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Detection and Examination of Anthrosols by Phosphate Analysis

Field and laboratory tests for phosphate, well known in soil science, find new applications in archeology.

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Among the nonconventional methods for detecting abandoned settlement sites whose physical remnants have disappeared from the earth, that of inorganic soil phosphate analysis has the most persistent and varied history of applications. Studies of abandoned settlements through phosphate methods, which first appeared in Sweden in the 1930's and spread gradually across Europe, spiraled in importance after World War II (*1–3*). Research in the United States, affected by this surge of interest, began in the 1950's, but stagnated until the introduction of a rapid field test for settlement phosphate in the 1970's. Moreover, during the Bicentennial period, major federal funding made available for the purpose of locating sites with potential historic or prehistoric value generated still further use of phosphate field tests (*4–7*). The swift diffusion of these investigations in the United States and an urgent desire for more efficient methods of disclosing the past have heightened the appeal of chemical analysis of soils.

Phosphorus in the form of phosphate is especially appropriate for detecting settlement-affected soils, known as anthrosols, because of its universal association with human activities. One of the basic ingredients of the DNA molecule, phosphorus increases through the life chain because of its chemical immobility. The element is an essential component of many manufactured items such as fertilizers, detergents, pesticides, oils, and foodstuffs, and remnants from all of them find their way into the soil. Curiously, their wholesale removal cannot be stimulated by normal oxidation, reduction, or leaching processes, as is true of compounds of nitrogen, calcium, carbon, sulfur, and other common elements. Consequently, when phosphorus is added to soil, it accumulates in situ across the broadest spectrum of soil types (*5*). Although phosphate levels decline extremely slowly in nature, they deteriorate rapidly during human-related activities such as harvesting, livestock grazing, and terrain modification. Since parent materials supply soils with minute amounts of phosphate over geologic rather than short periods of time, natural recycling does not mask human-caused alterations (*8–10*). By comparing background and anthrosol phosphate concentrations, therefore, the investigator can interpret abnormal soil phosphate readings as chemical evidence of human settlement. Hence, because nature ultimately destroys physical traces of human efforts in many soils, authorities have viewed changes in phosphate content with great expectations in the identification of locations, outlines, functions, and relative ages of past settlement phenomena.

Whereas persistent experimentation with phosphate detection has begun to produce a valuable if somewhat disorganized body of knowledge, the use of certain techniques has also produced disappointing and occasionally misleading results. An appraisal of some of the major aspects of settlement phosphate analysis would be appropriate at this time not only because of its rapidly growing and incidental problematic use in archeological research or because of recent improvements in the understanding of its difficult chemistry, but especially because of promise from a new two-part approach whose essentials are outlined in this article.

Forms of Phosphorus in the Soil

Because of the strong affinity of phosphorus for oxygen, the orthophosphate radical forms $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}, rather than the elemental form, appear in soils—a condition true of both inorganic and organic compounds of phosphorus. The most common source of inorganic phosphate is apatite, which occurs in small amounts in nearly all rocks. If sufficient phosphate is released as the soil forms, living organisms convert small amounts from the inorganic to the organic type. The conversion also depends on whether the released phosphorus exists in a form which is available to organisms. These critical relationships determine not only crop success, but entire native vegetation associations (*9*). The relationships also explain why soil tests may indicate adequate phosphate concentrations even though plant life suffers from phosphate deficiency. Thus, agronomists have devised tissue tests with plant material instead of soil to ascertain whether the phosphate is soluble enough for uptake by vegetation (*11*). Investigators of man's role in changing the phosphate landscape must not only diagnose the presence but also interpret the behavior of inorganic and organic soil phosphate forms.

