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Iron oxide impregnated filter paper (P_i test): a review of its development and methodological research

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Abstract

Iron oxide impregnated filter paper (FeO paper) has been used to study the availability of phosphorus (P) to plants and algae, P desorption kinetics and P dynamics in the field. Since its initial development a number of differences in the method of preparation of the paper and its application have been implemented. The purpose of this article is to (i) critically review studies on the various aspects of both preparation and use of the FeO paper and (ii) to suggest a standardized procedure.

Type of filter paper, FeO impregnation of the filter paper, neutralization of $FeCl_3$, washing and drying of the impregnated paper, all have a significant effect on the amount of P sorbed. It is suggested that the method for neutralization of $FeCl_3$ is checked on the release of acid when FeO paper is used, because the acid can release P compounds that would otherwise not desorb. Washing after neutralization is essential to remove loose FeO particles, which otherwise will cause incomplete P recovery. Modifications of the desorption procedure itself also affect the amount of P sorbed onto the paper. The ionic strength of the shaking solution, surface area of the FeO paper and the number and position of the paper in the shaking solution, and shaking strength and time all may introduce variations in the amount of P on the FeO paper. Differences in the dissolution of the Fe compounds on the filter paper and the subsequent determination of P in the solute may contribute to variations in P recovery. It is illustrated that the existing variation in the preparation and use of the FeO paper will cause differences in the amount of P extracted from soils, impeding the comparison of different studies.

Finally, we recommend a standardized procedure for the preparation and use of the FeO paper. Such a procedure will allow comparison between studies and may reduce or circumvent possible artefacts.

Introduction

The availability of phosporus (P) in soil or surface water for biota (e.g. plants or algae) has been studied extensively, and numerous tests for available P have been developed and used. These tests can roughly be divided into four categories: (1) shaking with acid solutions which dissolve P compounds or with (buffered) alkaline solutions which displace P from the soil, (2) measuring exchangeable P, using ^{32}P, (3) shaking with dilute salt solutions or water, which simulate the soil solution, and (4) as (3), with a sink added, acting more or less analogous to the withdrawing behaviour of a plant root. The use of resin beads as a sink for P was introduced by Amer et al. (1955). Stronger sinks for P were developed by Hsu and Rich (1960) and by Robarge and Corey (1979) who affixed hydroxy-Al to a cation exchange resin. This resin was used for the prediction of algal-available P in runoff by Huetll et al. (1979), Wendt and Corey (1980), Mueller et al. (1984) and Andraski et al. (1985). Since the method is laborious, it has not developed into a practical method (T.C. Daniel, pers. communication). Moreover, Dorich et al. (1985) found that results of chemical extractions correlated much better with algal uptake than those of the resin method.

Iron (hydr)oxide impregnated filter paper (FeO paper, also known as P_i paper or HFO paper) was initially developed for soil chemical studies. The amount of P already sorbed by the soil must be taken into account when determining an adsorption isotherm. This amount can be estimated by curve-fitting or it can be determined directly by, e.g., using a sink method like anion resin (Barrow, 1978). As a simpler alternative for resin, the FeO paper was developed by Sissingh in 1977. For fertilizer recommendations a water extraction procedure is used in the Netherlands (Sissingh, 1971). However, in tropical soils this method often results in very low amounts of extracted P, causing analytical problems. Therefore, FeO paper was added as a sink during the extraction. Since the use of water as an extractant gave too much dispersion of the soil and contamination of the FeO paper with soil particles, 0.01 *M* $CaCl_2$ was chosen as an alternative for water.

Although the description of the preparation of the FeO paper and its application was only published in an internal report (Sissingh, 1983), its use became widespread. The application for plant availability studies was reviewed by Menon et al. (1990), and the use for water quality studies was described by Sharpley et al. (1995).

Since the initial development of the FeO paper, a number of modifications in the method of preparation of the FeO paper and its application have been implemented. Some of these modifications cause differences in the amount of P extracted from soils, thus impeding the comparison of different studies. Also, a number of studies were published on various aspects of the method. This article critically reviews these studies on the various aspects of both preparation and use of the FeO paper, in a historical perspective. Suggestions are given for standardization of the procedure and for further research.

1. Initial procedure / method

The method proposed by Sissingh (1983) can be summarized as follows:

A. take a 15-cm disc of ash-free, hard filter paper (e.g. Schleicher & Schuell 589^5 red ribon),

B. cut paper to a rectangle (12×12.5 cm^2), and wax 1.25 cm at two ends using paraffine; thus leaving an uncovered rectangle of 12×10 cm^2; (for the purpose of waxing see step H),

C. immerse the paper in 0.37 *M* $FeCl_3$, acidified with 1.32 *M* HCl L^{-1},

D. let the paper drip dry at room temperature for 1 h,

E. pull the paper rapidly and uninterrupted through a bath containing 2.7 *M* NH_4OH (5% w:v) to neutralize the $FeCl_3$ and produce amorphous iron (hydr)oxide (ferrihydrite, denoted as FeO),

