Relationship between phosphorus availability and phosphorus saturation index

W.J. Chardon

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DLO Instituut voor Agrobiologisch en Bodemvruchtbaarheidsonderzoek
Oosterweg 92, Postbus 129,
9750 AC HAREN

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Addresses:

Location Wageningen:
P.O. Box 14, 6700 AA Wageningen
The Netherlands
Phone (+)31.8370.75700
Fax (+)31.8370.23110
e-mail postmaster@ab.agro.nl

Location Haren:
P.O. Box 129, 6750 AC Haren
The Netherlands
Phone (+)31.50.337777
Fax (+)31.50.337291
e-mail postmaster@ab.agro.nl

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1. Introduction

Under the project "Non-avoidable decrease in soil phosphorus availability" it was assumed that a relationship exists between the Pw value (Sissingh, 1971) and the phosphorus (P) saturation index (Lexmond et al., 1982). Such a (lineair) relationship was used by Schoumans et al. (1991). Based on existing knowledge about the soil chemical behaviour of P and on existing datasets remarks are being made on this (assumed) relationship.

2. Theoretical background

Inorganic phosphorus in the soil is distributed over the soil solution and over the solid compounds. For the total amount of P the symbol T can be used, leading to the mass balance equation:

$$T = g.Q + v.C \qquad (1)$$

g = weight soil (kg), Q = adsorbed P (mMol kg^{-1}), v = volume (l),
C = P in solution (mMol l^{-1}).

The relationship between the concentration of P in solution (C) and the content in the solid phase (Q) is usually described with an adsorption isotherm: Q = f(C). The so-called Freundlich equation is often used for this purpose:

$$Q = k.C^n \qquad (2)$$

The Langmuir equation can also be used:

$$Q = Q_{max} \frac{K.C}{1 + K.C} \qquad (3)$$

where k, n, K and Q_{max} are parameters, calculated using regression.

In terms of an adsorption isotherm, the Pw value (the P concentration in a 60:1 (v:v) water:soil extract, expressed in mg P_2O_5 l^{-1} soil) can be seen as a measure of C, the P concentration in the soil solution.

However, it is more difficult to express the Phosphorus Saturation Index (PSI) in these terms. The PSI is defined as:

$$PSI - \left| \frac{P}{Fe + Al} \right|_{ox} \qquad (4)$$

where P, Fe and Al denote the amount of each element dissolving in an acid extract of ammoniumoxalate/oxalic acid, expressed in mMol/kg. The extraction procedure was developed by Tamm (1922) and further developed by Schwertmann (1964) and McKeague & Day (1966). The PSI-index was first used by Beek (1979) for the estimation of the capacity of a soil to retain P from wastewater applied to a soil. It is assumed that P only adsorbs to amorphous hydroxides which dissolve in the oxalate extract, and that the PSI will have a maximum; when this maximum is approached relatively more P will dissolve. It is also assumed that Fe and Al, dissolving in the oxalate extract, have the same capacity to adsorb P. However, the Al in the extract can partly originate from clay minerals like kaolinite, which have a low sorption capacity for P (J. Bril, pers. comm.).
From 308 field measurements of Pw and Pox (see par. 3.1) it was calculated that, on average, v.C accounted for only 0.03% of Pox. For this purpose the following relationship was used, which is valid during the determination of Pw, in which 1 cm^3 soil is shaken with 60 cm^3 of water (Van Noordwijk., et al, 1990):

$$Pw = 71 \,.\, 60 \,.\, C \tag{5}$$

where $Pw = \text{mg } P_2O_5 \text{ dm}^{-3}$ soil and $C = \text{mMol P l}^{-1}$

When this equation is used to calculate C from Pw, a correction has to be made for the solid:solution ratio in a field situation, for which a ratio of 1:0.3 can be assumed. A further assumption was made that an increase in the soil:solution ratio from 1:60 to 1:0.3 has a limited effect on C, due to the buffering capacity of the soil. An increase in C by a factor 3 would show that v.C accounts for only ≈ 0.1% of Pox. Thus, in the mass balance equation (1):

$$T = g.Q + v.C$$

the term v.C is negligible compared with g.Q, and the following approximation can be made:

$$T \approx g.Q \tag{6}$$

Introducing the Freundlich equation (2), and rearranging gives:

$$C = k' \,.\, T^m \tag{7}$$

with $m = 1/n \ (m > 1)$ and $k' = (k.g)^{-m}$

implying that, when C is plotted on a double-log scale against T, this gives a linear relationship, and thus also when Pw is plotted against Pox or PSI.

