# Phosphorus supplying potential of European soils

Helinä Hartikainen and Asko Simojoki

Department of Food and Environmental Sciences, University of Helsinki, Finland, Email helina.hartikainen@helsinki.fi

## Abstract

The P supplying power of 26 European benchmark soils was investigated by means of desorption/sorption isotherms (Q/I plots) and by desorption graphs determined at increasing water-to-soil ratios (x). The desorption followed the equation $y = c\, x^{a}$ where the parameters *c* and *a* stand for the P concentration in the soil solution at 100% moisture level and the P supplying power of soil, respectively. The parameter *c* correlated closely with the Al-bound P (r = 0.88***) and the P saturation of Al oxides (r = 0.92***) and with labile P ($Q_0$) (r = 0.83***) and the equilibrium P concentration ($EPC_0$) (r = 0.92***) derived from Q/I plot. In contrast, the parameter *a* did not correlate very closely with the P quantity parameters, the correlation coefficient with Al-bound P and the P saturation of Al oxide being -0.59** and -0.57**, respectively. Similarly, its correlation with the P buffering power of the sorption isotherm ($EBC_0$) remained rather weak (r = 0.47*), suggesting that the slope of the Q/I graph will change at concentrations below the $EPC_0$ value. This means that the labile P ($Q_0$) derived from the Q/I plot at a fixed solution to soil ratio may underestimate the labile P reserves of the solid phase.

## Key Words

P buffering, P supplying power, P desorption, Q/I plots, P exchange

## Introduction

In soil, the release of labile phosphorus (P) from soil particles resupplies P taken up by plants from the soil solution. The same mechanism maintains a dynamic equilibrium between solid and solution phase, and explains the eutrophication risk caused by the runoff water in contact with surface soil and carrying erosion material to watercourses. The dissolved P in runoff water correlates positively with readily extractable P in surface soil (e.g. Sharpley *et al.* 1977; Culley *et al.* 1983; Pote *et al.* 1996). However, the common P tests based on single extractions do not describe adequately the capacity of soil material to buffer the changes in the solution phase. The P buffering power is a function of the quantity of sorbed P (Q) and its intensity (I) controlled by the coverage of sorption components by phosphate and ligands competing with it.

The quantity/intensity model (Q/I) model by White and Beckett (1964) can be applied to determine the P release from soil or sediment to the ambient solution (e.g. Fox and Kamprath 1970; Hartikainen 1991, Koski-Vähälä and Hartikainen 2001). It allows the prediction of both P sorption to and desorption from the soil, and the slope of the desorption-sorption curve at different points characterizes the P-buffering properties of the soil. Its limitation is, however, that it describes the situation at a given solution-to-soil ratio and easily underestimates the labile P reserves (Yli-Halla *et al.* 2002). In this study, we investigated the P release potential of 26 contrasting European agricultural soils in an extraction test using increasing water-to-soil ratios. The P supplying parameters derived from the desorption graphs were compared with the soil P characteristics and the P exchange parameters obtained from desorption/sorption graphs (Q/I plots).

## Material and methods

### *Soil samples*

Twenty-six topsoil samples of "benchmark" soils were collected from across Europe (Austria (AU), Finland (FI), Hungary (HU), Italy (IT), United Kingdom (UK)) as part of the EU DESPRAL project. The soils differed markedly in their weathering degree and other chemical properties, fertilization history, as well as in their lithological origin, a total of five being calcareous (details given in Withers *et al.* 2007).

### *Methods*

Soil samples were analyzed for pH($CaCl_2$), for the easily soluble ($NH_4Cl$-extractable), Al-bound ($NH_4F$-extractable) , Fe-bound (NaOH-extractable) and Ca-bound ($H_2SO_4$-extractable) P pools (Chang and Jackson fractionation method slightly modified by Hartikainen 1979) and for the oxalate soluble Al and Fe oxides ($Al_{ox}$, $Fe_{ox}$) (Loeppert and Inskeep 1996). The degree of P saturation (DPS) on the oxide surfaces was calculated as molar ratios of $NH_4F\text{-}P/Al_{ox}$ ($DPS_{Alox}$) and $NaOH\text{-}P/Fe_{ox}$ ($DPS_{Feox}$) according to Hartikainen (1979), and also as a molar ratio $P_{oxal}/Al_{ox}+Fe_{ox}$ ($DPS_{Poxal}$) of the oxalate soluble P and oxides according to Lookman *et al.* (1995). Total P was determined as described in Withers *et al.* (2007).