F. rinse the paper with water to remove adhering particles of FeO,

G. after air drying, cut the paper into 2×12.5 cm^2 strips, having a reactive surface of 2×10 cm^2 and two waxed ends of 1.25 cm each,

H. shake 1 g of soil in 40 ml 0.01 *M* $CaCl_2$ end-over-end at 30 rpm during 16 h, with one filter paper in a fixed position, mounted with the waxed ends on a holder attached to the cap of a 100 ml bottle,

I. take out the filter paper, rinse with distilled water to remove adhering soil particles, and let it dry at room temperature,

J. dissolve the FeO with adsorbed P by shaking 1 h in 40 ml 0.1 *M* H_2SO_4,

K. determine P in the acidic extract; the amount of P is called Pi-value, expressed in mg P (or P_2O_5) kg^{-1} soil.

Slightly modified, this version of the method was also published by Menon et al. (1989a).

In the following, studies dealing with various aspects of the preparation and use of the FeO paper are summarized and discussed. The material is grouped into chapters on preparation of the FeO paper, shaking of soil with FeO paper, and determination of P on FeO paper. We conclude with suggestions for further research.

2. Preparation of FeO paper

2.1 *Type of filter paper*

Hard filter paper was chosen by Sissingh to prevent damaging of the paper during shaking; ash-free paper was chosen because ash components can be released either when the paper is immersed in the acidified $FeCl_3$ solution (see 2.2) or when the FeO is dissolved in H_2SO_4 (Sissingh, 1983). Lin et al. (1991) investigated eight types of filter paper and found differences between these filter papers in the final Fe content (range 79–163 μmol strip^{-1}) and in the amount of P adsorbed (range 7.2-11.1 μmol strip^{-1}) on the paper. Buselli (1994) and Myers et al. (1995) showed that the use of filter papers with relatively large pores may lead to contamination of the paper with soil particles during the shaking procedure (see also 4.1).

Summarizing, we recommend the use of ash-free and hard filter paper with small pores.

2.2 *Impregnation with $FeCl_3$*

Menon et al. (1989b) suggested to replace part of the 0.37 *M* $FeCl_3$ with $AlCl_3$ in order to test if this would increase the sorption capacity of the paper. However, replacing Fe with Al was found to reduce the amount of P extracted from soils, so $AlCl_3$ was not recommended. Van der Zee et al. (1987) and Buselli (1994) used 0.4 *M*, Kuo and Jellum (1994) used 0.54 *M*, Lin et al. (1991) and Myers et al. (1995) used 0.65 *M* $FeCl_3$ for immersion. A higher concentration of $FeCl_3$ would make it more difficult to attain uniform impregnation; also, thick FeO precipitates are prone to detach from the paper (Lin et al., 1991).

Lin et al. (1991) investigated the effect of the $FeCl_3$ concentration on the amount of Fe deposited on the strips and on the amount of P adsorbed. The Fe content of the strip increased linearly with the $FeCl_3$ concentration (Fig. 1A), but slightly more than according to the 1:1 line. The more than proportional increase can be an effect of a decrease in surface tension of the $FeCl_3$ solution at higher concentrations. In Fig. 1B the dotted line shows P adsorption on the paper if this would depend linearly on its Fe content, but the amount adsorbed is clearly lower. The data correspond well with the solid line, which represents an increase in P adsorbed equal to the square root of the increase in Fe content. This can be explained as follows. A microscopic image of the strips shows brown, cylindric fibers, impregnated and coated with FeO. The volume of these cylinders increases with increasing FeO content of the strips. The surface area (calculated as $1 . 2\pi r$, with 1 = length, r = radius of the cylinder) of the cylinders increases with the square root of the increase in volume ($1 . \pi r^2$). Thus, the P adsorbed on the strips seems to be proportional to the surface area of the coated fibers, and not to the total amount of iron in the strips.

Schwertmann and Cornell (1991) mention the fact that $FeCl_3.6H_2O$ is hygroscopic; therefore, testing of the Fe content of the $FeCl_3$-solution is advisable.

No duration of the period of immersion in $FeCl_3$ was mentioned in the original procedure of Sissingh (1983). Menon et al. (1989c) mention that the filter paper is drawn through the solution. Buselli (1994) used three consecutive immersions of 30 s, Kuo and Jellum (1994) used one immersion of at least 10 min, Sharpley et al. (1994) 1 h, and Myers et al. (1994) left the filter paper overnight in the $FeCl_3$. The effect of the immersion period was investigated by Lin et al. (1991): increasing the period from 0.5 to 2.3 h increased the final amount of P adsorbed by 8%; longer periods gave no further increase.

Some studies mention acidification of the $FeCl_3$ solution with HCl (Sissingh, 1983; Menon et al. 1989a), other studies do not (Van der Zee et al., 1987; Lin et al., 1991; Sharpley, 1993; Buselli, 1994), so this step may be arbitrary (Myers et al., 1995). However, even at room temperature some nucleation of goethite can take place in an $FeCl_3$ solution (Schwertmann and Cornell, 1991), and this will decrease the P sorption capacity of the FeO paper. Acidification will strongly retard the formation of goethite, and is therefore recommended when the solution is kept for a longer period.