When phosphate is added to soils of relatively high *p*H, it bonds instantly to calcium cations. If the *p*H decreases, some calcium phosphate dissolves and becomes available to plants. Aluminum and iron components immediately resorb all or nearly all of the released phosphate ions to produce still other insoluble compounds. Aluminum, iron, and calcium are practically ubiquitous in soils and hold most of the inorganic phosphate

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which enters the solum in one or more of the insoluble forms. Only in theoretical cases where a scarcity of the primary retaining components emerges, such as in pure sand, would it be difficult for added phosphate to accumulate. Under the anaerobic (reducing) conditions of flooded soils, there appears to be loss of inorganic phosphate by conversion of ferric phosphate to the more soluble noncrystalline ferrous form. Organic anions may displace phosphate from the soil matrix under similar circumstances. By these mechanisms strengite ($FePO_4 \cdot 2H_2O$) becomes an available source of phosphorus for lowland rice and swamp plants (*12*).

Phosphate is bonded to organic compounds in the soil in amounts ranging from approximately 2.5 to 75 percent of the total in the surface layers (*13*). Organic phosphate differs from the inorganic form in that an ester rather than a metallic cation links itself to the phosphate radical. When phosphate displaces the hydroxyl groups on the surface of organic colloids and the solution envelops a metallic iron surface, insoluble complexes form which protect iron objects from corrosion—a fact well known to archeologists (*14*). Organic phosphate permeates all living things, from microbes to plants, animals, and humans, so that when their remains decompose in the ground, mineralization gradually converts small amounts in a seasonally variable fashion to an inorganic form (*15*). Part of this newly produced inorganic phosphate enters the soil solution; the retaining components aluminum, iron, and calcium immediately bond the rest. As such, converted phosphate accumulates steadily along with other inorganic additions and can be measured as part of the evidence of soil phosphate enrichment.

Problems of Testing for Phosphate

The Swedish agronomist O. Arrhenius (*16, 17*) first suspected the close correlation between abandoned settlements and native soil phosphate alteration. When his suspicions proved factual, investigators relied on soil sample analysis by agricultural techniques designed to reveal available phosphate, P_{av} (*18*). In this article P_{av} is defined as the minute amount of phosphate already in solution in the soil plus a labile part only loosely bound to the surface of colloidal particles containing aluminum, iron, and calcium. Plants, which require phosphorus for proper cell growth, fruit production, and resistance to disease, can extract P_{av} (*19*). Agronomists have never found completely adequate methods of testing for P_{av} because of the difficulty of simulating plant-soil chemistry in the root zone (*20*).

Table 1. Two-minute ring chromatography field-test results are identified according to length of striae, time of appearance, and color. Quantification of values is inadvisable because of variations in sample size, color perception, and temperature and unequal extraction of soil phosphate types.

Phosphate	Length of radiating lines (mm)	Time of appearance of lines (min)	Ring around sample (%)
5. Strong	8	0.5	100
4. Good	3–5	0.5–1	75
3. Average	2	1–2	50
2. Weak	≤1	2	<50
1. None	0	0	0

In spite of this problem, tests designed for P_{av} do detect phosphate in the soil. The soluble or available forms are $H_2PO_4^-$ and HPO_4^{2-} since they possess lower valences and hence lower bonding energies (*21*). The more efficient the extractant, the more the inorganic phosphate revealed. This explains the potential of these tests for simultaneously releasing the tightly bonded (unavailable) PO_4^{3-} form, which is the one most commonly associated with settlement phosphate, P_{set}. Following Arrhenius' work, most experiments with anthrosols have been performed in the laboratory, but procedures have been simplified to the point where testing in the field has become a reality, even for nonchemists (*2, 6*). However, because of the general lack of knowledge about the efficiencies of extractants and about the fate of phosphorus added to the soil, and because P_{set} represents a type of phosphate different in its chemistry from P_{av}, interpretive progress by these methods has been disappointingly slow and marked by misconceptions.

