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COMPARING DIFFERENT EXTRACTION METHODS FOR ESTIMATING PHOSPHORUS SOLUBILITY IN VARIOUS SOIL TYPES

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In areas with intensive animal livestock farming, agricultural soils are enriched with phosphorus (P). These soils exhibit an increased risk for P transfer to the sub-soil and surface water via leaching. Besides the presence of hydrological pathways between a field and surface water, P in soil solution should be studied for evaluating the environmental risk. For this purpose, soil P extraction methods can be used. In this study, we tested the relation between various extraction methods and P in soil solution, simulated by a water extraction at a soil-to-solution ratio of 1:2 (w/v) using field-moist topsoils sampled from the major Dutch soil types (noncalcareous and calcareous sand and clay, reclaimed peat, and peat). The following methods were used: P_w (1:60 [v/v] water-extractable P), 0.01 M $CaCl_2$ (1:10 [v/v]), FeO-strip, and acid ammonium oxalate-extractable P, Al, and Fe. Phosphorus in the 1:2 water extracts was mainly present as molybdate-reactive P (MRP). Extraction methods with the highest ability to predict MRP in 1:2 water extracts across different soil types were $CaCl_2$, P_w , and FeO-strip, the latter two normalized for $[Al + Fe]_{ox}$. However, for the peat and noncalcareous clay soils, also estimation of molybdate-unreactive P (MUP) is important because MUP dominates in the 1:2 water extracts of these soils. Thus, an extraction method that only determines MRP will not suffice, and further research is needed on the environmental risk of MUP in soil solution from these soil types. The calcareous sandy soils deviated significantly from the above mentioned relationships. For this soil type, it should be tested whether a single water extraction (e.g., P_w) suffices for determining the environmental risk. (Soil Science 2006;171:103–116)

Key words: Phosphorus, environmental risk, extraction methods, soil solution, leaching.

IN areas with intensive animal livestock farming in The Netherlands, agricultural soils are enriched with phosphorus (P). This is the result of high application rates of animal manure and

P fertilizer exceeding the P removal rate by crop harvest (Breeuwsma et al., 1995; Smaling et al., 1999). In The Netherlands where most of the agricultural land is flat and where groundwater tables are shallow, soils enriched with P exhibit an increased risk for the loss of P to surface water via (sub-surface) leaching of soil solution (Schoumans and Groenendijk, 2000; Sims et al., 1998). Phosphorus enrichment of surface waters contributes to eutrophication because P often limits the primary production in freshwater ecosystems (Correll, 1998).

Agricultural soils are generally considered to be a major (diffuse) source of P to surface

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waters. In 2002, the estimated contribution of agriculture to the total P (TP) load of surface waters in The Netherlands was 58% (RIVM, 2004), whereas this can be as high as 90% in some hot spot areas (Coppoolse and Kersten, 1992). The contribution of point sources such as industry and sewage treatment plants has decreased strongly in recent decades. Because of the high costs of further reducing P emissions by point sources (Boers and van der Molen, 1993), attention of policy makers has shifted to reducing the contribution of agricultural soils to the TP load of surface waters. From 1985 onwards, a series of policies and measures were implemented to reduce P accumulation in agricultural soils and the associated risk for P loss to surface water (Oenema et al., 2004; van der Molen et al., 1998). To evaluate the effectiveness of these policies, the risk of agricultural soils for P transfer needs to be monitored at the field level. Besides the presence of hydrological pathways between a field and surface water (Haygarth et al., 2000), the concentration of P in soil solution should be studied because a high concentration forms a risk for loss to the sub-soil and surface water. For estimating the solubility of P in soil waters such as soil solution and surface runoff, soil P extraction methods can be used. This is primarily because extraction methods are widely used for agronomic purposes, are inexpensive, and strong correlations have been found between various extraction methods and P in soil waters (Sims et al., 2000). For example, P in column leachate measured by the colorimetric acid molybdate method of Murphy and Riley (1962) (molybdate-reactive P; MRP) correlated well with 0.01 M of CaCl_2 -extractable and water-extractable P, as well as with P extractable in the presence of an FeO-strip (FeO-P) (Maguire and Sims, 2002). Pote et al. (1996, 1999) and Turner et al. (2004b) found strong correlations between MRP in surface runoff and 0.01 M CaCl_2 -extractable and water-extractable P and FeO-P. Pote et al. (1996, 1999) also found strong correlations with the acid ammonium oxalate-based degree of P saturation. Most of these extraction methods were, however, not able to predict MRP in surface runoff across all soil types used in these studies. Beauchemin and Simard (1999) and Turner et al. (2004b) attributed this to chemical differences between the different soil types studied. To develop a tool that can be applied to predict the risk of P loss from soil in The Netherlands, it is thus important to be able

to estimate the solubility of P in various soil types.

In this study, we tested the relationships between various soil P extraction methods and P in soil solution. For a large number of soil samples, however, it is difficult to obtain soil solution by extraction with *in situ* porous suction cups or by centrifugation. In a study of Chapman et al. (1997), the concentration of TP and its distribution over inorganic and organic species in water extracts with a narrow soil-to-solution ratio were in good agreement with results obtained by centrifugation. Therefore, we decided to simulate soil solution by a water extraction at a soil-to-solution ratio of 1:2 (w/v) (Sonneveld et al., 1990). Soil samples were obtained in 2002 and 2003 from the plough layer of arable land and the 0–5 cm layer of grassland soils on all major Dutch soil types. We chose taking samples from topsoils because in the case of P management measures of agricultural land such as mining soil P, changes in soil P are expected to occur first in the topsoil where plants take up P from soil solution (Koopmans et al., 2004). Furthermore, P transport from topsoil to the sub-soil determines the risk of P loss to surface water by leaching in the long-term. In 2003, a limited number of extraction methods were selected for validation of the relationships found in 2002. The use of field-moist samples is most appropriate for simulating soil solution via a 1:2 water extraction because drying and rewetting of soils have been shown to have a large effect on the release of P to soil-water extracts (Turner and Haygarth, 2001; Turner et al., 2003). However, sub-sampling of dry soils is much easier and storage of dry soil samples is less complicated. Therefore, we tested the influence of drying on both MRP and molybdate-unreactive P (MUP) in 1:2 water extracts. The objectives of our study were (i) to determine the influence of soil drying on MRP and MUP measured in 1:2 water extracts, and (ii) to investigate the relation between P extracted with different extraction methods and P in 1:2 water extracts, for different soil types.