*Determination of P buffering power*

The dynamic equilibrium between the P sorption and solution phase P was depicted by Q/I plots determined at solution to soil ratio of 50:1 using $KH_2PO_4$ solutions containing P 0-100 mg/l. The P exchange parameters were calculated using a modified Langmuir equation as in Hartikainen and Simojoki (1997):

$$\Delta Q = \frac{Q_{\max} I}{1/K + I} - Q_0$$

where $\Delta Q$ is the P amount sorbed or desorbed, $Q_{max}$ is the maximum P sorption, $Q_0$ is the amount of P that has to be desorbed to decrease the P equilibrium concentration to 0 mg/l (by extrapolation), $I$ is the concentration of P in the equilibrium solution and $K$ is a sorption/desorption equilibrium constant related to the binding strength. The intercept of the Q/I curve on the $I$ axis stands for the equilibrium P concentration $EPC_0$, where $\Delta Q = 0$. The slope of the curve at $EPC_0$ was termed the equilibrium buffering capacity ($EBC_0$). Desorption curves were determined by extracting the soils with water ($P_w$) at solution-to-soil ratios varying from 2:1 to 1000:1.

**Results and discussion**

The variation in the different P fractions was very large. Ca-bound P dominated in 16 out of 26 soils (range 58-738 mg/kg) and Fe-P (range 0-734 mg/kg) dominated over Al-P (range10-227 mg/kg) in 19 soils. As for the DPS values, $DPS_{Feox}$ (range 0-50%) was larger than $DPS_{Alox}$ (range 0.4-17%) in a total of 20 soils, but no correlation between the oxide bound P pools and their respective sorption components ($Al_{ox}$, $Fe_{ox}$) was found. In the 5 calcareous soils low in oxide bound P, $DPS_{Poxal}$ (range 5.5-36%) markedly exceeded the DPS based on P fractionation. These high $DPS_{Poxal}$ values were probably artefacts caused by the dissolution of Ca-bound P as demonstrated previously (Uusitalo and Tuhkanen 2000; Peltovuori *et al.* 2002).

The P exchange parameters derived from the Q/I plots varied widely, as expected (Table 1). In $EPC_0$ referring to the 'zero point' of P exchange at which no net desorption from or sorption to soil occurs (Taylor and Kunishi 1971), the range of values was largest as the values varied by more than two orders of magnitude. In contrast, in $EBC_0$ that stands for the buffering capacity at $EPC_0$, and in the instantly labile P ($-Q_0$), the variation was less than two orders of magnitude. The smallest relative variation was found in $Q_{max}$.

The P concentration in the water extracts was expressed as a function of the extraction ratio by the equation:

$$y = c\, x^{a} \qquad (2)$$

where y stands for the P concentration in the extract, x for the solution to soil ratio, *c* for the P concentration in soil solution at moisture level of 100% and *a* for the P buffering power. An example in Figure 1 shows the response of soil solution P to the increasing extraction ratio: in Gleadthorpe soil, the P concentration first sharply decreased when the ratio increased, but then levelled off gradually. The variation in the parameter *c* was larger than that in the parameter *a* (Table 1). The parameters *c* and *a* of desorption graphs correlated negatively with each other (r = -0.68***, n= 26), which means that the P supplying power decreased with an increase in P intensity in the soil solution.

