Evaluation of phosphorus mobility in soil using different extraction methods

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ABSTRACT

Soil samples (from Czech and German long-term field experiments) were used to estimate different soil phosphorus (P) fractions. More than 200 topsoil (0–30 cm) samples from different fertilizing treatments were taken. These were analyzed for P in soil solution (P_{CaCl_2}) [0.01M $CaCl_2$ extract], exchangeable sorbed P (P_{ex}) [anion exchange (AE) membranes] and bioavailable P [Doppel-Lactat and Mehlich 3 (P_{DL} and P_{M3})]. Other fractions analyzed were total inorganic (P_{in}), total ($P_{M\text{-}tot}$) and organic (P_{org}) P [fractionation after Marks], P sorbed on Fe and Al (P_{FeAl}) [fractionation after Schwertmann] and residual P (P_{ar}) [aqua regia extract]. Comparison of medians appeared to be better for evaluating extraction abilities. Phosphorus fractions were in the following order: (P_{ar} = 100%); P_{CaCl_2} (0.2%) < P_{ex} (9%) < P_{DL} (10%) < P_{M3} (16%) < P_{in} (24%) < P_{org} (37%) < P_{FeAl} (55%) < $P_{M\text{-}tot}$ (59%). Low amounts of P_{in}, P_{org} and $P_{M\text{-}tot}$ did not verify the applicability of the Marks' fractionation for the set of studied soils. Close correlations at $P \leq 0.001$ were found for all methods for estimating the fractions of bioavailable phosphates (P_{CaCl_2}, P_{ex}, P_{DL} and P_{M3}). Statistically significant relations were observed between P_{in} with P_{ar}, $P_{M\text{-}tot}$ and P_{FeAl}.

Keywords: phosphorus; soil; bioavailability; P fractions

Total P amounts, which range between 0.02 and 0.20%, depend on the composition and type of the soil (e.g. Mengel 1991, Schilling 2000, Blume et al. 2002) and are divided in different fractions. All of them may have an impact on the availability of P for plants. Therefore, it is important to have a good knowledge of all P fractions to gain a better insight of processes taking place in soils.

Phosphorus concentration is normally lowest in soil solution. This fraction is usually estimated by extraction with water (Luscombe et al. 1979) or with 0.01M $CaCl_2$ (Houba et al. 1994) and ranges between 0.8–8 mg P/kg (Marschner 1995). Exchangeable sorbed P (P_{ex}) is another important source of bioavailable P. It is the part of soil P that is exchangeable and adsorbed on the surface of soil particles and can be easily released to the soil solution. This fraction can be estimated for example with anion resins (Tiessen and Moir 1993, Lewis and McGechan 2002), or recently, via anion exchange (AE) membranes (Kuono et al. 1995, Sato and Comerford 2006).

The most commonly used methods are those for estimating total bioavailable P in soils: e.g. Mehlich 3 (Mehlich 1984), Olsen (Olsen et al. 1954), CAL and Doppel-Lactat (DL) (Hoffman 1991), Bray 1 and 2 (Bray and Kurtz 1945), etc. These extractions are focused on the determination of potentially quickly bioavailable P, i.e. P in soil solution and weakly bound P.

One of the most important fractions in non-calcareous soils are Fe and Al phosphates (P_{FeAl}). Adsorption runs commonly on the sesquioxides (Fe, Al oxides), allofans, clay minerals and organic Fe and Al complexes. Adsorption increases with increasing amorphous phases (Sharpley 1995). Adsorbed phosphates are released back to the soil solution with increasing pH value (desorption), resulting thus into plant available fractions (Schilling 2000). Fe and Al phosphates are estimated

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with different fractionation methods, e.g., Chang and Jackson (1957), Hedley et al. (1982) or separately with the method according to Schwertmann (1964).

