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Phosphorus Forms and Extractability from Three Sources in a Recently Exposed Calcareous Subsoil

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ABSTRACT

Irrigation-induced erosion and land leveling have decreased crop yields on ≈800 000 ha of south-central Idaho silt loam soils because of topsoil removal. Phosphorus availability is a known production problem after topsoil removal. This study evaluated the effect of three P sources on soil P solubility by three standard methods for calcareous soils. A long-term study was initiated on a Portneuf silt loam (Coarse-silty, mixed, superactive, mesic Durinodic Xeric Haplocalcid) by removing the surface 0.3 m of topsoil from strips between undisturbed topsoil strips. Phosphorus treatments applied across all strips were conventional fertilizer (applied according to soil test), dairy manure, and cheese whey. All treatments increased the freshly exposed subsoil bicarbonate extractable ortho-P concentrations up to or greater than the topsoil concentrations, which were more than adequate for economical crop production. The high-whey and manure treatments increased the subsoil saturation paste and 0.01 *M* $CaCl_2$ extractable ortho-P concentrations up to or greater than the untreated topsoil ortho-P concentrations. The initial topsoil ortho-P solubility was along the β-tricalcium phosphate (β-TCP) isotherm and the initial subsoil was well below the β-TCP isotherm. The ortho-P solubility of the subsoil monocalcium phosphate (MCP) treatment remained just below the β-TCP isotherm. The cottage cheese whey treatment increased subsoil P solubility up to the β-TCP isotherm and the manure treated subsoil ortho-P solubilities were between the β-TCP and octacalcium phosphate (OCP) isotherms. Most subsoil ortho-P concentrations by all three extraction methods decreased from spring to fall and then increased over winter in the subsequent spring samples. Soil solution ortho-P concentrations decreased with time in the subsoil treatments except immediately following treatment applications. The topsoil ortho-P extract concentrations by all three methods varied among samplings but remained about the same during the study period.

EROSION OF IRRIGATED SILT LOAM SOILS in south-central Idaho removes up to 140 Mg soil ha^{-1} per season, depending on crops grown and field slope (Berg and Carter, 1980). This does not represent the total topsoil movement, since additional soil moves from the upper end of fields and is redeposited on the lower end of fields by irrigation water, exposing more subsoil than indicated by net topsoil loss. Land leveling to increase field size and reduce irrigation labor also exposes subsoil on additional areas. Mixing subsoil with topsoil, without loss of topsoil, by deep tillage also reduces crop yields on these soils (Cary and Rasmussen, 1979). Erosion and land leveling has decreased crop yields on at least 800 000 ha in south-central Idaho (Carter et al., 1985).

In the spring of 1991, Robbins et al. (1997) established a long-term study to find a method(s) to increase freshly exposed calcareous subsoil productivity to the levels of adjacent uneroded soils. Fertilizer treatments were applied to Portneuf silt loam subsoil plots in 1991 and crop rotation variables were applied for 3 yr (Fig. 1, Table 1). In 1994, all plots were planted to bean (*Phaseolus vulgaris* L., cv. Viva) as a test crop. Soil and whole bean plant N, P, K, Cu, Mn, Fe, and Zn availability and uptake were measured to determine why dairy manure increased bean yields to that of the topsoil, while acid cottage cheese whey and conventional fertilizer applications did not. Zinc uptake and soil organic C (OC) increases were the only measured factors that appeared to be associated with increasing subsoil bean yields to levels of the topsoil yields. Soil test and whole bean plant uptake of all other measured nutrients were more than adequate for maximum bean seed yield (Robbins et al., 1997).

The treatments applied in the previous study were an attempt to find a method of increasing subsoil productivity to that of the original topsoil (Robbins et al., 1997). No attempt was made to keep total or ortho-P rates uniform across treatments. The original treatments along with additional treatments in the fall of 1994 and four additional years of soil P data provided an excellent opportunity to track ortho-P solubility and saturation paste extract and 0.5 *M* $NaHCO_3$ extractable ortho-P soil test P (STP) concentration changes with time on topsoil and subsoil treated with different P-supplying materials.

Phosphorus availability and mobility in calcareous soils can be evaluated by several methods. In general, for soils with free lime, the standard extractant for relative plant available P is 0.5 *M* $NaHCO_3$ (Watanabe and Olsen, 1965). Water-soluble ortho-P gives an indication of potential ortho-P movement with leaching and is sometimes used as a measure of plant-available P (Nishimoto et al., 1977) and can be estimated with a dilute $CaSO_4$ solution after contact for 30 min, or in the saturation paste extract after 18 h of equilibrium. Alterna-

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Abbreviations: EC, electrical conductivity; F, fall; HA, hydroxyapatite [$Ca_5(PO_4)_3OH$]; MCP, monocalcium phosphate; OC, organic C; OCP, octacalcium phosphate [$Ca_4H(PO_4)_3{\cdot}2.5H_2O$]; S, spring; STP, soil test phosphate (0.5 *M* $NaHCO_3$ extractable ortho-P); β-TCP, beta tricalcium phosphate [β-$Ca_3(PO_4)_2$].