MATERIALS AND METHODS

Soils

Soil samples were taken from noncalcareous and calcareous sandy and clay, reclaimed peat, and peat soils under both arable (plough layer) and grassland (0–5 cm) at various locations

across The Netherlands in October 2002 ($n = 49$) and 2003 ($n = 37$). In 2003, samples were taken for validation purposes from the same soil types as in 2002, but from different locations. To avoid P in disequilibrium, we did not choose fields where cattle had been grazing or that had received animal manure, P fertilizer, or other soil amendments (e.g., lime or compost) six weeks before sampling. After sampling, soils were stored in the dark at 5 °C, until further processing. Soil samples were dried at 40 °C and passed through a 2-mm sieve. For 1:2 water extraction of the field-moist soils, a sub-sample was taken from the bulk soil after homogenization by mixing, without previous sieving and drying.

Soil Analyses

The pH (H₂O), CaCO₃, and organic matter (OM) were determined according to standard analytical procedures (Houba et al., 1995). The pH was measured in a settling 1:5 (w/v) suspension of soil in water, CaCO₃ was determined by measuring the volume of CO₂ produced after the addition of HCl, and OM was determined by loss-on-ignition. For simulating soil solution, field-moist soil was suspended in water according to a modified method of Sonneveld et al. (1990). Based on the moisture content determined at 105 °C, the water volume of the field-moist soil samples was adjusted to a soil-to-solution ratio of 1:2 (w/v). Soil suspensions were shaken reciprocally with 60 strokes per minute (spm) for 24 h. After centrifugation (1800g for 10 min), supernatants were filtered through a 0.45-μm filter (Aquatron, Schleicher & Schuell) and MRP was measured colorimetrically at 882 nm (Murphy and Riley, 1962). Furthermore, pH was determined in the extract, TP and major cations were measured by inductively coupled plasma (ICP) spectroscopy, and total and inorganic dissolved carbon were determined on a Shimadzu TC5000. Concentration of MUP was calculated as the difference between TP and MRP, and dissolved organic carbon (DOC) as the difference between total and inorganic dissolved carbon. To evaluate the effect of soil drying, the 1:2 water extraction and the same analyses were also performed on dry soils. The P concentrations in the 1:2 water extracts were related to P extracted with the following methods: CaCl₂, P_w, FeO-strip, and the acid ammonium oxalate-based α . Instead of using the 1:2 water extraction method, soil solution can also be

simulated with 0.01 M CaCl₂ (Houba et al., 1986). The 1:10 (w/v) 0.01 M CaCl₂ extracts were shaken on a reciprocating shaker at 165 spm. After centrifugation (1800g), MRP was measured. The P_w (1:60 [v/v]) was determined according to Sissingh (1971). After 22 h of pre-equilibrating 1.2 mL of soil with 2 mL of water, 70 mL of water was added and the soil suspension was shaken end-over-end at 30 rotations per min for 1 h. After filtration over a 0.45-μm filter (Schleicher & Schuell 602H), MRP was measured colorimetrically. The reversibly adsorbed inorganic P pool (FeO-P) was determined with the FeO-strip method according to a modified method of van der Zee et al. (1987) (for details, see Koopmans et al., 2004). The total pool of sorbed inorganic P (P_{ox}) was estimated using the acid ammonium oxalate extraction method of Schwertmann (1964). Concentrations of P, Al, and Fe were measured by ICP. Based on these results, the degree of P saturation of a soil with respect to its content of amorphous Al-(hydr)oxides and Fe-(hydr)oxides (van der Zee and van Riemsdijk, 1988) can be calculated. This parameter, α , was originally developed for noncalcareous sandy soils where sorption of inorganic P is dominated by these metal-(hydr)oxides (Beek, 1979); α was calculated as

$$\alpha = \frac{P_{ox}}{[Al + Fe]_{ox}} \times 100 \quad (1)$$

where α is expressed as a percentage and P_{ox} and [Al + Fe]_{ox} are expressed in mmol kg⁻¹.

Statistical Analyses

Linear and exponential relationships and the Langmuir isotherm were fitted to the data using GenStat 5, Release 7.1 (GenStat, 2003). Significance of R^2_{adj} values was determined using F tests.

Solubility Equilibrium Calculations

For the calcareous sandy soils sampled in 2002, chemical activities of Ca and P were calculated for the 1:2 water extracts using the chemical speciation model ORCHESTRA (Meeussen, 2003). Ionic strength was calculated from the concentrations of cations measured using ICP. For the construction of a calcium phosphate double function plot (Lindsay, 1979; McDowell et al., 2003; Sharpley et al., 2004), we used the thermodynamic constants given by Lindsay (1979).

RESULTS AND DISCUSSION

Soils

In Table 1, selected physical and chemical characteristics of the soil samples are presented as well as the surface area currently covered per soil type in The Netherlands. The largest area of agricultural land is found on noncalcareous sandy soils, which is mainly used as grassland for dairy farming. The smallest area is found on calcareous sandy soils along the Dutch coast, which is mainly used as arable land (calcareous dune sand) (Schoumans, 2004). The soil samples used exhibit a wide range in general characteristics, for example, pH (4.3–8.5), CaCO_3 (0–9.4%), OM (1.0–54.9%), P_{ox} (2–48 mmol kg^{-1}), and $[\text{Al} + \text{Fe}]_{\text{ox}}$ (7–460 mmol kg^{-1}). As such, the data presented in Table 1 reflect the variability encountered in major Dutch soil types.

Effect of Soil Drying on Water-Extractable Phosphorus

The MRP concentration in the 1:2 water extracts obtained from the field-moist soils ranged from 0.04–0.07 mg L^{-1} in the peat soils to 0.92–1.04 mg L^{-1} in the calcareous sandy soils (Table 2). In these extracts, MRP as a percentage of TP ranged from 68–70% in the noncalcareous sandy soils to 81–84% in the calcareous sandy soils (Table 2). For the peat and noncalcareous clay soils, this percentage was (much) lower. MRP is often assumed to represent ortho-P, which suggests that P in the 1:2 water extracts is mainly present as an inorganic species in most soil types. However, release of P from colloids containing Fe, Al, Ca, or Mg or from DOC-(Al, Fe)-P complexes by the acid molybdate reagent can cause an overestimation of the inorganic P concentration (Gerke, 1992; McDowell and Sharpley, 2001; Turner et al., 2004a). After soil drying, MRP in the 1:2 water extracts was on average 2.7 (2002) and 1.5 times (2003) higher across all soil types (based on data for individual samples). Both in 2002 and 2003, a strong linear relationship was found between MRP in the 1:2 water extracts before and after soil drying ($R^2_{\text{adj}} = 82.2$ and 88.0%) (Fig. 1). The increase of MRP due to soil drying can be attributed to the exposure of new desorption sites resulting from the disruption of soil aggregates and mineralization of organic P induced by drying and subsequent rewetting of soil during the water extraction (Chepkwony et al., 2001).