When the Langmuir equation (3) is combined with equation (6), it gives:

$$T = g.Q_{max}. \frac{K.C}{1 + K.C} \tag{8}$$

Rearranging yields:

$$C = \frac{T}{K.g.Q_{max} - K.T} \tag{9}$$

which is an equation of the form:

$$C = T / (a'-b'.T) = a.T / (1-b.T) \tag{10}$$

When $b.T \ll 1$ this gives a straight line, with slope a, and when b.T approaches 1, C increases sharply.

Both equations (7) and (10) were tested on field data. Results are given in the following paragraphs.

In practice, the parameters of adsorption isotherms vary, influencing the relationship between Pw and PSI. As an example, the effect of a variation of the Freundlich parameters on this relationship is shown.

Calculations were made for the amounts of soil and solution used for the determination of Pw (1 cm^3 soil and 60 ml water). The value of Pw can then be calculated from C using equation (5). As denoted above, the value of PSI is determined by oxalate extraction. During this, both the adsorbed P (Q) and the P that would normally be in solution (C) is extracted by the oxalate; the sum of both, Pox, equals the total amount of P:

$$\mathrm{Pox} = T = g.Q + v.C = g.k.C^n + v.C \tag{11}$$

g = weight 1 cm^3 soil (kg), Q = adsorbed P (mMol kg^{-1}), v = volume (0.06 l), C = P in solution (mMol l^{-1}), k and n parameters Freundlich equation.
Soil density was assumed to be 1.2 kg l^{-1}. From Pox, PSI follows by definition (eqn. 4); for (Fe+Al)ox a value of 30 mMol kg^{-1} was used.

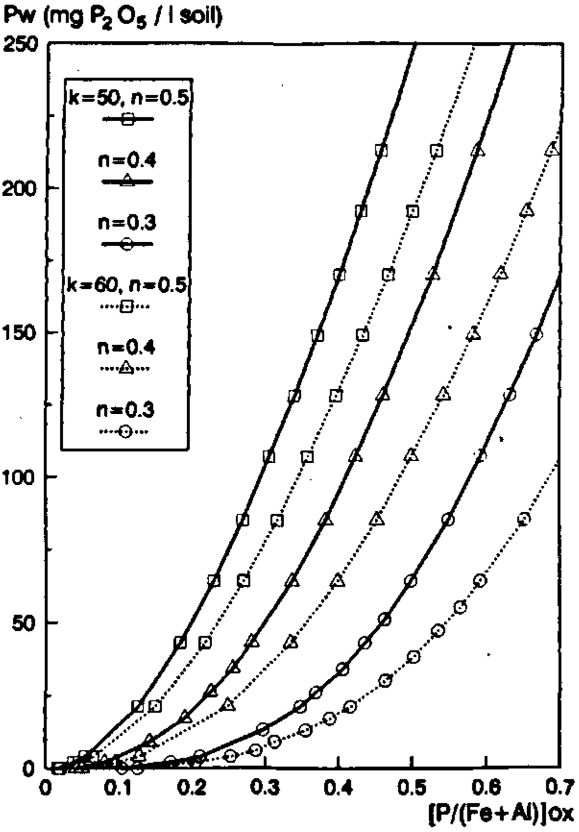

Figure 1. Effect of Freundlich parameters k and n on calculated relationship between Pw and PSI.

Figure 1 shows the calculated relationship between Pw and PSI. For k the values 50 and 70 (l kg^{-1}) were taken and for n the values 0.5, 0.4 and 0.3. The figure shows that the value of Pw decreases when k increases or when n decreases. Both changes in parameters cause a stronger sorption of P, and thus a decrease of Pw. In practice k will vary, e.g. through the effect of pH: lowering the pH will increase k, and Pw will decrease.

Figure 2 shows how the relationship between Pw and PSI will change with time in case the equation of Barrow & Shaw (1975) is used for the description of the effect of time on the Freundlich parameter k:

$$k = k_{t=1} \cdot t^m \tag{12}$$

where $k_{t=1}$ = k at t = 1 (e.g. year), and m = parameter; in the literature values for m between 0.1 and 0.3 are given.

