

## Relationship between phosphorus intensity and capacity parameters in Finnish mineral soils

### II Sorption-desorption isotherms and their relation to soil characteristics

HELINÄ HARTIKAINEN

*Department of Agricultural Chemistry, University of Helsinki, 00710 Helsinki 71*

**Abstract.** The relationship between P intensity and capacity parameters in 104 mineral soil samples was studied by means of sorption-desorption isotherms of two types. In the isotherm A the P exchange was expressed as a function of P concentration in the initial solution, in the isotherm B as a function of P concentration in the final equilibrium solution. Both isotherms conformed to the equation  $y = a + bx$ , where  $y$  stands for the amount of P sorbed or desorbed and  $x$  the P concentration in the solution.

In the isotherm A the constant  $a$  is the intensity factor expressing the amount of water soluble P at a given soil-solution ratio. The term  $a$  in the isotherm B, on the contrary, was only poorly related to water soluble P in soil. In both isotherms the slope  $b$  of the line seemed to be most effectively affected by oxalate extractable Al. The relative importance of oxalate soluble Fe appeared to be greater in affecting the effectiveness of sorption-desorption reactions than in affecting the buffer reactions. However, the slope  $b$  of both isotherms was found to be a semi-intensive parameter: it was quite markedly dependent also on soil characteristics which control the level of water soluble P in soil.

The ratio of the term  $-a$  to  $b$  (termed as EBS or EPC), expressing the zero point of net P exchange, varied from 0.003 to 13.89 mg P per liter, the lowest values tending to be in the heavy clay soils and the highest ones in the non-clay soils. The practical significance of this quantity was discussed.

### Introduction

The applicability of various isotherms to studies dealing with agricultural and environmental P problems has been subject to many investigations. A great deal of effort has been expended on trying to find the isotherm parameters of essential significance in predicting e.g. the fertilizer requirement of plants or the P loading of surface waters induced by eroded soil material.

The important soil factors controlling the P supply to plants are the intensity, quantity and P buffering power factors (HELYAR and MUNNS 1975, HOLFORD 1976). The intensity refers to P concentration in the soil

solution and the quantity to total labile P in soil. The intensity parameter, e.g. water soluble P, describes a transient situation in soil, but it does not exactly inform about changes in P intensity occurring when P concentration in the solution is reduced by P uptake or increased by P fertilization.

The purpose of the present study was to find out in more detail the relationship between the P intensity and capacity parameters and soil factors involved therein. The relationship was investigated by sorption-desorption isotherms of two kinds. The results were assumed to give further information about factors to be taken into account when developing methods for extracting plant available P as well as methods for determining the requirements of P fertilization. The isotherms were considered to give intimations also about factors in lakes controlling P exchange between the sediment and overlying water and, thus, being noteworthy when developing models for predicting the ability of a lake to tolerate P loading or in polluted waters the ability of bottom deposits to supply the water body with P.

## Materials and methods

The material consisted of 104 mineral soil samples, some characteristics of which are reported in Table 1. The means and range of other properties in various soil groups as well as the methods of soil analyses are presented in a previous study (HARTIKAINEN 1982 a). The method for preparing the isotherms is described in the first part of this study (HARTIKAINEN 1982 b). In some soil samples, however, no sorption was found to have taken place even at the highest P concentration (1 mg/l) in the bathing solution. In these cases, the sorption or desorption from and to a solution were investigated by using standard solutions of higher P concentrations (up to 14 mg/l).

## Results

The P exchange by soils was expressed in two ways: as a function of P in the initial solution (isotherm A) and as a function of the P concentration in the final equilibrium solution (isotherm B). The graphs being curved at high P concentrations, calculations of regressions and correlations were carried out after plotting of sorption or desorption *versus* concentration data in order to determine the upper end of the concentration range for linearity. For most soils this was 1.0 mg P per liter (in the initial solution), even if, on the whole it ranged from 0.2 mg to 6.0 mg P per liter or it was not reached. Points diverging from the linearity above this limit concentration were excluded from the analyses and only the straight-line sections of lower P concentrations, better simulating the circumstances in nature, were examined. Thus, both isotherms conformed to the equation  $y = a + bx$ , where y stands for the amount of P sorbed or desorbed, x the P concentration in the solution.

The values of the constants and the slopes of the lines obtained are reported in Table 1. The constant and the tangent for the isotherm A are

Table 1. Chemical characteristics of soil samples, constants ( $a_A$  and  $a_B$ ) and tangents ( $b_A$  and  $b_B$ ) for P isotherms.

