5 The phosphate analysis

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1 Introduction

During the excavations at Kootwijk a large number of soil samples were taken from the areas Kootwijk 2 and 3 specifically for the analysis of the phosphate content. The purpose was to establish whether any differences in phosphate concentration could be found between the living and stall areas of the excavated long-houses, whether the phosphate content could provide clues as to the duration of occupation of the houses, a difference in function between the houses from the Roman period (Kootwijk 3) and the medieval period (Kootwijk 2) (more emphasis on cattle raising in the Roman period?), the length of time that the medieval fields were in use, and any manuring patterns which might have been practised (Kamermans 1980)[1].

Over a period of time, human activity in a restricted area brings about changes in the natural soil phosphate levels. Soil phosphates are poorly soluble, difficult to extract by natural means and remain identifiable and, indeed, measurable for a long period of time. The analysis of phosphate in soil samples basically consists of releasing the phosphate from its compounds by means of treatment with an acid, and then measuring the amount with the aid of a colouring agent and a colorimeter. The chemical formula of the basic reaction is: $H_3PO_4 + 12H_2MoO_4 \rightarrow H_3P\ (Mo_3O_{10})_4 + 12H_2O$ (Jackson 1958).

2 Phosphate analysis at Kootwijk

Kootwijk lies nowadays in a region of wind-blown sands. The most common, original soil types are *haar* podzol soils and *holt* podzol soils (Heidinga 1984, 1987; de Bakker & Schelling 1966). The pH of these soils lies between 5 and 6. Following consultations with members of the Laboratory of Physical Geography and Soil Science of the University of Amsterdam, and taking into account the pH and the sandy base material (with high leaching), total analysis was selected as the most suitable method. The analysis itself was carried out at the IPP, following the method of analysis described below.

2.1 *Description of the method*

Weigh the sample material accurately (1 g or less) in a 250/400 ml glass beaker. Add 20 ml perchloric acid ($HClO_4$) and heat for ± hour on a gas ring until virtually all the liquid has evaporated. Transfer the residue with a little distilled water to a wide centrifuge tube, and centrifuge (2 min. at ± 3000 r.p.m.). Decant the clear liquid into a 50 ml flask. Wash the residue with a little distilled water, centrifuge and again decant the liquid into the flask. Repeat the process once more. To the solution add a couple of drops of an indicator (2,4-dinitrophenol). Then with a burette add 2N Na_2CO_3 until a yellow colour appears. Remove the colour carefully with 2N $HClO_4$: at the exact moment that the colour disappears, the pH of the solution is 3. Dilute the solution with distilled water to ± 35 ml. Within the time limit of 30 seconds add, one after the other, 1.6 ml reductor reagent (1,2,4-aminonaphtholsulphonic acid), 5.0 ml $HClO_4$ 60%, and 4.0 ml ammonium molybdate solution. After each addition shake well. Quickly top up to 50 ml with distilled water. The blue colour of the solution is measured at 690 μ exactly 15 min. after the addition of the ammonium molybdate. Now read off the extinction in ppm P.

1269 samples were analysed in this manner. The samples may be divided into four categories:

1 samples taken from two undisturbed podzol soil profiles in the neighbourhood (control samples)
2 samples from the fields, belonging to Kootwijk 2 (8th-10th century, fig. 2.1: Ph1)
3 samples from four house sites of Kootwijk 3 (2nd-3rd century (fig. 2.1: Ph2), and Kootwijk 2 (8th-10th century, fig. 2.1: Ph3-5) taken predominantly on transect lines
4 various samples from a buried podzol and from other interesting features.