Several fractionation methods, e.g., Chang and Jackson (1957), Marks (1977), Hedley et al. (1982) etc., are commonly used for estimating total inorganic P (P_{in}). One part of these fractionations is ever estimating of total P (P_{tot}). Based on data from these fractionation methods, it is possible to calculate the amount of total organic P (P_{org}) as the difference between P_{tot} and P_{in} (Olsen and Sommers 1982).

To estimate total P (P_{tot}) in soils many methods are available. Some of them are described in detail in the work of Kara et al. (1997). Commonly used extraction procedure is the aqua regia extraction (P_{ar}). According to Crossland et al. (1995) this method correlates well with alkaline fusion. Therefore, the aqua regia extraction for estimating of residual P is useful for indirect estimation of total P in soils.

The aim of this work was to evaluate selected methods used for estimating of different P forms in soil. The methods studied included 0.01M $CaCl_2$ extraction, use of anion exchange membranes, Mehlich 3 and Doppel-Lactat methods, estimating of Fe-, Al-P, and fractionation after Marks (1977) and the extraction with aqua regia.

MATERIALS AND METHODS

Soil samples (0–30 cm) were taken from 22 sites of long-term field experiments in the Czech Republic (16 sites) and Germany (6 sites). Characteristics of these sites are summarized in Table 1. The experiments have been running for more than 20 years at the time of sampling, except Lukavec, Humpolec, Červený Újezd and Hněvčeves sites,

Table 1. Characteristics of the experimental sites

Site	Soil type	Soil texture	pH (0.01M $CaCl_2$)
Horažďovice	Cambisol	loamy sand	5.9
Chrastava	Cambisol	loamy sand	5.8
Jaroměřice	Haplic luvisol	loamy	6.3
Krásné Údolí	Cambisol	sandy loam	5.5
Libějovice	Haplic luvisol	sandy loam	6.2
Lípa	Cambisol	sandy loam	5.9
Staňkov	Haplic luvisol	loamy	6.0
Svitavy	Haplic luvisol	sandy loam	6.2
Vysoká	Stagnosol	loamy	6.3
Pusté Jakartice	Haplic luvisol	loamy	5.8
Uherský Ostroh	Haplic luvisol	loamy	6.6
Žatec	Chernozem	silty clay	6.4
Červený Újezd	Haplic luvisol	loamy	6.5
Hněvčeves	Mollic luvisol	clay loamy	5.9
Humpolec	Cambisol	sandy loam	5.1
Lukavec	Cambisol	sandy loam	5.3
Dahlem (Germany)	Albic luvisol	loamy sand	5.4
Lauchstädt (Germany)	Chernozem	silt loam	6.9
Lauterbach (Germany)	Dystric cambisol	silt loam	5.3
Dikopshof (Germany)	Haplic luvisol	silt loam	5.6
Thyrow (Germany)	Albic luvisol	loamy sand	5.0
Halle (Germany)	Chernozem	loamy sand	6.0

where the samples were taken 6 years after experiment set up. Only sites with an average pH value under 7.0 were chosen. Commonly 228 samples from different fertilizing treatments were taken. More fertilizing treatments were chosen, to get higher variability of studied samples. Samples were air-dried and passed through a 2-mm sieve.

Soil samples were analyzed for different P fractions. The following methods were used: 0.01M $CaCl_2$ extraction (Houba et al. 1994) for readily available P (P_{CaCl_2}), anion exchange (AE) membranes (adapted after Kuono et al. 1995) for the extraction of exchangeable P (P_{ex}), Mehlich 3 (Mehlich 1984) and Doppel-Lactat (DL) (Hoffman 1991) methods for bioavailable P (P_{M3} and P_{DL}), P sorbed on Fe and Al compounds (P_{FeAl}) according to Schwertmann (1964), extraction with 0.2M $C_2H_8N_2O_4 \cdot H_2O$ and afterwards digestion with H_2SO_4 and H_2O_2 at 250°C for total inorganic (P_{in}), total organic (P_{org}) and total P ($P_{M\text{-}tot}$) contents according to Marks (1977). To estimate P_{in} soil samples were extracted with 1M NaOH after the DL extraction. Five ml of 1M NaOH extract were then digested with 1M H_2SO_4 at 120°C to obtain the total P ($P_{M\text{-}tot}$) content. Aqua regia extracts (EN 13346) were used for measuring residual P (P_{ar}). All reagents used were in per analysis quality. All extracts were measured spectrophotometrically after Murphy and Riley (1962) with SKALAR SANPLUS SYSTEM. Spearman correlation test, average, median, maximal and minimal values were used for the statistical evaluation.