Soil sample	pH	H <sub>2</sub> O-P mg/kg	Oxalate extr. mmol/kg		Isotherm A		Isotherm B		EBS = EPC mg/l
			Al	Fe	$a_A$ mg/kg	$b_A$ l/kg	$a_B$ mg/kg	$b_B$ l/kg	
Heavy clays									
43	4.2	2.4	134	74	- 2.8	41	-16.0	239	0.067
20	4.6	6.1	118	118	- 2.2	49	-79.0	1715	0.046
36	4.7	0.5	255	30	- 1.0	49	-29.9	1521	0.020
38	4.7	2.5	95	109	- 1.6	40	- 7.9	207	0.038
18	4.8	4.4	86	148	- 2.5	44	-16.0	288	0.056
22	4.8	4.7	98	82	- 3.1	43	-21.5	297	0.073
24	4.8	4.7	98	81	- 2.9	42	-16.9	247	0.068
35	4.9	2.8	137	116	- 3.3	41	-17.9	221	0.081
37	4.9	0.2	65	77	- 0.2	47	- 3.4	751	0.005
41	4.9	1.7	75	108	- 1.9	41	- 9.5	214	0.044
42	4.9	5.7	110	58	- 5.7	41	-30.9	223	0.139
40	5.0	3.2	78	108	- 3.6	40	-18.7	210	0.089
23	5.1	4.2	79	114	- 5.2	43	-36.0	295	0.122
21	5.2	8.6	71	102	- 5.2	41	-27.0	214	0.126
44	5.3	2.3	72	99	- 4.3	36	-19.8	171	0.116
45	5.4	4.3	61	73	- 5.2	40	-23.7	182	0.130
48	5.5	10.4	45	88	-11.9	25	-24.0	51	0.469
19	5.8	20.0	67	100	-15.6	31	-40.3	80	0.505
39	6.0	2.9	69	102	- 2.0	43	-14.7	317	0.046
$\bar{x}$	5.0	4.8	95	94	- 4.2	41	-23.8	392	0.118
s	0.4	4.5	46	26	3.7	6	16.3	455	0.136
Coarser clays									
15	4.3	4.9	94	171	- 4.2	45	- 43.9	473	0.093
73	4.4	4.0	85	65	- 4.1	41	- 23.5	240	0.098
13	4.5	6.7	74	71	- 5.7	37	- 21.5	140	0.154
59	4.5	1.7	64	144	- 0.7	44	- 5.5	373	0.015
61	4.5	5.5	82	150	- 5.4	45	- 49.2	404	0.122
109	4.5	3.5	77	56	- 4.0	41	- 21.3	214	0.099
72	4.6	9.3	76	61	- 9.7	33	- 28.1	95	0.296
47	4.7	1.3	81	102	- 2.5	43	- 14.7	278	0.053
54	4.7	5.0	88	75	- 4.3	40	- 22.2	209	0.106
80	4.7	3.2	59	43	- 2.4	40	- 11.5	187	0.061
82	4.7	0.2	76	49	- 0.9	45	- 7.3	415	0.018
49	4.8	3.1	76	59	- 4.5	33	- 16.5	125	0.132
62	4.9	6.7	111	71	- 7.8	36	- 27.7	129	0.214
63	4.9	41.3	68	83	-37.1	17	- 55.7	25	2.214
66	4.9	4.7	73	24	- 3.0	29	- 7.0	67	0.104
74	4.9	8.3	50	58	- 7.7	28	- 17.3	63	0.273
83	4.9	5.9	45	64	- 5.7	29	- 12.2	62	0.197
89	4.9	5.9	59	59	- 4.3	28	- 9.5	62	0.152
7	5.0	8.9	57	67	- 7.4	34	- 22.4	102	0.220
56	5.0	5.8	73	97	- 3.8	38	- 15.5	152	0.102
64	5.0	4.2	50	54	- 3.7	24	- 6.9	45	0.154
93	5.0	8.4	62	53	- 8.2	26	- 17.2	55	0.311
108	5.0	5.1	32	56	- 5.3	30	- 13.4	77	0.174

Table 1. Chemical characteristics of soil samples, constants ( $a_A$  and  $a_B$ ) and tangents ( $b_A$  and  $b_B$ ) for P isotherms.