2.2 *The undisturbed profiles*

Two undisturbed podzol profiles in the immediate neighbourhood of the excavation were sampled in order to establish the natural phosphate content for the area: the 'background noise' to the settlement. The phosphate values display two peaks, one in the A1 horizon and a higher one in the B horizon (tables 5.1-2, fig. 5.1). This picture is consistent with other

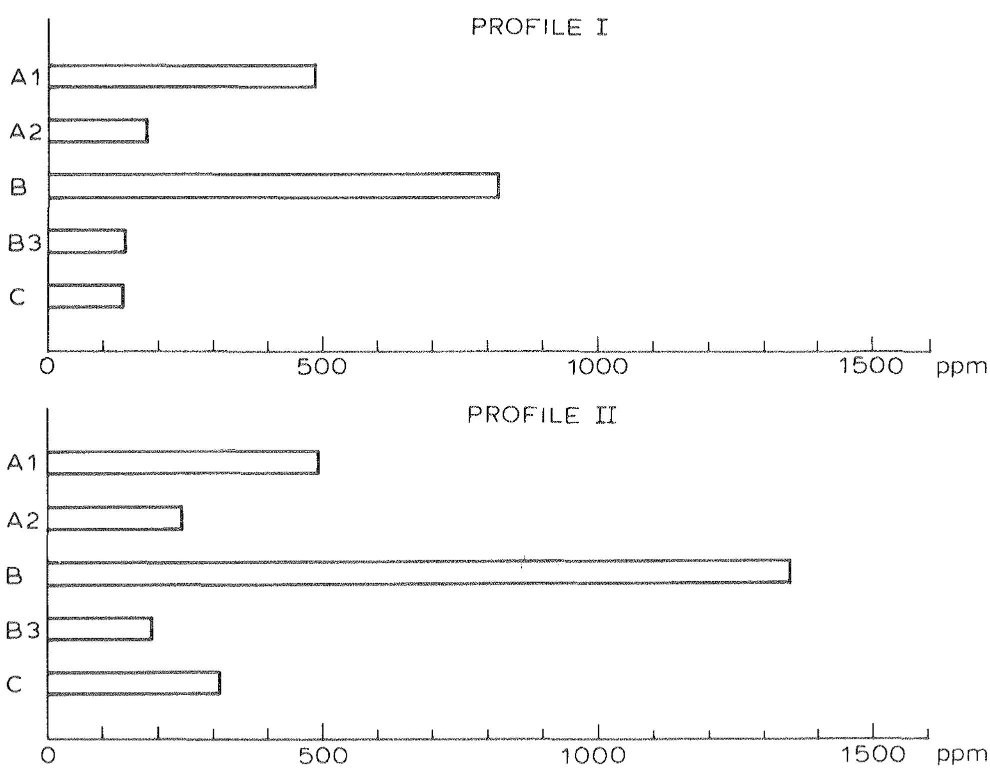

Fig. 5.1
The maximum phosphate values (ppm) for two undisturbed podzol profiles at Kootwijk.

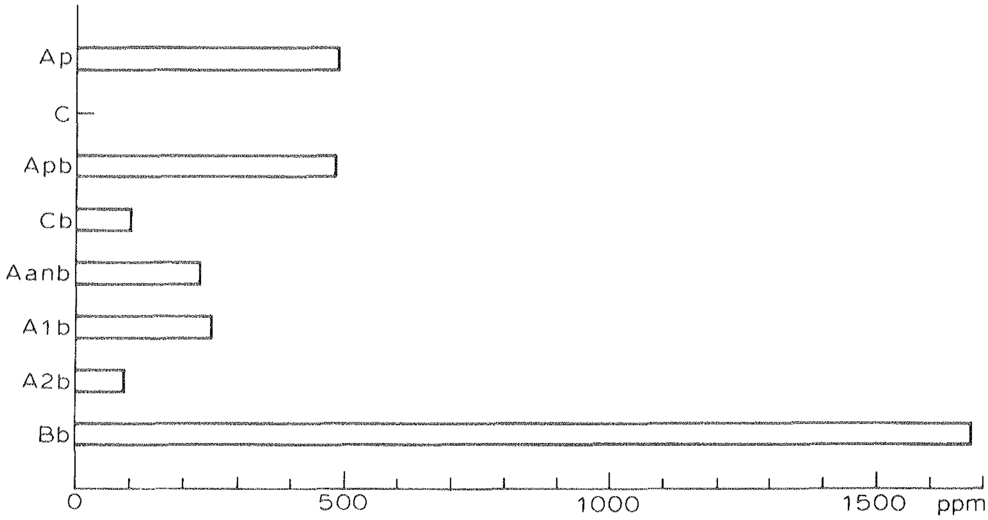

Fig. 5.2
The maximum phosphate values (ppm) for a buried podzol within the settlement of Kootwijk.

podzol analyses (cf. for example Pape 1966, 1970; Ceelen & van Diepen 1968).