2.3 *Treatment with NH_4OH and subsequent washing*

Kuo and Jellum (1994) used an immersion time in NH_4OH of 45 s, since a too short period caused incomplete FeO formation with a variable Fe content. During immersion, gentle agitation proved to produce more consistent results. Buselli (1994) used three consecutive immersions of 10 s, after which the paper was air-dried and the immersions were repeated (see below).

Myers et al. (1994) found that immersion of the $FeCl_3$ paper in NH_4OH for 30 s was sufficient; immersion times of 30 and 180 s gave the same amounts of P extracted from eight soils. During immersion the filter paper was inserted between two holders of fiberglass screen, clasped together with clips. This had the advantage that 25 filter papers could be treated at the same time. Vertical immersion gave a more uniform coating; however, it was not shown that a uniform coating influences the result of P extraction. Eye protection is recommended because of the hazardous nature of NH_4OH (Myers et al., 1994).

For the preparation of ferrihydrite the pH should not exceed 8 to avoid conversion to more crystalline compounds like goethite or hematite (Schwertmann and Cornell, 1991). The pH of the 2.7 *M* NH_4OH solution exceeds 12, thus a longer immersion time might induce formation of crystalline Fe compounds.

As an alternative for drawing the paper through a bath containing NH_4OH, Menon et al. (1989d) introduced exposure of the paper to NH_3 vapor, which gave a more uniform deposition of FeO on the filter paper than the use of an NH_4OH solution, as indicated by

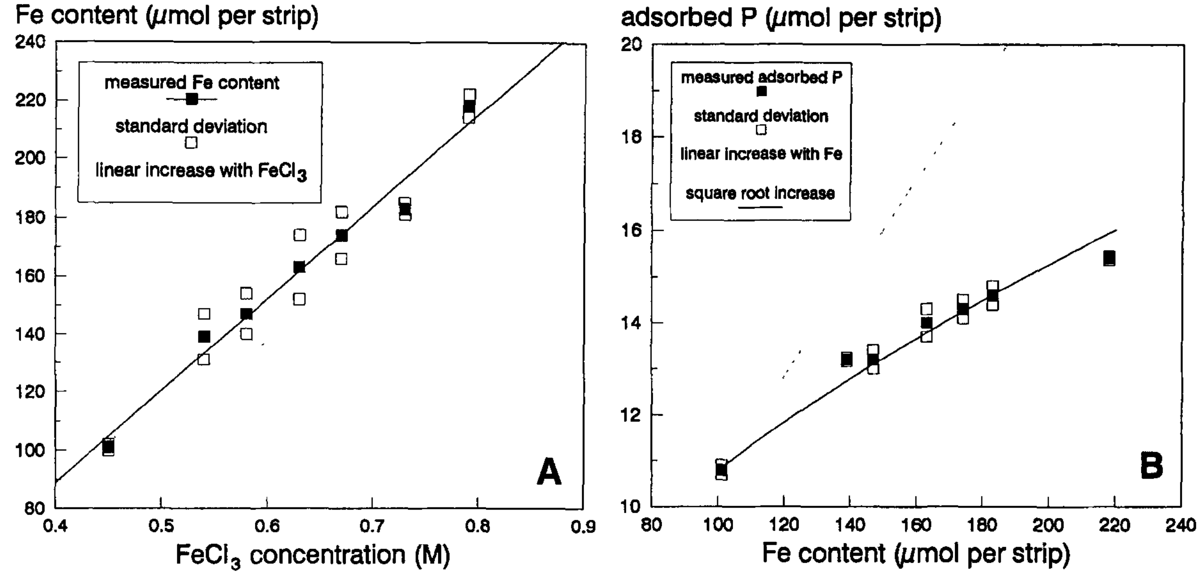

Figure 1. Effect of $FeCl_3$ concentration on the iron content of an FeO strip (A), and of the iron content on P adsorption (B). The iron content increases more than proportional with the $FeCl_3$ concentration; P adsorption does not increase linearly with Fe (dotted line), but is proportional to the square root of the increase in Fe content (solid line). Data of Lin et al. (1991).

the color. More P was extracted using vapor than using the solution for three soils out of four treated with triple superphosphate. The standard deviation was lower when vapor was used with three of the four soils.

Washing the paper after neutralization of the $FeCl_3$ was recommended to remove loosely adhering precipitates, which can be released during shaking with a soil suspension. When NH_3 vapor was introduced as an alternative for NH_4OH, Menon et al. (1989c) simplified the procedure of preparation by omitting washing. As a consequence, NH_4^+ and Cl^- ions will remain on the surface of the paper. Next, the NH_4Cl will dissolve again when a soil solution is shaken with the paper, thereby increasing ionic strength. Moreover, because $NH_4{}^+$ is a weak acid, its dissociation lowers pH. Thus, it is recommended that also the paper prepared with NH_3 vapor be washed with water to remove NH_4Cl.