Soil sample	pH	H <sub>2</sub> O-P mg/kg	Oxalate extr. mmol/kg		Isotherm A		Isotherm B		EBS = EPC mg/l
			Al	Fe	$a_A$ mg/kg	$b_A$ l/kg	$a_B$ mg/kg	$b_B$ l/kg	
6	5.1	25.3	37	63	-21.2	22	- 38.0	40	0.951
60	5.1	78.2	68	86	-85.4	17	-131.2	27	4.894
75	5.1	6.9	76	94	- 5.8	39	- 25.6	171	0.149
92	5.1	22.1	42	62	-19.5	18	- 30.1	27	1.112
14	5.2	9.5	47	71	- 7.8	31	- 20.5	82	0.252
17	5.2	6.3	69	91	- 5.3	39	- 22.0	164	0.134
53	5.2	0.4	49	86	- 0.2	47	- 2.1	634	0.003
58	5.2	7.6	59	60	- 3.8	28	- 8.7	66	0.132
69	5.2	6.5	55	60	- 3.7	17	- 16.4	75	0.220
81	5.2	11.8	39	64	-11.9	21	- 19.4	37	0.532
51	5.3	9.8	75	80	- 8.4	35	- 27.1	113	0.240
76	5.3	8.4	46	59	- 7.2	22	- 12.9	40	0.324
78	5.3	0.2	28	31	- 0.4	44	- 6.4	574	0.011
12	5.4	13.9	39	73	- 8.5	18	- 12.1	25	0.483
16	5.4	4.3	161	92	- 3.6	41	- 20.8	228	0.091
52	5.4	15.0	79	81	-14.5	25	- 29.2	50	0.579
55	5.6	3.8	69	69	- 2.4	37	- 8.6	136	0.063
50	5.7	32.7	47	46	-35.4	13	- 44.9	16	2.819
79	5.7	64.7	38	68	-50.5	6	- 57.7	7	8.186
95	5.7	8.3	45	49	- 8.5	23	- 15.5	41	0.379
8	6.0	38.2	43	79	-33.7	23	- 63.1	44	1.434
46	6.0	5.0	50	64	- 5.2	26	- 10.6	54	0.197
57	6.0	11.9	40	72	-10.0	21	- 12.4	26	0.478
77	6.1	17.1	106	68	-16.7	33	- 49.7	99	0.504
71	6.2	5.4	53	49	- 5.1	34	- 15.6	103	0.151
68	6.3	48.5	36	52	-46.0	9	- 56.9	11	5.337
84	6.5	35.7	50	63	-33.2	13	- 45.3	18	2.481
67	6.6	0.8	56	61	- 1.0	46	- 13.0	587	0.022
$\bar{x}$	5.2	12.8	63	71	-11.7	30	- 25.2	147	0.736
s	0.6	16.3	23	26	15.8	11	21.6	158	1.533
Non-clay soils									
90	3.8	1.9	95	84	- 1.7	47	- 24.2	660	0.037
96	4.2	1.7	56	44	- 2.7	34	- 8.4	109	0.077
99	4.5	9.4	61	56	- 7.9	30	- 20.2	77	0.261
113	4.5	4.5	38	80	- 5.7	26	- 11.9	53	0.222
3	4.6	0.5	141	50	- 0.3	49	- 16.6	2921	0.005
91	4.6	1.2	138	57	- 1.2	48	- 36.0	1519	0.024
110	4.6	5.0	61	85	- 6.0	40	- 30.1	199	0.151
111	4.6	0.9	59	112	- 3.0	40	- 14.4	191	0.075
4	4.7	0.8	133	63	- 0.6	47	- 11.1	875	0.012
114	4.7	1.5	17	84	- 2.3	30	- 5.4	72	0.075
100	4.8	6.6	53	63	- 8.1	29	- 18.8	66	0.282
102	4.8	22.9	72	57	-25.1	21	- 42.8	35	1.206
5	4.9	12.0	66	80	-10.4	37	- 41.3	148	0.279
106	4.9	4.5	78	50	- 5.7	33	- 16.5	96	0.171

Table 1. Chemical characteristics of soil samples, constants ( $a_A$  and  $a_B$ ) and tangents ( $b_A$  and  $b_B$ ) for P isotherms.

Soil sample	pH	H <sub>2</sub> O-P mg/kg	Oxalate extr. mmol/kg		Isotherm A		Isotherm B		EBS = EPC mg/l
			Al	Fe	$a_A$ mg/kg	$b_A$ l/kg	$a_B$ mg/kg	$b_B$ l/kg	
65	5.0	4.0	33	53	- 3.3	22	- 5.7	37	0.152
97	5.0	2.1	40	73	- 2.4	38	- 10.0	160	0.063
88	5.1	16.1	70	69	-16.5	29	- 38.4	66	0.578
87	5.2	11.4	43	33	- 7.0	15	- 9.7	20	0.480
101	5.2	14.0	54	50	-14.8	21	- 25.0	35	0.719
112	5.2	0.7	67	45	- 2.8	39	- 12.5	171	0.073
1	5.3	14.0	47	54	-10.9	21	- 18.7	36	0.518
10	5.3	17.9	29	46	-15.2	15	- 22.0	22	0.986
86	5.3	117.8	47	73	-97.0	7	-112.6	8	13.870
104	5.3	2.4	52	81	- 4.0	27	- 8.6	60	0.144
105	5.3	2.9	79	64	- 4.8	37	- 17.8	137	0.130
9	5.5	21.9	48	55	-18.1	20	- 29.9	33	0.917
103	5.5	18.7	44	69	-18.5	22	- 33.3	40	0.836
11	5.6	28.7	40	47	-14.9	9	- 17.8	11	1.687
85	5.7	18.5	69	64	-20.1	22	- 24.2	26	0.920
2	6.0	21.6	23	50	-17.7	19	- 28.3	30	0.937
98	6.0	0.3	26	64	- 0.8	45	- 7.6	448	0.017
115	6.1	10.2	38	44	-11.0	17	- 16.8	26	0.645
107	6.3	32.2	66	50	-31.3	19	- 51.8	32	1.608
94	6.4	22.4	44	60	-20.7	17	- 31.8	27	1.190
$\bar{x}$	5.1	13.3	60	62	-12.1	29	- 24.1	248	0.863
s	0.6	20.6	30	16	17.0	12	19.5	561	2.347