A buried podzol within the settlement area was also sampled. The phosphate values of the podzol itself were recorded for only the A1, A2 and the B horizons (table 5.3, fig 5.2). The content in the A1 varies between 200 and 250 ppm, that in the A2 remains below 100. The B horizon, however, displays values between 900 and 1700 ppm.

Table 5.1
Number (n), average ($\bar{x}$) and standard deviation (s) of profile I (undisturbed podzol) per horizon. $\bar{x}$ and s in ppm.

	A1	A2	B	B3	C
n	3	7	2	1	5
$\bar{x}$	309	121	798	142	61
s	175	39	113	-	40

Table 5.2
Number (n), average ($\bar{x}$) and standard deviation (s) of profile II (undisturbed podzol) per horizon. $\bar{x}$ and s in ppm.

	A1	A2	B	B3	C
n	3	8	2	1	7
$\bar{x}$	289	102	846	183	170
s	246	58	729	-	82

Table 5.3
Number (n), average ($\bar{x}$) and standard deviation (s) of profile III (buried podzol) per horizon. $\bar{x}$ and s in ppm.

	A1	A2	B
n	2	2	2
$\bar{x}$	232	72	1294
s	26	16	534

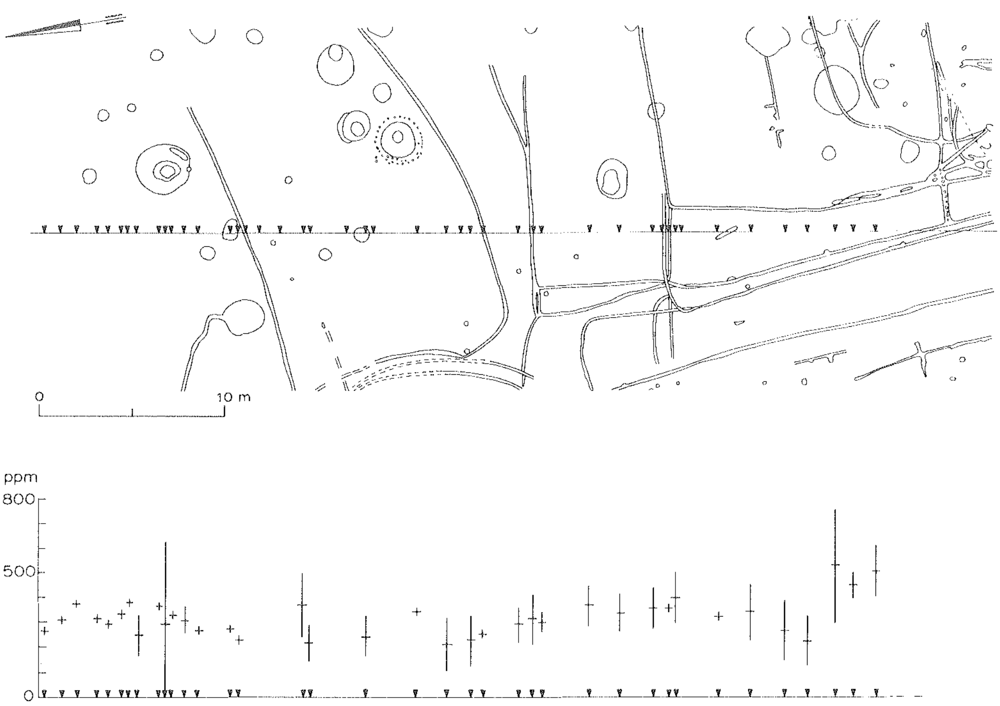

Fig. 5.3
Section over the medieval plough soil. Mean phosphate values (ppm) with their standard deviation.

