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SOME EFFECTS OF MOISTURE AND TEMPERATURE ON TRANSFORMATION OF MONOCALCIUM PHOSPHATE IN SOIL

W. C. HINMAN, J. D. BEATON¹ AND D. W. L. READ

*Experimental Farm, Research Branch, Canada Department of Agriculture,
Swift Current, Saskatchewan*

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ABSTRACT

Pre-weighed monocalcium phosphate pellets, containing about 15 milligrams of P, were placed in 200 grams of soil and stored for 2 weeks at four moisture tensions and three temperatures. Pellet residues were then removed and the amount of phosphorus remaining was determined. Small cores containing pellet residues and the surrounding soil contacted by fertilizer solution were removed for determination of water-soluble and total inorganic P. Phosphate phases present at the granule sites and the surrounding soil were identified by their optical properties.

The mean amount of phosphorus remaining at the granule sites was 20.2 per cent. Although both moisture tension and temperature significantly affected the quantity of phosphorus retained, no consistent trend was apparent. Residues remaining at the site of application were found to be mixtures of anhydrous and dihydrated dicalcium phosphate, with the latter predominating. Moisture tension and temperature did not greatly alter the proportion of the two phases.

Periodic precipitates or Liesegang rings of dicalcium phosphate were formed in the soil surrounding monocalcium phosphate pellets. Dicalcium phosphate dihydrate was the predominant phase. The proportion of dihydrated to anhydrous dicalcium phosphate increased as the temperature decreased and as the moisture tension increased.

Water-soluble P increased significantly with increased moisture tension and was significantly greater at 5°C. than at either 16 or 27°C. The mean of all treatments was 5.6 per cent. Increased amounts of dicalcium phosphate dihydrate in the surrounding soil seemed to be responsible for the increase in water solubility.

Between 89.5 and 99.2 per cent of the added phosphorus was recovered in the water and acid extracts of soil cores containing about 1.4 cm.³ of soil.

INTRODUCTION

Robinson (15) found in a greenhouse study that uptake of P by Ladino clover from an acid soil limed to pH 6.5 and fertilized with monocalcium phosphate (MCP) was greater when the soil was incubated at 3°C. prior to planting than when it was incubated at 15 to 45°C. Soil moisture was also important since high incubation temperatures only reduced P uptake when the soil was moist. Laboratory investigations have shown that the fixation of other P salts such as K_2HPO_4 , KH_2PO_4 and $(NH_4)_2HPO_4$ was reduced at low soil temperatures (7, 9). Plant uptake of P has been reported to increase with increasing moisture content during the initial soil-MCP reaction period (5). The increased uptake was believed to be the result of differences in reaction products which were formed in the soil at the various moisture levels during the initial reaction period.

¹Formerly Physical Chemist, Soil Section, Experimental Farm, Swift Current, Sask.; now Soil Scientist, Research and Development Division, Consolidated Mining and Smelting Company of Canada Ltd., Trail, B.C.

Dicalcium phosphate dihydrate (DCPD) is the usual initial product of hydrolysis of MCP in soil. It is formed at the original granule site as well as in the immediate surrounding soil (6, 10). This salt exists in the soil for considerable periods of time, although it is instable with respect to anhydrous dicalcium phosphate (DCPA) at normal soil temperatures and moisture contents. Such is the case whether it is formed during the hydrolysis of MCP or added as a fertilizer (6, 12).

It is predicted that 21 per cent of the P added to soil as MCP remains at the granule site as DCPD (6). Calculations indicate that residues of DCPA should contain some 28 per cent of the original P (6). Lehr *et al.* (11) found that under a wide range of conditions residues of dicalcium phosphate accounted for 18 to 33 per cent of the applied P. The average fraction of added P remaining as DCPD in an acid soil treated with three rates of MCP and stored at three moisture contents was observed to be 20.7 per cent (5). In the same study an average of 28.2 per cent was obtained for an alkaline soil stored at three moisture levels and three temperatures.

Environmental factors, such as moisture and temperature and soil organic matter, have been shown to influence both the amount and form of dicalcium phosphate remaining at the granule site. Lehr *et al.* (11) and Bouldin *et al.* (5) reported that increasing moisture generally resulted in slightly lower P content of residues. However, Lehr *et al.* (11) found that increased soil moisture also increased the proportion of residual P when humus was added. They also found that elevation of soil temperature alone increased residual P, whereas increase in temperature simultaneously with soil moisture tended to decrease residual P. The data of Bouldin *et al.* (5) showed that residual P increased as the temperature increased from 9° to 20°C. and then decreased slightly when the temperature was raised to 31°C. Organic matter apparently affected the retention of dicalcium phosphate more than did temperature or moisture (11).