Those who work with P_{set}, for example, still commonly believe that phosphate is not easily extractable at low *p*H values (*22, 23*). Such ideas may stem from confusion over the fact that transformation within the soil from one phosphate form to another may occur during reactions which are *p*H-dependent (*24*). But regardless of *p*H, the principal retaining components, whether mainly aluminum and iron in acidic soils or calcium in basic soils, so quickly bond or "fix" most of the phosphate in insoluble compounds that it accumulates precisely at the point where it is added. Thus, fertilizer mixed in farm soil does not move laterally and stabilizes within a few millimeters of entry in the vertical profile, where it remains as evidence of one type of human activity. Recent tests show that even on anthropic Oxisols with low *p*H, calcium-oriented P_{set} (designated commonly as Ca-P) remains bound at the place of deposition in spite of heavy tropical rainfall, and it is just as easily detected as it would be in soils of much higher *p*H (*25*).

Others believe, moreover, that phosphate is readily leached from the soil at nearly neutral *p*H values (*26*). However, only some of the small amount of P_{av} already in solution may escape the retaining system just described. In any case, dissolved phosphate constitutes an insignificant portion of total P_{av} and, therefore, a negligible percentage of P_{set} (*27*). The small amounts in field drainage waters, which average less than 0.5 microgram per liter, attest to the low degree of solubility of phosphate in soil (*28, 29*). For practical purposes, nearly all the soil phosphate may be considered bound to the Al, Fe, and Ca retaining components with so many kilocalories of energy that it cannot be dislodged from the point of application either by leaching or by the physical action of vadose waters. Of course, natural erosion or human-induced transport of the soil mass would remove the phosphate.

During the last few years scientists, inspired by agricultural needs and by soil and water pollution problems, have produced a more complete understanding of phosphate chemistry as well as improved analytical procedures, thereby intensifying hopes for archeometric progress with the phosphate method (*30–34*). Some of the new knowledge would appear to offer significant breakthroughs in the analysis of anthrosols in terms not only of field mapping but of feature function (land use) interpretation and possibly settlement dating as well. The proper use of this new knowledge in anthrosol phosphate determination depends on correct understanding of the forms of phosphate in the soil and of the problems of testing, as explained earlier. On the basis of this knowledge and understanding, I have developed a two-part method which involves a rapid qualitative field test for P_{set} and a quantitative laboratory determination of land use and dating. This new method is presented in the sections that follow along with some recent theoretical considerations that explain its function.

Qualitative Method of Soil Phosphate Analysis: New Approach, Part 1

Since the time of J. von Liebig's work in soil chemistry, investigators have been aware that an acid-molybdate solution can be applied to orthophosphate to form molybdophosphoric acid (*35*). The latter may then be selectively reduced to create a heteropoly or molybdenum-blue complex. Various acids (H_2SO_4, HNO_3, HCl) and various reducing agents [$SnCl_2$, $(CH_3CO_2)_2C_6H_4$, $C_6H_8O_6$] have been employed in experiments with P_{set}. My research with hundreds of soil samples, as well as the work of others, shows that H_2SO_4 is a less efficient color producer because of interference from Fe^{2+} and organic materials and that HNO_3 should not be used because of its known ability to complex organic phosphate (*6, 36, 37*). Organic substances also increase resorption of phosphate liberated by HNO_3, and this occurs at a greater rate than with other acids (*37*). Experience indicates that the best extraction results with soils of any *p*H are obtained with a solution of 35 milliliters of 5*N* HCl mixed with 5 grams of ammonium molybdate dissolved in 100 ml of distilled water. The reducing reagent is prepared by dissolving 0.5 g of ascorbic acid ($C_6H_8O_6$) in 100 ml of water. Attempts at combining these two reagents fail because of instability of the single solution. However, if two drops of the first reagent are placed on a 50-milligram soil sample that rests on a small phosphate-free filter paper, and 30 seconds later two drops of the reducing reagent are applied, a blue ring forms whose color traits and proportions indicate different amounts of P_{set} (*6*). The much-used procedure can be carried out in the field between 5° and 27°C but should be performed at normal room temperatures otherwise.