2.3 *The field transects*

Samples were taken at various points along a section containing a medieval plough soil (phase 4C-D), in the area of the former pool at Kootwijk 2 (fig. 2.1: Ph1). The composition of the section from the bottom upwards was as follows: undisturbed sand, on which sporadic traces of the B horizon of a podzol occur, over this a dark layer which is interpreted as the plough soil (originally the A horizon of a podzol, in places mixed with the B horizon) and finally, wind-blown sand. Fig. 5.3 shows the phosphate content of the various samples taken from the plough soil, together with their position. Where different samples were taken one above the other in this layer, the averages were calculated and are given with their standard deviation. For the most part, the values vary between 80 and 500 ppm, only the three southernmost samples display values between 400 and 800 ppm. The B horizon has an average value of 463 ppm (table 5.4).

Table 5.4
Number (n), average ($\bar{x}$) and standard deviation (s) of the phosphate content of the plough soil and the B horizon of the transect over the fields. $\bar{x}$ and s in ppm.

	plough soil	B
n	72	21
$\bar{x}$	321	463
s	126	254

2.4 *The house sites*

Nowhere has the actual floor level of the houses survived. Analysis of the highest surface present reveals low phosphate values of ca. 200 ppm (table 5.5).

For the western house of Kootwijk 3 (2nd-3rd century, fig. 2.1: Ph3; Heidinga 1984, 12, fig. I,1:4) the picture is not very clear. The sample transects do not extend beyond the house (fig. 5.4). The graph of phosphate values taken down the length of the house is almost even, and the cross sections also differ little from one another.

Table 5.5
Number (n), average ($\bar{x}$) and standard deviation (s) of the phosphate content within the houses. $\bar{x}$ and s in ppm.

	Kootwijk 3	Kootwijk 2	
	w house	house 35	house 9
n	25	20	20
$\bar{x}$	227	150	244
s	46	97	86

