



Soil Phosphorus Analysis as an Integrative Tool for Recognizing Buried Ancient Ploughsoils

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Two different methods of analysis of the phosphorus content of the soil were applied to two different archaeological areas, already interpreted as probable Roman ploughsoils through the study of the archaeological indicators. Both the fractionation method and the comparison of the organic versus total phosphorus content supported the interpretation of an ancient agricultural use of these soils, but it is worth underlining that the latter method is quicker and less expensive. The work confirms the usefulness of soil phosphorus analysis for archaeological purposes.

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Introduction—Archaeological Data and Problems

Archaeological discoveries connected with Pre-historic and Roman agricultural activities have been made in two places on the outskirts of Padua (north-eastern Italy) (Figure 1) at the Archaeological Area of Centro Universitario Sportivo-Piovego (hereafter: CUS) (Leonardi, 1990; Stocco, 1992) and the so-called Cittadella dello Sport (hereafter: CdS) (Leonardi, 1993). Here systematic, archaeological research has been done since the 1980s in connection with the needs of the building industry and of territorial organization. In both cases agricultural structures were found, consisting of water drains of varying importance.

At CUS these agricultural structures were very complex because of changes in the agricultural system. These changes were, in chronological order: (a) changes in the orientation of the hydraulic network and (b) a change in the dimensions of the cultivated fields, evident in the last phase through the general obliteration of the agricultural channel network marking the field boundaries. These changes happened

within the Roman period, between the 2nd/1st century BC and the 2nd/4th century AD as demonstrated by the few artefacts found. At CdS the drains were lateral to a possible road. In this case the drains are datable to Late Prehistory, very probably to the centuries of the beginning of the Roman conquest (Leonardi, 1993: 24). From a territorial and geomorphological point of view, in both cases the agricultural structures cut the alluvial plains created by the ancient floods of two rivers, the Brenta and the Bacchiglione. Because of their common origin the two areas show a similar sedimentary substratum.

From an archaeological point of view, a further element common to both areas (Figure 2) is the presence of ancient agricultural deposits. They are connected with the drains, as they occur within them in the upper fill and are buried under Mediaeval and/or modern–contemporary agricultural layers. Our research concentrated on the stratified segments of agricultural sediment preserved in an almost “fossilized” condition. These segments of ancient ploughsoils have been preserved because they have sunk into the upper part of the agricultural drains and have therefore been protected from damage by later ploughing. This

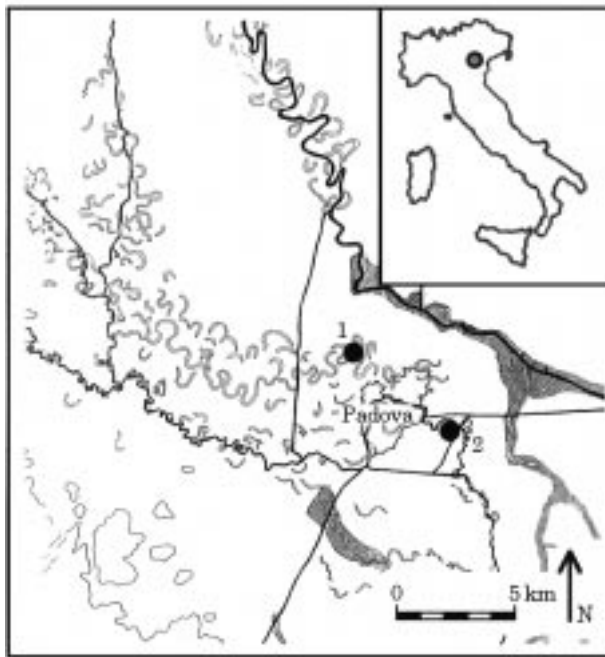


Figure 1. The archaeological areas quoted in the text: 1—Cittadella dello Sport (CdS), 2—CUS-Piovego (CUS).

sinking of the ploughsoils was caused by the compaction of the upper sediment forming the fill of the drains after their abandonment.

At CUS the analysis of the physical and spatial features of the materials included in the soil provided a scientific demonstration of the presence of what had already, on customary criteria, been identified as a ploughsoil. By extension, the subsequent discovery of a similar situation in the layers at CdS allowed the probable identification of a ploughsoil here also.

In order to validate this interpretation, it was decided to back up the archaeological evidence with chemical proof from phosphate analysis of soil, following well-established scientific precedents (Eidt, 1977, 1984; Edwards, Hamond & Simms, 1983; Prosch-Danielsen & Simonsen, 1988).

