. (2015), Chernozem soils had higher amounts of labile P and lower P adsorption compared to Ferrasol and Nitisol soils with more acidic pH, large amounts of sesquioxides and higher clay contents.

In 2013, the long-term cultivation of crops without P fertilization in Zero and NK treatments has, however, depleted total and available P reserves due to the continual removal of P by crops. Therefore, application of P fertilizer is essential for maintaining soil fertility and P balance in the long-term even in highly fertile Chernozem soils. The NK treatment showed the most negative P balance compared to the other treatments. This is because application of NK fertilizer has resulted in

yield increases, and therefore higher P removal from the soil with crops. The ongoing crop cultivation without P fertilization will result in a further decrease of available soil P.

Role of deeper Chernozem soil layers in plant P nutrition

The vertical gradient in P distribution with the higher contents in the topsoil, and a gradual decrease with depth is in line with the observations at other long-term fertilization experiments conducted on Chernozem soils (Garz et al. 2000; Zhan et al. 2015) (Table 4). Similarly to Schliephake et al. (1997) and Deubel et al. (2011), the differences in P contents between fertilized and unfertilized treatments were noticeable up to 60 cm depth. The higher P contents in the fertilized topsoils are related to the application of fertilizers and manure, as well as to more plant residues, which after decomposition contributes to increased soil P stocks. As P is not very mobile in soil due to the quick sorption to soil particles, the effect of the applied fertilizer should be more obvious in the top 0-30 cm soil layer. The downward movement of soil P is nevertheless possible due to the leaching of dissolved P or movement of particulate organic material, which also increased P contents at 30-60 cm depth in fertilized treatments. As reported by Andersson et al. (2013) this downward P distribution varies between different soils, and depends on soil P saturation and sorption capacity. In soils less saturated with soil P, sorption in the topsoil in high, while in soils well saturated, sorption capacity is reduced, and more P may enter deeper soil layers with percolating water. It is likely that in our study, the continuous addition of P fertilizers over a long period has resulted in high P saturation, which is evident from the higher DPS values (Table 1). This reduced sorption capacity of fertilized soils, and enabled higher P movement down the soil profile, compared to the Zero treatment, which had a lower soil P concentration, and thus lower saturation. This was most noticeable for the FYM+NPK treatment, which has the highest P application rates and where sorption sites could be more blocked through metal-chelate linkages mediated by humic- and fulvic- acids, which reduced phosphorus sorption. Besides vertical transport, the higher contents of P in the 30-60 cm soil layer in treatments fertilized with P may also be related to more root residues. Fertilized soils had higher crop yields, and therefore more root residues, which after decomposition increase the soil P stocks in the deeper soil layers. Our findings confirmed our first two hypotheses showing that P fertilization increase total and available

phosphorous not only in the ploughed soil layer, but also, in deeper Chermozem layers, and that vertical transport of soil P is related to the P contents in the topsoil layer and to the P saturation of soils.

P limitation of crop yields on Chernozem soils

As a result of breeding of high-yielding and disease-resistant cultivars, crop yields have largely increased over the last few decades globally (Rothamsted Research 2006; Roy et al. 2006; Hejcman et al. 2012; Hlisnikovsky et al. 2016). Similarly in our study, more productive crop varieties, adapted to particular site conditions, were seeded over the last few decades, which has resulted in increased crop yields (Fig. 3).