Perrott and Wise (1993), using unwashed FeO paper prepared with the vapor method, showed that adding the FeO paper to a soil suspension lowered pH. Shaking a paper with water gave a pH of 3.6. This pH lowering was attributed to aging of $Fe(OH)_3$: if part of the Fe in the precipitate on the paper is coordinated with Cl^-, this can be replaced with OH^- from solution, thus lowering pH of the solution (Lahann, 1976). Myers et al. (1995) also found that the pH of a soil suspension, when shaken using unwashed paper prepared with NH_3 vapor, was lower than the original soil pH. This was the case for two soils with a low buffering capacity, but not for a highly buffered soil. Buselli (1994) found that when filter paper was neutralized in NH_4OH during one cycle (3 × 10 s) both H^+ and Cl^- were released thereafter when the FeO paper was shaken in distilled water. The use of two neutralization cycles reduced the release of H^+ and Cl^-. However, in the procedure of Buselli the FeO paper was dried before washing, which may have reduced the effectiveness of washing.

Bramley and Roe (1993) compared both neutralization methods and the influence of washing. When the paper was shaken in a $CaCl_2$ solution containing 20 μg P ml^{-1}, they found that unwashed paper released more Fe than washed paper, which lowered the adsorption of added P on the paper. The variation coefficient of adsorbed P was lowest with washed paper neutralized with NH_4OH.

Summarizing, washing the paper after neutralization is an essential step, regardless of the neutralization procedure.

2.4 Drying

Lin et al. (1991) compared oven-drying (70–75°C) of the strips with air-drying and found that oven-drying during 2 h decreased the amount of P adsorbed on the paper by 9% (18% after 25 h drying). This decrease must be attributed to the partial conversion of ferrihydrite into hematite during heating in the oven (Lewis, 1992). Air-dry storage does not seem to influence the binding capacity of the paper. Robinson et al. (1994) found no differences in binding of P between paper that was stored for 100 weeks and paper that was used immediately. Myers et al. (1994) neither found difference in P binding between paper stored air-dry for 0 or 120 days. When paper was stored in water in the refrigerator until use, the recovery from the paper after shaking with a solution containing 500 μg P was somewhat larger than from paper stored air-dry. However, 500 μg P in solution is much beyond the amount that is generally present in 1 g of soil, and approaches the sorption maximum of the paper (see 3.2). Long-term storage of FeO paper can affect the dissolution of Fe after use (see 4.2).

Summarizing, the paper should be air dried after washing. Storage for a longer period does not affect the P sorption capacity of the paper.

2.5 General characteristics of the FeO paper

Van der Zee et al. (1987) measured that a 20 cm^2 paper strip has a BET-specific surface (paper and hydroxide) of 1.5 m^2; it contains approximately 120 μmol Fe. For this determination, Schleicher and Schuell 602 h filter paper was used and 0.4 *M* $FeCl_3$.

Menon (1992) found an Fe content of 160-170 μmol strip^{-1} using 0.37 *M* $FeCl_3$ and NH_3 vapor for neutralization. Lin et al. (1991) investigated eight types of filter paper and, using a 0.45 *M* $FeCl_3$ solution, and found Fe contents ranging from 79 to 163 μmol strip^{-1}. Increasing the concentration of the $FeCl_3$ solution from 0.45 *M* to 0.79 *M*, increased the Fe content of a 20 cm^2 Whatman no. 50 strip from 100 μmol to 218 μmol strip^{-1}. Kuo and Jellum (1994) also used a Whatman no. 50 strip, and immersion in 0.54 *M* $FeCl_3$ during 10 min, and found 109 ± 9 μmol Fe per strip. Buzelli (1994) used Whatman no. 42 and 0.4 *M* $FeCl_3$, and found 143 ± 15 μmol Fe strip^{-1}.

Summarizing, a variety of filter papers is used in practice, containing different amounts of Fe, which may lead to different amounts of extracted P for the same soil.

3. Shaking of soil with paper

3.1 Shaking solution

A solution of 0.01 *M* $CaCl_2$ was initially chosen as extraction medium in order to reduce dispersion of the soil, and thus reduce contamination of the FeO paper (Sissingh, 1983). However, a concentration of 0.01 *M* Ca^{2+} is higher than in most soil solutions, and it is known that increasing the Ca^{2+} concentration or ionic strength reduces the desorption of P from soils (Barrow and Shaw, 1979; Traina et al., 1986). Van der Zee et al. (1987) used a solution containing 5.10^{-3} *M* $CaCl_2$ and 5.10^{-4} *M* KCl, which more approaches the soil solution. Kuo and Jellum (1994) compared P sorption on FeO paper using different shaking solutions (10^{-4}, 10^{-3}, 10^{-2} and 0.1 *M* $NaNO_3$). Above 10^{-3} *M* less P was sorbed from three soils when the concentration of $NaNO_3$ increased. However, it is also possible that this decrease in sorption was caused by a decrease in contamination of the paper, due to a decrease in dispersion of the soil (see 4.1).