The archaeological area of CUS-Piovego, Padua East

In this archaeological area the Roman agricultural structures overlaid a cemetery datable to the 5th–3rd centuries BC. The only chronological indications came from the artefacts found during the fieldwork. As the pit-tombs were removed and transported to the laboratory still sealed in their sedimentary deposit, the chronology might be revised in the future when these funerary contexts are analysed. In the areas adjacent to the agricultural drains, mixed sediments were often found in the contact zone between the modern ploughsoils and the sterile substratum. These mixed sediments consisted of silt and sand together with mostly miniscule brick and tile fragments, bits of charcoal. They were interpreted as the remains of ancient ploughsoils, although this could not be demonstrated scientifically (Leonardi, Balista & Vanzetti, 1989). A possible, partial solution to the problem arose when macroscopic remains of buried ploughsoils were discovered in the upper part of the agricultural drain called St. 101. This structure was accurately studied and published (Leonardi, 1990; Leonardi *et al.*, 1992). These remains were interpreted as the traces of a “young” ploughsoil on the basis of the fragmentation of the bricks, especially considering the grading of their dimensions in combination with their spatial arrangement. In fact the process of fragmentation of the bricks by the plough was just beginning (Stocco, 1992). Extending this interpretative model, the almost flat

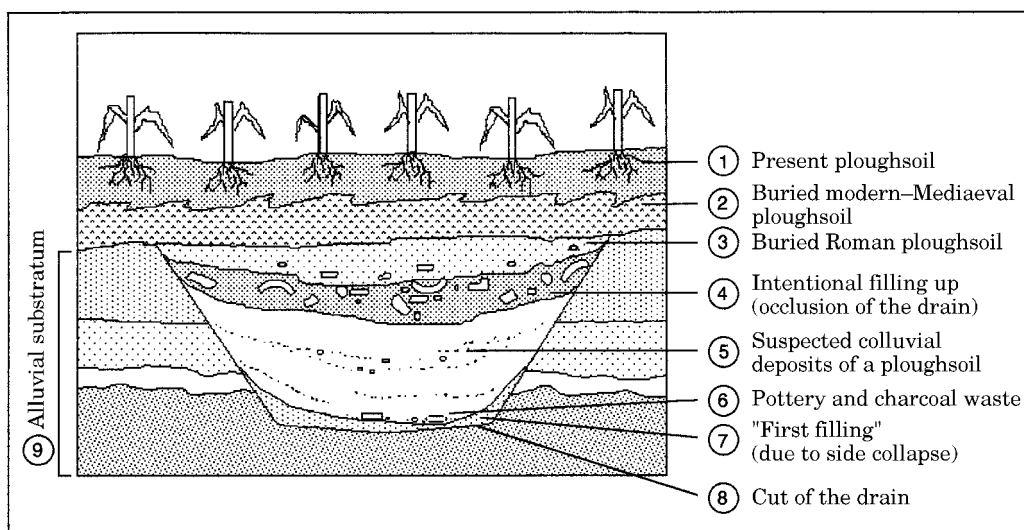


Figure 2. Model of the layers with agricultural drains and buried ploughsoils of CUS-Piovego and CdS.

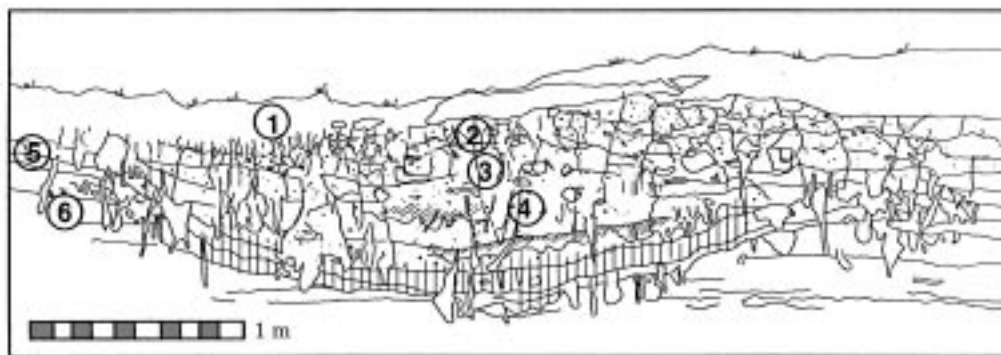


Figure 3. Oblique section of the agrarian drain St. 101 of the Archaeological Area of CUS-Piovego (PD). Location of the samples collected: 1, present ploughsoil; 2, Roman ploughsoil, upper zone; 3, Roman ploughsoil, lower zone; 4, layer under the ploughsoil, inside the drain; 5, layer under the ploughsoil, outside the drain; 6, sterile soil (modified from Leonardi *et al.*, 1992).

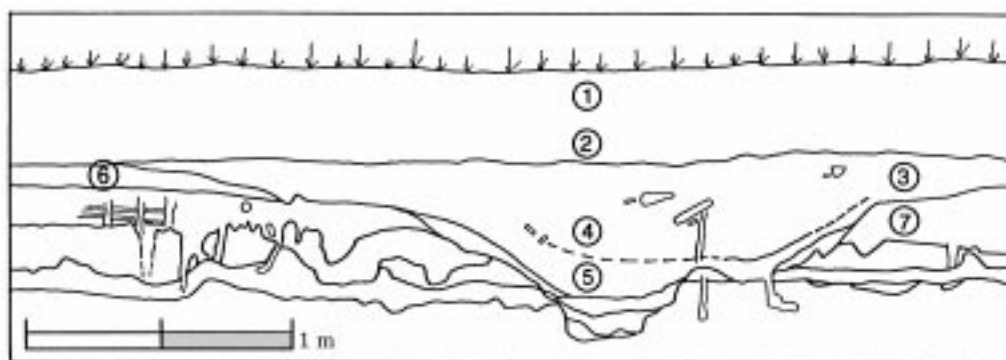


Figure 4. Section of the agricultural drain Str. 1 of CdS. Location of the samples collected: 1, present-modern ploughsoil; 2, modern-Mediaeval ploughsoil; 3, Roman ploughsoil; 4, colluvial layer under the ploughsoil, inside the drain; 5, basal silt, inside the drain; 6, suspected sterile soil; 7, sterile soil (scale 1:20).

layers lying under the modern ploughsoils were interpreted as very “mature” ploughsoils because of the presence of miniscule brick fragments.