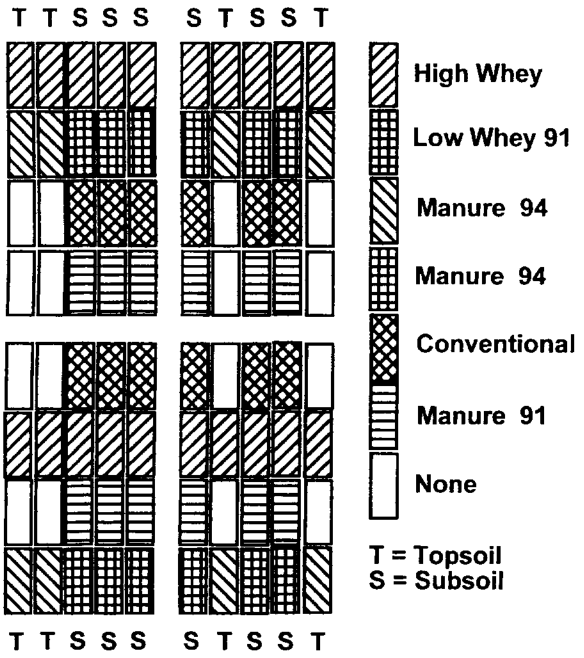

Fig. 1. Experimental design and treatment plot layout at the end of the 1997 growing season. Topsoil, subsoil, and crop rotations were positioned along the length of the field and fertilizer treatments were across the field. (Wide spaces represent replication boundaries for illustration purposes only.)

tively, soil solution P concentrations can be estimated using 0.01 *M* $CaCl_2$ solutions equilibrated for 24 h with continuous, mild shaking or with intermittent shaking for 6 d. This latter estimate is also used to compare soil P solubility relationships with known mineral solubilities and for developing adsorption isotherms (Lindsay, 1979). Both the saturated $CaSO_4$ and 0.01 *M* $CaCl_2$ solutions have Ca concentrations approximately equal to calcareous soil solutions.

In this paper, we report 0.5 *M* $NaHCO_3$, saturation paste, and 0.01 *M* $CaCl_2$ extractable ortho-P concentration and ortho-P solubility changes across 7 yr caused by treating topsoil and subsoil plots with monocalcium phosphate (MCP), cheese whey, and fresh dairy manure.

MATERIALS AND METHODS

The study was conducted on a Portneuf silt loam (Coarse-silty, mixed, superactive, mesic Durinodic Xeric Haplocalcid) having a noncontinuous 0.20- to 0.45-m-thick lime–silica cemented hard layer that starts 0.30 to 0.45 m below the surface in native soils. The native topsoil is pale brown (10 YR 6/3), and the hard layer is white (10 YR 8/2). The material below the hard layer is a light gray (10 YR 7/2) silt loam. Silt increases from 62% in the surface to 67% at 1.3 m. The sand fraction is fairly constant at ≈18% down to 1.3 m. The clay content decreases from ≈20% in the surface to 15% at 1.3 m on uneroded sites (Robbins, 1977). The topsoil contained 80 g $CaCO_3$ equivalent and the subsoil contained 240 g $CaCO_3$ equivalent kg^{-1} soil. The plot area has a 1.1% slope and was surface irrigated for more than 90 yr. There is a slight but definite redistribution of topsoil from the top to the bottom of the field.

In 1991, topsoil was removed from three long narrow strips, along the full length of the field, between undisturbed strips of topsoil plots to create freshly exposed subsoil plots (Fig. 1). The topsoil was spread on an adjacent field. The strip arrangement was necessary because the plot area is furrow irrigated and the study was to last for at least 8 yr. Each plot is 9 m wide and 21 m long. Crop rotations were randomized across the field (Fig. 1); however, crop rotations did not significantly affect STP or P uptake by subsequent crops (Robbins et al., 1997), consequently crop rotations are not discussed here. The four fertilizer treatments were applied only to the subsoil strips in 1991. Phosphorus treatments were not applied to any topsoil plots until after the 1994 cropping season (Table 1). Following the 1994 cropping season, manure was applied to two topsoil and three subsoil plots in each replication, and whey was applied to two topsoil and three subsoil plots in each replication (Fig. 1, Table 1). Four topsoil plots in each replication were left untreated for the entire study.

The four 1991 fertilizer treatments were conventional (fertilized according to soil tests for calcareous soils), manure, high-whey, and low-whey. Only the P fertilizer rates and re-

Table 1. Treatment dates, materials, total P, and ortho-P portion of total P applied to subsoil and topsoil plots.

	Treatment material					
Treatment	**Apr. 1991**	**Nov. 1991**	**Oct. 1994**	**Apr. 1991**	**Nov. 1991**	**Oct. 1994**
					kg total P ha^{-1} (kg ortho-P ha^{-1})	
Subsoil conventional†	MCP¶	MCP	None	135	130	0
Subsoil high-whey†,‡	Whey	Whey	Whey	970 (825)	420 (360)	225 (135)
Subsoil low-whey†,§	Whey	Whey	–	242 (205)	210 (180)	–
Subsoil manure 1994‡,§	Whey	Whey	Manure	242 (205)	210 (180)	450 (225)
Subsoil manure 1991†	Manure	Manure	None	380 (210)	800 (450)	0
Topsoil	None	None	None	0	0	0
Topsoil manure 1994‡	None	None	Manure	0	0	450 (225)
Topsoil whey 1994‡	None	None	Whey	0	0	225 (135)

† Treatments were applied after the spring 1991 and fall 1991 soil samples were taken.
‡ Treatments were applied after the fall 1994 soil samples were taken.
§ Manure was applied to the low-whey plots after the fall 94 soil samples were taken.
¶ MCP is monocalcium phosphate.

Table 2. Bicarbonate-extractable ortho-P concentrations in soil samples collected in the spring (S) and fall (F) of the respective years.