expressed by  $a_A$  and  $b_A$ , respectively, and those for the isotherm B by  $a_B$  and  $b_B$ , respectively. Both graphs intersect the x-axis on the same point, termed equilibrium bathing solution (EBS) for isotherm A and, according to TAYLOR and KUNISHI (1971), equilibrium phosphate concentration (EPC) for isotherm B. Also the intersecting points are presented in Table 1.

In the isotherms A, expressing the retention or removal of P as a function of P in the initial solution, the absolute values of the constants  $a_A$  describe the solubility of soil P in pure water. When comparing them with the quantities of water extractable P, obtained in an earlier study (HARTIKAINEN 1982 a), close correlations were found:

	r
Heavy clays (19)	0.92***
Coarser clays (51)	0.99***
Non-clay soils (34)	0.99***

Table 1 shows that the absolute values of the constant  $a_A$  tended to be somewhat lower than the amounts of P extracted by water, because the soil-solution ratio 1:50 used in the present study was a little higher than that used in water extraction (1:60).

The correlation analyses showed that, contrary to  $a_A$ , the constant  $a_B$  was quite poorly related to water soluble P. The following correlation coefficients were found for the relation between water soluble P and the logarithm of the absolute value of the term  $a_B$ :

	r
Heavy clays (19)	0.51*
Coarser clays (51)	0.72**
Non-clay soils (34)	0.56***

The values of the slopes of the lines ranged widely: those of  $b_A$  from 49 to 6 and those of  $b_B$  from 2921 to 7. On the average, the values of  $b_A$  for the isotherms of the type A, which expresses the P exchange as a function of P addition, were highest in the heavy clay soils and lowest in the non-clay soils. There was 33 samples with  $b_A$  values exceeding 40: 15 heavy clays, 12 coarser clays and 6 non-clay soils. In this group the corresponding value of  $b_B$ , describing the P buffering power of the soil, ranged from 2921 to 199.

It was observed that the correlations found for the relation between the slope  $b_A$  and the soil characteristics were linear and those for the relation between the slope  $b_B$  and soil characteristics were logarithmical (Table 2).

Table 2. Total correlation coefficients for the relation between soil characteristics and the slope  $b_A$  as well as the logarithm value of slope  $b_B$ .

	Heavy clays		Coarser clays		Non-clay soils		All samples	
	$b_A$	log $b_B$	$b_A$	log $b_B$	$b_A$	log $b_B$	$b_A$	log $b_B$
pH	-0.53*	-0.48*	-0.44**	-0.42**	-0.56***	-0.41*	-0.49***	-0.47***
Oxal. extr. Al	0.52*	0.62**	0.50***	0.45***	0.63***	0.73***	0.57***	0.62***
" " Fe	ns	ns	0.36**	0.36**	0.35*	ns	0.41***	0.34***
NH <sub>4</sub> F-P/Al	ns	ns	-0.64***	-0.63***	-0.64***	-0.58***	-0.66***	-0.59***
NaOH-P/Fe	ns	ns	-0.63***	-0.63***	ns	ns	-0.36***	-0.27**
H <sub>2</sub> O-P	-0.64**	-0.53*	-0.71***	-0.66***	-0.62***	-0.57***	-0.67***	-0.63***

ns = not significant

This was due to the fact that distribution of the values of  $b_B$  appeared to deviate markedly from the normal distribution, the Pearson's coefficient of skewness  $S$  being 0.94. The utilization of the logarithms of the  $b_B$  values decreased this coefficient to 0.07. Nevertheless, all correlation coefficients for the relation between the  $b$  parameters and soil properties were relatively low, indicating that the sorption-desorption system of the soil is of multi-component nature.