The samples for soil phosphorus analysis were taken from different kinds of sediment according to the interpretative model (Figure 3), i.e.:

- (1) modern ploughsoil
- (2) upper part of the Roman ploughsoil, sampled in order to analyse the amount of phosphorus present in definite agricultural layers
- (3) lower part of the Roman ploughsoil, probably partially mixed with the sediment gradually filling the drain
- (4) sediment possibly representing a ploughsoil which had washed down into the drain, together with material from the ditch sides, while it was still in use
- (5) soil possibly partly involved in ancient agricultural activity (“under the ploughsoil”) redeposited from the area outside, but close, to the drain
- (6) sterile sediment, that is not affected by human activities.

The archaeological area of Cittadella dello Sport, Padua North-west

The drains found in the central area of CdS (Figures 4 & 5) show features very similar to St. 101 of CUS-Piovego. Both Str. 1 and Str. 2 were characterized by an artificial fill sealing the colluvial deposits which had progressively obliterated the agricultural structures. The upper part of this fill bore traces of ploughing, at least on the basis of the interpretative model suggested at CUS. Therefore the sampling procedure was the same as at the CUS drain, i.e.:

— Str. 1:

- (1) present day-modern ploughsoil
- (2) modern-Mediaeval ploughsoil underlying present day-modern ploughsoil
- (3) Roman ploughsoil
- (4) sediment possibly representing a ploughsoil which had washed down into the drain, together with material from the ditch sides, while it was still in use; sediment (4) was in contact with the lower part of the Roman ploughsoil

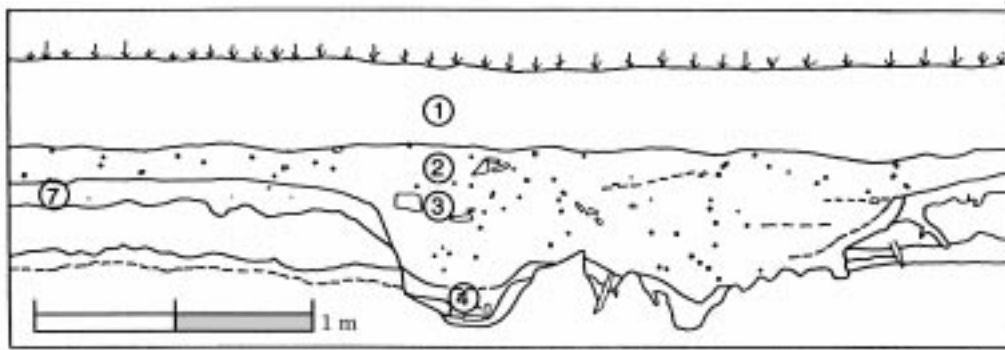


Figure 5. Section of the agricultural drain Str. 2 of CdS. Location of the samples collected: 1, modern ploughsoil; 2, Roman ploughsoil; 3, colluvial layer under the ploughsoil inside the drain; 4, basal silt with rubbish; 7=sterile soil (scale 1:20).

- (5) basal colluvial silt deposits inside the drain, similar to the previous sample
- (6) possible sterile sediment under the ploughsoil
- (7) sterile silt outside the drain.

— Str. 2:

- (1) present day—modern ploughsoil
- (2) Roman ploughsoil
- (3) sediment possibly representing a ploughsoil which had washed down into the drain, together with material from the ditch sides, while it was still in use
- (4) basal silt associated with a rubbish deposit consisting mainly of pottery fragments
- (5) sterile silt outside the drain.

From archaeological analysis to soil phosphate analysis

The analysis of the phosphorus content of the soil was applied to four different, but inter-related, types of deposit. They have the same natural origin, in thin alluvial sediments, but are differentiated by subsequent transformations due to human activity:

- (1) *substratum*: fluvial sediment not affected by agricultural activity, therefore archaeologically “sterile”
- (2) *colluvial archaeological sediment*: same type of fluvial sediment, altered by ploughing and cultivation, and subsequently washed down into the drains, in secondary deposition. This type of deposit probably consisted predominantly of ploughsoil mixed with a smaller quantity of sterile sediment derived from erosion of the sides of the drain
- (3) *transitional deposit between the ploughsoil and the sterile substratum*: a mixture of sediments 1 and 4
- (4) *archaeological ploughsoil*: same type of fluvial sediment, altered by ploughing and cultivation, still in primary deposition, and buried.

The analysis of the amounts of phosphorus present in the sequence was expected to reveal different values in the different types of deposit. Subsequent

comparison between the CUS and the CdS sequences was expected to show similar values, demonstrating the same anthropogenic origin for the two archaeological deposits and their agricultural function (G.L.).