Treatment	*n*	S1991	F1991	S1992	F1992	S1993	F1993	S1994	F1994	F1995	S1996	S1997	S1998	LSD¶
		mg P kg^{-1}												
Subsoil conventional†	12	9	12	31	25	36	29	32	21	26	32	30	28	4
Subsoil high-whey†,‡	12	9	48	71	57	74	49	48	35	77	82	64	57	13
Subsoil low-whey†,§	12	9	27	51	38	55	37	31	25					9
Subsoil manure 1994‡,§	12									118	137	142	126	20
Subsoil manure 1991†	12	9	70	114	124	134	122	125	88	85	118	111	104	33
Topsoil	16	25		25	24	28	24	22	19	22	26	22	21	3
Topsoil manure 1994‡	8	23		21	22	27	26	19	18	105	121	95	94	7
Topsoil whey 1994‡	8	22		22	21	25	22	19	17	47	42	40	37	21

† Treatments were applied after the S1991 and F1991 soil samples were taken.

‡ Treatments were applied after the F1994 soil samples were taken.

§ Manure was applied to the low-whey plots after the F1994 soil samples were taken.

¶ Least significant difference (LSD) across years for each treatment is calculated at $P < 0.05$.

sults will be discussed here. Please refer to Robbins et al. (1997) for N, K, and Zn application rates. The conventional subsoil plots received 135 kg P ha^{-1} as MCP on 23 Apr. 1991 (Table 1). The following day, fresh dairy manure was applied at an air-dry rate of 44 Mg ha^{-1}. It contained 0.6 g water g^{-1} of wet manure and 8.6 g total P kg^{-1} of air-dry manure, providing 380 kg total P ha^{-1}. The subsoil plots were then furrowed with large shovels on 0.50-m centers and 0.25 m deep to make large ridges. This covered the manure and commercial fertilizer and provided the maximum surface possible for applying the whey treatments. Berms were made at each end of the whey plots for whey containment. Cottage cheese whey (acid) was surface applied to the whey plots through gated irrigation pipe. The acid whey was the byproduct of cottage cheese produced by adding 3 kg of H_3PO_4 to each 1000 kg of milk and contained 1050 mg P kg^{-1} of whey (as opposed to sweet whey from hard cheeses coagulated by biological culture as applied in the fall of 1994). The low-whey plots received 230 m^3 whey ha^{-1} (equivalent to 23-mm depth of whey) and the high-whey plots received 920 m^3 whey ha^{-1} (92-mm depth). Total and ortho-P applications are shown in Table 1. Based on initial soil test concentrations (Watanabe and Olsen, 1965), P was not added to the topsoil plots (Tables 1 and 2). The entire plot area was moldboard plowed 0.3 m deep after the fertilizer treatments were applied.

At the end of the 1991 growing season, each plot was sampled and tested for STP. On the basis of the soil tests, 130 kg P ha^{-1} as MCP were added to the conventional fertilizer subsoil plots. Fresh dairy manure was again applied to the manure treatment plots at 93 Mg ha^{-1} on an air-dry basis to add additional organic matter. This application rate was not based on P test or crop need. The low-whey plots received 200 m^3 ha^{-1} (20-mm depth) of acid whey, and the high-whey plots received 400 m^3 ha^{-1} (40-mm depth) of acid whey. The whey was added to give additional readily decomposable organic matter, and its application was not based on soil test or crop need. The plots were then moldboard plowed to mix the added materials with the soil. No treatments were applied to the topsoil plots.

After the 1994 bean harvest, 74 Mg ha^{-1} of fresh dairy manure (dry weight basis) was applied to the original subsoil low-whey plots and the topsoil plots in the same rows (Fig. 1). The high-whey subsoil plots and the topsoil plots in the same rows received 500 m^3 (50-mm depth) of sweet whey (whey from cultured cheese) on 8 and 9 Nov. 1994 (Table 1). The 1991 manure plots received no additional treatments.

Ortho-P concentrations in the manure were measured in 1:20 manure/0.5 *M* $NaHCO_3$ extracts and in water dilutions of the whey (Watanabe and Olsen, 1965). Total-P was determined by ashing manure or whey samples at 500°C, dissolving the ash in 10 mL of 1.0 *M* HNO_3, heating for 10 min just below boiling and then determining total P in an appropriate-sized aliquot (Kitson and Mellan, 1944). No attempt was made to identify P forms beyond ortho- and total-P.

Soil samples were taken each spring from 1991 to 1998, except spring 1995, and each fall from 1991 to 1995. Topsoil samples were not taken in the fall of 1991 because of unusually early adverse weather (Table 2). All soil samples were taken before treatments were applied each spring or fall. The entire plot area was moldboard plowed each spring following soil sampling to 0.30 m, except in the spring of 1997. Five soil samples 75 mm in diameter by 300 mm deep (plow depth) were taken from each plot, combined, and thoroughly mixed. A 5-kg subsample was air dried and saved for chemical analysis.

Bicarbonate extractable (STP) (Table 2) and water-soluble (saturation paste extract) (Robbins and Wiegand, 1990) (Table 3) ortho-P was measured on all soil samples (Watanabe and Olsen, 1965). Ortho-P concentrations in 0.01 *M* $CaCl_2$ (Table 4) were measured each spring from 1991 to 1997 except for the spring of 1995 (the spring following the second treatment application year) and in the fall of 1994 and 1995 by shaking 2.0 g of air-dried ground soil in 40 mL of 0.01 *M* $CaCl_2$ for 22 h at one cycle per second at 20°C (Fox and Kamprath, 1970). The samples were centrifuged and the pH and electrical

Table 3. Saturation paste ortho-P concentrations in soil samples collected in the spring (S) and fall (F) of the respective years.