Concentration of MUP in the 1:2 water extracts obtained from the field-moist soils ranged from 0.05–0.10 mg P L^{-1} in the calcareous clay soils to 0.19–0.37 mg P L^{-1} in the reclaimed peat soils (Table 2). MUP is often assumed to represent organic P (e.g., Chardon et al., 1997), although polyphosphates and inorganic P bound to colloids can contribute to MUP as well (Haygarth and Sharpley, 2000). After soil drying, MUP in the 1:2 water extracts was on average 4.8 (2002) and 1.2 (2003) times higher across all soil types (based on data for individual samples). Soil drying had especially a large effect on MUP in the extracts obtained from the peat and noncalcareous clay soils. After drying, MUP was about 10 times higher for the samples from 2002. The increase in MUP can be attributed to the release of organic P to water extracts from soil microbial biomass resulting from osmotic shock and lysis of microbial cells after drying and rewetting of soil (Turner and Haygarth, 2001; Turner et al., 2003). Furthermore, solubilization of organic P through the disruption of soil aggregates by drying and rewetting of soil can play a role (Chepkwony et al., 2001). The effects of soil drying also become apparent in the increase found in DOC for the soils sampled in 2002; values were on average 5.8 times higher across all soil types (based on data for individual samples).

In summary, soil drying resulted in an increase in both the MRP and MUP concentrations in 1:2 water extracts. Based on these results, we decided to use field-moist soil samples for the 1:2 water extraction instead of dry soils to test whether soil P extraction methods can be used to predict P in soil solution under field conditions. In the 1:2 water extracts of the field-moist soils, P was mainly present as MRP, with the exception of the peat and noncalcareous clay soils. The dominance of MRP in soil solution in topsoils of intensively managed agricultural land has been reported many times before (e.g., Chardon et al., 1997). Because the largest part of P in animal manures is contained in inorganic species (e.g., Sharpley and Moyer, 2000), accumulation of P in topsoils mainly takes place in the inorganic form, which is reflected in increased concentrations of MRP in water extracts (Koopmans et al., 2003). With increasing depth, concentration of TP in soil solution decreases, but the contribution of organic P typically increases (Chardon et al., 1997). This has been attributed to the higher mobility of organic P species (Chardon et al.,

TABLE 1
Selected physical and chemical characteristics (average \pm S.D.) and area of agricultural land of the soils sampled in 2002 and 2003 from the major soil types in The Netherlands

Soil type	Area [†]		Year	n	Moisture content [‡] (%)	pH (H ₂ O)	CaCO ₃ (%)	OM (%)	[Al + Fe] _{ox} (mmol kg ⁻¹)	P _{ox} (mg kg ⁻¹)	α^{\S} (%)
	ha	%									
Noncalcareous sand	977,482	41	2002	12	16 \pm 4	6.0 \pm 0.3	ND [¶]	4.3 \pm 0.9	66 \pm 28	394 \pm 111	21 \pm 8
			2003	12	13 \pm 2	6.2 \pm 0.4	ND	5.3 \pm 1.1	98 \pm 31	654 \pm 177	22 \pm 3
Calcareous sand	63,983	2.7	2002	11	15 \pm 6	7.4 \pm 0.2	2.5 \pm 1.7	2.9 \pm 1.8	20 \pm 8	232 \pm 73	38 \pm 10
			2003	11	9 \pm 2	8.0 \pm 0.3	2.1 \pm 1.9	1.6 \pm 0.2	14 \pm 3	206 \pm 51	50 \pm 17
Noncalcareous clay [#]	399,516	17	2002	5	34 \pm 5	6.3 \pm 0.3	ND	12.1 \pm 4.9	133 \pm 12	506 \pm 174	13 \pm 5
Calcareous clay	609,412	26	2002	10	19 \pm 4	7.6 \pm 0.2	4.8 \pm 3.1	4.7 \pm 2.7	84 \pm 29	333 \pm 118	13 \pm 4
			2003	10	17 \pm 2	8.3 \pm 0.3	7.1 \pm 1.8	4.3 \pm 2.4	78 \pm 14	354 \pm 77	15 \pm 3
Reclaimed peat	88,398	3.7	2002	6	21 \pm 3	5.9 \pm 0.1	ND	9.0 \pm 2.8	83 \pm 58	385 \pm 181	16 \pm 4
			2003	2	22 \pm 0	5.9 \pm 0.1	ND	10.3 \pm 0.2	62 \pm 5	309 \pm 30	16 \pm 3
Peat	247,534	10	2002	5	56 \pm 5	5.2 \pm 0.7	ND	46.6 \pm 9.1	387 \pm 70	1403 \pm 101	12 \pm 2
			2003	2	57 \pm 1	5.6 \pm 0.0	ND	48.7 \pm 0.3	402 \pm 18	1207 \pm 164	10 \pm 2

[†]Data from Schoumans (2004); percentage of total agricultural land in The Netherlands.

[‡]Moisture content of field-moist soils determined at 105 °C.

[§]Values of α were calculated as the molar ratio between P_{ox} and [Al + Fe]_{ox}.

[¶]Not determined.

[#]Noncalcareous clay soils were not sampled in 2003.

TABLE 2
Characteristics of the 1:2 (w/v) water extracts obtained from the studied field-moist and dry soils (average \pm S.D.)