The Phosphorus Cycle and the Archaeological Record

It is well known that human activities cause changes in the chemical content of the soils on which they take place so that these human affected soils are different from the sterile ones. The rate of soil change depends on the power of retention or fixation of the chemical elements involved as well as on soil features and climatic conditions; nevertheless the soil chemical content reflects human activities—their function, intensity and duration (Eidt, 1984; Cresser, Killham & Edwards, 1993).

As a consequence, buried soils can be considered a palimpsest of evidence for past human presence, especially when traditional archaeological material is absent and the only evidence of past human occupation is due to the decay of organic remains recorded in the soil (Figure 6).

The major chemical elements involved in human activities before the Industrial Revolution are nitrogen, potassium, phosphorus, calcium, magnesium and sulphur.

Phosphorus is by far the most reliable of the chemical elements connected with human activities because of its very low “loss factor”: once deposited, in most soils it remains bound to the original deposition site with negligible horizontal and vertical migration and no gaseous escape. In addition to this, it is very easily examined both through laboratory and field methods.

The primary source of phosphorus in soils is the rocks underlying them as parent materials (Cook & Heizer, 1965; Provan, 1971; Eidt, 1977, 1984). The quantity of “native phosphorus” may vary widely from place to place and from soil to soil, so that the background of soil phosphorus must be experimentally assessed in any study area.

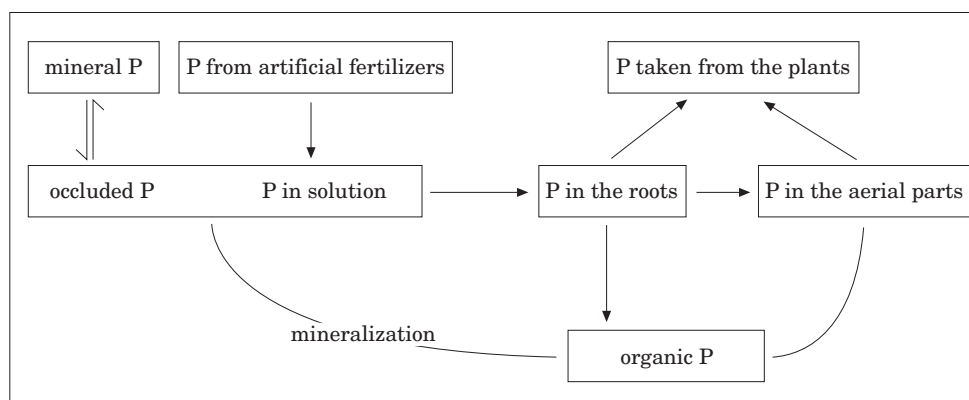


Figure 6. The phosphorus (P) cycle (after Cremaschi & Rodolfi, 1991).

Of course animals living in an area provide soil with both the inorganic and organic phosphorus they contain in their body through their waste products and at the same time they remove soil phosphorus when they graze.

Plants contain organic and, to a lesser extent, inorganic phosphorus. Through their roots they remove phosphorus at a certain depth from the soil surface, taking it from the small amount of available phosphorus (i.e., in solution as orthophosphate ions) which they find in the soil (Brady, 1974; Bethell & Mate, 1988). If these plants are part of a crop the loss is permanent (loss from the system) but in the case of naturally growing plants, when they die the phosphorus they contain in their tissues is returned to the surface of the soil, mostly as organic phosphorus.

We can therefore regard the action on soil phosphorus content of natural-growing plants and animals as one of mobilization and transformation of phosphorus rather than accumulation and depletion (Cook & Heizer, 1965).

We have very little information about the fate of the organic phosphorus which is deposited on the surface of the soil (Brady, 1974), although in different ways, both phytin and nucleic acids rapidly become available to plants, that is to say “fixed” in insoluble compounds. This happens both in alkaline and acid conditions for phytine, while nucleic acids are less available in acid conditions. In the long-term, anyway, the organic phosphorus tends to become inorganic (Provan, 1971).

Inorganic phosphorus enters only to a minimal extent into the available (i.e., in solution) pool of the soil. Most of it is “fixed”, becoming insoluble and unavailable to plants.

When the soil pH is alkaline (pH > 7) the inorganic phosphorus reacts with the calcium ions present in the soil forming insoluble calcium compounds (the most common is $\text{Ca}_3(\text{PO}_4)_2$). In acid situations (soil pH < 7) iron and aluminium ions are usually predominant and immediately react with the orthophosphate ions forming mineral insoluble phosphate (Brady, 1974; Bethell & Maté, 1988).

In a native (i.e., not human-affected) system the two significant pathways of net loss of phosphorus are erosion and leaching.

The total amount of phosphorus in a native soil is relatively stable; by far the most important changes in the conditions of this element come from human activities, which make phosphorus extremely mobile as an output of an economic system (Bethell & Maté, 1988).

Agriculture and soil phosphorus

The direct effect of cropping is the depletion of soil phosphorus content because the losses due to plant removal are not replaced by the decomposition of their dead tissues on the soil’s surface.

So, in the most primitive types of farming the level of soil phosphorus will decrease below the natural phosphorus content (Eidt, 1984).

Losses of phosphorus in arable land are often losses from the system and must be replaced by adding manure and artificial fertilisers. The late (1849) introduction of artificial fertilizers, the possibility of controlling many variables involved in the chemical and agrarian history of the studied soils, and the conjunction with other archaeological methods make possible the use of the analysis of soil phosphorus content for archaeological purposes, as is evident from many applications (Gurney, 1985; Buck, Cavanagh & Litton, 1989).