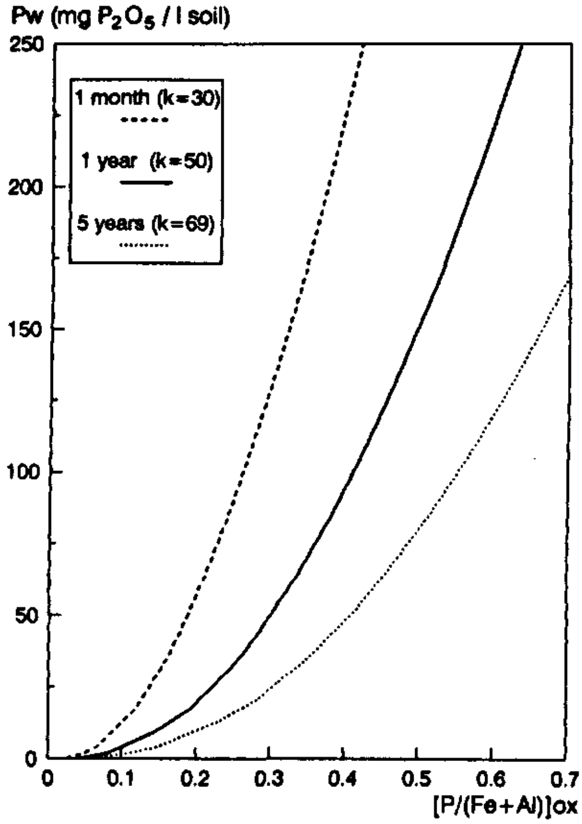

Figure 2. Effect of time, via Freundlich parameter k, on calculated relationship between Pw and PSI.

Figure 2 gives, with $m = 0.2$, $k_{t=1} = 50$ and $n = 0.4$, lines for k after 1 month ($k = 30$), 1 year ($k = 50$) and 5 years ($k = 69$), respectively. Again, the increase of k with time gives a decrease of Pw, and gives a 'band' for the relationship shown in the figure. In practice this has to be taken into account since P, analyzed in field samples, will often be applied at different periods before sampling, and thus will have had different periods of incubation.

3. Field data

Four datasets are available for testing equations (7) and (10).

The first dataset is given by Lexmond et al. (1982) and contains plough layer and sub-soil samples (0-50 cm) of 84 locations on -mostly- sandy soils. A small part of the samples were taken on clay soils or organic soils; soils which received animal manure as well as reference soils were sampled.

The second dataset was published by Schoumans et al. (1991). All samples were taken from the plough layer (0-30 cm) of both sandy and organic soils.

The other two datasets contain data from samples taken from the sandy loam soil of the AB-DLO experimental farm in Haren (Hesterberg et al., 1993).

The third dataset is formed by a combination of sampling events on field plots where different amounts of pig manure were applied previously (an experiment of De la Lande Cremer). Sampling depths were both 0-20 and 20-30 cm. A small number of the samples were taken in 1975/1977, the largest part was taken in 1988/1989, as described by Del Castilho et al. (1993).

The fourth set contains (unpublished) data of samples of an experiment carried out by Bril and Blaauw (AB-DLO) in 1990. On a small plot (12 m^2) a large amount of pig manure was applied, corresponding with 65 t (wet) manure per hectare (10.7 t dry matter). The amount of P applied was 255 kg/ha. The manure was mixed through the top 5 cm of the soil. Samples were taken during 120 days after mixing; the soil was dried, sieved, and Pw and PSI were determined.

3.1 Field data: different soil types

Data from several soil types (dataset 1 and 2) were published and interpreted by the respective authors.

A power function relationship (eqn. 7) between Pw and PSI was calculated by Lexmond et al. (1982) for the plough layer samples ($n = 84$); they found a b value of 1.2 with a (visual) lack of fit.

Schoumans et al. (1991) calculated similar parameters, giving a b value of 1.55 ($r^2 = 0.63$). They also fitted a linear relationship between Pw and PSI, and used this for the calculation of the Pw value that corresponds with a given PSI value (0.125). However, their dataset hardly contains any samples at lower Pw values (< 20).

There are several ways to calculate a line through both datasets:
1. using linear regression after conversion of Pw and PSI,
2. using unweighted non-linear regression,
3. using weighted non-linear regression.