Treatment	*n*	S1991	F1991	S1992	F1992	S1993	F1993	S1994	F1994	F1995	S1996	S1997	S1998	LSD¶
		mg P L^{-1}												
Subsoil conventional†	12	0.05	0.25	0.59	0.27	0.51	0.34	0.39	0.26	0.21	0.31	0.20	0.24	0.11
Subsoil high-whey†,‡	12	0.05	0.53	1.65	0.76	1.09	0.67	0.56	0.29	1.51	1.71	0.78	0.85	0.41
Subsoil low-whey†,§	12	0.05	0.23	1.12	0.41	1.04	0.51	0.36	0.19					0.32
Subsoil manure 1994‡,§	12									3.04	3.87	3.23	3.32	0.50
Subsoil manure 1991†	12	0.05	0.47	2.65	1.80	3.24	2.86	2.20	1.68	2.20	3.23	2.35	2.34	0.64
Topsoil	16	0.78		0.78	0.64	0.69	0.56	0.50	0.44	0.54	0.72	0.48	0.48	0.13
Topsoil manure 1994‡	8	0.58		0.48	0.31	0.46	0.34	0.31	0.26	3.01	3.82	3.24	3.35	0.62
Topsoil whey 1994‡	8	0.53		0.61	0.39	0.65	0.43	0.35	0.30	2.02	1.82	1.10	1.15	0.42

† Treatments were applied after the S1991 and F1991 soil samples were taken.

‡ Treatments were applied after the F1994 soil samples were taken.

§ Manure was applied to the low-whey plots after the F1994 soil samples were taken.

¶ Least significant difference (LSD) across years for each treatment is calculated at $P < 0.05$; 0.03 mg P L^{-1} is about the lower detection limit for these samples.

Table 4. Ortho-P concentrations in 0.01 *M* $CaCl_2$ extracts of soil samples collected in the spring (S) and fall (F) of the respective years.

Treatment	*n*	S1991	S1992	S1993	S1994	F1994	F1995	S1996	S1997	S1998	LSD¶
		mg P L^{-1}									
Subsoil conventional†	12	0.05	0.16	0.13	0.11	0.09	0.06	0.12	0.06	0.07	0.08
Subsoil high-whey†,‡	12	0.05	0.34	0.28	0.21	0.12	0.37	0.36	0.25	0.21	0.09
Subsoil low-whey†,§	12	0.05	0.23	0.20	0.15	0.09					0.08
Subsoil manure 1994‡,§	12						1.01	1.00	1.02	0.86	0.22
Subsoil manure 1991†	12	0.04	0.86	1.02	0.97	0.41	0.67	0.80	0.70	0.63	0.23
Topsoil	16	0.30	0.28	0.25	0.28	0.21	0.18	0.25	0.17	0.24	0.12
Topsoil manure 1994‡	8	0.27	0.19	0.20	0.16	0.15	0.82	1.48	1.34	1.04	0.32
Topsoil whey 1994‡	8	0.27	0.26	0.24	0.20	0.16	1.09	0.54	0.41	0.34	0.12

† Treatments were applied after the S1991 and F1991 soil samples were taken.

‡ Treatments were applied after the F1994 soil samples were taken.

§ Manure was applied to the low-whey plots after the F1994 soil samples were taken.

¶ Least significant difference (LSD) across years for each treatment is calculated at $P < 0.05$; 0.03 mg P L^{-1} is about the lower detection limit for these samples.

conductivity (EC) of the supernatant were measured immediately (Robbins and Wiegand, 1990) and solution ortho-P was determined (Watanabe and Olsen, 1965). Sulfate and F were determined by ion chromatography (Robbins, 1989), and Ca and Mg were determined by atomic absorption spectrophotometry in the 0.01 *M* $CaCl_2$ extracts.

The appropriate ortho-P ion pairs and activities were added to an existing iterative procedure to calculate Ca^{2+} and HPO_4^- activities corrected for $CaSO^4_0$, $CaCO_3^0$, $CaHCO_3^+$, $CaH_2PO_4^+$, $CaPO_4^-$, CaF_2^0, $MgSO_4^0$, $MgCO_3^0$, $MgHCO_3^+$, $MgHPO_4^0$, $MgH_2PO_4^+$, and MgF^+ ion pairs and ionic strength (Robbins et al.,1980). The Davies equation was used to estimate activity coefficients (Stumm and Morgan, 1970, p. 83) and ionic strength was estimated from EC (Griffin and Jurinak, 1973). The calculated log $H_2PO_4^-$ pH and log Ca^{2+} + 2pH data were plotted along with the double function solubility diagrams for OCP, β-TCP, and hydroxyapatite (HA) (Fig. 2–7). The solubility product (K_{sp}) values and the equilibrium equations for OCP, β-TCP, and HP calculations are shown in Table 5 (Lindsay, 1979).

The bivariant ortho-P solubility means and significant differences, by time, for each treatment were calculated at $P <$ 0.05 using the SAS GLM Tukey procedure (SAS Institute, 1989).

RESULTS

The initial freshly exposed subsoil (spring [S] 1991) STP concentration was 9 mg P kg^{-1} (Table 2). The initial topsoil STP was 22 to 25 mg P kg^{-1}. Adequate STP values for these calcareous soils vary between 10 to 15 mg P kg^{-1}, depending on the crop (University of Idaho, 1998). The fresh subsoil saturation paste ortho-P was 0.05 mg P L^{-1} and 0.53 to 0.78 mg P L^{-1} in the topsoil (Table 3). The untreated subsoil 0.01 *M* $CaCl_2$ extractable ortho-P concentration was 0.04 to 0.05, and 0.27 to 0.30 mg P L^{-1} in the initial topsoil (Table 4).