Eidt (1977, 1984) applied the soil fractionation procedure for identifying the different kinds of soil phosphorus induced by human activities in order to detect areas of ancient cultivation.

It was that last study by Eidt that influenced this attempt to find chemical traces of the agricultural use of the soils under study. The limitations of Eidt’s work should also be emphasized, as it was based on a very small number of samples coming from very different situations (ranging geographically from northern to southern America and even to India, and chronologically from our times to AD 700) (M.M.).

Materials and Methods

As previously described, soil phosphorus is made up of an inorganic fraction (bound and/or dissolved) and an organic fraction with varying percentages of between 5% and 95% of the total for each. Only a small part appears in the soil solution (0.1–1 mg/l).

The soil phosphorus cycle is almost restricted to the soil, water and plant compartments, as it lacks wet or dry inputs from and gaseous output to the atmosphere and a limited output to headwater streams or the groundwater. However, the latter may occur in soils with low absorption capacity and high water permeability, or erosion of soils heavily fertilized with phosphorus applications.

Soil microbes are involved both in the mineralization of phosphorus to phosphorus-inorganic forms and in the dissolution of inorganic phosphorus. The dissolution is promoted by the emission of carbon dioxide and organic acids by micro-organisms. Essentially the inorganic phosphorus in soil exists in the form of orthophosphates or derivatives of phosphoric acid.

Knowledge of the forms of phosphorus in soil has come largely from chemical fractionation based on the ability of selective chemical reagents to dissolve different types of phosphorus compounds.

Sampling

We assessed the natural “background” phosphate level of the sites, sampling the ploughsoil and the subsoil in areas where, as far as can be ascertained, there is little evidence of settlement.

For each archaeological horizon, 10 soil samples of 30 g each were collected, using a clean trowel, avoiding obvious sources of contamination, roots and large stones. We stored them in sealable plastic bags of an appropriate size with write-on panels.

Once in the laboratory, the 10 samples taken from the same archaeological horizon were mixed together to form a unique sample.

To minimize contamination, the water used to prepare the solution and rinse glassware was always deionized, distilled and sterilized by filtration (Millipore[®], type GS, 0.22 µm).

All glassware was cleaned in chromic acid (24 h) and then rinsed with deionized, distilled and sterilized water.

Data are the result of 10 replications and the deviation standard was always under 5%.

Soil pH was determined by pH meter utilizing a soil–water ratio of 1:2.5.

Estimation of total phosphorus (method Bowman, 1988, see Alef & Nannipieri, 1995)

Principle of method. The soil sample is treated with concentrated sulphuric acid and hydrogen peroxide to dissolve phosphorus in organic and non-silicate inorganic forms. Phosphorus in the silicate lattice is released by hydrofluoric acid treatment.

Materials and apparatus
hotplates or heated sand bath
Teflon beakers (100 ml)

Chemicals and solutions
concentrated sulphuric acid (95–97%)
hydrogen peroxide (30%)
concentrated hydrofluoric acid (40%)

Procedure. Three millilitres of hydrogen peroxide and 3 ml of sulphuric acid were added to 1 g of soil sample, in a beaker, then it was swirled vigorously and when the reaction had subsided, 1 ml of hydrofluoric acid was added. The beaker was placed on a hot plate at 150°C for 20 min to eliminate hydrogen peroxide, then the beaker content was transferred to a volumetric flask, passing it through a quantitative filter paper and the filtrate was made up to volume. On this extract was determined the quantification of phosphorus.

Extraction of organic phosphorus (method Bowman, 1989 modified, see Alef & Nannipieri, 1995)

Principle of method. Soil is extracted with concentrated sulphuric acid followed by sodium hydroxide; inorganic and total phosphorus are determined by colorimetry. Organic phosphorus is calculated by the difference between total and inorganic phosphorus.

Materials and apparatus
high-speed centrifuge
analytical balance
100 ml volumetric flasks
horizontal shaker with holding device for centrifuge tubes

Chemical and solutions
concentrated sulphuric acid (95–97%)
0.5 M sodium hydroxide

Procedure. One gram of soil sample was put into a centrifuge tube, 1.5 ml of sulphuric acid was added, then 5 ml of distilled water was added and when the mixture was cooled the other 40 ml of distilled water was introduced into the tube. The tubes were centrifuged and the supernatants were filtered. Some 100 ml of 0.5 M of NaOH was added to the filtrate and then it was shaken for 2 h. The shaken solution was centrifuged and the extract was filtered and utilized for the quantification of phosphorus (inorganic phosphorus).

Extraction of labile phosphorus (Stevenson, 1986)

Principle of method. Phosphorus that is thought to be available to plants is usually extracted with 0.5 M NaHCO₃.

Materials and apparatus. The same utilized for the organic phosphorus determination.

*Chemicals and solution*0.5 M NaHCO₃

Procedure. One gram of soil sample was treated with 0.5 M NaHCO₃ and the solution was shaken for 2 h. Then the extract was centrifuged and the supernatant was utilized for the phosphorus estimation.