The weight assigned to each measurement is based on the fact that low Pw values are less reliable than high values. The standard deviation (s) of a Pw value was assumed to follow the equation: $s = 0.75 + 0.04*Pw$ (Lepelaar, pers. comm.). The weight was calculated as ($1/s^2$).

The parameters of the Freundlich type line (eqn. 7) could be calculated in all three ways; linear regression could be applied to log(Pw) versus log(PSI). Linearization of eqn. (10) is possible after conversion to 1/C (1/Pw) and 1/T (1/PSI). However, it is known from the literature that this procedure is very sensitive to deviations of datapoints from the fitted line; it appeared that no reliable parameters could be calculated for eqn. (10) this way. Table 1 shows the parameters calculated for both line types using the different procedures. The lines F1, F2, L1 and L2 (for explanation see Table 1) are plotted in Figure 3. In the range 0 < PSI < 0.4 there is little difference between the four lines; at higher values of PSI the prediction of Pw according to L2 is higher.

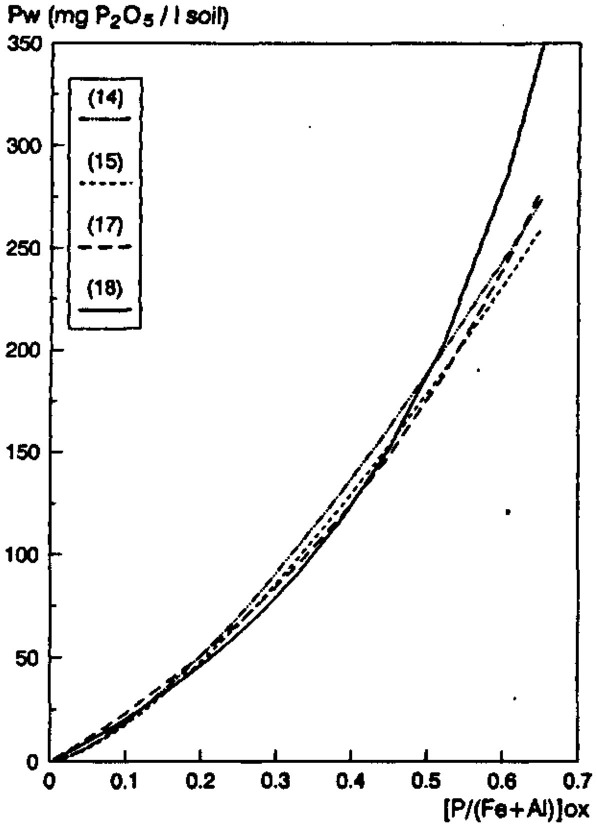

Figure 3. Calculated relationship between Pw and PSI, using different fitting procedures.

Table 1. Fitted parameters of equations of the Freundlich (F) type: $y = a.x^b$ and the Langmuir (L) type: $y = a.x/(1-b.x)$

Line	Type	Linearized	Weighted	a	b	r^2
F1	F	yes	no	505	1.426	0.80
F2	F	no	no	481	1.433	0.87
F3	F	no	yes	481	1.432	0.80
L1	L	no	no	216	0.763	0.87
L2	L	no	yes	184	1.009	0.79

Table 1 shows that the parameters of line F2 and F3 are similar, so that weighting has no effect on the non-linear fitting of the Freundlich type curve. In the following, only the parameters of line F2 will be used for the description of the relationship between Pw and PSI.

When Pw is plotted, according to line F1 (see Table 1), against Pox instead of Pox/[Fe+Al]ox, this gives a relationship with $r^2 = 0.66$. The correction for the sorption capacity, [Fe+Al]ox, thus gives a better relationship.