The yields in P-fertilized treatments were within or above the average values for Germany. Germany is a top producer of winter wheat, barley, potato and sugar beet with average yield values comprizing 7.7 t ha⁻¹ for winter wheat, 5.9 t ha⁻¹ for spring barley, 42 t ha⁻¹ for potato, and 60 t ha⁻¹ for sugar beet (FAOSTAT 2014). The higher than average yields in the P-fertilized treatments of our study for winter wheat (8-8.9 t ha⁻¹), spring barley (6.2-6.7 t ha⁻¹), and sugar beet (59-65 t ha⁻¹) could be related to the high natural fertility of Chernozem soils. Chernozems are characterized by high contents of organic matter, essential soil nutrients, and high water holding capacity, and thus they are considered to be the most productive soils in the world, which at adequate fertilization may produce higher yields than less fertile soil types (Campbell et al. 2005; Kunzova and Hejeman 2009; Krupenikov et al. 2011). The increase in the soil P contents up to the 60 cm depth in fertilized treatments of our study further contributes to the high productivity of this soil, as it is expected that more than two-thirds of the total plant nutrition comes from the 20-60 cm soil layers (Garz et al. 2000; Kautz et al. 2012).

The yield differences between treatments were small at the beginning, but increased with the duration of the experiment, which was in line with the other studies (Kunzova and Hejcman 2009; Hejcman et al. 2012; Hlisnikovsky et al. 2016) (Fig. 2). This is related to the gradual accumulation of soil nutrients in fertilized treatments, which enhanced soil fertility and therefore increased yields.

The lower yields in Zero treatment compared to the other treatments indicate that application of fertilizer is essential for maintaining soil fertility even in highly fertile Chernozem soils. Comparable yields for winter wheat (4.2 t ha⁻¹) on unfertilized black earth (Chernozem) were reported by Kunzova and Hejcman (2009). Application of the NK fertilizer in our study has increased yields between 37 and 104% compared to Zero, and application of P fertilizer in mineral or manure forms further increased yields between 12 and 63%, compared to the NK treatment (Fig. 3). This is in line with Johnston and Steen (2000), and Takahashi and Anwar (2007), who observed higher yields in NPK compared to NK treatments. Optimal P supply enhances crop productivity by controlling seed germination, photosynthesis and transport of carbohydrates to plant storage organs, such as roots of sugar beet, grain of wheat, and potato tuber (Johnston and Steen 2000; Sarkar et al. 2014; Rehim et al. 2016). As nutrient uptake is balanced, to maintain optimal nutrition, the inflow of N, P and K into plant tissues should follow the ratio of 1:0.1:1 (Sakar et al. 2014). The application of NK fertilizer increased crop yields, which in turn increased P demand. The missing P fertilization in NK treatment imbalanced nutrient stochiometry and consequently caused a strong negative soil P balance, even more negative than in the Zero treatment. The addition of P fertilizer balanced nutrition and therefore resulted in significantly higher yields compared to the NK treatment. Our findings support the statement made by Krupenikov et al. (2011) that although Chernozems are quite well supplied with P, appropriate P fertilization is essential to ensure high yield production. This fertilization should be based on the efficient use of P fertilizer by crops to minimise unnecessary and costly usage of limited mineral fertilizer.

P use efficiencies of crops

The P use efficiency represents the efficiency of fertilizer use by crops, and indicates whether fertilizer is applied in excessive amounts or in shortage in a particular cropping system. In our study, the average P use efficiency along all crops was below 70% in the P-fertilized treatments between 1902 and 1982 (Table 5), indicating that P removal was lower than the P input and that P fertilizer was applied in excess. As available P concentrations were above the recommended level, the excessive amount of added P was not used by the crops, and the strongly positive P balance resulted

in an accumulation of P compounds in the soil though sorption process. After reduction of P application rates in 1982, P use efficiencies increased (Table 5). This confirmed our third hypothesis that the reduction of P fertilization rates along with breeding-related crop yield increases would result in more balanced P input-output and increase P use efficiency.

Among the crop species, sugar beet and potato showed higher yield increases in response to P fertilization (38-63%) than the cereals (12-25%) (Fig. 2). This could be related to the P requirements and P acquisition strategies of crop roots. Phosphorus is a structural component of nucleic acids and lipids and is important for the production and transport of sugars and protein during sugar beet growth (Sinclair and Vadez 2002; Yara UK Limited 2015). It is especially important during early root development, when it ensures rapid root growth and enhances the uptake of other nutrients. At that period, the sugar beet root system does not produce many fibrous roots and the taproot dominates the root system (Murrell 2002). Short lateral roots develop from the taproot, but do not extend very far, and may only utilise available P which is located nearby the roots, in the topsoil. Therefore, adequate supply of phosphorus early in the season is critical for attaining high sugar beet yields.