Investigations of the forms of native inorganic phosphorus and transformations of phosphorus applied as fertilizer (Stevenson, 1986)

Principle of method. All phosphate was extracted with 0.1 M ammonium fluoride, iron phosphate with 0.1 sodium hydroxide, calcium phosphate with 0.5 sulphuric acid and phosphorus occluded with iron oxide and hydrous oxide is extracted with 0.3 M citrate–dithionite–bicarbonate solution.

Materials and apparatus. The same above described for organic phosphorus.

Chemicals and solutions

0.1 N sodium hydroxide

0.1 M ammonium fluoride

0.5 N sulphuric acid

0.3 M citrate–dithionite–bicarbonate solution

Procedure. For the determination of phosphorus linked to aluminium phosphate 500 mg of soil sample was treated with 25 ml of 1 N ammonium fluoride and the solution was shaken for 2 h, then the solution was centrifuged and utilized for the phosphorus quantification.

For the analysis of phosphorus bound to iron, 500 mg of soil was shaken for 2 h in 0.1 N NaOH solution. Then, after the extract was centrifuged, the phosphorus content was determined.

For the calculation of phosphorus linked to calcium, 500 mg of soil was mixed with 0.5 N sulphuric acid solution and shaken for 2 h. After the extract was centrifuged the phosphorus amount was evaluated.

For the iron occluded with iron oxide and hydrous oxides 500 mg of soil sample was added to 100 ml of 0.3 M citrate–dithionite–bicarbonate solution, it was shaken for 2 h and after centrifuging, the phosphorus content was estimated.

Quantification of phosphorus in the different soil extract

Principle of the method. Orthophosphate reacts with molybdenum and antimony in an acid medium to form a phosphoantimonyl–molybdenum complex. This complex is subsequently reduced with ascorbic acid to form a mixed valence complex. Light absorption is measured at 880 nm.

Material apparatus

spectrophotometer equipped with 1 cm cuvette
test tube shaker

Chemicals and solutions

antimony potassium tartrate

ammonium molybdate

concentrated sulphuric acid (95–97%)

ascorbic acid

Colour reagent (25 ml sulphuric acid+85 ml antimony potassium tartrate+1.7 g ascorbic acid+17 ml ammonium molybdate)

Procedure. One millilitre of the extract was introduced in a test tube. The final phosphorus concentration in the test should be 0.01–0.06 mg/l. For the calibration curve 0, 20, 40, 60 µl of the phosphorus standard stock solution was put into the test tube. In each test tube 1 ml of colour reagent was added and the total volume was made up to 10 ml total volume with a suitable volume of distilled–bidistilled water. The test tubes were shaken well and allowed to stand for 30 min. The adsorption was read on the spectrophotometer on 880 nm.

Calculation. A calibration curve was made plotting the absorption values versus concentration. To determine sample and blank concentrations it is necessary to subtract the mean of the blanks from sample values to give the corrected sample solution concentration (Cs). The concentration in the original soil sample

$$C_p \cdot (\text{mg P/kg}) = C_s \cdot 10 \cdot V_e/V_a \cdot W$$

where V_a is the volume of the aliquot in ml, V_e is the volume of the extract in ml and W is the sample weight in g; the final volume of the analyte is 10 ml (S.N.).

Results

As shown in Table 1, total phosphorus content is high in sample 4 (3.52 mg P₂O₅/g of soil) followed by samples 1 and 3 (2.16; 2.12), sample 5 (1.96) and sample 6 (1.84). As far as inorganic phosphorus is concerned, samples 1, 3 and 4 show the same content, while samples 5 and 6 exhibit a lesser amount (1.77; 1.27, respectively). Organic phosphorus shows a trend similar to total phosphorus, except for sample 6, which shows a high amount of organic phosphorus.

The phosphorus linked to aluminium is homogeneous in all the samples, while the phosphorus linked to iron is higher in samples 1 and 2. Also the phosphorus linked to calcium is homogeneous except for sample 6.

The pH value is alkaline, ranging from 8.0 to 8.6.

In Table 2 total phosphorus is more elevated in samples 2, 1 and 5 (1.05; 1.16; 1.27). Total phosphorus is high also in sample 4 (0.9) and decreases in samples 7, 6 and 3 (0.81; 0.79; 0.64). Samples 2, 1 and 4 exhibit a similar value of inorganic phosphorus, while samples 3, 4, 7 and 6 reveal lower values of inorganic phosphorus. Organic phosphorus demonstrates a trend

Table 1. Absolute values of the phosphorus content of the samples from St.101 of CUS—Piovego. The values are expressed in mg/g P_2O_5

	No.	P total	P inorg	P org	P Al	P Fe	P Ca	pH
Present ploughsoil	1	2.16	1.92	0.24	0.03	0.01	1.03	8.35
Roman ploughsoil, upper zone	2				0.03	0.01	0.91	8.33
Roman ploughsoil, lower zone	3	2.12	1.96	0.16	0.02	0.008	0.92	8.12
Layer under the ploughsoil, inside the drain	4	3.52	1.93	1.59	0.02	0.006	0.99	8.03
Layer under the ploughsoil, outside the drain	5	1.96	1.77	0.19	0.03	0.005	1.04	8.38
Substratum under the ploughsoil	6	1.84	1.27	0.57	0.01	0.003	0.73	8.6

*Sample 2 lacks some values as the analysis of the organic and inorganic soil phosphorus was introduced at a later stage in the research, when the archaeological deposit had already been destroyed.