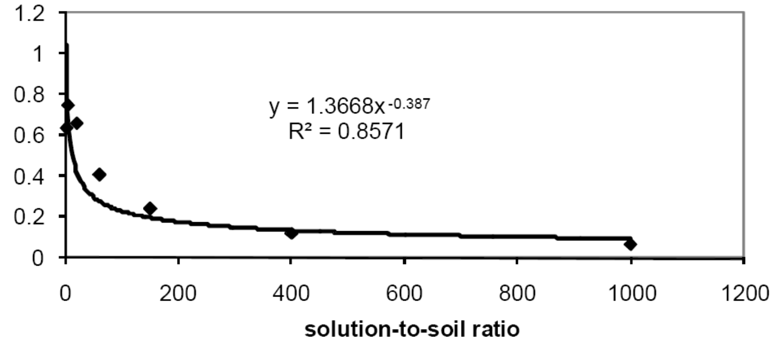

**Figure 1. Desorption graph describing the P concentration (y) as a function of water-to-soil extraction ratio (x) in Gleadthorpe soil (Great Britain).**

**Table 1. The ranges in the parameters derived from the Q/I plots and the desorption graphs in European "benchmark" soils.**

| Q/I plot parameters | Range | Desorption graph parameters | Range |
|---|---|---|---|
| - $Q_0$ (mg/kg) | 2 – 75 | $c$ (mg/l) | 0.14 – 5.89 |
| $EPC_0$ (mg/l) | 0.00 – 10.3 | $a$ | -0.026 – -0.610 |
| $EBC_0$ (l/kg) | 5 – 343 | | |
| $Q_{max}$ (mg/kg) | 43 – 515 | | |

The estimate for soil solution P at 100% moisture level ($c$) seemed to be most closely related to the Al-bound P ($NH_4F$-P) and the P saturation degree of Al oxide surfaces, whereas the correlation with the Fe-bound reserves remained low (Table 2). The correlations between $c$ and the Q/I plot parameters revealed that the higher was the P concentration in the soil solution, the higher were also $EPC_0$ and $Q_0$. These two parameters $EPC_0$ and $Q_0$ explained 85% and 69% of the variation in the parameter $c$, respectively.

The parameter $a$ describing the buffered nature of soil P supplying power did not correlate very closely with the P quantity parameters (Table 2), even though it seemed to increase as the $NH_4F$-bound P and the P saturation of Al oxides decreased. Interestingly, the correlation between $EBC_0$ and $a$ remained rather weak, even if both parameters describe the buffering of soil solution P. This is probably due to the fact that at concentrations below $EPC_0$, the actual buffering power will become larger than that estimated on the basis of the $EBC_0$ values obtained at a fixed solution-to-soil ratio at $EPC_0$. We also note that the parameter $a$ values vary relatively more than the $EBC_0$ values (Table 1). These results lead to the conclusion that in the conventional Q/I plots determined at a fixed solution-to-soil ratio, the estimate $Q_0$ will underestimate the labile P, especially at such large solution-to-soil ratios typical of surface runoff waters containing soil particles eroded from topsoil.

**Table 2. Correlation coefficients for the relationship between the desorption parameters *c* (the P concentration in the soil solution) and *a* (the P supplying power) with the parameters describing soil P reserves and P exchange (parameters derived from Q/I plots).**

| | P parameter | Parameter $c$ | Parameter $a$ |
|---|---|---|---|
| P reserves | $NH_4F$-P | 0.88*** | -0.59** |
| | NaOH-P | 0.22 | -0.25 |
| | Total P | 0.48** | -0.58** |
| | $DPS_{Alox}$ | 0.92*** | -0.57** |
| | $DPS_{Feox}$ | 0.19 | -0.21 |
| | $DPS_{sesq.ox}$ | 0.52** | -0.41* |
| Q/I plot | $Q_0$ | 0.83*** | -0.50** |
| | $EPC_0$ | 0.92*** | -0.46* |
| | $EBC_0$ | 0.57** | 0.47* |
| | $Q_{max}$ | 0.27 | -0.38* |

n = 26; Significance: * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$

## Conclusions

The 26 “benchmark” European agricultural soils covered a wide range in P sorption and desorption properties. The soil solution P estimated from the desorption graph at 100% moisture level increased with increase in the equilibrium P concentration of the Q/I curve and with the P bound to Al oxides. However, it is noteworthy that the ability of soil to maintain high solution P concentration also at higher solution-to-soil ratios decreased more rapidly as Al-bound and soil solution P increased. This P supplying power tended to increase with increase in the equilibrium buffering capacity derived from the Q/I curve. Our results show that European agricultural soils vary widely in their capacity to supply P to surface runoff waters. They also indicate that the traditional determination of P reserves and Q/I curves with a fixed solution-to-soil ratio is likely of limited use for predicting the P loading by eroded soil particles transported to watercourses.