The relationship between the soil properties and the parameters describing the effectiveness of the desorption or sorption ( $b_A$ ) as well as the buffer power of soil ( $b_B$ ) was investigated by the regression analysis. The coefficients of multiple determination  $R^2$  were calculated for the equations with the following variables:

- $x_1$  = oxalate extractable Al mmol/kg
- $x_2$  = " " Fe "
- $x_3$  = molar ratio NH<sub>4</sub>F-P/Al ( $\cdot 10^2$ )
- $x_4$  = " " NaOH-P/Fe ( $\cdot 10^2$ )

In 104 samples studied the relationship between the parameter  $b_A$  (l/kg) =  $y$  and these soil characteristics was found to conform to the following regression equation:

$$y = 0.169x_1 + 0.094x_2 - 0.845x_3 - 0.483x_4 + 23.459 \quad (F = 58.89^{***}) \quad R_2 = 0.66$$

$$S = 6.17$$

$$s_{b1} = 0.022$$

$$s_{b2} = 0.025$$

$$s_{b3} = 0.178$$

$$s_{b4} = 0.206$$

In the corresponding equation, calculated for the relationship between the parameter  $\log b_B$  and soil characteristics, the molar ratio NaOH-P/Fe was not statistically significant: it explained only 2 % of the variation in  $\log b_B$ . Thus, the regression equation was:

$$y = 0.0078x_1 + 0.0035x_2 - 0.0488x_3 + 1.519 \quad (F = 63.62^{***}) \quad R_2 = 0.70$$

$$S = 0.312$$

$$s_{b1} = 0.00096$$

$$s_{b2} = 0.00123$$

$$s_{b3} = 0.00621$$

The relative importance of these soil factors affecting the parameter  $b_A$  and  $\log b_B$  may be compared on the basis of  $\beta$ -coefficients ( $\beta_A$  and  $\beta_B$ , respectively) which were as follows:

	$\beta_A$	$\beta_B$
Al	0.50	0.49
Fe	0.22	0.17
NH <sub>4</sub> F-P/Al	-0.39	-0.48
NaOH-P/Fe	-0.20	

Oxalate extractable Al had the highest values of  $\beta$ -coefficients, but in the equation for  $\log b_B$  the role of NH<sub>4</sub>F-P/Al seemed to be nearly as appreciable. Further, it can be seen that the oxalate extractable Fe is of importance, affecting relatively more the parameter  $b_A$  than the parameter  $\log b_B$ .

The zero point of net P exchange (EBS of EPC) expresses the P concentration in a solution where  $y = 0$ . Table 1 shows that these points ranged widely: 0.003 – 13.89 mg P per liter. In all samples the average value was 0.665 mg P per liter. The non-clay soils tended to have the highest values and the heavy clay soils the lowest ones. The magnitude sequence of average EBS (= ECP) values of the soil groups was the same as that of water soluble P and high values of correlation coefficients were found for the relation between water soluble P and EBS (=EPC) values.

The calculation of these correlations is, however, questionable. This is due to the fact that e.g. the EBS is determined by dividing the constant  $-a_A$  which represents water soluble P by the slope  $b_A$ . Thus, the water soluble P is included in the EBS values.

As expected on the basis of the associations stated above, the EBS (=EPC) values correlated moderately with the soil characteristics found by HARTIKAINEN (1982 a) to regulate the extractability of soil P into water (Table 3). Like in water soluble P, the relationship between the EBS and the molar ratio

Table 3. Total correlation coefficients for the relation between the EPC (EBS) values and soil characteristics.

	Heavy clays (19)	Coarser clays (51)	Non-clay soils (34)	All samples (104)
pH	0.57*	0.35*	ns	0.26**
NH <sub>4</sub> Cl-P	0.79***	0.95***	0.96***	0.95***
NH <sub>4</sub> F-P	ns	0.56***	0.72***	0.57***
NH <sub>4</sub> F-P/Al	0.52*	0.80***	0.86***	0.79***
NaOH-P	ns	0.55***	0.51**	0.43***
NaOH-P/Fe	ns	0.77***	0.47**	0.43***

NH<sub>4</sub>F-P/Al tended to become the closer and that between the EBS and soil pH the poorer the coarser the soil material was. However, the values of the correlation coefficients for the EBS were somewhat lower, but in NH<sub>4</sub>F-P/Al, statistically significantly lower than those found for the water soluble P (tested by the z-transformation test according to SNEDECOR and COCHRAN 1972,  $P = 0.05$ ). This indicates the role of the factor  $b$ . In general, the EBS and EPC increased with a decrease in  $b_A$  and  $b_B$ , respectively.

## Discussion

The equations obtained differ from the Langmuir and Freundlich as well as Temkin isotherms often used to describe the interaction between soils and phosphate solutions (OLSEN and WATANABE 1957, KAILA 1963, BACHE and WILLIAMS 1971, MEAD 1981, etc.). Also these isotherms, generally applied to sorption studies, normally fit the sorption data only within a limited range of phosphate concentrations in solution (MEAD 1981). These equations are hardly used in sorption-desorption studies, because quite low phosphate concentrations are needed in experiments of this kind.