Bouldin *et al.* (5) and Lehr *et al.* (11) observed that during the transformation of monocalcium phosphate increased soil moisture restricted the production of DCPA in favor of the dihydrated salt in the residues left at the fertilizer granule site. They also reported that increased temperature promoted the formation of DCPA, whereas high moisture level with high temperature level inhibited its formation. Increased generation of DCPD is desirable since, per unit of surface area, its availability coefficient is about 2.3 times that of DCPA (3).

It is apparent from the above discussion that both the amount and form of dicalcium phosphate remaining at MCP granule sites have been the object of considerable study. Residual P, however, constitutes less than one-fourth of the total P added as MCP. Further study should, therefore, be made of the remaining three-fourths of the added P which moves into the surrounding soil. Investigation of this portion of the added P may be facilitated by using a calcareous soil where periodic or irregular precipitation of the soil-MCP reaction products occurs.

The objectives of this study were to determine how temperature and moisture tension of a calcareous soil affected: (a) amount and form of P remaining at pellet site; (b) form of P in the soil surrounding pellet site, and (c) water solubility of the P in the complete soil-MCP reaction zone. This information should assist in understanding why the availability of MCP to plants has been influenced by soil moisture and temperature.

MATERIALS AND METHODS

Soil

A surface sample (0 to 6 inches) of the Bradwell very fine sandy loam (formerly called Asquith), which is calcareous and is a member of the Dark Brown great soil group (13), was obtained from near Outlook, Saskatchewan. It was air-dried, sieved through a 6-mesh screen and used for laboratory study. The following properties were measured: pH = 7.7; total carbon = 1.4 per cent; cation exchange capacity = 10.5 me./100 grams and 6.6 per cent CaCO_3 .

Treatments and Design

Pellets of monocalcium phosphate monohydrate were prepared from reagent grade salt which had been washed with dry acetone to remove free acid. Sufficient quantities of this phosphate salt to supply approximately 15 milligrams of P were placed in a steel die with a diameter of 5 millimeters. A pressure of 20,000 pounds per square inch was applied, using a Carver laboratory press. The resulting pellets had a thickness of approximately 1.80 millimeters.

The pellets were subjected to reaction with the soil for 2 weeks at 5, 16 and 27°C. and four levels of moisture tension, namely 0.4, 0.8, 2.0 and 6.0 bars, which corresponded to 17.2, 13.6, 10.8 and 9.6 per cent moisture by weight respectively. These levels of moisture and temperature were combined factorially into a randomized block design with five replicates. Due to the high degree of accuracy with which the temperature could be controlled in the tanks, and the equal accuracy of mixing soil and water to obtain the desired moisture content, the five samples of each treatment were considered to be from separate replicates. The results were analysed using an analysis of variance. Duncan's (8) multiple range test was used to indicate the reliability of the conclusions drawn from the data.

Adequate soil to provide for all the treatments of a particular tension was moistened by the addition of appropriate volumes of water to weighed quantities of air dry soil spread evenly in a thin layer on a sheet of rubber dental dam. The wetted soil was thoroughly mixed by kneading it while enclosed in the rubber sheet. The equivalent of 200 grams of air dry soil was placed in 8-ounce screw cap specimen jars (approximately 7 centimeters in diameter and 7 centimeters in height). The bulk density of the soil was adjusted to about 1.2 gram per cm^3 . Cavities 5 millimeters in diameter and approximately 3 millimeters in depth were formed in the center of the soil surface, using a cork borer. Pre-weighed pellets of monocalcium phosphate monohydrate were placed in the hole and pressed firmly into place. The

jars were then placed in 1-gallon plastic pots with close fitting lids made of 2-inch thick styrofoam and stored for 2 weeks in constant temperature baths at 5, 16 and 27°C.

Experimental Measurements

At termination of the reaction period, cores 15 millimeters in diameter and about 8 millimeters in depth were removed from the pellet site of two replicates of each treatment. The pellet residues and the soil contacted by fertilizer solution were included in these samples. These plugs, which had a volume of approximately 1.4 cm.³, were transferred to 100-millimeter centrifuge tubes and analysed for water-soluble P and subsequently inorganic P (hot 6N HCl extraction), according to the methods of Bouldin and Sample (4). Unfertilized soil samples were treated in the same way to obtain a correction for the contribution of native soil P.