## References

Culley JLB, Bolton EF, Bernyk V (1983) Suspended solids and phosphorus loads from a clay soil: I Plot studies. *Journal of Environmental Quality* **12**, 493-498.

Fox RL, Kamprath EJ (1970) Phosphate sorption isotherms for evaluating the phosphate requirements of soils. *Soil Science Society of America Proceedings* **34**, 902-907.

Hartikainen H (1979). Phosphorus and its reactions in terrestrial soils and lake sediments. *Journal of the Scientific Agricultural Society of Finland* **51**, 537-624.

Hartikainen H (1991) Potential mobility of accumulated phosphorus in soil as estimated by the indices of Q/I plots and by extractant. *Soil Science* **152**, 204-209.

Hartikainen H, Simojoki A (1998) Changes in solid-and solution-phase phosphorus in soil on acidification (vol 48, pg 494, 1997). *European Journal of Soil Science* **49,** 160-160. Erratum **48,** 493-498.

Koski-Vähälä J, Hartikainen H, Tallberg P (2001) Phosphorus mobilization from various sediment pools upon increased pH and silicate concentration. *Journal of Environmental Quality* **30**, 546-552.

Peltovuori T, Uusitalo R, Kauppila T (2002). Phosphorus reserves and apparent phosphorus saturation in four weakly developed cultivated pedons. *Geoderma* **110**, 35-47.

Pote DH, Daniel TC, Sharpley AN, Moore PA, Edwards DR, Nichols DJ (1996) Relating extractable soil phosphorus to phosphorus losses in runoff. *Soil Science Society of America Journal* **60**, 855-859

Loeppert RH, Inskeep P (1996) Iron. *In* 'Methods of soil analysis. Part 3.' (Eds. Sparks DL, Page AL, Helmke PA, Loeppert RH, Soltanpour PN, Tabatabai MA, Johnston CT, Summer), pp. 649-650. Soil Science Society of America, Inc. Madison.

Lookman R, Vandeweert N, Merckx R, Vlassak K (1995) Geostatistical assessment of the regional distribution of phosphate sorption capacity parameters ($Fe_{ox}$ and $Al_{ox}$) in northern Belgium. *Geoderma* **66**, 285-296.

Sharpley AN, Tillman RW, Syers JK (1977) Use of laboratory extraction data to predict losses of dissolved inorganic phosphate in surface runoff and tile drainage. *Journal of Environmental Quality* **6,** 33-36.

Taylor AW, Kunishi HM (1971) Phosphate equilibria on stream sediment and soil in a watershed draining an agricultural region. *Journal of Agricultural and Food Chemistry* **19**, 827-831.

Uusitalo R, Tuhkanen H-R (2000) Phosphorus saturation of Finnish soils: evaluating an easy oxalate extraction method. *Agricultural and Food Science in Finland* **9**, 61-70.

White RE, Beckett PHT (1964) Studies on the phosphate potentials of soils. *Plant and Soil* **20,** 1-16.

Withers PJA, Hodkinson RA, Barberis E, Presta M, Hartikainen H, Quinton J, Miller N, Sisak I, Strauss P, Mentler A (2007) An environmental soil test to estimate the intrinsic risk of sediment and phosphorus mobilization from European soils. *Soil Use and Management* **23** (Supplement 1), 57-70.

Yli-Halla M, Hartikainen H, Väätäinen P (2002) Depletion of soil phosphorus as assessed by several indices of phosphorus supplying power. *European Journal of Soil Science* **53**, 431-438.