Buselli (1994) determined the effect of pH of the $CaCl_2$ solution on the binding of P from solution (520 μg P in 80 ml). Above pH 6.5 sorption of P onto the FeO paper decreased, and at pH $\geq$ 10 colloidal precipitates were visible. This implies that comparing data from calcareous soils with data for neutral or acid soils has to be done with care.

3.2 Number of strips

Sissingh (1983) found that increasing the surface area of FeO paper increased the amount of P desorbed from the soil. A 20 cm^2 FeO paper strip has a sorption capacity of about 18 μmol P without leaving measurable P in solution (Van der Zee et al., 1987). When 1 g of soil is extracted, this corresponds with about 550 mg P kg^{-1} soil. Buselli (1994) found a comparable sorption capacity. In most cases, the use of one strip would thus suffice for binding all P that desorbs when the external concentration is kept at a very low level. Nevertheless, Van der Zee et al. (1987) also found that the use of four strips resulted in a larger amount of P desorbed than the use of one strip. This increase was attributed to a faster decrease in the P concentration in solution, thus giving slow desorption processes the chance to proceed longer. Lin et al. (1991) also determined the effect of the number of strips on the amount of P desorbed. They found a maximum P desorption with four strips. Four strips extracted 50% more P than one strip from a sandstone-shale alluvial soil, and 30% more from a slate alluvial soil. Menon (1992) compared the amount of P extracted from four soils by FeO paper with different surface areas (5, 10, 20, 40 and 80 cm^2). Increasing the surface from the standard size (20 cm^2) increased the amount of P extracted. A practical problem of using more than one strip is that they have a tendency to stick together, which reduces the effective surface area. Without justification, Yli-Halla (1989) used three strips, Kuo and Jellum (1994) used five strips per gram of soil.

Myers et al. (1994) used 5.5-cm diameter circles (23.8 cm^2 surface). The use of these circles instead of strips avoids the time-consuming cutting of 15-cm circles into strips (Myers et al., 1995). Cutting is also a source of variation in the final Fe content of the strips (Kuo and Jellum, 1994). Myers et al. (1994) compared P extracted from five soils using either one or three circles. In contrast with the studies mentioned above, only one soil showed more P extracted with three circles. However, with this specific soil also the amount of soil retained on the FeO paper increased. Thus, when contamination of the filter paper with soil particles cannot be prevented, or removed after shaking (see 4.1), it is difficult to interpret the real influence of increasing the surface of FeO paper because the risk of contamination is proportional to the surface area of the paper (Myers et al., 1994). Additionally, imperfectly hydrolyzed FeCl_3 could also be partly responsible for the apparent relationship between the number of strips and the amount of P extracted.

In the short term, the rate of sorption of P onto the FeO paper will mainly depend on the transport velocity of P from the soil particles towards the paper, which in turn will depend on the efficiency of mixing of the solution. The use of more strips, and the form of the FeO paper (strip or circle), will probably enhance mixing, thus having an indirect influence on the kinetics of P desorption from the soil.

Summarizing, a number of studies indicate that increasing the number of FeO strips increases P desorption from soil. However, it is unclear whether this effect is partly the result of an increased bias due to contamination of the paper with soil particles.

3.3 Position of strips during shaking

Initially, a fixed position of the FeO paper was chosen to reduce direct contact between soil and paper, thus minimizing abrasion of the paper. The paper was mounted on a holder attached to the cap of a glass bottle (Sissingh, 1983). This was considered as a complicated procedure, and simplifications were introduced. Menon et al. (1989c) enclosed the paper in nylon mesh bags. This was also done by Whelan et al. (1994), their bags had apertures from 25 to 150 μm. Buselli (1994) mounted a square paper on a slide mount (without glass covers). Yli- Halla (1989), and Kuo and Jellum (1994) used no protection. All authors let the strips move freely in the solution.

Myers et al. (1995) mention as a possible problem of shaking with a loose paper strip that it can adhere to the flask during shaking, reducing P uptake by the strip. Placing the paper between circles of polyethylene screen (925 μm), and leaving this in a fixed position during shaking, reduced contamination of the paper with soil particles and P loss from the paper due to erosion by sand particles. For these reasons, both protection of the strips and a fixed position during shaking is recommended. The position during shaking can also affect mixing of the suspension, and thus enhance P desorption from the soil. This aspect should be studied by measuring the decrease in P concentration with time when pure P solutions are shaken with FeO paper.

3.4 Soil:solution ratio, shaking strength

A soil:solution ratio of 1:40 is used in most studies. Buselli (1994) and Myers et al. (1995) used a ratio of 1:80. Sissingh (1983) compared P sorption on FeO paper at ratios of 1:30 and 1:60 for one soil; the lower ratio was less effective. Menon (1992) compared sorption from ten soils at ratios of 1:5, 1:10, 1:20, 1:40 and 1:60. Generally, the amount of P sorbed tended to increase when the ratio decreased, but decreased again at the lowest ratios. Compared with a high ratio, a lower ratio will promote P desorption from the soil by dilution. However, at very low ratios sorption of P on the FeO paper will be hampered by the increased diffusion distance to the paper.