Residues remaining at the pellet sites were removed from two replicates of each treatment by the vacuum procedure described by Bouldin *et al.* (5). For collection of the residue, one-half of a 7.0-centimeter circle of No. 42 Whatman filter paper, folded tightly over a large bore end of the glass receiving tube, was found to be more convenient than a glass-wool pad. The residues were dissolved in 15 milliliters of a cold 2 per cent hydrochloric acid solution (11), and P was determined by the method of Shelton and Harper (16).

The residue retained at the pellet site of the fifth replicate was recovered by vacuum, transferred to the porous surface of clean unglazed porcelain tiles and washed with acetone. Small portions of the reaction products in the soil immediately surrounding the residue were probed from the soil and similarly cleaned. The solid phases present in both the residues and the immediate surrounding soil were then identified by their optical properties (10). Proportions of the two major phases present, namely dicalcium phosphate dihydrate (DCPD) and dicalcium phosphate, anhydrous (DCPA), were computed by crystal count.

RESULTS AND DISCUSSION

Figure 1 shows the periodic or irregular precipitation of dicalcium phosphate following the reaction of MCP with soil. The retention of about one-fourth of the added P at the tablet site is well established (cf. Introduction). However, the occurrence of reaction products in rather discrete zones in the soil surrounding MCP pellets is not so well known. Bouldin and Black (2) reported that periodic precipitates or Liesegang rings formed upon the reaction of MCP solutions with Muscatine soil, pH = 4.9 and with Miami soil, pH = 6.5. Ostwald's supersaturation theory is usually adopted to explain the phenomenon of Liesegang ring formation (17). According to this theory, essentially the only requirement for the formation of rings in the presence of seed crystals is that the velocity of crystallization be slow compared to the rate of diffusion and interaction of the reacting ions (17). The tendency for solutions of calcium phosphates to be supersaturated with respect to anhydrous dicalcium phosphate (DCPA) was believed by Bouldin

FIGURE 1. Distribution of monocalcium phosphate reaction products after 14 days' reaction at 5°C. in the Bradwell very fine sandy loam.

and Black (2) to be one of the factors leading to periodic precipitation of MCP reaction products. In our study collection of these products from the soil surrounding the pellet sites for subsequent characterization was facilitated by the accumulation of relatively coarse crystals in these Liesegang rings or periodic precipitation.

P Remaining in Residues

The proportion of P left at the application site was affected significantly by moisture tension and temperature (Table 1). At 16°C., decreasing tension (increased soil moisture) tended to lower slightly the P content of the residues. Increasing moisture was found by Bouldin *et al.* (5) and Lehr *et al.* (11) to similarly affect residue P. Moisture tension did not consistently alter it at the two other temperatures. The mean of the 2.0 bar treatments was significantly greater than the 0.4 and 0.8 bar means. Residual P increased when the temperature was increased from 5 to 16°C. at the two higher moisture tensions and then decreased upon raising the temperature to 27°C. These results are in agreement with those of Bouldin *et al.* (5). Temperature did not uniformly influence the amount of P remaining in the residues at the two lower moisture tensions. The 5° and 16° means were not significantly different, whereas the 16° mean was significantly greater than that of the 27°C. treatments. The mean of all treatments from our work (20.22 per cent) is very close to the average of 20 per cent found by Lehr *et al.* (11) for water-saturated non-porous soils. It also compares favorably with the predicted value of 21 per cent for residues comprised only of DCPD (6). Most of the experimental values are within the range of 18.7 to 21.7 per cent predicted for metastable invariant-points between 0 and 30°C. (6).

TABLE 1.—INFLUENCE OF MOISTURE AND TEMPERATURE ON THE PER CENT OF PHOSPHORUS ADDED AS MONOCALCIUM PHOSPHATE REMAINING AT THE GRANULE SITE IN THE BRADWELL VERY FINE SANDY LOAM

Temperature °C.	Per cent of original P present remaining at granule site (mean of two replicates)				Temperature means ¹
	Moisture tension (bars)				
	0.4	0.8	2.0	6.0	
5	20.2	20.6	21.0	20.1	20.5 cd
16	18.7	19.4	21.7	22.6	20.6 c
27	20.3	19.2	20.2	18.6	19.6 d
Moisture means ¹	19.7 b	19.7 b	21.0 a	20.4 a b	20.2

S.E. of moisture means = ± 0.3

S.E. of temperature means = ± 0.3

S.E. of a given treatment (in body of table) = ± 0.6

¹Any two means not having letters in common are significantly different at the 5 per cent level by the Duncan test (8). Any two means with the same letter are not significantly different.