The results in Table 1 and the correlation analyses show that the constant  $a_A$  in the isotherm A which expresses the P exchange as a function of P concentration in the initial solution, really corresponds to the quantity of water soluble P at the soil-solution ratio used and is thus the intensity factor in the isotherm.

As stated in the first part of this study (HARTIKAINEN 1982 b), the physical meaning of the constant  $a_B$  cannot be interpreted as exactly and explicitly as the meaning of the constant  $a_A$ . The equation of the isotherm B presented in this study is to some extent similar to the Freundlich sorption isotherm modified by FITTER and SUTTON (1975) into the form  $\Delta P = bC^k - a$ , where  $C$  stands for the P concentration in the final solution and  $\Delta P$  the amount of sorbed P. According to the authors, the third term,  $a$ , theoretically represents the phosphate which must be removed in order to reduce P concentration in the final solution to zero, since  $\Delta P = -a$  when  $C = 0$ . When the equation was fitted to the sorption data, a close relationship was found



between  $a$  and the resin-P values, with the calcareous and acid soils falling into two distinct groups.

However, in the present study there existed quite a poor association between the water extractable P in the soil and the term  $a_B$  corresponding to the term  $a$  of FITTER and SUTTON (1975). This result supports the concept discussed by HARTIKAINEN (1982 b) that, with increasing solution-soil ratio the isotherm expressing the P exchange as a function of final P concentration can be assumed in practice to converge the y-axis without intersecting it. This is due to the fact that the intersecting point on the y-axis would express the equilibrium P concentration  $x = 0$  which, in turn, does not allow any net phosphate exchange.

As can be seen in Table 2, water soluble P and some soil properties involved were correlated to some extent also with the slope  $b_A$  and the logarithm value of the slope  $b_B$ . In addition, on the basis of the  $\beta$ -coefficients, the soil characteristics controlling the level of water soluble P in soil seem to be important factors in both equations, which indicates the factor  $b_A$  as well as the factor  $b_B$  to be semi-intensive parameters.

Water extraction has been shown to illustrate the P status determined by the quantity and quality of sorption components in soil, soil pH, and the content of organic carbon (HARTIKAINEN 1982 a). These factors seemed not to affect the amounts of P dissolved in water directly, but indirectly, by controlling the nature of P bonding which, in turn, seemed to be of decisive importance in the extractability of P into water.

The importance of various P fractions differed in the equations for  $b_A$  and  $\log b_B$ . It can be concluded that, with an increase in the molar ratio  $\text{NH}_4\text{F-P/Al}$ , the buffer power ( $b_B$ ) is decreased more markedly than the effectiveness of sorption-desorption reactions ( $b_A$ ). On the other hand, the molar ratio  $\text{NaOH-P/Fe}$ , an insignificant variable in the equation for the buffer power parameter, was of importance in affecting the effectiveness of sorption-desorption reactions. These facts give intimations also about the role of sorption components. As anticipated, Al seemed to play a more appreciable role than Fe, but some difference was really found between the isotherms. The relative importance of Fe appeared to be greater in affecting the effectiveness of sorption reactions than in affecting the buffering reactions. Thus, it is obvious that in the rapid P exchange reactions (i.e. in P buffering) Al and P bound by it are more decisive factors, because Al forms a weaker bond with phosphate than Fe (see AURA 1980). If these assumptions are valid, the result is of interest also as far as limnological studies are concerned in which the role of Al generally fails being noticed.

The ratio of the term  $-a_A$  to  $b_A$ , or  $-a_B$  to  $b_B$ , expressing the zero point of net P exchange, tended to be lowest in the heavy clay soils and highest in the non-clay soils. This gives reason to suppose that the heavy clay soils in general were able to sorb P from more diluted phosphate solutions than the coarser soils.

TAYLOR and KUNISHI (1971) observed the EPC values of fertilized soils somewhat to change with changing soil-solution ratio. Thus, the EPC does not necessarily correspond to the actual pre-existing P equilibrium level in

the soil solution, but is probably closely related to it. Taking all this into consideration, the EPC value may be a practical index. It can be used, for instance, in predicting the direction and extent of P exchange reactions between suspended soil material and recipient water. The data in Table 1 give reason to suppose that, under suitable conditions, some samples may be able to sorb P even from very pure surface waters. The water conducted from Lake Päijänne to Helsinki, for instance, used to making drinking water, contains about 10  $\mu\text{g PO}_4\text{-P}$  per liter (data obtained from the Water Works of Helsinki) which is more than the EPC of the samples 3, 37 and 53. A greater number of the samples studied would have been able to retain P from the polluted water of Lake Tuusulanjärvi, containing 14–280  $\mu\text{g PO}_4\text{-P}$  per liter in the hypolimnion in 1981 (analyzed by the Water District of Helsinki). On the other hand, many of the soil samples would cause P load, if carried into watercourses.