The MCP-treated subsoil conventional treatment soil STP increased from 9 to 31 mg ortho-P kg^{-1} (S1991–S1992) after the second phosphate application (Table 2). With no additional P application for the next 7 yr, STP varied between 21 and 36 mg P kg^{-1} and showed no long-term change during the sampling period. The saturation paste ortho-P concentrations increased from 0.05 mg L^{-1} in the freshly exposed subsoil samples (S1991) to a maximum 0.59 mg L^{-1} in the S1992 samples after a second MCP application, then decreased with time (Table 3). The 0.01 *M* $CaCl_2$ extract ortho-P con-

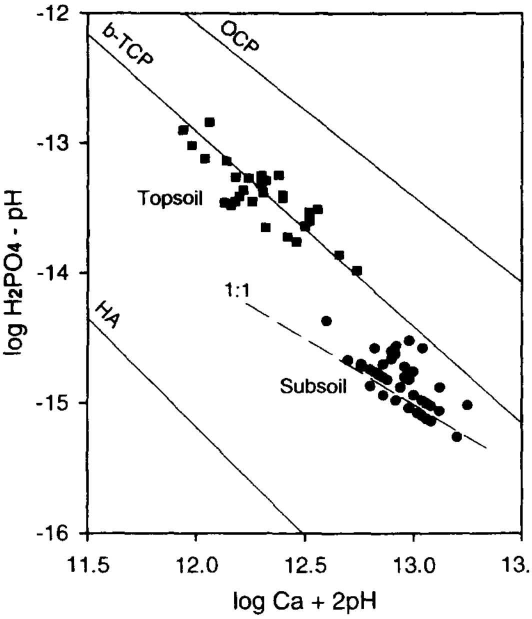

Fig. 2. Topsoil and subsoil ortho-P solubilities prior to treatment applications in the spring of 1991. The dashed isotherm line through the subsoil data has a 1:1 slope.

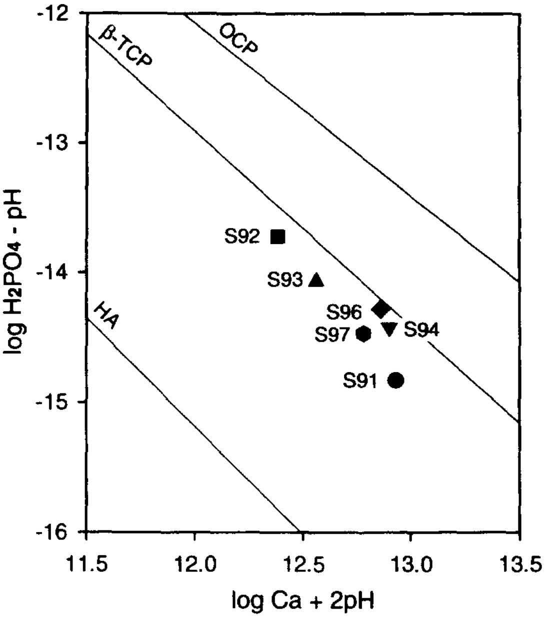

Fig. 3. Subsoil conventional treatment ortho-P solubility changes with time. The spring (S) 1994, S1996, and S1997 means are not different from each other at P = 0.05. All other combinations are different.

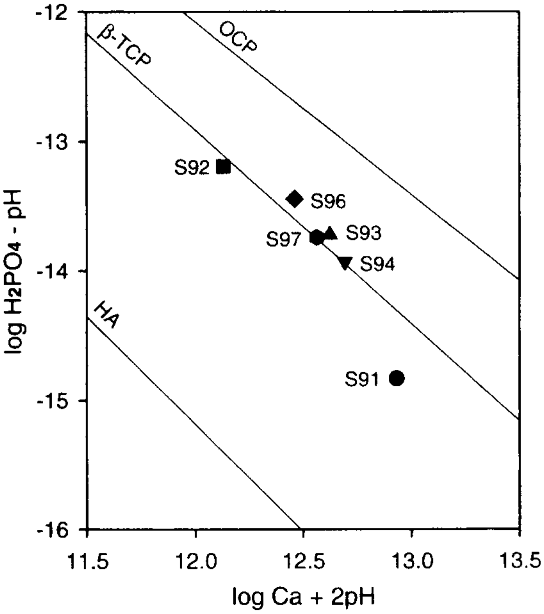

Fig. 4. Subsoil high-whey treatment ortho-P solubility changes with time. The spring (S) 1993 and S1997 means are not different from the S1994 or S1996 means at $P = 0.05$. All other combinations are different.

centrations followed the same trends, although samples were analyzed from fewer sampling dates (Table 4).

The high-whey subsoil treatment STP increased from 9 to 48 (S1991– fall [F] 1991), then to 71 mg ortho-P kg^{-1} soil by the S1992 sampling (Table 2). It steadily decreased to 35 mg P kg^{-1} in the F1994 sampling. Additional whey applied after the F1994 sampling increased the STP to 77 (F1995), to 82 (S1996), and then it decreased to 57 mg P kg^{-1} in S1998. Saturation paste extract ortho-P increased from 0.05 mg L^{-1} in the fresh subsoil to 1.65 in the S1992 samples and decreased to 0.29 prior to additional whey application (Table 3). It increased to 1.51 mg ortho-P kg^{-1} after the fall 1994 whey application and to 1.71 by S1996, followed by a substantial decrease the S1997 and S1998 samples. The 0.01 M $CaCl_2$ extract concentrations increased from 0.05