RESULTS AND DISCUSSION

The obtained data did not meet normal distribution with the statistical tests. Therefore, basic statistical characteristics (average, median, maximal and minimal contents) were used for the evaluation of results. These are depicted in Table 2.

The comparison of extraction ratios of all methods yielded almost always statistically significant differences. Only between P_{ex} and P_{DL}; $P_{M\text{-}tot}$ and P_{FeAl} no statistically significant differences were obtained.

The lowest content of P was, as expected, measured in soil solution with 0.01M $CaCl_2$ (P_{CaCl_2}). Maximal content of P was 8.90 mg P/kg. The value of median was only 1.70 mg P/kg. It corresponds with our previous results (Kulhánek et al. 2007), where we obtained values between 0.20 and 2.80 g P/kg.

A relatively low content of P was also measured with AE membranes (P_{ex}) where similar values of average and median were reached, which varied around 60.0 mg P/kg. This method should estimate exchangeable sorbed P, which has the ability to easily pass to the soil solution and become available for plants.

No significant differences (based on the box-plot comparison) were found between the methods Mehlich 3 and Doppel-Lactat commonly used for estimating total bioavailable P. With both of them we did not reach any outlaying observations. The median of P_{DL} was 70.3 mg P/kg and when using P_{M3} the estimate was about 35.5 mg P/kg higher. Both methods yielded higher values than P_{ex}. It is also likely that with the Doppel-Lactat and especially Mehlich 3 method results into nonbioavailable fractions of P. This does not, however, limit the possibility of using these methods to estimate bioavailable P, because according to Tiessen and Moir (1993) the Mehlich 3 and Doppel-Lactat methods should not only estimate significant contents of nonbioavailable P fractions.

The fractionation after Marks (1977) was used for estimating the contents of total inorganic (P_{in}), organic (P_{org}) and total P ($P_{M\text{-}tot}$). The results showed that in the analyzed soils, usually higher contents of P were bound in organic matter. The median of P_{in} was 190 mg/kg and 250 mg P/kg for P_{org}. Analyzing the median values appeared to be more suitable in this case, because of the presence of outlaying observations that inadequately influenced the values of averages.

The content of P_{FeAl} averaged 446 mg P/kg. Regarding the outlaying observations in the area of extremely high values, it appeared to be more

Table 2. Portions of different P fractions in soils (mg P/kg)

	P_{CaCl_2}	P_{ex}	P_{DL}	P_{M3}	P_{in}	P_{org}	$P_{M\text{-}tot}$	P_{FeAl}	P_{ar}
Average	1.70	61.4	84.4	116	190	317	506	446	705
Median	1.30	59.1	70.3	106	162	250	397	374	676
Max	8.90	147	326	297	696	910	1440	1430	2024
Min	0.00	8.6	12.2	19.8	47.0	19.5	130	142	273

Table 3. Correlations between observed P fractions (Spearman correlation coefficient *r*)