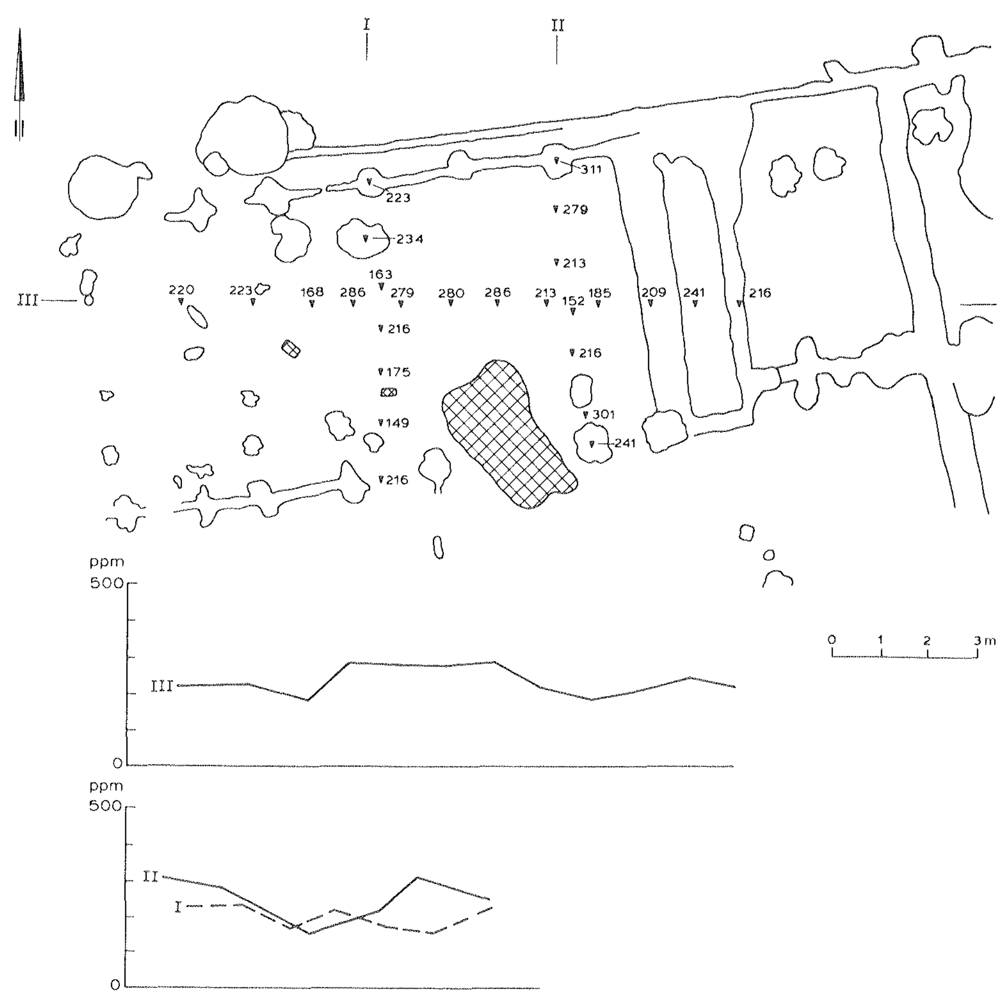

Fig. 5.4
Kootwijk 3. The phosphate values (ppm) along the sample transects across the western house.