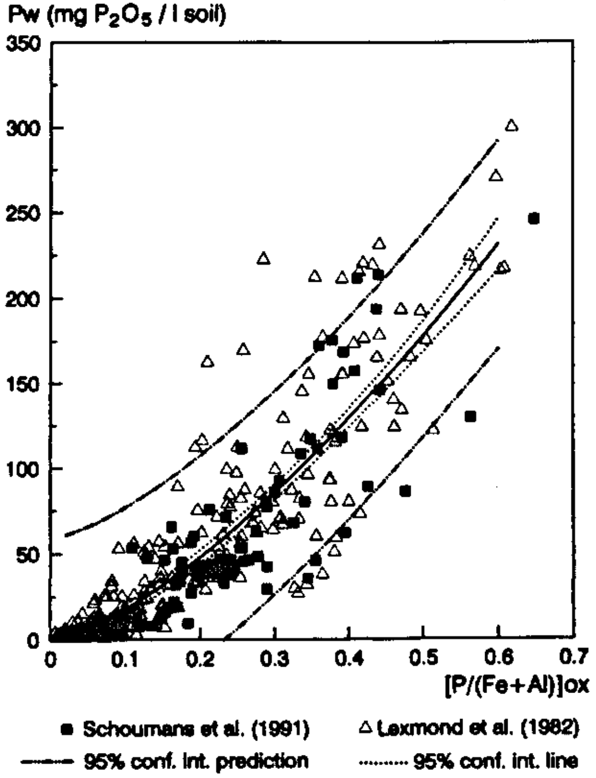

Figure 4. Relationship between Pw and PSI, using the data as given by Schoumans et al. (1991) and Lexmond et al. (1982)

Figure 4 shows all data of both Lexmond et al. (1982) (n = 234) and Schoumans et al. (1991) (n = 74). The data show a band of points around an average line, which is drawn with the (95%) confidence interval of the line and of the predictions of Pw.

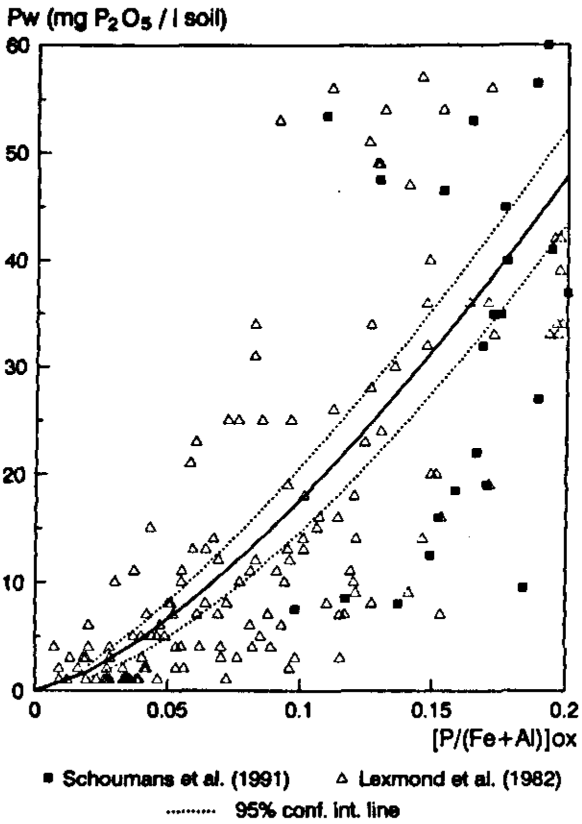

Figure 5. As Figure 4, only data from the low concentration range are shown, with the line as calculated for the complete dataset.

The data points with Pw < 60 and 0 < PSI < 0.2 are shown in Figure 5, with the curve as calculated for all data. The deviation between data and the curve is very large, and the calculation of Pw at a given value of PSI is questionable. Nevertheless, when this is done for PSI = 0.125 a value of 24 is found for Pw. This value differs strongly from Pw < 10, wich was the value found when the linear relationship of Schoumans et al. (1991) was used.

The shape of the band with data points corresponds with Figure 1 and 2, and indicates a compilation of curves. The complete dataset originates from a large number of locations, with their own characteristic form of Fe- and Al-hydroxides and (presumably) a different pH. Both lead to different values of the Freundlich parameters k and n, and thus to a different relationship between Pw and PSI.

Lexmond et al. (1982) give descriptions of the soil profiles from which their samples were taken. For six groups of samples the parameters of line F1 were fitted.

Table 2. Parameters for the equation log(Pw) = a + b.log(PSI) calculated for different locations from Lexmond et al. (1982); n = number of samples.