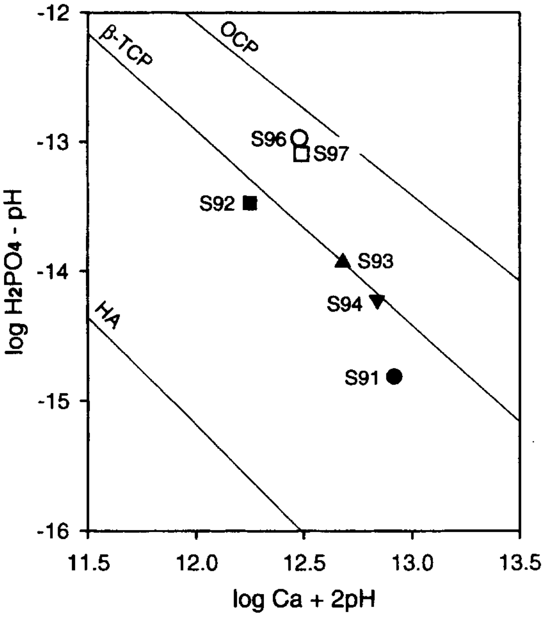

Fig. 5. Subsoil low-whey spring (S) 1993 and S1994 treatment ortho-P solubility values (solid points) are not different from each other but are different from all other values at $P = 0.05$. Manure was applied to these plots in the fall of 1994 to became the subsoil manure 1994 plots (open points). The S1996 and S1997 manure values are not different from each other, but are different from the low-whey treatment values ($P = 0.05$).

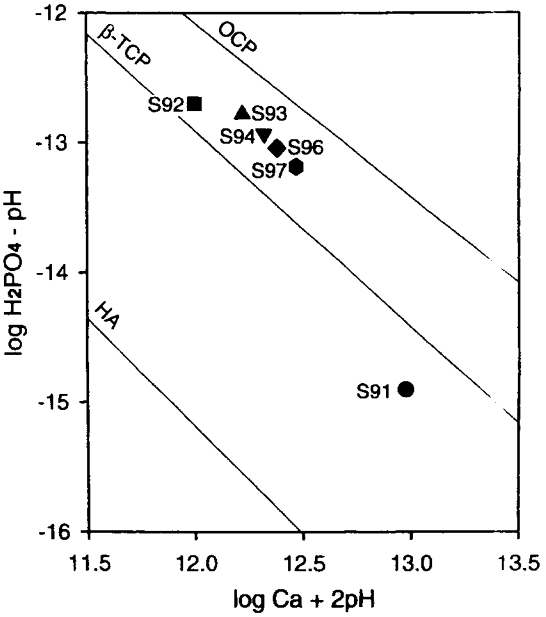

Fig. 6. The spring (S) 1993 subsoil manure 1991 treatment ortho-P solubilities were not different from S1992, S1994, and S1996; and S1994, S1996, and S1997 were not different from each other ($P = 0.05$). All other combinations are different.

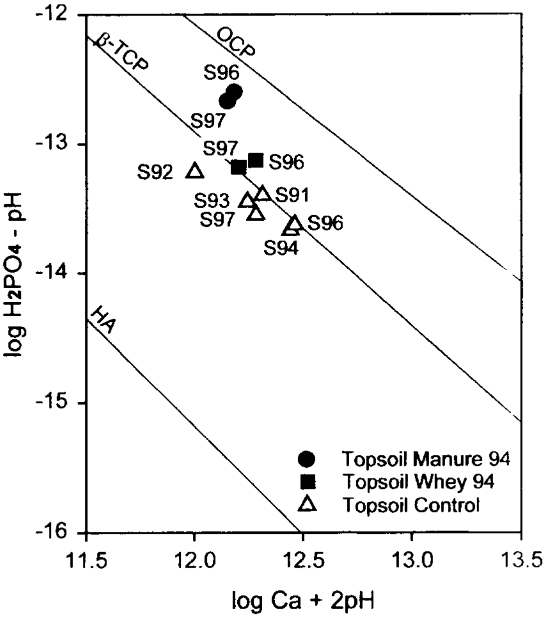

Fig. 7. The untreated topsoil (open points) and the topsoil whey 1994 (solid squares) treatments: ortho-P solubility means are not different, except that spring (S) 1992 and topsoil S1996 and S1994 were different from each other at $P = 0.05$. The topsoil manure 1994 S1996 and S1997 (solid circles) means are not different from each other, but are different from all other treatment means.

Table 5. Equations and solubility product pK_{sp} used for the double function plots (Lindsay, 1979).

Mineral†	Equilibrium equation	pK_{sp}‡
OCP	$pH - \log H_2PO_4^- = 8/3(pH + 1/2\log Ca^{2+}) - 3.91$	46.9
β-TCP	$pH - \log H_2PO_4^- = 3(pH + 1/2\log Ca^{2+}) - 5.09$	49.3
HA	$pH - \log H_2PO_4^- = 10/3(pH + 1/2\log Ca^{2+}) - 4.82$	14.46

† OCP is octocalcium phosphate; β-TCP is beta tricalcium phosphate; HA is hydroxyapatite.

‡ pK_{sp} is the negative log of the solid phase solubility product.

in S1991 to 0.34 mg ortho-P L^{-1} in S1992, and decreased to 0.12 in F1994. Adding more whey increased it to 0.37 in F1995 then it decreased to 0.21 by S1998. (Table 4).

The low-whey results followed the same pattern as the high-whey but with less intensity with respect to STP, saturation paste extract, and the 0.01 *M* $CaCl_2$ extractable ortho-P (Tables 2, 3, and 4). Following the F1994 soil sampling, manure was applied to the low-whey subsoil plots and the topsoil plots in the same rows. For the remainder of the study they were designated the Manure 94 plots (Table 1). The STP increased to 118 in F1995, 137 in S1996, 142 in S1997, and decreased to 126 mg ortho-P kg^{-1} soil in the S1998 samples (Table 2). The saturation paste and 0.01 *M* $CaCl_2$ extractable ortho-P concentrations also increased following the manure additions (Tables 3 and 4).