Potatoes also have a relatively high P demand and a root system that is not particularly well suited for P uptake (Mikkelsen 2015). The root system of potatoes is shallow, with the majority of the roots found in the upper 30 cm of soil. The density of potato root hairs is low, comprising only about 20% of the total root mass, compared to 30 to 60% in corn crops. The total root length is also low, comprising about one-fourth of wheat root density (Mikkelsen 2015). For this reason, potato may be less efficient for the P aquisition than cereals, and may respond more profoundly to addition of P fertilizer.

Crops with higher specific root length may be more effective in absorbing P due to the larger soil volume per unit of root surface area (Sandaña and Pinochet 2014). In line with this and also with the results of Föhse et al. (1988), winter wheat showed the highest P use efficiency, which in our case was in average 117% since 1982 (Table 5). This is related to the high root-to-shoot ratio of winter wheat. As reported by Johnston and Steen (2000), a 1 m tall winter wheat plant has a total length of root

system of 100 m. Wheat roots reach depths of more than 1 m, and have a large root hair density, which enables exploring a greater volume of soil and greater acquisition of available P compared to short-rooted crops. The P use efficiency found for winter wheat was above 100% in our study, which indicates that more P is removed with crops than supplied with fertilizer. A further reduction of fertilization rates may lead to a depletion of P reserve in soil, as the output would exceed the input. However, the crop rotation leads to near-balanced P levels in soil, because the higher removal of P by winter wheat is compensated by lower P removal by the other crops grown in crop rotation. The unused P fertilizer by the other species will contribute to the building up of P reserves in the soil, which can be used by succeeding crops.

The small difference between the crop yields in NPK, FYM+NK and FYM+NPK, irrespectively of different P application rates, showed that increases in P fertilizer application beyond a certain treshhold has only little effects on crop yields. This is in line with Johnston and Syers (2009), who reported that winter wheat yields did not change significantly with the increase in P application rates above the optimum level.

P use efficencies at different treatments

Among the P-fertilized treatments, the treatment with the lowest P application rates, NK+FYM, showed the highest P use efficiency (Table 5). Although the balance in this treatment slightly decreased over the last years due to the yield increase, the soil content of available P grew up and was above recommended values. This could be attributed to the organic form of P in manure, which is not immediately available to the crop, and may stay in soil over a long period, gradually mineralising to plant-available inorganic form (Johnston and Steen 2000). As P in this treatment is exclusively in manure form, it enables reducing fertilization costs compared to the costly mineral fertilizer. This is of particular importance as rock phosphate, which represent the raw material for mineral P fertilizer production is limited, and efficient usage of mineral P fertilizer is of great concern of agricultural producers. In addition, application of manure in this treatment promotes building up of soil organic matter, which in turn increases microbial activities, and availability of other essential plant nutrients

in soil. At the same time, FYM+NK treatment enables a comparable high yield production as more expensive mineral NPK and FYM+NPK fertilization. Therefore, this management practice likely presents the most efficient strategy for Chernozem soils. However, a reduction of P balances since the 1982 in FYM+NK suggest that the contents of P in soils should be regularly checked to avoid P depletion and soil fertility loss in the future.

Conclusions

Application of P fertilizer is essential for maintaining soil fertility and high crop production even in highly fertile Chernozem soil. Organic fertilization combined with mineral N and K was found to be the most P efficient fertilization strategy for the studied Chernozem. It enables maintaining optimum available P levels, reduces fertilizer costs, and in addition may increase soil organic matter. Soil phosphorus contents should be regularly checked to adjust fertilizer application rates, as new more productive crop varieties may change phosphorus balance. Subsoil layer should be included in the assessment of soil P status, as it may substantially contribute to crop nutrition.