Code	Profile	Location	n	a	b	r^2
MER	1–6	Merselo	12	2.385	1.186	0.93
BAR	1–6	Barneveld	12	2.659	1.457	0.91
MIL	1–2	Milheeze	18	2.726	1.892	0.95
YSS	1–8	IJsselstein	29	2.766	1.414	0.93
BAEX	1–6	Baexem	25	2.782	1.786	0.94
AST	3–10	Asten	16	2.887	1.702	0.77

Table 2 presents: the name of the location (taken from the report), the code and the numbers of the profiles, the number of samples used for fitting, the values of the parameters of the function log(Pw) = a + b.log(PSI), and the r^2 value.

Table 2 shows that the r^2 values are rather high when only a limited amount of -more coherent- data is analyzed.

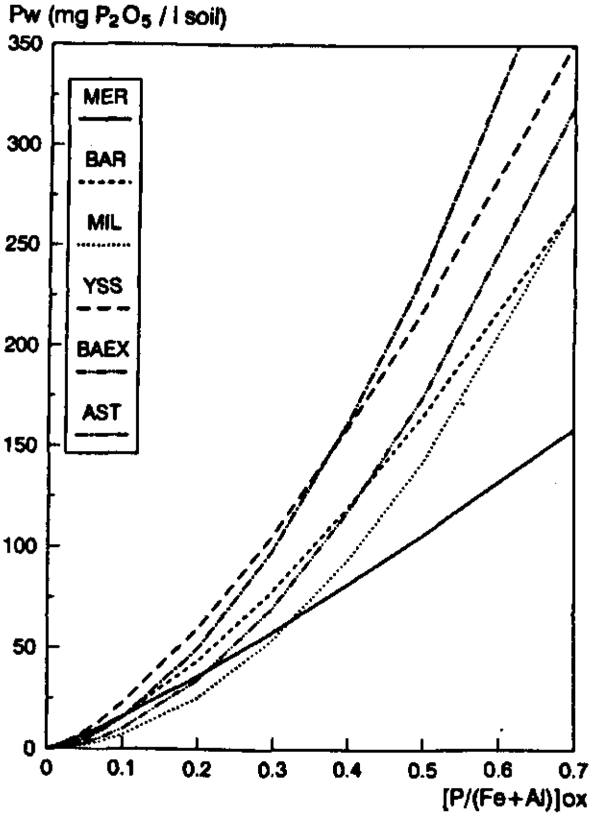

Figure 6. Calculated relationships between Pw and PSI for coherent subsets of the dataset of Lexmond et al. (1982).

Figure 6 shows the different curves, using the values of a and b from the table. It follows from the figure that the six curves diverge, especially at a higher PSI level. This justifies the hypothesis that the deviation of data points from the mean curve, as shown in Figure 4, is mainly caused by the use of data from different locations for the calculation of the (mean) curve.

3.2. Field data: sandy loam soil

Pw and PSI (datasets 3 and 4) were determined in samples taken at the experimental AB-DLO farm in Haren. In Figure 7 both datasets are presented in one figure, with the calculated line, using line F1 (see Table 1).

$$Pw = 633 \,.\, PSI^{1.957} \qquad n = 98 \qquad r^2 = 0.86$$

This relationship has a higher r^2 value than calculated for the combined datasets 1 and 2 (r^2 = 0.80), which can be ascribed to the fact that all samples were taken from the same soil.

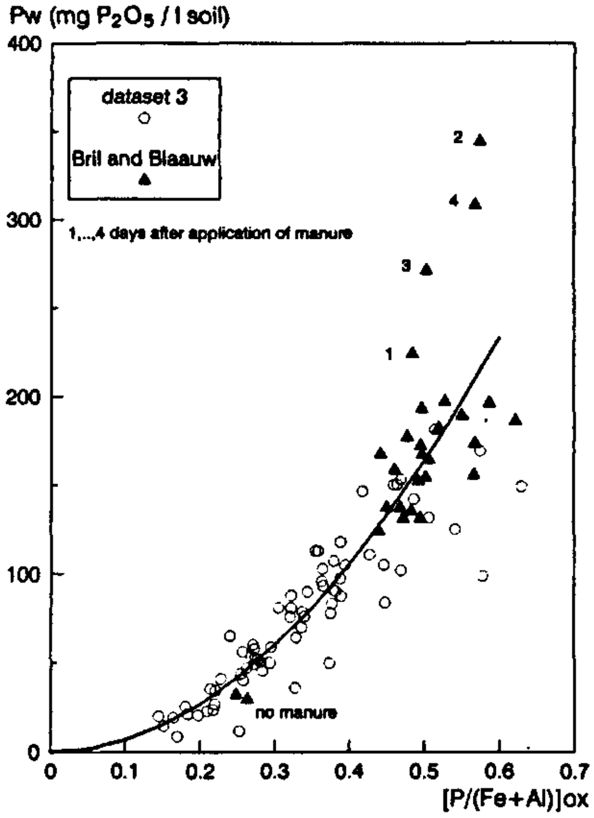

Figure 7. Relationship between Pw and PSI, calculated using dataset 3 and the data from the experiment by Bril and Blaauw.