Soil type	Year	Condition [†]	n	DOC	Ca	Al	Fe (mg L ⁻¹)	MRP [‡]	TP	MUP [‡]
Noncalcareous sand	2002	Field-moist	12	30.1 \pm 15.6	11.4 \pm 3.5	1.10 \pm 0.32	1.52 \pm 1.55	0.48 \pm 0.39 (70)	0.64 \pm 0.44	0.16 \pm 0.07
	2002	Dry	12	106.0 \pm 41.0	13.6 \pm 4.4	1.42 \pm 0.55	1.32 \pm 1.54	0.61 \pm 0.49 (54)	1.08 \pm 0.61	0.47 \pm 0.25
	2003	Field-moist	12	30.6 \pm 15.5	8.5 \pm 2.9	0.64 \pm 0.15	0.58 \pm 0.52	0.56 \pm 0.33 (68)	0.81 \pm 0.40	0.25 \pm 0.10
	2003	Dry	12	ND [§]	12.8 \pm 2.9	1.10 \pm 0.34	0.72 \pm 0.69	0.66 \pm 0.36 (68)	1.03 \pm 0.58	0.37 \pm 0.32
Calcareous sand	2002	Field-moist	11	19.0 \pm 13.1	29.7 \pm 13.1	0.42 \pm 0.39	0.66 \pm 0.53	0.92 \pm 0.79 (84)	1.06 \pm 0.87	0.13 \pm 0.09
	2002	Dry	11	69.4 \pm 18.3	35.5 \pm 15.2	0.23 \pm 0.19	0.39 \pm 0.32	1.34 \pm 0.75 (76)	0.72 \pm 0.92	0.38 \pm 0.23
	2003	Field-moist	11	13.3 \pm 1.9	28.7 \pm 6.4	0.30 \pm 0.28	0.34 \pm 0.25	1.04 \pm 0.42 (81)	1.28 \pm 0.49	0.24 \pm 0.07
	2003	Dry	11	ND	33.9 \pm 5.2	0.14 \pm 0.13	0.17 \pm 0.09	1.73 \pm 0.73 (93)	1.85 \pm 0.77	0.12 \pm 0.05
Noncalcareous clay [¶]	2002	Field-moist	5	28.8 \pm 4.7	39.6 \pm 27.9	6.18 \pm 8.15	7.44 \pm 9.89	0.16 \pm 0.16 (48)	0.27 \pm 0.22	0.11 \pm 0.06
	2002	Dry	5	168.3 \pm 21.4	62.1 \pm 42.5	5.39 \pm 5.98	4.82 \pm 5.26	0.33 \pm 0.10 (29)	1.12 \pm 0.26	0.80 \pm 0.17
	2002	Field-moist	10	7.8 \pm 7.6	48.4 \pm 12.9	0.49 \pm 0.64	0.40 \pm 0.45	0.33 \pm 0.41 (82)	0.37 \pm 0.44	0.05 \pm 0.04
	2002	Dry	10	65.8 \pm 23.8	71.1 \pm 17.4	0.15 \pm 0.22	0.07 \pm 0.16	0.38 \pm 0.46 (57)	0.58 \pm 0.53	0.20 \pm 0.12
Calcareous clay	2003	Field-moist	10	16.6 \pm 22.1	49.6 \pm 22.5	0.49 \pm 0.30	0.55 \pm 0.33	0.35 \pm 0.30 (75)	0.44 \pm 0.34	0.10 \pm 0.07
	2003	Dry	10	ND	70.4 \pm 43.0	0.45 \pm 0.28	0.32 \pm 0.19	0.54 \pm 0.45 (82)	0.65 \pm 0.56	0.12 \pm 0.14
	2002	Field-moist	6	38.5 \pm 13.4	15.8 \pm 6.9	1.16 \pm 0.37	0.93 \pm 0.85	0.76 \pm 0.54 (77)	0.95 \pm 0.63	0.19 \pm 0.09
	2002	Dry	6	60.2 \pm 13.7	19.9 \pm 7.3	1.50 \pm 0.33	0.87 \pm 0.75	0.92 \pm 0.62 (68)	1.27 \pm 0.75	0.34 \pm 0.16
Reclaimed peat	2003	Field-moist	2	43.2 \pm 19.5	11.3 \pm 1.2	1.09 \pm 0.07	0.71 \pm 0.03	1.27 \pm 0.55 (77)	1.65 \pm 0.68	0.37 \pm 0.13
	2003	Dry	2	ND	21.1 \pm 1.0	1.69 \pm 0.20	0.98 \pm 0.01	1.44 \pm 0.65 (80)	1.79 \pm 0.75	0.35 \pm 0.10
	2002	Field-moist	5	83.7 \pm 17.9	122.7 \pm 18.2	1.48 \pm 1.12	0.88 \pm 0.25	0.04 \pm 0.02 (18)	0.21 \pm 0.04	0.17 \pm 0.02
	2002	Dry	5	248.3 \pm 57.6	77.5 \pm 14.6	2.16 \pm 1.41	1.38 \pm 0.44	0.20 \pm 0.06 (11)	1.88 \pm 0.24	1.68 \pm 0.27
Peat	2003	Field-moist	2	107.1 \pm 64.4	143.2 \pm 1.9	0.97 \pm 0.33	1.04 \pm 0.45	0.07 \pm 0.01 (21)	0.32 \pm 0.01	0.26 \pm 0.01
	2003	Dry	2	ND	76.2 \pm 2.0	2.85 \pm 1.38	2.08 \pm 0.82	0.12 \pm 0.03 (10)	1.23 \pm 0.39	1.10 \pm 0.36

[†]MRP as a percentage of TP in parentheses.
[‡]MUP was calculated as the difference between TP and MRP.
[§]Not determined.
[¶]Noncalcareous clay soils were not sampled in 2003.