On the basis of the idea introduced by BECKWITH (1965), OZANNE and SHAW (1967) developed a method for predicting the phosphate requirements of pasture plants. The method is based on the measurement of phosphate sorption by soil at a standard equilibrium concentration. In the experiments performed by the authors, the variations in phosphate sorbed accounted for over 80 % of the variation found in the phosphate requirement of plants.

The determination principle of OZANNE and SHAW (1967) presupposes the use of an isotherm corresponding to the graph of type B, presented in this study. However, more accurate information may be obtained, if the isotherm of type A is used simultaneously. As can be concluded from the paper of HARTIKAINEN (1982 b), the sorption data derived from the isotherm B give no information about P quantities to be added to the soil. The following example elucidates this fact. The heavy clay soil sample 20 and 39 have the same EPC value, i.e. 0.046 mg/l (see Table 1). If the equilibrium concentration of 0.100 mg/l is to be achieved, it can be calculated from the equation B that 92.5 and 17.0 mg/kg should be sorbed by the sample 20 and 39, respectively. In experimental conditions (soil-solution ratio 1:50) the initial P concentration in the solution to be added (as calculated from the corresponding equation A) should be 1.933 and 0.442 mg/l, respectively. These calculations show that, in order to achieve the same P concentration in the equilibrium solutions, sample 20 has to retain 5.44 times more P than sample 39, but the P addition needed is only 4.37 times greater. If the P added were distributed evenly in the surface soil, 20 cm in thickness, and if one liter of soil were assumed to weigh one kilogram, these additions would correspond to 193.4 kg (soil 20) and 44.2 kg (soil 39) per hectare.

Further, it can be concluded from the equations of the isotherms B that a given desorption decreases the P concentration in a solution the more markedly the lower the buffer power of the soil is. Also HOLFORD and MATTINGLY (1976) have emphasized the importance of the buffering factor. They claim that, in P requirements of plants, the critical level of P quantity in soil increases and P intensity decreases as the buffer power of soil increases.

An ideal extractant would account for the P intensity as well as the P supplying capacity in a wide range of soil types. The results obtained in the

present study show the water soluble P in soil to be closely related to parameters describing the interaction between soil material and surrounding P solution. As compared to other soil characteristics studied, it seems to be of a relatively greater importance because it is related to both the term  $a$  and the term  $b$  in the equations of the isotherms. This supports the conclusion presented in some earlier studies (e.g. AURA 1978, SCHACHTSCHABEL and BEYME 1980) that the water soluble P gives intimations about P intensity as well as P capacity in soils.

However, simple water extraction seems not to indicate adequately the P exchange properties of a soil, but the amount of Al and Fe must also be taken into account. Thus, the use of sorption-desorption isotherms, including all the parameters discussed above, is justified. By applying simultaneously the isotherms of both types investigated in this study, the lines can be used as a dynamic model to describe P exchange. The advantage of this method is that the data on both isotherms are obtained by the same analysis and no additional measurements are needed.

**Acknowledgement.** The author wishes to thank the Maj and Tor Nessling Foundation for supporting this study financially.

## References

- AURA, E. 1978. Determination of available soil phosphorus by chemical methods. *J. Scient. Agric. Soc. Finl.* 50: 305–316.
- AURA, E. 1980. Oxygen as an exchangeable ligand in soil. *J. Scient. Agric. Soc. Finl.* 52: 34–44.
- BACHE, B. W. & WILLIAMS, E. G. 1971. A phosphate sorption index for soils. *J. Soil Sci.* 22: 289–301.
- BECKWITH, R. S. 1965. Sorbed phosphate at standard supernatant concentration as an estimate of the phosphate needs of soils. *Aust. J. Exp. Agric. Anim. Husb.* 5: 52–58.
- FITTER, A. H. & SUTTON, C. D. 1975. The use of the Freundlich isotherm for soil phosphate sorption data. *J. Soil Sci.* 26: 241–246.
- HARTIKAINEN, H. 1982 a. Water soluble phosphorus in Finnish mineral soils and its dependence on soil properties. *J. Scient. Agric. Soc. Finl.* 54: 89–98.
- 1982 b. Relationship between phosphorus intensity and capacity parameters in Finnish mineral soils. I Interpretation and application of phosphorus sorption-desorption isotherms. *J. Scient. Agric. Soc. Finl.* 54: 245–250.
- HELYAR, K. R. & MUNNS, D. N. 1975. Phosphate fluxes in the soil-plant system: a computer simulation. *Hilgardia* 43: 103–130.
- HOLFORD, I. C. R. 1976. Effects of phosphate buffer capacity of soil on the phosphate requirements of plants. *Plant and Soil* 45: 433–444.
- & MATTINGLY, G. E. G. 1976. Phosphate adsorption and plant availability of phosphate. *Plant and Soil* 44: 377–389.
- KAILA, A. 1963. Dependence of the phosphate sorption capacity on the aluminium and iron in Finnish soils. *J. Scient. Agric. Soc. Finl.* 35: 165–177.
- MEAD, J. A. 1981. A comparison of the Langmuir, Freundlich and Temkin equations to describe phosphate adsorption properties of soils. *Aust. J. Soil Res.* 19: 333–342.
- OLSEN, S. R. & WATANABE, F. S. 1957. A method to determine a phosphorus adsorption maximum of soils as measured by the Langmuir isotherm. *Soil Sci. Soc. Amer. Proc.* 21: 144–149.
- OZANNE, P. G. & SHAW, T. C. 1967. Phosphate sorption by soils as a measure of phosphate requirement for pasture growth. *Aust. J. Agric. Res.* 18: 601–612.