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List of Abbreviations

P – phosphorus

NK - treatment with application of mineral nitrogen and potassium fertilizers

NPK - treatment with application of mineral nitrogen, phosphorus and potassium fertilizers

FYM+NK – treatment with application of organic manure and mineral nitrogen and potassium fertilizers

FYM+NPK - treatment with application of organic manure and mineral nitrogen, phosphorus and potassium fertilizers

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Tabl	e 1.
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Soil depth (cm)	Zero	NPK	FYM+NPK
Sand, %			
0-30	7 (0.9)	7 (1.0)	10 (1.4)
30-60	9 (0.4)	11 (3.5)	11 (2.5)
60-90	7 (0.6)	8 (3.0)	11 (0.6)
Silt, %		. ,	
0-30	69 (1.0)	69 (1.1)	67 (1.9)
30-60	68 (2.0)	66 (1.2)	69 (1.5)
60-90	70 (2.1)	73 (0.5)	70 (1.0)
Clay, %			
0-30	24 (1.6)	24 (1.0)	23 (0.6)
30-60	23 (1.4)	23 (4.6)	20 (1.0)
60-90	23 (1.7)	19 (3.5)	19 (0.6)
рН			
0-30	6.8 (0.8)	6.3 (0.8)	7.0 (0.1)
30-60	7.5 (0.2)	7.3 (0.4)	7.4 (0.2)
60-90	7.8 (0.1)	7.7 (0.2)	7.7 (0.1)
OC, %			
0-30	1.6 (0.0) <i>a</i>	2.0 (0.1) <i>b</i>	2.6 (0.1) <i>c</i>
30-60	1.4 (0.1) <i>a</i>	1.8 (0.1) <i>b</i>	1.7 (0.1) <i>b</i>
60-90	0.7 (0.1)	0.8 (0.0)	0.8 (0.1)
Ca, mg g⁻¹			
0-30	8 (0.7)	8 (0.6)	9 (0.8)
30-60	14 (1.8)	13 (1.2)	17 (1.8)
60-90	56 (11.2)	52 (9.6)	68 (10.0)
Fe _{total} , mg g ⁻¹			
0-30	20 (0.4)	19 (0.2)	19 (0.3)
30-60	18 (1.1)	19 (1.0)	18 (0.6)
60-90	14 (0.6)	15 (0.7)	15 (1.5)
Fe _d , mg g ⁻¹			
0-30	5 (0.7)	6 (0.5)	5 (0.4)
30-60	5 (0.8)	5 (0.8)	5 (0.7)
60-90	4 (0.4)	4 (0.3)	4 (0.4)
Fe _{ox} , mg g ⁻¹			
0-30	1.2 (0.1)	1.5 (0.1)	1.4 (0.1)
30-60	1.1 (0.2)	1.3 (0.2)	1.2 (0.1)
60-90	0.6 (0.1)	0.7 (0.1)	0.6 (0.1)
Al _{totak} , mg g ⁻¹			
0-30	26 (0.6)	26 (0.5)	25 (0.5)
30-60	24 (1.7)	23 (1.9)	24 (0.8)
60-90	15 (0.7)	17 (1.0)	18 (2.2)
-1			