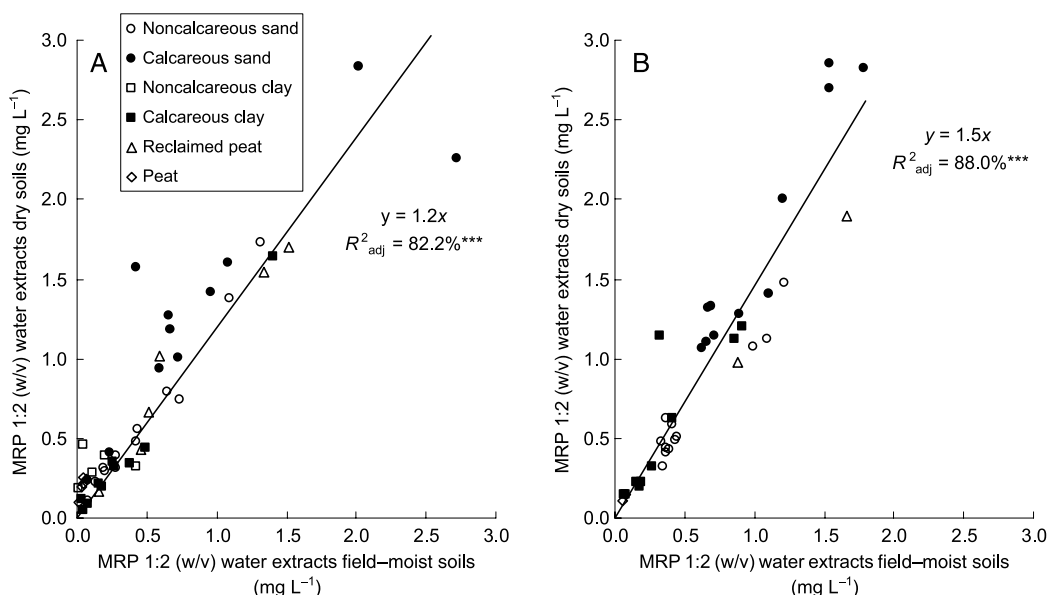


Fig. 1. Relationships between MRP in 1:2 (w/v) water extracts before and after soil drying for 2002 (A) and 2003 (B).

1997; McDowell and Koopmans, 2006; Toor et al., 2003; Turner and Haygarth, 2000). For estimating the potential of a soil for P loss to surface water, the contribution of organic P therefore cannot be neglected. For the purpose of estimating the potential mobility of P in topsoils, however, it is legitimate to focus on MRP. Obviously, to predict MRP in the 1:2 water extracts, extraction methods indicative of the behavior of inorganic P have to be used. As mentioned before, we used CaCl₂, P_w, the FeO-strip method, and the acid ammonium oxalate-based α for this purpose. All methods were first applied on field-moist samples taken in 2002. For a limited number of extraction methods, the relationships found in 2002 were validated on samples taken in 2003.

Relationships Between Soil Phosphorus Extraction Methods and MRP in Water Extracts from Field-Moist Soils

In Tables 1 and 3, the results of the soil P extraction methods used in this study are presented. Largest amounts of P were extracted by acid ammonium oxalate, with smaller amounts extracted by the FeO-strip method, P_w, and CaCl₂; this was also found by Koopmans et al. (2001).

Phosphorus extractable with CaCl₂ shows a strong linear relation with MRP in the 1:2 water extracts ($R^2_{adj} = 78.5\%$) (Fig. 2).

However, the peat and calcareous sandy soils deviated significantly from this relationship. For the peat soils, the measured MRP concentrations in the CaCl₂ extracts were much higher than expected from the linear relationship. This can probably be explained by the large amounts of P_{ox} and [Al + Fe]_{ox} in the peat soils compared to those in the other soil types (Table 1). This may have caused more desorption of P from peat soils to the CaCl₂ extracts than with other soil types, facilitated by the wider soil-to-solution ratio of this extraction method (1:10 [w/v]). After normalizing CaCl₂-extractable P for [Al + Fe]_{ox} and plotting this molar ratio against MRP in the 1:2 water extracts, the peat soils do not deviate anymore from the other soil types (not shown).

In the CaCl₂ extracts of the calcareous sandy soils, P desorption seems to reach a plateau at approximately 4 to 5 mg P kg⁻¹ (Fig. 2). This suggests the presence of a solid Ca-P mineral phase in our calcareous sandy soils controlling the solubility of P in these CaCl₂ extracts. To evaluate whether or not the presence of Ca-P minerals could explain the observed P concentration patterns, a mineral stability plot can be constructed. Although these plots do not provide conclusive evidence for the presence of specific minerals (Shenker and Bloom, 2005), an indication of whether or not a theoretical equilibrium is likely can be obtained. In Fig. 3,

TABLE 3
Soil-extractable P of the studied soils (average \pm S.D.)
Results of acid ammonium oxalate-extractable P (P_{ox}) are presented in Table 1.

Soil type	Year	<i>n</i>	CaCl ₂	P _w	FeO-P
			mg kg ⁻¹		
Noncalcareous sand	2002	12	1.75 \pm 1.45	14.4 \pm 5.2	19.9 \pm 10.1
	2003	12	1.50 \pm 0.92	11.4 \pm 2.3	ND [†]
Calcareous sand	2002	11	2.89 \pm 1.41	11.7 \pm 4.8	14.5 \pm 6.2
	2003	11	3.14 \pm 1.22	8.8 \pm 1.9	ND
Noncalcareous clay [‡]	2002	5	1.11 \pm 0.84	12.4 \pm 5.3	14.4 \pm 5.5
Calcareous clay	2002	10	1.33 \pm 1.37	15.2 \pm 9.7	16.8 \pm 9.6
	2003	10	1.27 \pm 1.24	11.6 \pm 4.7	ND
Reclaimed peat	2002	6	3.35 \pm 2.09	16.1 \pm 4.3	25.4 \pm 7.1
	2003	2	3.60 \pm 1.43	14.6 \pm 4.1	ND
Peat	2002	5	2.66 \pm 1.73	13.7 \pm 4.7	21.7 \pm 6.7
	2003	2	1.01 \pm 0.09	10.9 \pm 3.6	ND

[†]Not determined.

[‡]Noncalcareous clay soils were not sampled in 2003.

we plotted pH and the calculated activities of MRP and Ca in the 1:2 water extracts in a calcium phosphate double function plot to determine which Ca–P mineral most likely controlled P solubility in the calcareous sandy soils. Our data points corresponded most closely to β -tricalcium phosphate and octacalcium phosphate. For confirmation of these indications, however, mineralogical techniques should be used (Shenker and Bloom, 2005). Our results

are typical for soils with a pH > 7 (Pierzynski et al., 1990). Sharpley et al. (2004) found that these compounds also determined P solubility in water extracts of manured soils. At the high Ca concentration as used in the 0.01 M CaCl₂ extracts, dissolution of Ca–P minerals will be limited, which could explain the plateau in Fig. 2.