This simple ring chromatography field test produces a continuous reaction so that, all things being equal, the investigator must read color characteristics after precisely 2 minutes. Afterward, the molybdenum blue spreads over the entire filter paper and obliterates any interpretable patterns. Until recently, it has been necessary to tabulate data regarding the physical traits of the blue color, such as length of striae, completeness of ring formation, and saturation of chroma (Table 1). With a new technique that I have developed the reaction is stopped after 2 minutes by thoroughly washing the filter paper in a small tray filled with sodium citrate solution (two parts water to one part sodium citrate). Papers dry rapidly and may be stored as part of a permanent record (*38*).

Although this ring test serves well in identifying past settlement areas without using expensive excavation methods and is especially helpful where artifacts cannot be found to corroborate evidence of settlement, two major limitations detract from its accuracy. First, the phosphate intensities revealed cannot be scientifically compared. Values are only qualitatively determined and may change from place to place depending on sample size, color perception, temperature, and, most significantly, unequal extraction of soil phosphate types. The results may even vary seasonally in places where P_{av} is the major type extracted. It is therefore inadvisable to quantify the readings. Second, the test cannot make a distinction between occasional soils that possess sizable amounts of native phosphate and anthrosols, whose phosphate is derived principally from settlement activities.

Unfortunately, these limiting factors may cast serious doubts on some field analyses because erroneous conclusions can be drawn about past settlement duration (vertical soil phosphate profile) and precise areal extent (horizontal soil phosphate profile). Under the circumstances, the field phosphate ring test merely assists in locating probable abandoned settlement sites and making rough estimates of their vertical and horizontal distribution. The investigator can then more exactly determine and interpret areal and temporal boundaries by traditional methods of excavation, provided interpretable artifacts are to be found. If the latter are not present, and this may occur either within the settlement proper or in its associated work areas, only a system of chemical analysis that produces more reliable (that is, justifiably quantifiable) values of P_{set} will help. It is evident that a chemical method which would overcome the two major field test limitations and simultaneously reveal enough about phosphate origins for a thorough site interpretation would be highly desirable. The growing need to analyze not just the settlement proper but the abandoned work areas as well, where few or no artifacts can be ex-