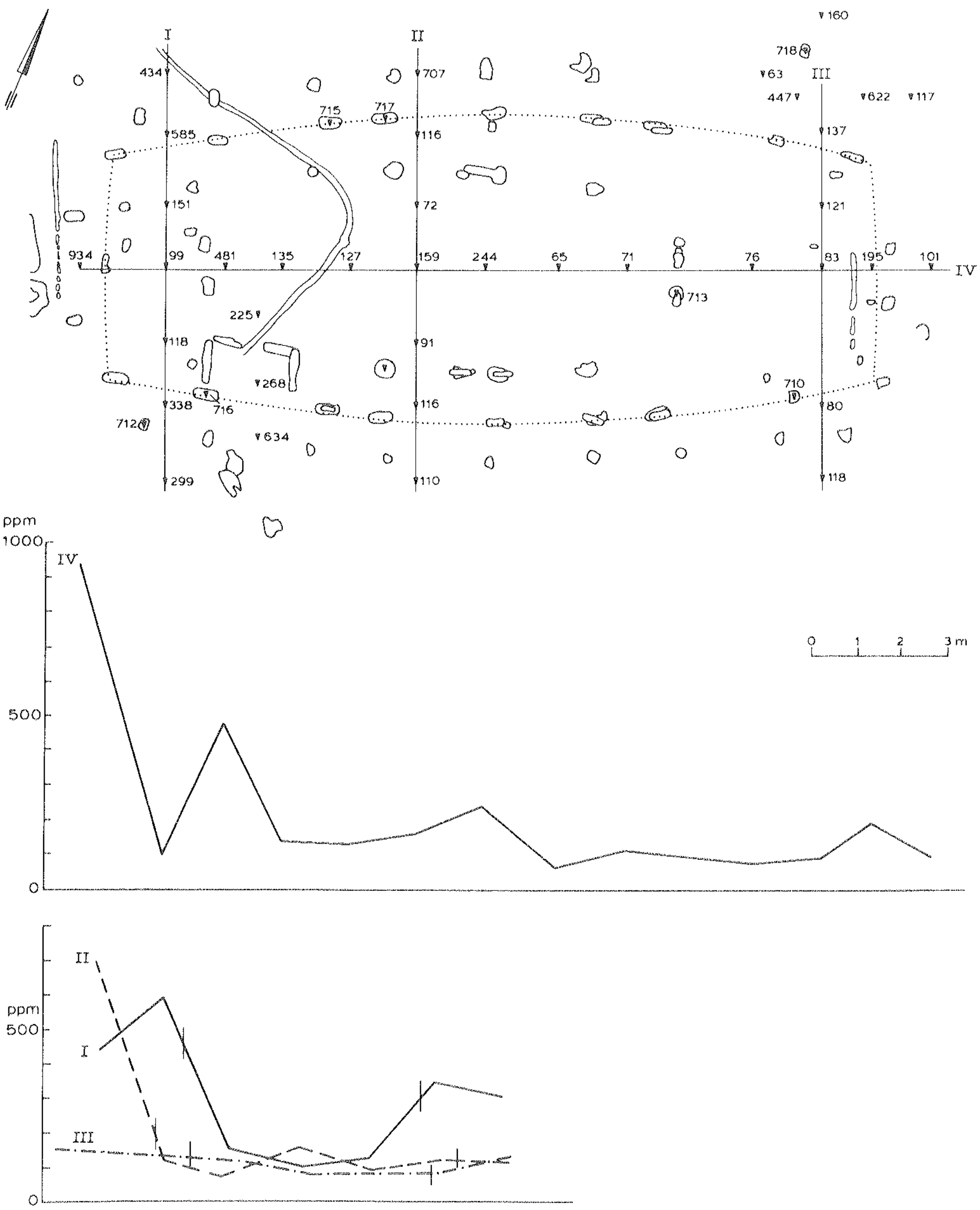

Fig. 5.5
Kootwijk 2. The phosphate values (ppm) along the sample transects across house 35.

House 2 of Kootwijk 2 (phase 1A-B, fig. 2.1) was sampled on two levels. The phosphate content of the upper level appears to be slightly greater outside the house than within it, but this difference is no longer discernible on the lower level. Here, however, the amount of phosphate increase with depth: on level 1 it is on average 453 ppm (standard deviation 100) and on level 2 602 ppm (standard deviation 129).

House 35 of Kootwijk 2 (phase 1B-2A, fig. 2.1: Ph4) displays high values immediately to the west of the house. Furthermore, the entire western half of this house seems on average to have higher phosphate levels than the eastern part (fig. 5.5). The values outside the house are, on average, 373 ppm, with a standard deviation of 286. The sections confirm this picture. The westernmost section (I) has high values outside the house, the central section (II) also displays high values to the north of the house, while the eastern section (III) is virtually undifferentiated. Within the house the phosphate values for section III are somewhat lower than is the case for the other sections. A lean-to to the north of the house is characterised by rather high phosphate values, especially to the centre (447 and 622 ppm).

The axial section of house 9 of Kootwijk 2 (phase 2A, fig. 2.1: Ph5) again reveals an increase in phosphate levels to the west of the house, and the cross section also shows higher values towards the house walls (fig. 5.6).