In Fig. 4A, P_w is plotted against MRP in the 1:2 water extracts. Although separate curves could have been drawn per soil type (not shown), no general relationship could be found, that is valid for all soil types. The lack of a single relationship suggests that the solubility of P in the various soil types studied is controlled by different processes. However, the observed variation in desorption behavior can, for a large part, be explained by differences in the soil content of $[Al + Fe]_{\text{ox}}$. After normalizing P_w for $[Al + Fe]_{\text{ox}}$, a strong, single, nonlinear relationship ($R^2_{\text{adj}} = 90.1\%$) was obtained across all soil types, with the exception of the calcareous sandy soils (Fig. 4B). In noncalcareous sandy soils, sorption of P is known to be dominated by Al-(hydr)oxides and Fe-(hydr)oxides (Beek, 1979; van der Zee and van Riemsdijk, 1988), but also in noncalcareous and calcareous clay and peat soils, these metal-(hydr)oxides play an important role in P sorption (Freese et al., 1992; Solis and Torrent, 1989). A nonlinear relationship such as presented in Fig. 4B can be encountered when two methods that extract different fractions of the amount of reversibly adsorbed P are compared on soil samples exhibiting a range of P accumulation. The nonlinearity of this relationship can be attributed

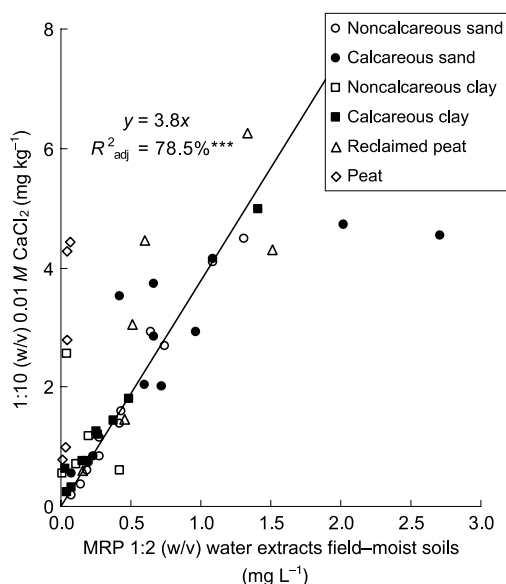


Fig. 2. Relationship between CaCl₂-extractable P and MRP in 1:2 (w/v) water extracts obtained from field-moist soils for 2002. The calcareous sandy and peat soils were not included in the linear relationship.

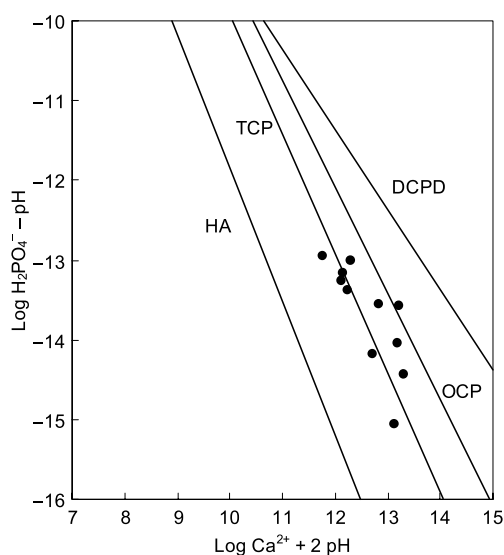


Fig. 3. Calcium phosphate double function plot of solubilities for 1:2 water extracts of calcareous sandy soils, in relation to the following Ca-P minerals: hydroxyapatite, HA; β -tricalcium phosphate, TCP; octacalcium phosphate, OCP; and dicalcium phosphate dihydrate, DCPD.

to the nonlinear character of P (de)sorption (Koopmans et al., 2002; van der Zee et al., 1987). As with CaCl_2 -extractable P (Fig. 2), the data points for the calcareous sandy soils deviate

from the relationship (Fig. 4B). This may be caused by the limited dissolution of Ca-P minerals in 1:2 water extracts. With P_w , a much wider soil-to-solution ratio (1:60 [v/v]) is used, leading to much better Ca-P mineral dissolution (Kleinman et al., 2002). The relatively high MRP concentrations in the P_w extracts from the calcareous sandy soils may also be the result of the presence of colloidal Ca-P minerals (Turner et al., 2004a). A low ionic strength of the P_w extracts from these soils may have increased dispersion of soil, and consequently the detachment of colloidal particles (Koopmans et al., 2005).

The FeO-strip method has been proposed to determine the amount of reversibly adsorbed P (van der Zee et al., 1987). Plotting FeO-P against MRP in 1:2 water extracts leads to the construction of a desorption isotherm. For each individual soil type, the Langmuir isotherm was able to fit the data very well, but the model coefficients varied strongly across the soil types included here (Table 4). After normalization of FeO-P for $[\text{Al} + \text{Fe}]_{\text{ox}}$, a single Langmuir isotherm could describe the desorption isotherm ($R^2_{\text{adj}} = 87.9\%$) across all soil types, with the exception of the calcareous sandy soils (Fig. 5). A desorption isotherm can also be constructed by plotting α (i.e., the molar ratio of P_{ox} and $[\text{Al} + \text{Fe}]_{\text{ox}}$) against MRP in the 1:2 water

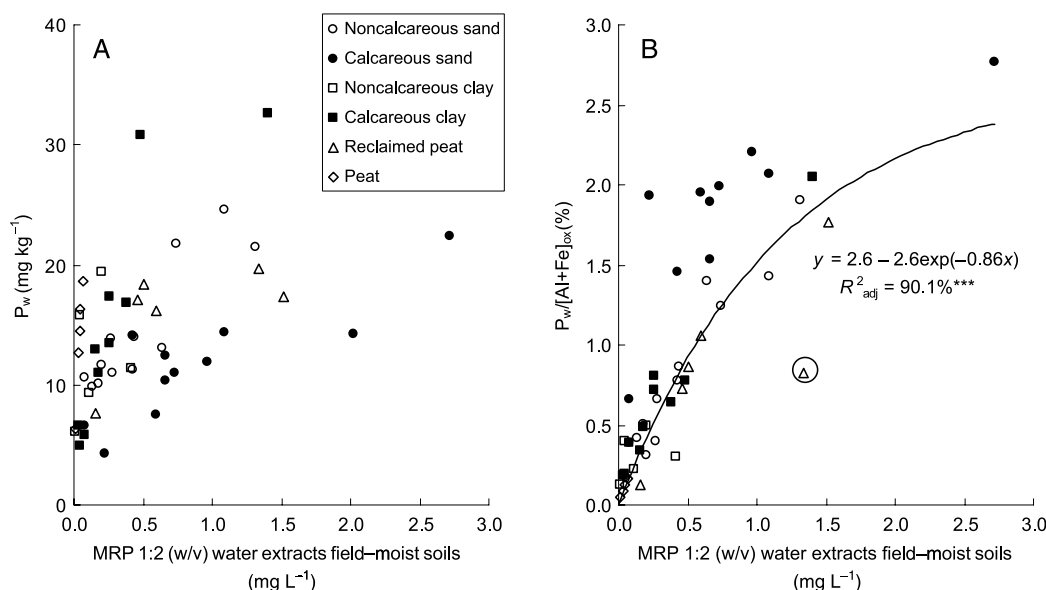


Fig. 4. Relationships between P_w (A) and P_w normalized for $[\text{Al} + \text{Fe}]_{\text{ox}}$ (B) and MRP in 1:2 (w/v) water extracts obtained from field-moist soils for 2002. In panel B, the data point surrounded by a circle was not included in the exponential relationship.