Table 2. Absolute values of the phosphorus content of the samples from St. 1 of CdS. The values are expressed in mg/g P_2O_5

	No.	P total	P inorg	P org	P Al	P Fe	P Ca	P Fe II	pH
Present ploughsoil	1	1.16	0.68	0.48	0.1	0.22	0.23	0.19	6.94
Modern/Mediaeval ploughsoil	2	1.05	0.56	0.49	0.04	0.21	0.19	0.18	7.22
Roman ploughsoil	3	0.64	0.33	0.31	0.02	0.16	0.12	0.1	7.49
Colluvial layer, inside the drain	4	0.9	0.57	0.33	0.08	0.16	0.12	0.15	7.66
Basal silt, inside the drain	5	1.27	0.45	0.82	0.07	0.19	0.1	0.18	7.81
Suspected substratum under the ploughsoil	6	0.81	0.29	0.52	0.02	0.15	0.14	0.13	7.74
Substratum under the ploughsoil	7	0.79	0.34	0.45	0.01	0.15	0.15	0.13	7.87

Table 3. Absolute values of the phosphorus content of the samples from St.2 of CdS. The values are expressed in mg/g P_2O_5

	No.	P total	P inorg	P org	P Al	P Fe	P Ca	P Fe II
Modern ploughsoil	1	4.86	4.33	0.53	0.16	0.41	1.98	0.71
Roman ploughsoil	2	3.16	2.63	0.53	0.1	0.12	1.19	0.65
Colluvial layer, inside the drain	3	3.44	2.97	0.47	0.08	0.21	1.4	1.17
Basal silt with rubbish	4	3.82	3.14	0.68	0.1	0.19	1.67	1.14
Substratum under the ploughsoil	7	0.79	0.34	0.45	0.01	0.15	0.15	0.03

similar to total phosphorus. Samples 1 and 2 show a higher amount of phosphorus linked to iron and calcium, while the other samples show similar values.

The pH value is almost neutral, ranging from 6.94 to 7.87.

In Table 3, samples are endowed with a high amount of total phosphorus, except sample 5. Total and inorganic phosphorus show the same trend, while organic phosphorus is lower in samples 3 and 5.

Sample 1 presents a high amount of phosphorus linked to iron, calcium and aluminium. Samples 3 and 4 show a high amount of phosphorus linked to calcium and to occluded iron (M.M., S.N.).

Discussion

A significant result is that the ploughsoils—both contemporary ones and suspected Roman ones—of all three sections investigated present a percentage of organic versus total phosphorus lower than that of soils not affected by humans. This phenomenon is

explained by the agricultural exploitation of the soils, as plants and micro-organisms mineralize the organic phosphorus and use it; if these plants are part of a crop the loss is permanent.

In the *Piovego area* (Table 1), samples 4 and 6 (the level underlying the ploughsoil inside the drain and the not human affected soil) show a higher percentage of organic phosphorus due to their being buried, and therefore protected from erosion, and their not being exploited by people.

In the area of CdS *section 1* (Table 2), the contemporary and suspected ancient ploughsoils show a percentage of organic versus total phosphorus of about 40%. Sample 4, taken from the level underlying the suspected Roman ploughsoil, seems to have been the more exploited soil (36.6% organic P), so a possible human exploitation (as ploughsoil or similar) can be hypothesized: the chemical datum therefore supports the previous archaeological hypothesis (Figure 7). In the “sterile” samples the higher percentage of organic phosphorus means a lower human exploi-

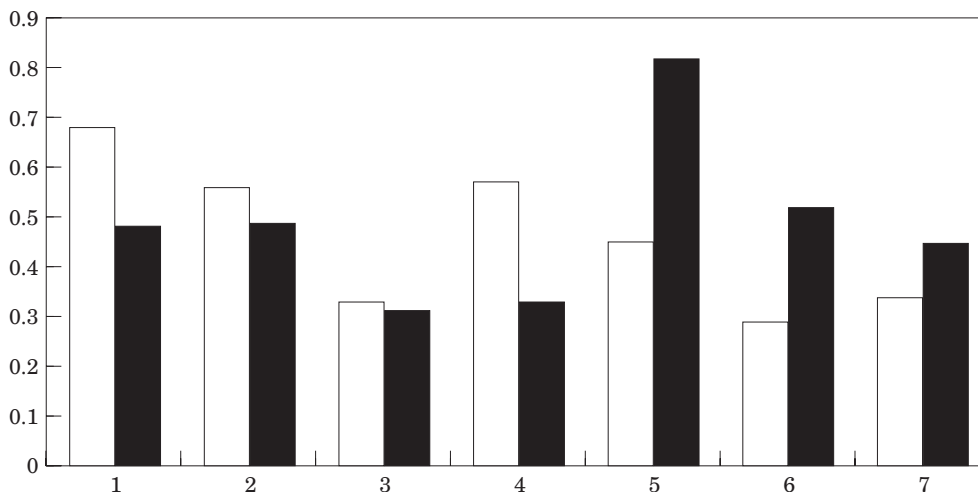


Figure 7. Barchart showing the absolute values of organic (□) versus inorganic (■) soil phosphorus of the drain St. 1 of CdS. The chart shows the contrast between the ploughsoils (samples 1–3) and the sterile soils (samples 6–7); sample 4, which was archaeologically interpreted as the agricultural sediment washed down into the drain, shows a chemical behaviour similar to the ploughsoils; sample 5 on the other hand seems to be similar to the sterile soils, but the high values of organic phosphorus can be interpreted in terms of use as a rubbish dump, as was archaeologically demonstrated in the nearby drain Str. 2.

tation; in other cases it can be interpreted as indicating a particular land use when especially high (sample 5 = a rubbish dump).