The original procedure of shaking end-over-end at 30 rpm (Sissingh, 1983) was changed by Menon et al. (1989c) to the use of a reciprocating shaker at 180 oscillations min^{-1} (opm). Menon (1992) mentions both shaking end-over-end at 30 rpm and reciprocating shaking at low speed (180 opm). Perrot and Wise (1993) used a rotary shaker at 24 rpm, Kuo and Jellum (1994) used a platform shaker at 120 opm, and Whelan et al. (1994) mention that they rolled the suspension gently. Buselli (1994) found that a mixing rate of 300 rpm (orbital shaking) caused more erosion of the paper than a rate of 150 rpm.

Barrow and Shaw (1975) measured P desorption in 0.01 *M* $CaCl_2$ using different shaking strengths, and found that the use of a reciprocating shaker at 240 opm gave a different desorption behavior of P than shaking end-over-end at 30 rpm. They attributed this to the breakdown of soil particles and the exposure of new surfaces when the reciprocating shaker was used; in their study this caused re-adsorption of previously desorbed P. Using FeO paper breakdown of soil particles would probably cause more P extracted by the paper. Although the wide variation in shaking conditions may affect the amount of P sorbed on FeO paper, to our knowledge this aspect has never been studied. In summary, a shaking strength should be chosen which gives enough mixing of the solution without breaking down of soil aggregates.

3.5 Shaking time

Sissingh (1983) observed that increasing extraction time, up to 64 h, increased the amount of P extracted. However, the rate of release decreased. An extraction time of 16 h was chosen by Sissingh (1983) because these results gave the best correlation with uptake of P in a pot experiment, and because of its convenience in the laboratory. Van der Zee et al. (1987) stated that a period of 20 h is reasonable to assess the total amount of desorbable P. However, their data also showed a continuing desorption of P, even after 60 h (Fokkink, 1983). Continuous desorption between 20 and 50 h was found for five soils by Myers et al. (1994); after this period, only one soil still showed further desorption. Myers et al. (1995) found for one out of three soils that measurable amounts desorbed between 16 and 24 h. Testing four soils, Menon (1992) found that desorption was complete after 16 h; Sharpley (1993) found the same for four samples of runoff sediment.

A sandy, a loamy sand and a loess soil were extracted for up to 21 days by shaking gently 1 g of soil with 40 ml 0.01 *M* $CaCl_2$ end over-end at 4 rpm. One FeO strip was used in a fixed position. Shaking ended after 1, 3, 7 or 21 days; for the 21 day period the strip was refreshed after 7 and 14 days. Fig. 2 shows the cumulative amount of P desorbed as a function of time. For all soils it was found that desorption continued after 1 day, but for the sandy and loess soils the rate appeared to decrease much faster than for the sandy loam soil.

Barrow and Shaw (1975) found that desorption of P continued after 96 h when soil was shaken with 0.01 *M* $CaCl_2$ at a low soil:solution ratio. Lookman et al. (1995) used a sink method in which FeO was put in a dialysis membrane because the mechanical stability of FeO paper during longer desorption times (weeks) was doubted. Using this technique, it was found that desorption of P continued for up to 67 days.

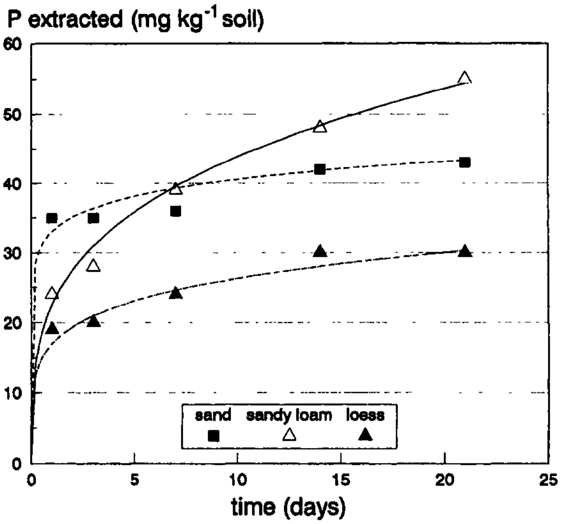

Figure 2. Effect of time on the cumulative amount of P extracted from a sandy, a loamy sand and a loess soil by one FeO strip (Chardon, unpubl. results). The rate of extraction for the sandy loam soil decreased much faster than for the sand and loess soil.

A complicating factor in prolonged desorption studies is the possible breakdown of soil particles, especially when the soil is shaken vigorously. In that case the continuation of desorption can at least partly be ascribed to exposure of new desorption sites. Shaking gently will prevent soil breakdown, but will also decrease the kinetics of P sorption on the FeO paper. Summarizing, the statement that 16 h is sufficient to measure all desorbable P (Van der Zee et al., 1987) seems to be true for a minority of the soils. For plant-availability studies, we recommend a shaking time of 16 h. For the determination of total desorbable P (much) longer shaking times must be used.