The subsoil manure 1991 STP increased with each sampling and manure application from S1991 to S1993, starting at 9 and peaking at 134 mg P kg^{-1} in the S1993 samples (Table 2). The STP then slowly decreased with time across the next seven samplings. The saturation paste and 0.01 *M* $CaCl_2$ extract ortho-P concentrations in the manure 1991 samples were the highest of the 1991 subsoil plot treatments and remained very high over the study period (Tables 3 and 4).

Adding 450 kg P ha^{-1} in manure and 225 kg P ha^{-1} in whey to the topsoil after the F1994 sampling increased the STP, saturation paste, and 0.01 *M* $CaCl_2$ extractable ortho-P in the F1995 and S1996 samples followed by slight decreases in the S1997 samples (Tables 2, 3, and 4).

Using the data used to produce Tables 2, 3, and 4, linear regressions were calculated among bicarbonate, saturation paste, and 0.01 *M* $CaCl_2$ extractable ortho-P for all data, subsoil data, and topsoil data (Table 6). These data suggest that good relationships exist among the three extraction methods for the topsoil and the subsoil, but that the relationships are different for the topsoil and the subsoil due to the differences in the slopes of the regressions.

There was a significant annual cycling of STP and saturation paste ortho-P concentrations in both the subsoil and topsoil treatments with two exceptions. These two P extraction method concentrations decreased from spring to fall and then increased from fall to spring samplings except in the F1993 to S1994 samples and when added P sources offset the P uptake by the growing crops (Tables 2 and 3). Insufficient fall data were collected to measure the spring to fall cycle effect in the 0.01 *M* $CaCl_2$ samples.

The freshly exposed subsoil ortho-P solubilities fell along or slightly above a 1:1 slope isotherm between the HA and β-TCP isotherms (Fig. 2). The initial topsoil P solubilities were about equally spaced above and below the β-TCP isotherm. The ortho-P solubilities in the MCP-treated subsoil conventional treatment moved closer to and up along the β-TCP isotherm by the S1992 sampling, then moved back down but remained below the β-TCP isotherm during the sampling period (Fig. 3). The high-whey S1992 P solubility moved up to and along the β-TCP isotherm past the conventional treatment subsoil and higher than most of the topsoil treatment samples for the same date (Fig. 2, 3, and 4). By S1994, the P solubility had moved back down along the β-TCP isotherm. Whey addition in the fall of 1994 moved the S1996 solubility up and above the β-TCP isotherm. The S1997 solubilities then moved to a slightly lower position and onto the β-TCP isotherm. Each low-whey P solubility for a particular sampling was down the isotherm from the corresponding high-whey concentration but remained near the β-TCP isotherm (Fig. 4 and 5). With the fall 1994 manure addition to the low-whey soil, the ortho-P solubility increased to well above the β-TCP isotherm in S1996 and S1997 (Fig. 5). Ortho-P solubility in the subsoil manure 1991 treatments moved up along and above the β-TCP isotherm in the S1992 samples (Fig. 6). The S1993 through S1997 solubilities moved closer to the OCP isotherms and slightly down along the isotherm. All untreated topsoil ortho-P solubility means were near to or below the β-TCP isotherm (Fig. 7). With whey or manure additions, the phosphate solubilities moved above and slightly up along the β-TCP isotherms, but remained below the OCP isotherm (Fig. 7).

Table 6. Regression equations for comparison of saturation paste (SPP), calcium chloride ($CaCl_2P$), and bicarbonate extractable (STP) ortho-P.

All data

$SPP = 0.2078 + 0.02557STP,\ r^2 = 0.8492$
$CaCl_2P = -0.0102 + 0.0077STP,\ r^2 = 0.7206$
$CaCl_2P = 0.0288 + 0.3026SPP,\ r^2 = 0.8968$

Subsoil

$SPP = -0.4404 + 0.02604STP,\ r^2 = 0.9129$
$CaCl_2P = -0.1329 + 0.0079STP,\ r^2 = 0.9306$
$CaCl_2P = 0.0070 + 0.2847SPP,\ r^2 = 0.9346$

Topsoil

$SPP = -0.2494 + 0.03530STP,\ r^2 = 0.9547$
$CaCl_2P = -0.0202 + 0.0118STP,\ r^2 = 0.8459$
$CaCl_2P = 0.0421 + 0.3458SPP,\ r^2 = 0.9178$

DISCUSSION

We would remind the reader that uniform P application rates and forms were not applied in this study. What is shown is how STP, saturation paste, and 0.01 *M* $CaCl_2$ extractable ortho-P and ortho-P solubilities changed with time and cropping following each treatment application.

The untreated freshly exposed subsoil STP mean was 9 mg P kg^{-1}, as compared with 23 mg P kg^{-1} in the topsoil at the beginning of the study. The first 135 kg P ha^{-1} added to the subsoil as MCP increased the STP by 3 mg P kg^{-1} in the F1991 sampling, which was not significant at $P < 0.05$. The high P immobilization was probably due to freshly exposed lime minerals (240 g $CaCO_3$ equivalent kg^{-1}) that reacted with the added P. The second 130 kg P ha^{-1} added to the same plots after the F1991 soil sampling increased the STP by 19 mg kg^{-1}, or 6.8 kg P ha^{-1} added for each mg P kg^{-1} increase in STP by the S1992 sampling (Table 2). When Westermann (1992) added MCP to other Portneuf soils that were deep-mixed 18 yr earlier, or to Portneuf topsoil treated with CaO or $CaCO_3$, more MCP was required to increase the STP one unit than for the topsoil, which required about 7.1 kg P ha^{-1} for each mg STP kg^{-1}. This same comparison is hard to make with the whey and manure treatments since the whey contained H_3PO_4 and both contained ortho-P, as well as organic P, which mineralizes at various rates, depending on composition and soil conditions. The very high P application rates with the whey and manure increased the STP well above that needed for economical crop production and remained adequate for the duration of the study.