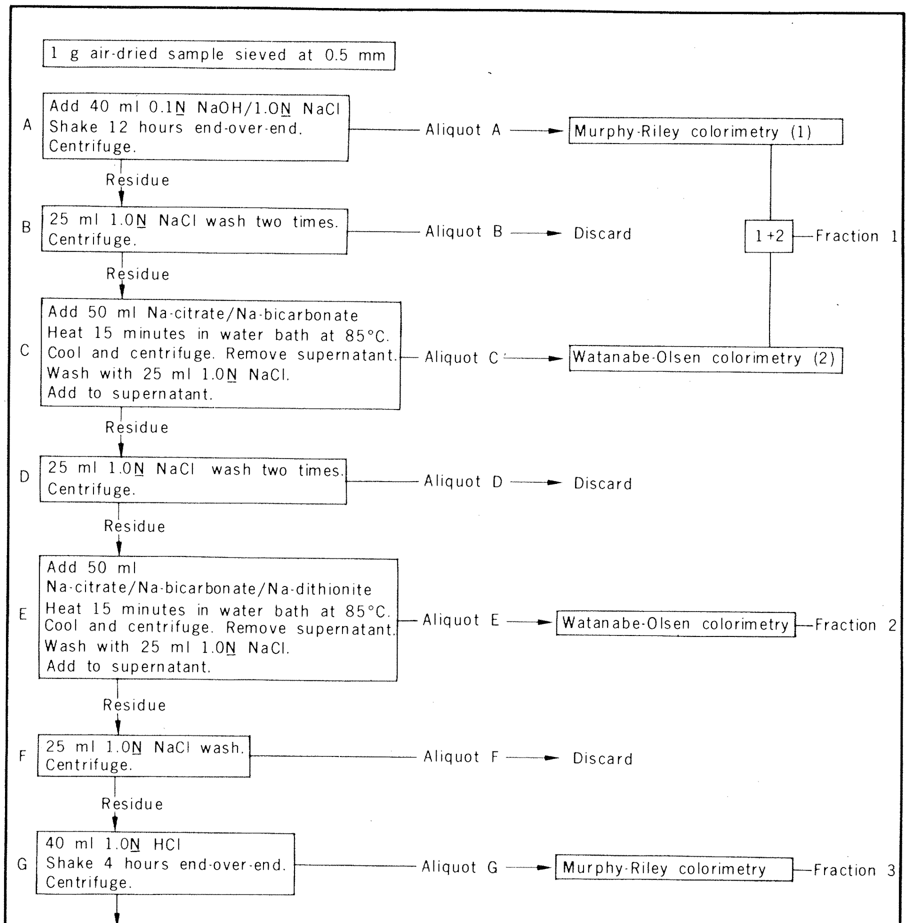


Fig. 1. Flow chart of soil fractionation procedure for identifying anthrosol phosphate types.

pected, would be satisfied by such a method. Furthermore, chemical analysis depends only on minute soil samples, which may be taken even where disturbing the landscape is forbidden—this, of course, is a plus for the method.

Quantitative Method of Soil Phosphate Analysis: New Approach, Part 2

The most common methods of soil phosphate analysis based on quantitative chemistry measure a precise amount of elemental phosphorus, represented usually by P_{av} or by total inorganic phosphate. However, methods designed to reveal only P_{av}, such as the calcium lactate and citrate types employed by European geographers and archeologists in the analysis of abandoned settlements, probably extract more than this kind of phosphate (*39*). Interpretation difficulties arise from the uncertainties of duplicating plant-root chemistry as mentioned earlier. Therefore, the quantifiable amounts of phosphate determined are not strictly comparable from one soil type to another. Considering this and the other problems with P_{av}, it follows that only methods that disclose total inorganic phosphate should be used in simplified P_{set} quantification.

Although quantification of total inorganic phosphate is easily performed in the laboratory (*40*) and solves some problems of accurate feature mapping, it has the two serious drawbacks that (i) it is not possible to distinguish between native phosphate, which occasionally produces very high noise levels (as in the band of diatomaceous earth along the west shore of Lake Michigan), and P_{set} and (ii) no information is added about the role of P_{av} and other forms of phosphate.

Chemists looked for a quantitative method that would reveal different kinds of phosphate, especially after the 1950's, and identified several so-called fractions, including those related to industrial contamination. From this research there emerged in 1957 a highly innovative sequential fractionation system proposed by Chang and Jackson (*32*). The method consists of seven steps, involving NH_4Cl (wash), NH_4F (Al-P removal), NaOH-H_2SO_4 (Fe-P removal), H_2SO_4 (Ca-P removal), sodium citrate-sodium dithionite (occluded Fe-P removal), NH_4F (occluded Al-P removal), and Na_2CO_3 fusion (total P). In later modifications a sodium citrate–sodium bicarbonate–sodium dithionite step was added (the sodium bicarbonate buffered the solution) and HCl was substituted for H_2SO_4 (*34*). Theoretically, the steps fractionate aluminum, iron, and calcium types of phosphate in a nonoverlapping system because of differences in their solubilities in carefully selected extracting reagents. The procedure has been used by soil chemists to analyze phosphate retention in soils, the role of phosphate in anion exchange, available versus nonavailable types of phosphate, and the transformation of fertilizer phosphate in soils.

Over the years, the desire for more information than that given by the ring chromatography test developed for anthrosols and acquaintance with soil phosphate fractionation methods being developed led me to experiment with fractionation of P_{set}. The full Chang-Jackson procedure outlined above embodies operational elements ultimately considered both unnecessary and too time-consuming to employ in P_{set} analysis. Consequently, certain aspects of the original soil science method were discarded, as illustrated in Fig. 1. Elimination of the NH_4Cl wash permits inclusion of the small amount of P_{av} that it would have removed with the rest of the loosely bound phosphate in an initial NaOH extraction. A sodium citrate–sodium bicarbonate step introduced by Syers *et al.* (*34*) corrects interference caused in calcareous soils by $CaCO_3$. The NH_4F treatment has been abandoned since the distinction between Al-P and Fe-P is nonabsolute (*15, 41*) and hence unnecessary in P_{set} determination. Finally, dropping Na_2CO_3 fusion for measuring a small amount of residual material that does not contain P_{set} further simplifies the procedure.