4.0 Determination of P on FeO paper

4.1 Contamination of FeO paper with soil particles

After shaking with soil, the FeO paper must be washed to remove adhering soil particles because any acid soluble P adhering to the paper will be included in the Pi-value. Sissingh (1983) clearly showed that a 0.01 *M* $CaCl_2$ solution gave much less dispersion of the soil and contamination of the FeO paper compared with water as an extractant solution. Similar results, using either $CaCl_2$ or a mixture of KCl, $MgCl_2$ and $CaCl_2$ were obtained by Buselli (1994). Myers et al. (1995) showed that contamination with soil particles after shaking in a soil suspension was higher on filter paper with large pores (Whatman 541, 20-25 μm) than with small pores (Whatman 50 (2.7 μm) or Schleicher & Schuell 589 rr (2-5 μm)). Contamination was also found to be influenced by the way of shaking (see 3.3). Buselli (1994) also found that paper with large pores (Whatman 541, 20-25 μm) was more contaminated than paper with small pores (Whatman 42, 2.5 μm). The problem of adhering soil particles was also investigated by Perrot and Wise (1993). Soil particles adhered to Whatman 541 filter paper (pores 20-25 μm) could partly be removed by ultrasonic treatment, which, however, also removed part of the P sorbed from a P solution. Perrot and Wise (1993) doubted if the presence of adhering soil particles reduces the effectiveness of FeO paper as plant-availability- test because P present in soil particles on the FeO paper might also be available for plants.

Whelan et al. (1994) used an air brush to remove adhering soil particles and showed, using SEM, that hardly any Si was left on the filter paper, indicating that all contamination was removed.

Summarizing, contamination of the FeO paper complicates the interpretation of methodological work and of most applications. It can be reduced by using filter paper with small pores and protecting the filter paper with a mesh screen in a fixed position. Further testing of the air brush technique is highly recommended.

4.2 Dissolution of FeO

Van der Zee et al. (1987) increased the time of shaking with H_2SO_4 from 1 to 4 h because not all P was recovered after 1 h. They used 0.2 M H_2SO_4 instead of 0.1 M; the 0.2 M value was also adopted by Lin et al. (1991) and Myers et al. (1995). Pierzynski et al. (1994) used 0.4 M H_2SO_4. Perrot and Wise (1993) compared 0.1 M and 0.5 M H_2SO_4 and found no differences in amount of P dissolved from the paper during 1 h. To our knowledge, the necessity of a concentration > 0.1 M has not been shown yet; it has neither been proven that all Fe dissolves during 1 h in 0.1 M H_2SO_4. Increasing the Fe content of the paper (see 2.2) will increase the time or amount of H_2SO_4 needed to dissolve all Fe. As P mainly adsorbs on the surface of the FeO coating (see 2.2), a complete recovery of the adsorbed P can be obtained even when not all Fe has been dissolved (see 4.3).

Myers et al. (1994) found that the Fe dissolution was much faster in H_2SO_4 when the FeO paper had been stored moist until use than when stored air-dry, indicating that some conversion of the FeO had taken place. This was probably due to the formation of hematite or goethite from ferrihydrite by dehydration, which is promoted by high temperature and low humidity (Schwertmann, 1988).

Buselli (1994) used 0.25 M $NH_2OH.HCl$ - 0.25 M HCl, which is suitable for the selective dissolution of amorphous Fe (Chao and Zhou, 1983). This solution was chosen because it leaves more crystalline Fe compounds intact, thus reducing the influence of crystalline-embedded particles. When FeO papers were stored for 70 days the fraction of total Fe that could be dissolved in $NH_2OH.HCl$ - HCl was halved, which indicates a partial conversion of the Fe into more crystalline compounds (Buselli, 1994).

Robinson and Sharpley (1994) showed that organic P compounds are also bound by FeO paper. Due to the large binding capacity of the paper, adsorption of organic P will not have a negative effect on the binding of inorganic P. However, during the treatment with H_2SO_4 organic P compounds can hydrolyze, as was the case with sodium inositol hexaphosphate (NaI6P), leading to an over-estimation of inorganic P. Therefore, when NaI6P is present in large amounts, Robinson and Sharpley (1994) suggested to use NaOH to dissolve P from the FeO paper, leaving the FeO unimpaired. However, since NaI6P is strongly bound in soils, it will probably not often disturb the use of FeO paper for availability studies.

4.3 Recovery of P

After shaking a P solution with an FeO paper most P will be adsorbed on the paper and a small part will remain in solution. The sum of the amounts of P determined on the paper and in the solution can be defined as the recovery of P. Perrot and Wise (1993) measured the binding of 99% of the total amount of 290 μg P in 40 ml after 17 h. Whelan et al. (1994) determined more than 99.5% binding from 20 μg P in 40 ml. Bramley and Roe (1993) investigated the effect of the neutralization method and washing after neutralization on the amount of P bound by a FeO strip, also using 20 μg P in 40 ml (see 2.3). Their results are summarized in Table 1. The highest recovery was found with neutralization using NH_4OH followed by washing, the lowest with

NH_3 vapor without washing. In all three studies 0.1 *M* HSO_4 was used for 1 h to dissolve the FeO, which thus seems to be sufficient to completely dissolve P from the paper (see 4.2).