- SCHACHTSCHABEL, P. & BEYME, B. 1980. Löslichkeit des anorganischen Bodenphosphors und Phosphatdüngung. Z. Pfl. ern. Düng. Bodenk. 143: 306–316.
- SNEDECOR, G. W. & COCHRAN, W. G. 1972. Statistical methods. 593 p. Ames.
- TAYLOR, A. W. & KUNISHI, H. M. 1971. Phosphate equilibria on stream sediment and soil in a watershed draining an agricultural region. J. Agric. Food Chem. 19: 827–831.

Ms received June 2, 1982

## SELOSTUS

# Fosforin intensiteetti- ja kapasiteettiparametrien välisestä suhteesta suomalaisissa kivennäismaissa

## II Sorptio-desorptioisotermit ja niiden riippuvuus maan ominaisuuksista

Helinä Hartikainen

*Helsingin yliopiston maanviljelyskemian laitos, 00710 Helsinki 71*

Maan fosforin helppoliukoisuutta sekä maan kykyä ylläpitää tiettyä fosforin pitoisuutta maanesteessä selvitetiin kahden erityyppisen fosforin pidättymistä ja vapautumista kuvaavan isotermin avulla 104 kivennäismaanäytteellä. Fosforin pidättyminen tai vapautuminen esitettiin isotermissä A lisätyn liuoksen ja isotermissä B saadun tasapainoliuoksen fosforin pitoisuuden funktiona. Molemmille isotermeille saatiin yhtälö  $y = a + bx$ , jossa  $y$  vastaa pidättynyttä tai vapautunutta fosforin määrää ja  $x$  liuoksen fosforin pitoisuutta.

Isotermissä A vakion  $a$  todettiin ilmaisevan maan vesiliukoisen fosforin määrää käytetyssä uuttosuhteessa ja kuvaavan fosforitilan intensiteettitekijää. Sen sijaan isotermissä B vakio  $a$  näytti kytkeytyvän varsin heikosti vesiuuttoisen fosforin määrään. Suoran kulmakerroin  $b$  kuvaa isotermissä A pidättymis- ja vapautumisreaktioiden tehokkuutta ja isotermissä B maan fosforinpuskurikykyä eli kykyä vastustaa fosforin pitoisuuden muutoksia maanesteessä. Molemmissa tapauksissa  $b$ :n arvo näytti voimakkaimmin riippuvan maan oksalaattiuuttoisen alumiinumin määrästä. Oksalaattiin liukenevalla raudalla näytti olevan suhteellisesti suurempi merkitys isotermissä A kuin isotermissä B. Tekijä  $b$  on ilmeisesti yhteydessä maan fosforitilan intensiteettitekijöihin, sillä  $b$ :n arvoon vaikuttivat huomattavasti myös vesiliukoisen fosforin pitoisuutta säätelevät maan ominaisuudet.

Isotermien yhtälöistä ratkaistiin fosforinvaihdon nollapistettä vastaavan liuoksen fosforikonsentraatio ( $-a/b$ ), ts. fosforin pitoisuus liuoksessa, josta ei sitoudu fosforia maahan ja johon ei myöskään maasta vapaudu fosforia. Tästä pisteestä käytettiin lyhennettä EBS tai EPC ja se vaihteli koko aineistossa 0.003 mg:sta 13.89 mg:aan litrassa. EBS:n (=EPC) arvoista voitiin päätellä, että aitosavimaat pystyivät pidättämään fosforia keskimäärin ottaen laimeammista liuoksista kuin muiden ryhmien maanäytteet. Tulosten tarkastelussa kiinnitettiin huomiota fosforinvaihdon nollapistettä kuvaavan suureen merkitykseen lannoitus- ja vesitötutkimuksen kannalta.