In the P_{set} analysis we are therefore left with separation of the three principal types of inorganic phosphate now recognized.

1) Easily extractable phosphate, consisting mainly of loosely bound Al-P and Fe-P and that resorbed by $CaCO_3$, as well as the minute amount of phosphate already in solution. This type is removed with NaOH and sodium citrate–sodium bicarbonate reagents and is called the NaOH + CB fraction.

2) Tightly bound or occluded phosphate absorbed by diffusive penetration or by incorporation with aluminum and iron oxides and hydrous oxides. This form is extracted with a sodium citrate–sodium bicarbonate–sodium dithionite reagent and is called the CBD fraction.

3) Occluded calcium phosphate and apatite extracted with HCl (the HCl fraction) (*42*). The flow chart in Fig. 1 portrays the steps recommended for P_{set} analysis. Once quantitative values are obtained for all three fractions, they are

Table 2. Inorganic soil PO_4^{3-}-P fractionation percentages. Values for sample 2c. were calculated from data of Khin and Leeper (*33*).

Soil	Fraction 1 (NaOH +CB)	Fraction 2 (CBD)	Fraction 3 (HCl)	PO_4^{3-}-P (total ppm)	Land use	Ring value
1a. U.S. Indian settlement, southeast Wisconsin, ~1200, 50 cm	37	30	33	836	Residential	4
1b. Colonial Indian mission, northeast Argentina, ~1600, 20 cm	38	28	34	2324	Residential	5
1c. Northern India settlement, Varanasi, ~700, 30 cm	34	34	32	3237	Residential	5
2a. Chibcha Indian settlement, Bogotá, Colombia, ~1600, 20 cm	78	10	12	186	Planting ridge	4
2b. Modern farm, Bogotá, Colombia, 1976, 20 cm	75	7	18	665	Planting ridge (potatoes)	4
2c. Modern farm, Melbourne, Australia	71	6	24	1084	Potato field	
3a. U.S. Indian settlement, southeast Wisconsin, ~1200, 30 cm	48	27	25	322	Suspected planting ridge	4
3b. U.S. Indian settlement, southeast Wisconsin, ~1200, 50 cm	3	2	95	355	Suspected planting ridge subsoil	4
3c. U.S. vegetable farm (modern), southeast Wisconsin, 30 cm	47	28	25	702	Mixed corn, beans, and others	4

added to calculate total inorganic settlement phosphate. Because the latter amounts differ from sample to sample, the fractional values are computed as percentages. Elimination of this factor of variability allows more accurate comparison of P_{set} form, distribution, and intensity patterns. The method has the advantage that it discloses what phosphate types and amounts have been extracted, rather than only uncertain P_{av} at one end of the scale or simply total inorganic phosphate at the other.

Results Obtained with the Quantitative Method

The results of fractionating soil phosphate from anthrosols are rewarding, judging from initial efforts (*43*). First, the distribution and concentration of phosphate in anthrosol fractions differ conspicuously from those of phosphate in nonsettlement or native soils. Sizable amounts of native phosphate, which cause interference with the ring test, are concentrated almost entirely in one of the three fractions—a feature which depends on the particular mix of retaining components, the soil texture, and the age of the system. On the other hand, P_{set} is distributed among all three fractions in recognizable patterns, as explained below. In practical terms, this means that the investigator can easily determine whether the rapid ring test used in the field is producing reliable information. In cases where native phosphate causes false settlement images or blurs the horizontal and vertical outlines of legitimate abandoned settlement remains, spot checks can be made in the laboratory by fractionating a few samples from the questioned areas. Second, the form, distribution, and concentration of phosphate in the separate fractions are directly correlated with variations of areal function, or land use, within settlements. These correlations have a rational explanation in terms of the different amounts of phosphate removed from soil by grazing animals, harvesting, irrigation, and drainage, for example, or added to the soil by fertilization, waste disposal, elimination, and other normal human activities. Table 2 presents examples of typical form, distribution, and concentration patterns of P_{set} fractions.