	P_{CaCl_2}	P_{ex}	P_{DL}	P_{M3}	P_{in}	P_{org}	P_{FeAl}	$P_{M\text{-}tot}$	P_{ar}
P_{CaCl_2}	1.00	0.50**	0.50**	0.58**	–0.08	0.22	–0.08	–0.19	–0.05
P_{ex}		1.00	0.79**	0.58**	0.28*	0.10	0.27*	0.18	0.36*
P_{DL}			1.00	0.65**	0.25*	–0.02	0.24	0.08	0.37*
P_{M3}				1.00	0.52**	0.26*	0.53**	0.38*	0.43**
P_{in}					1.00	0.63**	0.88**	0.84**	0.87**
P_{org}						1.00	0.70**	0.96**	0.49**
P_{FeAl}							1.00	0.84**	0.75**
$P_{M\text{-}tot}$								1.00	0.68**
P_{ar}									1.00

**highly significant relations at $P \leq 0.001$, *significant relations at $P \leq 0.01$

suitable to use the median as well. The value of median was 374 mg P/kg.

The highest contents were obtained with the estimation of residual P (P_{ar}). Here the average value was 705 mg P/kg and the median 676 mg P/kg. The highest content (2024 mg P/kg) was found at the Lauterbach site and the lowest (273 mg P/kg) at the Thyrow site. All of the measured values ranged between 0.02 and 0.20%. This range has been determined for total P by many authors (e.g. Mengel 1991, Schilling 2000, Blume et al. 2002, etc.). Due to the high extraction efficiency of the aqua regia extraction, it is possible to assume, that the obtained values were close to the total content of P in soil. This corresponds with the results of Crossland et al. (1995). These authors obtained very low differences between P_{ar} and total P estimated using the alkaline fusion.

Our results showed that the Marks fractionation did not probably estimate the corresponding P fractions. This is possible to derive from the fact that the P_{FeAl} content was very close to $P_{M\text{-}tot}$. Therefore almost all P was sorbed to Fe and Al compounds, which is not probable. Additionally, the $P_{M\text{-}tot}$ content was significantly lower compared to P_{ar} content. It is clear, that the Marks' fractionation is usable only as a rough tool for estimating the ratios between P_{in} and P_{org} in the analyzed soils. A similar ratio between P_{in} and P_{org} was published by Bünemann et al. (2007) using Saunders and Williams (1957) extraction method.

Figure 1 shows the percentual distribution of different P fractions in soils based on median comparisons. According to the low contents of $P_{M\text{-}tot}$, P_{ar} was chosen as 100%.