 AI_{dr} mg g⁻¹

0-30	0.6 (0.0)	0.7 (0.1)	0.6 (0.1)
30-60	0.6 (0.1)	0.7 (0.1)	0.6 (0.1)
60-90	0.3 (0.1)	0.4 (0.1)	0.3 (0.1)
Al _{ox} , mg g ⁻¹			
0-30	1.1 (0.2)	1.2 (0.1)	1.0 (0.1)
30-60	1.0 (0.1)	1.2 (0.1)	1.0 (0.1)
60-90	0.5 (0.0)	0.6 (0.1)	0.5 (0.0)
P _{ow} mg kg ⁻¹			
0-30	195 (18) <i>a</i>	397 (99) <i>b</i>	476 (65) <i>b</i>
30-60	118 (4) <i>a</i>	238 (79) <i>ab</i>	302 (75) <i>b</i>
60-90	102 (7) <i>a</i>	205 (76) <i>b</i>	275 (39) <i>b</i>
DPS, %			
0-30	8 (1.5) <i>a</i>	15 (3.7) <i>b</i>	19 (3.0) <i>b</i>
30-60	6 (0.4) <i>a</i>	10 (2.7) <i>b</i>	13 (3.6) <i>b</i>
60-90	10 (0.2) <i>a</i>	16 (6.7) <i>ab</i>	24 (4.9) <i>b</i>
Martin differences have		the last state of the state of	

Note: different lowercased italic letters indicate significant differences between treatments at the P < 0.05 level.

	٦	N	Р			К
	1903-1970	1971-2012	1903-1981	1982-2012	1903-1970	1971-2012
NK	63	120	-	-	93	117
NPK	63	120	32,5	30	93	117
FYM+NK	133	200	22	26	182	140
FYM+NPK	133	200	54.5 (32.5 NPK + 22 FYM) ^a	32 (6 NPK + 26 FYM) ^a	182	140

Note: ^{*a*} amounts of P applied with NPK fertilizer and FYM.

Table 3.

Treatment	Total P			P available			
	1986 ^a	2013	change ^b	1986 ^{<i>a</i>}	2013	change ^b	
	m	g kg⁻¹	%	m	g kg⁻¹	%	
Zero	623	474(61) <i>a</i>	-24	67	42(25)a	-37	
NK	621	448(75) <i>a</i>	-28	40	31(15) <i>a</i>	-23	
NPK	870	692(27)b	-20	116	110(41) <i>b</i>	-5	
FYM+NK	822	711(35)b	-14	152	178(16) <i>c</i>	17	
FYM+NPK	1063	969(65) <i>c</i>	-9	395	347(62)d	-12	

Note: different lowercased italic letters indicate significant differences between treatments at the P < 0.05 level.

^{*a*}values for 1986 were obtained from Wechsung and Pagel (1993).

^bchange in total and available P values from 1986 to 2013.

Table 4.

Soil depth (cm)	Zero	NK	NPK	FYM+NK	FYM+NPK
			P (t ha⁻¹)		
0-30	2.0 (0.3) <i>a</i>	1.9 (0.3) <i>a</i>	2.9 (0.1) <i>b</i>	3.0 (0.1) <i>b</i>	4.1 (0.3) <i>c</i>
30-60	1.6 (0.1) <i>a</i>	1.5 (0.1) <i>a</i>	2.0 (0.2) <i>b</i>	1.9 (0.1) <i>b</i>	2.5 (0.1) <i>c</i>
60-90	1.3 (0.1) <i>ab</i>	1.2 (0.1) <i>a</i>	1.4 (0.1) <i>b</i>	1.3 (0.1) <i>ab</i>	1.4 (0.1) <i>b</i>
0-90	4.9 (0.5) <i>a</i>	4.6 (0.4) <i>a</i>	6.3 (0.3) <i>b</i>	6.2 ((0.2) <i>b</i>	8.0 (0.4) <i>c</i>

Note: different lowercased italic letters indicate significant differences between treatments at the P < 0.05 level.

Table 5.

	P use efficiency, %				
<u>1903-1981</u>	Sugar	Spring	Potato	Winter	Mean
	beet	barley		wheat	
NPK					
	53	36	45	46	45
FYM+NK	84	57	69	70	70
FYM+NPK	34	24	31	29	30
<u>1982-2013</u>					
NPK	77	72	76	102	82
FYM+NK	98	90	96	117	100
FYM+NPK	80	74	79	95	82