TABLE 4

Values of Q_{\max} and K (\pm S.E.) of the Langmuir isotherm[†] fitted to the relationships between FeO-P and the MRP concentrations in 1:2 (w/v) water extracts obtained from the field-moist soils sampled in 2002[‡]

Soil type	<i>n</i>	Q_{\max} (mg kg ⁻¹)	K (L mg ⁻¹)	R^2_{adj} (%)
Noncalcareous sand	12	51.3 \pm 13.3	1.62 \pm 0.84	68.8***
Calcareous sand	11	27.8 \pm 7.1	1.56 \pm 0.99	46.4***
Calcareous clay	10	44.7 \pm 4.9	2.72 \pm 0.63	92.7***
Reclaimed peat	6	34.2 \pm 5.2	5.59 \pm 3.59	59.8***
Peat	5	34.6 \pm 4.5	52.3 \pm 21.1	91.2***

[†]Langmuir isotherm: $Q = Q_{\max}(KC) / (1 + KC)$, with FeO-P taken as Q and MRP in the 1:2 (w/v) water extracts taken as C .

[‡]Langmuir isotherm did not fit the results of the noncalcareous clay soils.

extracts, where P_{ox} includes both reversibly adsorbed P and strongly sorbed pools (Schoomans and Groenendijk, 2000; van der Zee and van Riemsdijk, 1988; van der Zee et al., 1987). However, even without the calcareous sandy soils, the Langmuir isotherm gave a poor description of these data points ($R^2_{\text{adj}} = 38.2\%$) (not shown). If only the data of the noncalcareous sandy soils were used, the R^2_{adj} of the Langmuir isotherm improved to 84.5%, and the estimated α_{\max} and K values were 40% and 3.4 L mg⁻¹, respectively (not shown). Thus, the applicability of α to predict MRP in 1:2 water extracts seems to be limited to noncalcareous sandy soils. This is not surprising because the concept of α was originally developed for this soil type (van der Zee et al., 1990).

In summary, the soil P extraction methods with the highest ability to predict MRP in 1:2 water extracts across different soil types were CaCl₂, P_w , and the FeO-strip, the latter two both normalized for $[Al + Fe]_{\text{ox}}$. Ideally, an extraction method suitable for monitoring purposes should be able to predict P in soil solution across various soil types. Furthermore, an ideal extraction method should be responsive to changes in the P management of agricultural land. The decrease in α after the implementation of mining soil P as a measure to decrease the risk of P leaching from hot spot areas is expected to be relatively small (Koopmans et al., 2004), which reduces the applicability of α . The relative decrease in soil P extracted with CaCl₂, P_w ,

and the FeO-strip method is expected to be much larger (Koopmans et al., 2004). Furthermore, an ideal method suitable for monitoring purposes should be a simple, routine method that can be easily and rapidly determined in private or public laboratories. The FeO-strip method, however, is rather laborious and therefore too time consuming and expensive for routine use. Based on these findings, we selected CaCl₂ and P_w normalized for $[Al + Fe]_{\text{ox}}$ for further research in 2003. An important aspect was the validation of the relationships of these extraction methods with MRP in the 1:2 water extracts obtained in 2002 using the data from 2003.

Validation of Relationships Between Selected Soil Phosphorus Extraction Methods and MRP in Water Extracts from Field-Moist Soils

In Fig. 6, CaCl₂-extractable P is plotted against MRP in 1:2 water extracts for the soils sampled in 2003, combined with the relationship found in 2002. The calcareous sandy and peat soils deviate again from the relationship found in 2002. In Fig. 7, a comparable plot is given for P_w normalized for $[Al + Fe]_{\text{ox}}$, and again the calcareous sandy soils deviate. However, also the noncalcareous sandy and the

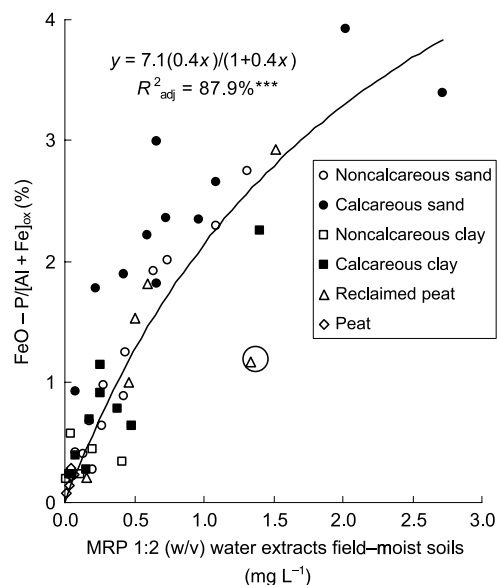


Fig. 5. Relationship between FeO-P normalized for $[Al + Fe]_{\text{ox}}$ and MRP in 1:2 (w/v) water extracts obtained from field-moist soils for 2002. The data point surrounded by a circle was not included in the Langmuir isotherm.

reclaimed peat soils sampled in 2003 deviate from the relationship established in 2002 and the measured MRP concentrations in the 1:2 water extract are consistently higher than predicted. A possible explanation for this deviation is the noticeable difference in weather conditions between 2002 and 2003. In 2002, total rainfall measured during the first 9 months of the year on six locations across The Netherlands amounted to 639 ± 48 mm (average \pm SD). In 2003, total rainfall was only 407 ± 65 mm (Royal Dutch Meteorological Institute, 2004). Thus, the soils in 2003 were subjected to much dryer conditions, but apparently, before sampling soils must have been rewetted by rainfall as we did not find differences between the moisture content of the soil samples from 2002 and 2003 (Table 1). As mentioned before, P can be released to water extracts by drying and rewetting of soil and this may partly become available as MRP. Due to the increased drying–wetting intensity in the field in 2003, MRP in the 1:2 water extracts obtained from the field-moist soils sampled in 2003 may be higher than expected based on the relationships found in 2002. This could also explain why soil drying had a larger effect on the concentrations of MRP and MUP in the 1:2 water extracts in 2002 compared to 2003 (Table 2). In 2003, the