In our own laboratory P solutions with initial concentrations between 0.05 and 3.2 mg P L^{-1} were shaken with one FeO paper strip for 24 h. The strips were put in 40 ml 0.1 *M* H_2SO_4, and were shaken by hand several times over 2 h. Using ^{32}P, it could be shown that on average only 1% of the P was left on the filter paper after the acid treatment; this percentage was independent of the initial P concentration. Higher concentrations of H_2SO_4 or longer shaking times were not tested (Chardon, unpubl. results).

Sharpley (1993) and Robinson and Sharpley (1994) used paper prepared with a NH_4OH solution; no final washing was mentioned in their description of the preparation. Initial amounts between 40 and 200 μg P in 50 ml were used, giving removal percentages > 99.9%; however, only 90% of P was recovered from the strip at low amounts of P added (40-120 μg P), increasing to 98% at higher amounts (160-200 μg P). Robinson et al. (1994) also used non-washed paper; when it was shaken with 50 ml solution containing between 0.5 and 150 μg P not all P was recovered on the strip: above 2.5 μg P the percentage recovered decreased from 94% to 90%. A possible explanation of these results is the binding of P to loose FeO particles. This P will generally not be included when the P concentration in the shaking solution is determined, unless the FeO particles are dissolved before P determination.

Summarizing: a single FeO paper strip is able to bind more than 99% of P in solution within 17 h. However, washing of the strip after NH_4OH treatment is necessary to remove adhering salts and precipitates of FeO, which will remove P from solution without being measured on the FeO paper. It has to be investigated whether washing paper prepared with NH_3 vapor will solve the problem of the lower recovery of P.

5. Recommended procedure / method

In order to make results of studies using FeO paper for plant-availability tests comparable, the following procedure is recommended.

Use hard and ash-free filter paper, with small pores. Immerse the paper in 0.37 *M* $FeCl_3$ (acidified if the $FeCl_3$-solution is kept for a long period), and let the paper drip dry at room temperature for 1 h. Pull the paper rapidly and uninterrupted through a bath containing 2.7 *M* NH_4OH to neutralize the $FeCl_3$, rinse the paper with water to remove adhering particles of FeO, and let the paper air dry. Use paper, either rectangular or circular, having a reactive surface of 20 cm^2. Shake 1 g of soil in 40 ml 0.01 *M* $CaCl_2$ during 16 h, with one filter paper in a fixed position and protected by polyethylene screen. Take out the filter paper, thoroughly rinse with distilled water to remove adhering soil particles, and let it dry at room temperature. Dissolve the FeO with adsorbed P by shaking 1 h in 40 ml 0.1 *M* H_2SO_4, and determine P in the acidic extract.

For the determination of the total pool of desorbable P, the strength of the $FeCL_3$-solution can be increased, more strips can be used and/or a longer shaking period.

6. Concluding remarks

The use of FeO paper in P availability and desorption studies has become widespread in recent years. However, types of filter paper used, ways of preparation of the FeO coating, and ways of shaking with a soil suspension vary greatly (Myers et al., 1995). These variations in procedure can strongly influence the result of the determination of desorbable P, making comparisons between different studies extremely difficult.

The following conclusions can be based on the foregoing:

- unless the use of an air-brush has proven to remove all adhering soil particles, contamination of the paper should be minimized by:
  - using filter paper with small pores, and by
  - protecting the filter paper with a mesh screen in a fixed position;
- the capacity of the paper can be increased by using a stronger $FeCl_3$ solution;
- washing after neutralization is essential to remove salts and loose FeO particles;
- breakdown of soil particles should be avoided during shaking with soil, but good mixing of the solution is necessary.

7. Research needs for further standardization of the procedure

Contamination of the FeO paper with soil particles may lead to an over-estimation of desorbed P. This phenomenon makes it difficult to interpret results of some methodological studies. Therefore, the promis-

Table 1. Effect of neutralization method and washing on P recovery by FeO strips (data Bramley and Roe, 1993)

Neutralization method	NH_4OH	NH_3 vapor	NH_4OH	NH_3 vapor
Washing after neutralization	yes	yes	no	no
P recovery on strip (%)	98.2	94.6	79.8	28.3
Standard error recovery (%)	0.4	2.0	0.4	2.1

ing results of the use of an air-brush to clean the FeO paper after shaking should be tested further.

Results on the desorption of P during longer periods are conflicting; some studies showed no further release after e.g. 16 h, other studies show a continuous release during weeks. Therefore, the soil factors which determine the long-term desorption kinetics should be quantified.

The form of the FeO paper (strip or circle) and its position during shaking (fixed or free moving) may influence mixing rate. In turn, mixing rate affects P adsorption on the paper, and thus influences the kinetics of P desorption from soil. These aspects should be studied by measuring the decrease in P concentration with time when pure P solutions are shaken with FeO paper.

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