TABLE 2.—[INFLUENCE OF MOISTURE AND TEMPERATURE ON THE PROPORTION OF DICALCIUM PHOSPHATE DIHYDRATE (DCPD) TO ANHYDROUS DICALCIUM PHOSPHATE (DCPA) IN RESIDUES AND IMMEDIATE SURROUNDING SOIL

Treatment		Residues remaining at granule site		Immediate surrounding soil	
Temperature °C.	Moisture tension bars	Number of crystals counted	Proportion of DCPD to DCPA	Number of crystals counted	Proportion of DCPD to DCPA
5	0.4	429	61:39	92	96: 4
	0.8	328	62:38	86	95: 5
	2.0	377	64:36	105	95: 5
	6.0	418	72:28	79	95: 5
16	0.4	367	64:36	47	55:45
	0.8	376	63:37	47	66:34
	2.0	334	67:33	55	73:27
	6.0	356	73:27	61	69:31
27	0.4	289	69:31	61	44:56
	0.8	351	68:32	53	43:57
	2.0	386	68:32	65	54:46
	6.0	232	68:32	49	65:35
Mean of all treatments					
Moisture tension	0.4	362	65:35	67	65:35
	0.8	352	64:36	62	68:32
	2.0	366	66:34	75	74:26
	6.0	335	71:29	63	76:24
Temperature	5°C.	388	65:35	91	95: 5
	16°C.	358	67:33	53	66:34
	27°C.	315	68:32	57	52:48

Composition of Granule Residues

The ratios of DCPD and DCPA in the residues (Table 2) show that DCPD was predominant in all the treatments. Moisture tension and temperature did not greatly alter the proportion of the two phases. There was, however, a weak tendency for the amount of DCPD to increase with temperature and to decrease with a decrease in moisture tension. Other investigators (5, 11) have indicated that formation of the dihydrate form was greatest at low temperatures and high moisture contents. Composition of the residues approaches that found by Bouldin *et al.* (5) when monocalcium phosphate was reacted with an alkaline soil at 31°C.

Form of Phosphorus in Soil Surrounding Pellet

The only calcium phosphate phases found in the Liesegang or periodic precipitates which formed in the soil surrounding MCP pellet sites were DCPD and DCPA. Table 2 shows that DCPD was usually the most prevalent phase. Lindsay and Stephenson (12) reported that in a slightly calcareous soil DCPD precipitated throughout the soil zone contacted by MCP fertilizer solution. However, on a heavy textured calcareous soil Lehr *et al.* (1) found that a precipitate of DCPA and DCPD was formed in the soil around MCP tablets. Dissolved Ca from the soil should favor precipitation of DCPD (12).

The proportion of DCPD to DCPA was found to increase drastically as the temperature decreased from 27° to 5°C. It is difficult to explain how low soil temperatures contributed to the formation of DCPD since temperature has little effect on the solubility of CaCO₃ (18). The conversion of DCPD to more stable DCPA (12) might be retarded at low temperatures.

TABLE 3.—INFLUENCE OF MOISTURE AND TEMPERATURE ON PER CENT OF ADDED PHOSPHORUS EXTRACTED IN 1:15 SOIL-WATER EXTRACTS OF THE SOIL-MONOCALCIUM PHOSPHATE REACTION ZONE

Temperature °C.	Per cent of original P present extracted in 1:15 soil-water extracts (mean of two replicates)				Temperature means ¹
	Moisture tension (bars)				
	0.4	0.8	2.0	6.0	
5	4.4	5.3	5.1	12.6	6.9 d
16	4.9	4.7	5.3	5.5	5.1 e
27	4.3	4.4	5.5	5.0	4.8 e
Moisture means ¹	4.5 c	4.8 b c	5.3 b	7.7 a	5.6

S.E. of moisture means = ± 0.1

S.E. of temperature means = ± 0.2

S.E. of a given treatment (in body of table) = ± 0.3

¹Any two means not having letters in common are significantly different at the 5 per cent level by the Duncan test (8). Any two means with the same letter are not significantly different.