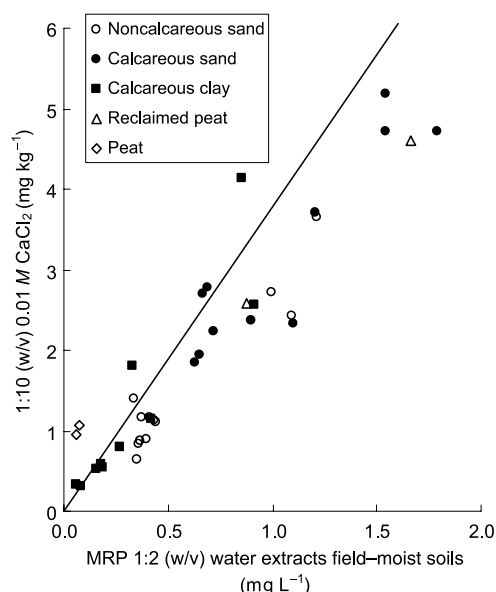


Fig. 6. Relationship between CaCl_2 -extractable P and MRP in 1:2 (w/v) water extracts obtained from field-moist soils for 2003. The line represents the model fitted to the results from 2002.

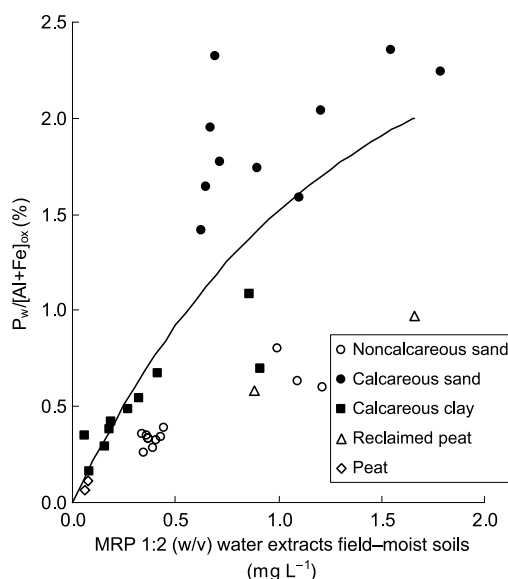


Fig. 7. Relationship between P_w normalized for $[\text{Al} + \text{Fe}]_{\text{ox}}$ and MRP in 1:2 (w/v) water extracts obtained from field-moist soils for 2003. The line represents the model fitted to the results from 2002.

soil probably had already undergone a cycle of drying and rewetting in the field before sampling. Therefore, in the field-moist soils sampled in 2003, the amounts of soil microbial biomass and unstable soil aggregates may have been smaller, resulting in a smaller effect of soil drying.

Based on our study, it is difficult to decide which soil P extraction method is most suitable to assess risk of P loss from agricultural soils, and whether one extraction method suffices for all soil types. Using normalized for P_w $[\text{Al} + \text{Fe}]_{\text{ox}}$, the risk of P loss is assessed with two extractions, whereas CaCl_2 requires only one. This seems to be an advantage because costs play a role in the selection of a suitable extraction method for monitoring purposes. On the other hand, determination of P_{ox} together with $[\text{Al} + \text{Fe}]_{\text{ox}}$ gives an indication of the accumulation of the total potentially available amount of P and the binding capacity of the soil for P. This is important when measures are considered to reduce the environmental risk of a specific field, for example, mining soil P (Koopmans et al., 2004; van der Zee et al., 1992) or increasing the binding capacity of the soil via the application of water treatment residuals to decrease the solubility of P (Elliott et al., 2002). Beauchemin et al. (1996) suggested to use two parameters, P_w

and the molar ratio of P_{ox} and $[Al + Fe]_{ox}$, to fully access the risk of contamination of drainage waters by leaching. In calcareous sandy soils, however, MRP seems to be in equilibrium with solid phases of β -tricalcium phosphate and octacalcium phosphate. It should be tested whether a single water extraction (e.g., P_w) suffices for determining the environmental risk for these soils. However, in addition to the estimation of MRP in soil solution of peat and noncalcareous clay soils, estimates of MUP seem to be important. For both soil types, concentrations of MUP in the 1:2 water extracts exceeded those of MRP (Table 2), and an extraction method only determining MRP will not suffice. Our results indicate the importance of drying and rewetting on the potential loss of P from topsoils. This is in accordance with results reported by Turner et al. (2003). In the latter study, drying and rewetting cycles of organic soils controlled the transport of P to surface water, occurring mainly in the form of organic P. Further research is needed on the environmental risk of MUP in soil solution, especially on the influence drying and rewetting may have on MUP.

CONCLUSIONS

- Soil drying resulted in a significant increase in the MRP and MUP concentrations measured in the 1:2 (w/v) water extracts, especially in the peat and noncalcareous clay soils.
- Phosphorus in the 1:2 water extracts obtained from the field-moist soils was mainly present as MRP. Thus, to predict MRP in soil solution, soil P extraction methods indicative of the behavior of inorganic P can be used. However, this is apart from peat and noncalcareous clay soils because MUP dominates in the 1:2 water extracts obtained from these soils.
- Differences in desorption behavior (P_w and $FeO-P$) between the noncalcareous sandy, noncalcareous and calcareous clay, reclaimed peat, and peat soils can be explained to a large extent by differences in soil content of $[Al + Fe]_{ox}$.
- Methods with the highest ability to predict MRP in the 1:2 water extracts were $CaCl_2$ -extractable P and P_w normalized for $[Al + Fe]_{ox}$. However, for the peat and noncalcareous clay soils, a separate relationship has to be developed, which requires more research on MUP in soil solution.
- In calcareous sandy soils, MRP is probably in equilibrium with solid phases of β -tricalcium phosphate and octacalcium phosphate. The calcareous sandy soils deviate significantly from the above mentioned relationships. It should be tested whether a single water extraction (e.g., P_w) suffices for determining the environmental risk for these soils.

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