In Table 2, soil set 1 includes samples from residential areas of abandoned settlements in northeast Argentina, the north-central United States, and northern India. The phosphate results indicate that residential land use leads to a specific and parallel distribution of phosphate among the three fractions. It is significant that this occurs irrespective of soil types and of total inorganic settlement phosphate accumulation. Moreover, the total inorganic phosphate values (expressed in parts of PO_4^{3-}-P per million because the standards are measured in units of elemental phosphorus) reflect intensities of residential land use which are well correlated with what is known about the population densities of the respective settlements (Table 3). The mathematical nature of this correlation will have to be determined as control data are analyzed from a broad range of settlement sizes.

Table 3. Relationships between settlement density and total parts per million PO_4^{3-}-P for three samples from Table 2.

Soil	Estimated population	PO_4^{3-}-P (total ppm)
Ia.	Several hundred	836
Ib.	~ 2000	2324
Ic.	> 3000	3237

Soil set 2 in Table 2 illustrates the results obtained for representative pre-Columbian and modern vegetable-growing areas in Colombia, South America. The same method of farming on planting mounds—ridges where one row crop is raised, beds where there are two to four rows, and platforms where there are many rows—has been preserved for centuries (Fig. 2) (*44*). One sample from southern Australia is included with this set because it, like the modern Colombian soil, represents a field in which potatoes were raised for many years (*45*). Once again, the fractional distribution and concentrations reflect specific land use irrespective of soil types. Moreover, the pre-Columbian sample fractions are so similar to the modern Colombian and Australian ones that after considerable laboratory analysis it has been concluded that Chibcha Indians were raising potatoes in these ridged fields. Chibcha farming resulted in a slightly higher level of phosphate in fraction 1, which is to be expected because the less intensive agricultural methods employed removed less P_{av} from the soil, and more fraction 1 phosphate accumulated during prolonged soil rest since the Spanish Conquest. The somewhat higher fraction 3 phosphate in the modern soil probably results from liming. The difference between the fraction 2 concentrations, although not large, indicates the greater age of the Chibcha feature, as explained below.

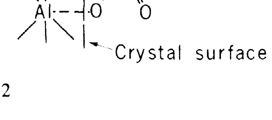
Set 3 in Table 2 includes a representative sample from modern field tests in southeast Wisconsin, where corn, beans, and other crops have been raised for many years, and samples from two depths in what appear to be old planting ridges at an aboriginal site in southeast Wisconsin. Sequential phosphate extraction from modern mixed vegetable soils produces another distinctive set of fractions. On the basis of this, the unknown ridged field has also been classified as a mixed vegetable raising area. The 50-centimeter fractions from the aboriginal ridged field are likewise of considerable significance. Judging from experience with similar soils, values from this level show purely native phosphate, since

Fig. 2. Ridged field remains about 8 km west of Bogotá, Colombia, along the Río Bogotá. Soil samples were taken from the central, U-shaped ridge.

concentration occurs almost entirely in one fraction. It should be noted that if only the ring value from the field test were available for analysis, the investigator would conclude that human activity was long-lasting here because of the same high phosphate readings throughout the vertical profile. If only total inorganic phosphate data were available, it would appear that the same land-use intensity occurred at both levels over a long period of time. However, fractionation proves that such conclusions would be in error.

From the comments above, it can be seen that examination of the vertical profile of an anthrosol is useful in establishing the relative ages of settlement phenomena. In other words, the thicker the P_{set} horizon, the older the settlement activity. If there are complete breaks in this horizon, then settlement phenomena were intermittent. If phosphate fractions within the vertical profile change, settlement function changed. A continuous and stable P_{set} horizon implies continuity of a specific settlement activity. For example, by fractionating a thick vertical chronosequence—one in which all soil-forming state factors except time vary inconsequentially (*46*)—dated from 700 B.C. to A.D. 700 at Varanasi, India, I was able to establish that residential settlement during this time span was uninterrupted. This conclusion helped substantiate a claim by Indian specialists that the site is the original center of one of the oldest continuously occupied modern cities in the world (*47*).