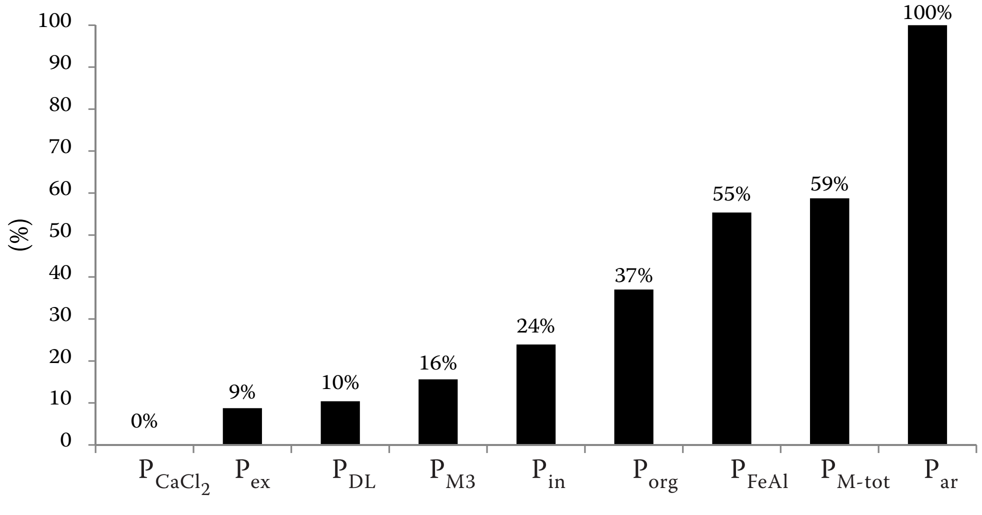

Figure 1. Percentage distribution of different P fractions in soils

The lowest percentage of different fractions represented P in soil solution (0.2%). Similar values of 9% and 10% were reached with AE membranes and the Doppel-Lactat method, respectively. The amount estimated with the Mehlich 3 method was 16%. That corresponds well with results of many authors, that the content of bioavailable phosphates in soil is relatively low and reaches usually about 10% of total P content (Mengel 1991, Marschner 1995, Blume et al. 2002, Bünemann et al. 2007). The P_{org} content was about 13% higher compared to the content of P_{in}. More than 50% of P_{ar} constituted of phosphates adsorbed on iron and aluminum compounds.

Correlation analysis was used for comparison of different P fractions (Table 3). Spearman correlation coefficients, which are suggested for comparison of data with non-normal distribution, were used for the calculating of relations. The relations were calculated at $P \leq 0.01$ and $P \leq 0.001$.

Comparing the different methods for estimating bioavailable P fractions in soils (P_{CaCl_2}, P_{ex}, P_{DL} and P_{M3}) led to close correlations at the $P \leq 0.001$. It means that with the mentioned methods it is possible to estimate mutually dependent P fractions and in this case it shows close relations between P in soil solution and exchangeable and total bioavailable P, respectively. Tightness of relations between P_{ex} and phosphates estimated with the Mehlich 3 and Doppel-Lactat methods shows that these methods probably did not estimate significant contents of nonbioavailable P. Significant relations between P_{M3} and P_{ex} were obtained in the work of Zheng et al. (2003). Close correlations between P in soil solution and P_{M3} was also found by Magdoff et al. (1999), who reached $r = 0.8$ at $P \leq 0.01$ in 28 noncalcareous soils. Zbíral and Němec (2002) compared the P_{M3} and P_{CaCl_2} fractions using regression analysis and obtained significant relations as well (coefficient of determination $r^2 = 0.56$).

Close correlations at $P \leq 0.001$ were obtained between P_{M3} and $P_{in.}$ Therefore, it is probable that the Mehlich 3 method estimated a significant content of total mineral P. Despite the low extraction efficiency of the Marks fractionation it is possible to presume that this method did not estimate the fraction of total inorganic P, but only a fraction of it. Relations between P_{in} with P_{ex}, P_{CaCl_2} and P_{DL} were not statistically significant at $P \leq 0.001$.

In most of cases, statistically significant relations between bioavailable forms of P and P_{org} were not reached.

High correlation coefficients between P_{in}, P_{org} and $P_{M\text{-}tot}$ were obtained, because these fractions originated from one fractionation. The correlation coefficient between P_{org} and $P_{M\text{-}tot}$ was even 0.96.

Close relations between P_{FeAl} and $P_{M\text{-}tot}$ and P_{ar} showed that a considerable content of P in noncalcareous soils can be adsorbed on Fe and Al compounds.

Regression analysis was used for evaluating the results of all the studied P fractions. Similar results to correlation analysis were obtained. In most cases linear regression appeared to be the most suitable.

As a conclusion it is possible to state that P contents in different fractions in soils can be written as: $P_{CaCl_2} < P_{ex} < P_{DL} < P_{M3} < P_{in} < P_{org} < P_{FeAl} < P_{M\text{-}tot} < P_{ar}$.

The Marks' fractionation probably does not estimate the corresponding contents of different P fractions. Therefore, this fractionation is only usable as guidance about ratios between P_{in}, P_{org} and P_{tot} in the analyzed soils.

Close correlations between the methods estimating bioavailable phosphates (P_{DL} and P_{M3}) with P in soil solution (P_{CaCl_2}) and exchangeable P (P_{ex}) verified the usability of the Mehlich 3 and Doppel-Lactat extraction schemes in noncalcareous soils.

High contents of phosphates in analyzed noncalcareous soils were bound in Fe and Al compounds. This was verified by the high percentage of this fraction compared to P_{ar}.

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