TABLE 4.—RECOVERY OF PHOSPHORUS FOLLOWING REACTION OF MONOCALCIUM PHOSPHATE PELLETS WITH THE BRADWELL VERY FINE SANDY LOAM

Treatment		mg. of P (mean of two replicates)				Per cent recovery
Temperature °C.	Moisture tension bars	Water soluble ¹ (1:15 soil to water extracts)	Acid soluble ² (hot 6N HCl)	Total P recovered	P added in monocalcium phosphate pellet	
5	0.4	0.67	14.2	14.8	15.4	96.3
	0.8	0.82	14.5	15.3	15.5	98.5
	2.0	0.76	14.2	14.9	15.1	99.0
	6.0	1.90	11.6	13.5	15.1	89.5
16	0.4	0.76	14.6	15.4	15.6	98.8
	0.8	0.72	14.4	15.1	15.4	98.1
	2.0	0.81	14.5	15.3	15.4	99.2
	6.0	0.82	13.9	14.7	14.8	98.8
27	0.4	0.66	14.0	14.7	15.2	96.7
	0.8	0.68	14.3	15.0	15.4	97.2
	2.0	0.81	13.4	14.2	14.8	95.9
	6.0	0.77	14.4	15.1	15.3	98.7

¹Contribution of native soil P was negligible.
²Corrected for native soil P which was 4 per cent.

Moisture tension did not influence the proportion of DCPD to DCPA to the same extent as did temperature. There was a consistent trend, however, indicating that the proportion of DCPD to DCPA increased slightly as the moisture tension increased. High soil moisture tension may have increased the proportion of DCPD to DCPA by reducing disproportionate diffusion of Ca and P ions (6).

Water-Soluble P

Table 3 reveals that water-soluble P in the reaction zone, which includes pellet residues and immediate surrounding soil, increased with decreases in temperature and increases in moisture tension. Significantly more water-soluble P was extracted following reaction of MCP with soil at 5°C. than when the reaction took place at either 16° or 27°C. The greatest release was obtained from the 6.0 bar moisture tension treatment at 5°C. It is interesting to note that Robinson (15) obtained greater uptake of P by Ladino clover from MCP treated soil when the soil was incubated prior to planting at 3°C. than when it was incubated at 15 to 45°C. Fraps (9) found that the fixation of K_2HPO_4 solutions in soil was less when the soils were kept in an ice bath for 5 hours than when they were kept at either 31 or 40°C. Dadykin (7) reported that the amount of readily available P was highest when $(NH_4)_2HPO_4$ and KH_2PO_4 were added to cold soils. Recently, Beaton and Read (1) observed that P uptake was greater following reactions of $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$ with the Bradwell soil at 5°C. than when the reactions took place at either 16 or 27°C. Temperature had little or no effect upon P uptake from MCP in their study.

Significant increases in water-soluble P occurred as the moisture tension increased. Release from the 6.0 bar treatments was significantly greater than that from the three lower tensions. It was also significantly greater from the 2.0 bar tensions than from the 0.4 bar treatments. Robinson (15) found that P uptake from MCP treated soil was not reduced by high incubation temperatures when the soil was dry. Studies with the Bradwell soil at first suggest that the greater release of water-soluble P following the reaction of soil and MCP at low temperatures was not reflected in greater subsequent uptake of P by plants. This anomaly may be explained by differences in soil moisture. Only one moisture tension, i.e., 0.8 bar, was used in the uptake study (1), whereas in the present study much more water-soluble P was extracted following reaction at 5°C. from the 6.0 bar moisture tension treatment than from the 0.8 bar treatment.

Increased formation of DCPD may be partially responsible for the increases in water solubility since it dissolves more rapidly than DCPA (14). Changes in the proportion of DCPD to DCPA throughout the surrounding soil contacted by the fertilizer solution are likely to be more important than in the residue because considerably more of the original P is found in the former location. The proportion of DCPD to DCPA formed in the soil surrounding the pellet was much greater at 5°C. than at the two higher temperatures. It also tended to increase as the moisture tension increased.

The mean of all treatments, 5.6 per cent, is quite similar to values reported by Bouldin and Sample (4). They found 5.2 and 6.5 per cent of P from MCP was soluble in 1:15 soil-water extracts of a calcareous and an acid soil, respectively.

Recovery of P

Most of the P originally added as MCP was recovered in the water and acid extracts (Table 4). Where it was not fully regained sampling of the reaction zone could have been incomplete. The relatively complete recovery of P within the core (15-millimeter diameter by 8 millimeters deep) indicates that this was the maximum volume of soil affected by the fertilizer solution.

The precipitation of DCPD and DCPA in Liesegang rings or periodic precipitates appears to have confined these MCP reaction products to a rather limited volume of soil. In a calcareous silty clay soil migration of P from the center of MCP pellets containing 15 mg. of P was found to be about 15 millimeters (4). They found on an acid fine sandy loam soil that P moved about 25 millimeters from the center of MCP pellets.

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