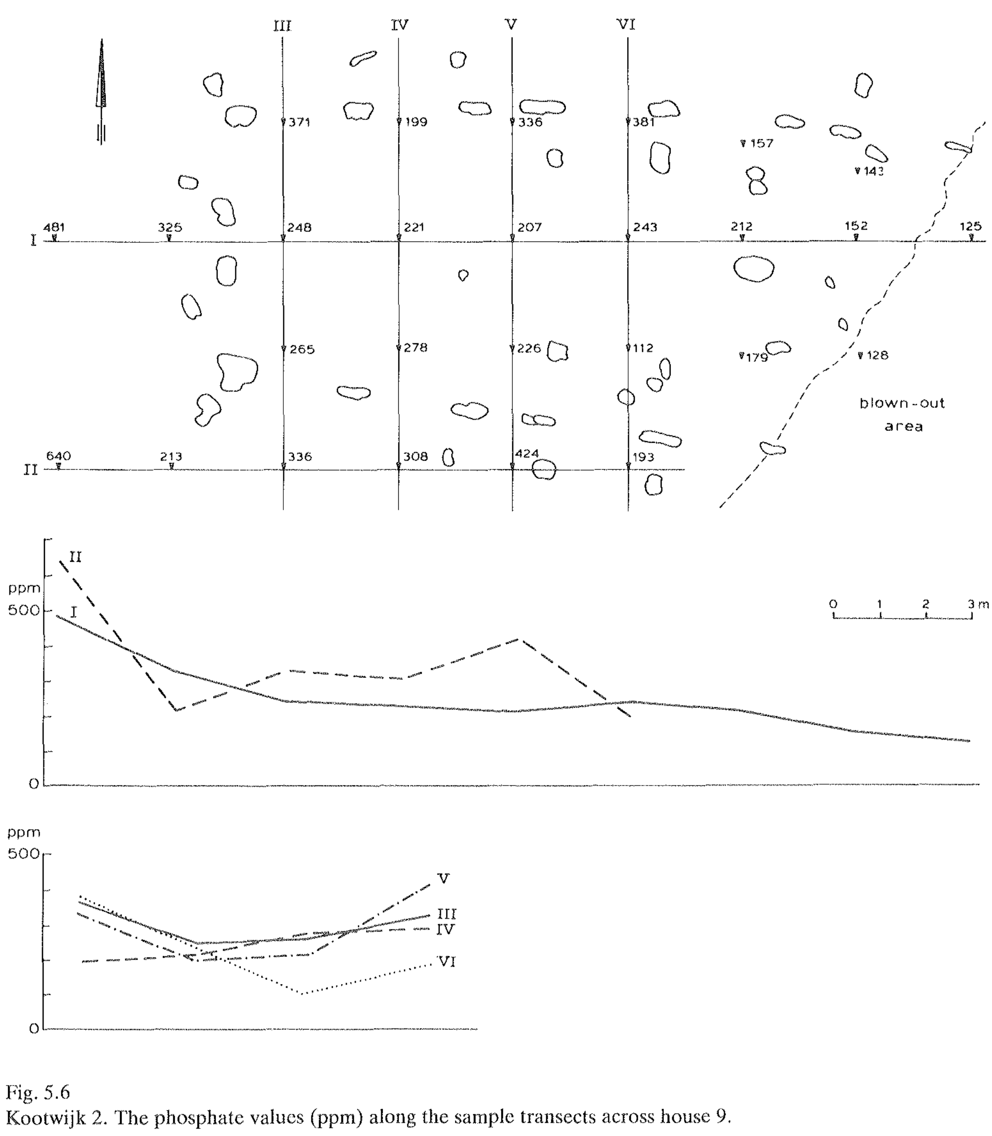

Fig. 5.6
Kootwijk 2. The phosphate values (ppm) along the sample transects across house 9.

3 Discussion

The undisturbed profiles display phosphate values which would be expected on the basis of comparative research (Pape 1966, 1970; Ceelen & van Diepen 1968). Only the buried podzol (fig. 5.2, table 5.3), with its average content of 1294 ppm in the B horizon, is clearly aberrant. The answer lies in the soil above the podzol: two plough soils and an occupation level, separated by wind-blown sand. The phosphate content of these levels does not exceed 500 ppm (a normal level for an A1 horizon) and the 'surplus' which must originally have been incorporated seems to have been leached down into the B horizon. Statistically, however, the difference in phosphate values between the B horizon of the buried podzol and those of the B horizons of the undisturbed podzols are not significant (table 5.6, test 1).

Table 5.6
t tests with significance level and calculated t (for an explanation of tests 1-5 see text).

	n	n	significance level = 0.05	calculated t
test 1	4	2	2.776	0.92
test 2	4	21	2.069	1.22
test 3	6	9	2.160	3.704
test 4	20	19	2.042	0.493
test 5	83	70	1.980	6.842

Comparison of the field transects and the undisturbed sections gives no clear indications of human activities. The phosphate values of the transect lines vary between 100 and 500 ppm; the phosphate values in the A1, A2 and B horizons of an undisturbed podzol are of the same order of magnitude. Comparison of the B horizon of the undisturbed sections with the remnants of the same horizon in the transect samples shows that the phosphate values of the latter are even lower than normal. This may well signify the absence of manuring, since continual cropping without the replacement of phosphate (manure) would result in a lowering of the phosphate level in the soil. The difference between the B horizon of the undisturbed podzols and the B horizon under the medieval plough soil is, however, not statistically significant (table 5.6, test 2). The higher phosphate levels in the three southernmost samples could be explained by the presence of an adjacent roadway, since the frequent passage of animals over a track results in a marked increase in the phosphate values (Bakkevig 1980).

Additional samples for phosphate analysis were taken from another trackway in Kootwijk, but not in the immediate vicinity of the samples discussed above, which hampers comparison. The phosphate values of samples taken from this road average 459 ppm with a standard deviation of 83. If we test the phosphate values taken from the road against those of the A1 of the undisturbed podzols (I and II, tables 5.1-2) then the phosphate content of the road is significantly higher (table 5.6, test 3).