A number of datapoints from the experiment of Bril and Blaauw strongly deviate from the calculated line, however. These points are designated in the figure with numbers, indicating the number of days the samples were taken after application of manure. It is clear that after 1, 2, 3 and 4 days there is a relatively high availability of the applied P (high Pw): sorption has not fully taken place.

Figure 8 shows, for the dataset of Bril and Blaauw, the deviation between measured and calculated Pw values as a function of time after the start of the experiment. The ratio between measured values and calculated values -using the regression line- is plotted on the y-axis: a ratio of 1 denotes that the calculated value is the same as the measured Pw value. During the first 15-20 days it appears that the measured Pw is underestimated; after this period there is a better relationship between measured and calculated Pw.

The figure also shows the measured Pox values there is a large variation between the data. Peaks of Pox are found after 20 and 80 days, which correspond with an overestimation of Pw (ratio < 1). A high Pox value gives a high PSI value, and thus a high predicted Pw value.

However, a surplus in Pox can consist of, e.g., calciumphosphates dissolving in the acid oxalate extract. These salts do not necessarily fully contribute to Pw, and a sample that contains a large amount of these salts may show a lower Pw value than the value predicted by the general relationship between Pw and PSI. Otherwise, some organic P compounds will show a relatively high solubility, and thus give a higher Pw value than the predicted value.

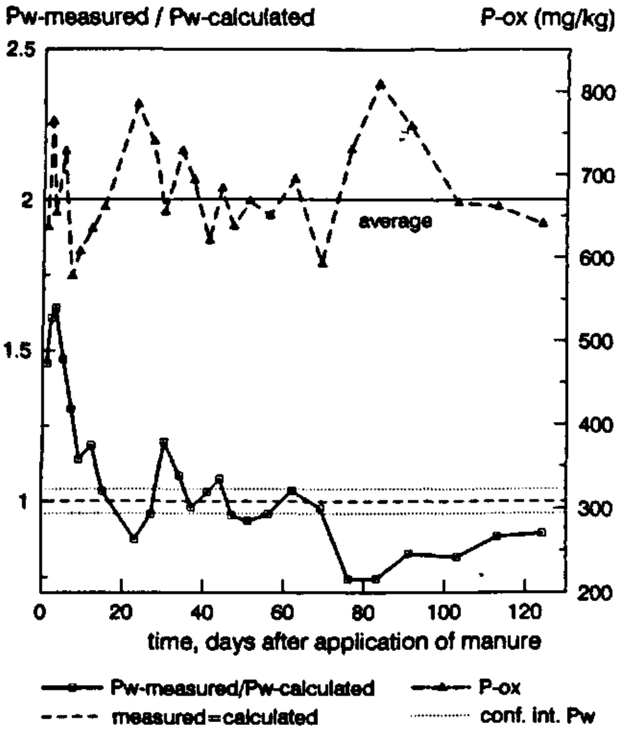

Figure 8. Deviation between measured and calculated Pw values, and measured Pox, as a function of time. Data from the experiment by Bril and Blaauw.

4. Summary and conclusions

The interpretation of existing datasets shows that a power function yields the best description of the relationship between Pw and PSI. This corresponds with expectations based on existing knowledge of adsorption isotherms describing the sorption of P.

It has to be emphasised that a calculated relationship between Pw and PSI will only be valid for one soil type, since, e.g., soil pH will have a large effect on P availability, and thus on Pw. The effect of (incubation) time on sorption of P will lead to deviations between measured and predicted Pw values.

Calculating a PSI value at a measured Pw, or the reverse, will be precarious, since many factors influence Pw. Only when a relationsip between Pw and PSI is calculated for a specific soil type or location, using enough field data, this can be justified.

5. Acknowledgements

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