At CdS section 2 (Table 3), sample 3, from the soil filling the drain, shows a percentage of organic phosphorus even lower than the contemporary and Roman ploughsoils. This could be explained either by the history of the filling of the drain, which has not yet been studied, or by the presence of sandy silt: lime helps the drainage of waters and therefore makes mineralization easier.

The fractionation method also yielded interesting results.

The soils in the Piovego section are alkaline (pH around 8), and therefore phosphorus tends to form calcium compounds as is especially evident in the sample taken from the sterile soil. The highest percentage of phosphorus linked to iron compounds is in the ploughsoils, both the modern and the suspected ancient ones. This happens because the percentage of phosphorus linked to iron compounds is the more stable: it becomes more evident in the ploughsoils where plants and micro-organisms use the more available forms of phosphorus (Figure 8).

In the CdS sections 1 and 2, as the pH of the soils are neutral, the percentages of phosphorus linked to calcium compounds and to iron compounds tend to remain balanced in the soils which are not affected by human activity, while this equilibrium is broken to various degrees in the anthropogenic soils. In particular, the ploughsoils tend to show a percentage of phosphorus linked to iron compounds higher than in the soils not affected by human activity. The very high percentage of phosphorus linked to occluded iron in samples 3 and 4 from CdS section 2 suggest a very

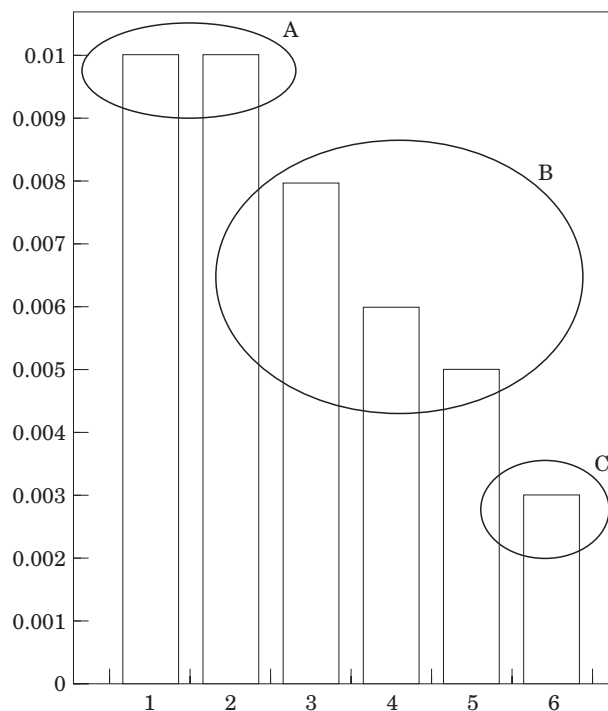


Figure 8. The absolute values of phosphorus linked to iron in the soils of drain St. 101 of CUS-Piovego. 1, Present ploughsoil; 2, Roman ploughsoil, upper zone; 3, Roman ploughsoil, lower zone; 4, layer under the ploughsoil, inside the drain; 5, layer under the ploughsoil, outside the drain; 6, sterile soil. The chart shows a direct correspondence with the archaeological interpretation: group A, with the maximum phosphorus linked to iron, represents the ploughsoils; group B corresponds to the layers linking the Roman ploughsoil with the colluvial deposit or the sterile soil; group C corresponds to the sterile soil.

ancient age for these soils (Russell, 1982).

In conclusion, the analysis of the phosphorus content of the soils helped to validate the previous archaeological interpretation.

Both the fractionation method and the comparison of the organic versus total phosphorus content supported the interpretation of an ancient agricultural use of these soils, but this study recommends *the latter method as quicker and less expensive*. Moreover, since this latter method is based on the observation of the presence of organic phosphorus, the influence of modern fertilizers (containing inorganic phosphorus easily available to plants) is minimal. The last is a problem that archaeologists tend to emphasize, forgetting that experimental studies have proved that the fixation of modern fertilizers tends to happen only in the first 30 cm of topsoil (Gurney, 1985).

The study of the CUS and CdS soils shows the great usefulness of soil phosphorus analysis for archaeological purposes when used in addition to the battery of techniques available to the field archaeologist.

This last is a point that cannot be stressed enough: phosphorus analysis is most effective when used in conjunction with other analytical archaeological methods: in this case the *archaeological recognition* of the internal elements forming ancient ploughsoils and of their distribution is successfully combined with the *chemical identification* of a particular relationship between organic versus total soil phosphorus and of a specific pattern of distribution of soil phosphorus fractions (M.M.).

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