In the case of the house sites, the phosphate values do not exceed those of the undisturbed sections (table 5.7), neither do the values within house 35 differ statistically from those outside (table 5.6, test 4). At house 2, the average phosphate values inside and outside the house are so little differentiated that a t test seemed to be superfluous.

Table 5.7
Number (n), average ($\bar{x}$) and standard deviation (s) for Kootwijk 2, houses 2 and 35. $\bar{x}$ and s in ppm.

	n ins	n outs	$\bar{x}$ ins	$\bar{x}$ outs	s ins	s outs
house 2	47	36	424	470	98	100
house 35	20	12	150	373	97	286

On the basis of the average phosphate content (table 5.5) no statements can be made about any differences in function within the houses, or about differences in the length of occupation between the Roman and medieval phases.

It does indeed appear that phosphates are more heavily concentrated near the house walls than elsewhere. This might indicate human activities such as cleaning, but might also be connected with the materials used to construct the wall. The clay used to daub wattlework is of fine grained structure which tends to retard leaching and would thus result in higher phosphate values (Zölitz 1980). The iron and aluminium content of clay is also rather high, which would permit the formation of rather more phosphate compounds than would be possible in the surrounding sandy soils (Poelman, pers. comm.). Another possibility is that the walls were formed of grass sods. Because of the increase in organic content, this would also tend to raise the phosphate levels. That phosphate values tend to be higher at house walls has also been observed previously (cf. Bleck 1965; Provan 1971). The excavator, however, supposes timber walls in the houses discussed here.

Where it was possible to make an internal division in the house on the basis of the phosphate content of the soil (house 35, fig. 5.5), the division does not correspond to the living quarters/byre distinction made on other criteria (Heidinga 1984, 1987). The increase in phosphate content with depth, as observed at house 2, is, however, of statistical significance (see table 5.6, test 5).

The high phosphate values to the north of house 35 in the shed suggests that the excavators were correct in calling this group of post holes 'the WC' (cf. Hamond 1983).

4 Conclusion

That the phosphate values of the settlement and the fields do not differ statistically from those of the undisturbed podzols cannot be a consequence of our chosen method of analysis. The values of our undisturbed sections correspond too well with those recorded in the available literature for that.

The fact that the floors of the houses are lost prevents us from testing the degree of phosphate retention here. It is, however, probable that most of the phosphate has been leached out. Podzols, the normal soils in such situations, develop by leaching out and percolation. A pH of 5-6 does not stimulate the fixation of phosphates. Cornwall (1958) states: 'Markedly acid soils, deficient in bases (pH 5.6), have no power to fix phosphate, which will rapidly be leached out'. The iron pan which occurs in some places at Kootwijk (Heidinga 1984, 1987) is an additional complication. Bakkevig (1980) remarks that the situation becomes extremely complex due to the development of intricate patterns of water transport, which result in greater lateral diffusion of the phosphates.

The podzol III (fig. 5.2) and the proportional increase in phosphate content with depth in house 2 indicates that the phosphates introduced by habitation on the site were leached out to a greater depth, where they were dispersed. Sampling on lower levels would not have resulted in a better picture. The even distribution of the phosphates both inside and outside house 2 on level 2 seems to corroborate this suspicion.

In general, it can be said that phosphate analysis at Kootwijk has added little to our knowledge of the settlement. Although the phosphate levels of the B horizon under the field suggests that manuring was not practised, it can not be statistically substantiated (but see, however, Pals, this volume, paragraph 5.2.2). A subdivision of houses into living quarters and byre can not be made on the evidence of the phosphate analysis.

A pedological study undertaken at an early stage would have clarified the migratory tendency of phosphates in these soils and would have confirmed the limited value of phosphate analysis as an aid to archaeological interpretation under these circumstances[1].

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NOTE

1 This analysis was undertaken as the practical part of the course ecological prehistory at the IPP, University of Amsterdam. The manuscript was completed in 1980, except for some minor additions.

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