The chronosequence examined at Varanasi further revealed that soil phosphate fractionation has potential use as a dating tool. This conclusion is obvious since the nonoccluded and occluded fractions form over different periods of time (*48*). Phosphate which enters the soil is immediately attracted to the surface of sorbing colloidal particles by means of anion exchange (*49*). This rapidly immoblizes most of the fertilizer phosphate employed in farming, which is why it must be replenished yearly in large amounts. In the following illustration of nonoccluded sorption (adsorption), the added phosphate becomes instantaneously attached to reactive aluminum sites on the edge faces of hexagonally shaped crystals of gibbsite (*50*). Iron present in the soil also adsorbs phosphate (*51*). In time, deposition of more hydrous oxides of iron and aluminum and addition of more phosphate occlude the previously formed phosphate adsorption products (*31*). Another process, that of diffusive penetration of ions toward adsorbing surfaces, assists in the occlusion of phosphate over extended periods of time (*52*). Long-term repetition of these activities causes more and more occlusion (absorption). Thus, nonoccluded and occluded phosphate types are generated at vastly different rates. Figure 3 demonstrates this relationship for the chronosequence at Varanasi. The (NaOH + CB)/CBD ratios, plotted against a time scale, produce such a smooth curve that once the relative fractional relationships are known, reasonably accurate dating becomes theoretically possible. To do it, an absolute date must be available for one end point in the sequence. It is clear that sequential dating is also feasible, as in seriation analysis (*53*). Further research is needed before these findings can be generalized.



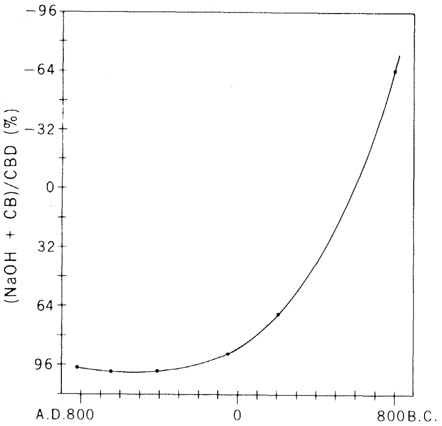


Fig. 3. Chronosequence of nonoccluded/occluded phosphate ratios, Varanasi, India.

Because the results described above were obtained from control samples with pH values between 5 and 8, it might be anticipated that soils with more extreme pH values but representing the same feature functions might have altered phosphate fractions. Hypothetically, this could occur because of masking induced by marked changes in the composition of the ionic environment at extreme pH values. Masking might similarly be predicted from other extreme landscape conditions such as long-term flooding or permanent waterlogging (*54*). In all forms of analysis it may be useful to consider the effects of normal transformation of fractional percentages by measuring native and settlement soil phosphate redistribution rates and amounts (*55*). Continued research should determine the extent of calibration required because of these potential forms of masking. When they are accounted for, sufficient samples from clearly identified features within abandoned settlements may be analyzed to develop representative land use–fractionation correlations and dating curves for the creation of a master reference file. Establishment of numerous feature functions and ages from unknown samples by means of a matching system like that used in mass spectrum analysis should then be within reach.

Summary

Land-use analysis of anthrosols has been performed by a new, two-part method. A rapid qualitative field test assists in locating past settlements and determining their areal and temporal extent, even where artifacts are missing. The field-test results are verified and samples are analyzed further by quantitative soil phosphate fractionation. Laboratory fractionation reveals much more than the simple phosphate test used at present. Like the chemical field test, it uses minute soil samples and may be invaluable where disturbance of the landscape is forbidden. Phosphate fractions reflect the details of man-induced changes in the soil and the timing of their appearance.

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