Organic materials added with the whey and manure would be expected to coat the reaction surfaces of the freshly exposed subsoil particles and prevent or delay P sorption, thereby increasing P solubility. There was evidence that this was occurring. The regression line slope between STP and both the saturation paste and the 0.01 *M* $CaCl_2$ extractable ortho-P was 1.42 times greater for whey than for MCP (conventional) applied ortho-P. For the manure 1991 treatment, the regression line slope was 1.69 and 2.73 times greater than for the MCP treatment for the saturated paste and 0.01 *M* $CaCl_2$ extract estimates. The addition of 25 Mg OC ha^{-1} in 1991 by the whey did not affect the subsoil OC content, while the addition of 41 Mg OC ha^{-1} from the manure tripled the subsoil OC in 1992 and decreased to double the original subsoil OC after 7 yr, or slightly higher than the topsoil (9 g OC kg^{-1}). The organic materials in whey are primarily sugars and simple proteins (the fats and long chain proteins end up in the butter and cheese) and decompose rapidly (Jones et al., 1993). These observations suggest that P sources increase solution ortho-P concentrations in the order: manure > acid-whey > MCP.

We speculate that the STP, saturation paste, and 0.01 *M* $CaCl_2$ extractable ortho-P spring to fall decrease and the fall to spring increase were caused by P cycling from crop roots and residues. Plants take up P during the growing season, decreasing the extractable P. During and between growing seasons, plant roots, incorporated plant material, and residual organic matter (previously added plant material or manure) decompose and liberate extractable P. There was no seasonal saturation paste pH change that would explain this cycling. It is also possible that there was some conversion of mineral P to labile P, which is partially extracted by $NaHCO_3$ and influences solution-P concentrations (Westermann, 1992).

Initially the subsoil ortho-P solubility concentrations were along or slightly above a 1:1 slope isotherm lying between the HA and β-TCP isotherms (Fig. 2). The 1:1 slope of these data points suggests that with time an ortho-P mineral, with a different $Ca:H:PO_4$ ratio than HA or β-TCP, formed in the subsoil below the native vegetation root zone, probably before the soils were irrigated and cultivated. The ortho-P solubility in the subsoil–conventional treatment did not increase significantly and remained below the β-TCP isotherm as the extractable $H_2PO_4^-$ concentration increased after 265 kg P ha^{-1} was added as MCP in 1991 (Fig. 3).

The initial topsoil P solubilities were astride the β-TCP isotherm (Fig. 2) and the untreated topsoil P solubilities remained unchanged throughout the study (Fig. 7). The untreated topsoil STPs showed the annual tendency for the spring–fall–spring cycles in all but the F1993 to S1994 samplings. These P changes were not as significant as in the treated subsoils, but the trend was occurring. The only topsoil treatment with P solubilities nearer the OCP than the β-TCP isotherm line was that receiving manure (Fig. 7).

The horizontal shifts in the subsoil solubility points were primarily due to pH changes in the $CaCl_2$ extracts. The Ca activities changed very little among samplings and treatments for the topsoil and the subsoil, due primarily to the calcareous nature of the soils and buffering within the extract. The topsoil pH values changed very little with time and treatment. The vertical movement was a combination of pH and $H_2PO_4^-$ changes in the subsoil and primarily $H_2PO_4^-$ changes in the topsoil.

We would remind the reader that comparing calculated $H_2PO_4^-$ solubility from $CaCl_2$ extract data does not imply that the soil solution is in equilibrium with the listed minerals. The precipitation–dissolution reactions are very slow and solution and surface contaminations further perturb the soil P equilibrium compared with pure solutions in contact with a pure mineral surface.

With the second whey and manure application in the fall of 1991, the total P applied was slightly higher in the high-whey than in the manure treatment (Table 1). The STP, saturated paste, and 0.01 *M* $CaCl_2$ ortho-P concentrations in the subsoil high-whey treatment were significantly lower than those in the subsoil manure 1991 from S1992 through F1994 (Tables 3–5). This difference was probably caused by release of appreciable amounts of soluble Ca^{2+} from H_3PO_4 neutralization by soil lime in the whey treatments. This would tend to precipitate additional P as the soil pH returned to that of the matrix. An additional factor that may contribute to higher P availabilities after manure is its higher portion of organic P compounds compared with the acid whey (44 vs. 15%). These organic compounds will mineralize with time, releasing additional ortho-P.

Both the 1994 whey and manure applications increased the 0.01 *M* $CaCl_2$ ortho-P concentrations several fold in the subsoil and topsoil plots (Tables 3 and 4) and were appreciably greater than the 0.2 to 0.3 mg P kg^{-1} required for optimum plant growth (Nishimoto et al., 1977).

Soil P solubility was generally near equilibrium with β-TCP when the STP concentration was <100 mg P

kg^{-1} (Table 2 vs. Fig. 2–7). As the STP approached and exceeded 100 mg P kg^{-1}, the soil P solubilities approached the OCP isotherm line. In addition, ortho-P concentrations in the 0.01 *M* $CaCl_2$ extract generally exceeded 1 mg L^{-1} when the STP was >100 mg P kg^{-1}, both more than sufficient for optimum plant growth on calcareous soils and at concentrations that suggest that ortho-P would move deeper into the soil profile with leaching water.

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