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Geochemical Study of the Iron Age Settlement Occupational Layer and the Early Roman Time Agricultural Layer at Voorthuizen, The Netherlands

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Abstract: The application of geochemical analysis in archaeology provides a better understanding of ancient human activities. This paper presents the results of geochemical multi-element, LOI, MS, and geochronological analyses of a cultural layer at the Voorthuizen (The Netherlands) archaeological site. The study has revealed a difference in the geochemical composition of an occupational surface in the Iron Age settlement and an early Roman Time agricultural horizon. The former is enriched in Ba, Sr, Rb, Th, Cl, and Mg, while the latter displays elevated P, Pb, Ni, Mn, and V values. The study has provided a deeper insight into the agricultural techniques applied at the Voorthuizen site and on the so-called Celtic Fields, known as ancient field systems dating from the same period and widespread throughout north-west Europe. It seems that household waste was not used as a fertilizer at Voorthuizen, while the application of manure is characteristic of Celtic Fields. However, phosphorous values in the Voorthuizen agricultural horizon are comparable to those in the Celtic Fields, suggesting similar sources of P in both cases. Elevated Si and "mobile" Fe, Mn, V, Pb, As, and Sn, along with higher MS measurements, are indicative of the use of extra mineral matter for the fertilization of the Voorthuizen ancient arable field.

Keywords: geochemistry; archaeology; ancient human activities; pre- and protohistoric agriculture; settlement occupational layer; Celtic Fields; Iron Age; Roman Time; phosphorous value; Veluwe

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Citation: Druzhinina, O.; Gedminienė, L.; van den Berghe, K. Geochemical Study of the Iron Age Settlement Occupational Layer and the Early Roman Time Agricultural Layer at Voorthuizen, The Netherlands. *Minerals* **2022**, *12*, 373. https://doi.org/10.3390/min12030373

Academic Editor: Massimo D'Antonio

Received: 6 February 2022
Accepted: 16 March 2022
Published: 18 March 2022

1. Introduction

The application of geochemical analysis to archaeology provides a deeper understanding of the functional meaning of the different zones of settlements and within structures, the identification of economic activities, including the types of an anthropogenic impact on the environment, the recognition of phases in the existence of settlements, as well as some other practical problems approached by archaeologists [1–6].

In recent decades, various geochemical methods have been developed to study traces of human presence, and a number of reliable anthropogenic geochemical indicators have been identified, allowing geochemistry to take its rightful place in scientific research [3,6–10]. However, there is a gap between the use of geochemical analysis in scientific projects and its use during rescue archaeological excavations, at least when it comes to rescue excavations in The Netherlands. Financial and time pressures certainly limit the choice of research methods, but the main reason why geochemistry is seldom used in Dutch rescue archaeology is that field archaeologists are often unaware of the advantages and potential of the method [5]. This, in turn, is due to the current lack of publications presenting regional data and the results of the use of geochemistry in rescue archaeological investigations.

This paper is part of a scientific study undertaken by a field team during rescue excavations of an Iron Age settlement at Voorthuizen in the central Netherlands (Figure 1).

In addition to geochemistry, the entire study comprised geochronological, phytolith, pollen, and non-pollen palynomorph (NPP) analyses with the aim to obtain more information on ancient economic activities at the site and their impact on the surrounding landscape. While this study is still in progress [11], the present contribution discusses the selective results of the geochemical investigation of Voorthuizen anthropogenic layers, such as the occupational surface of the settlement and the ancient agricultural horizon.

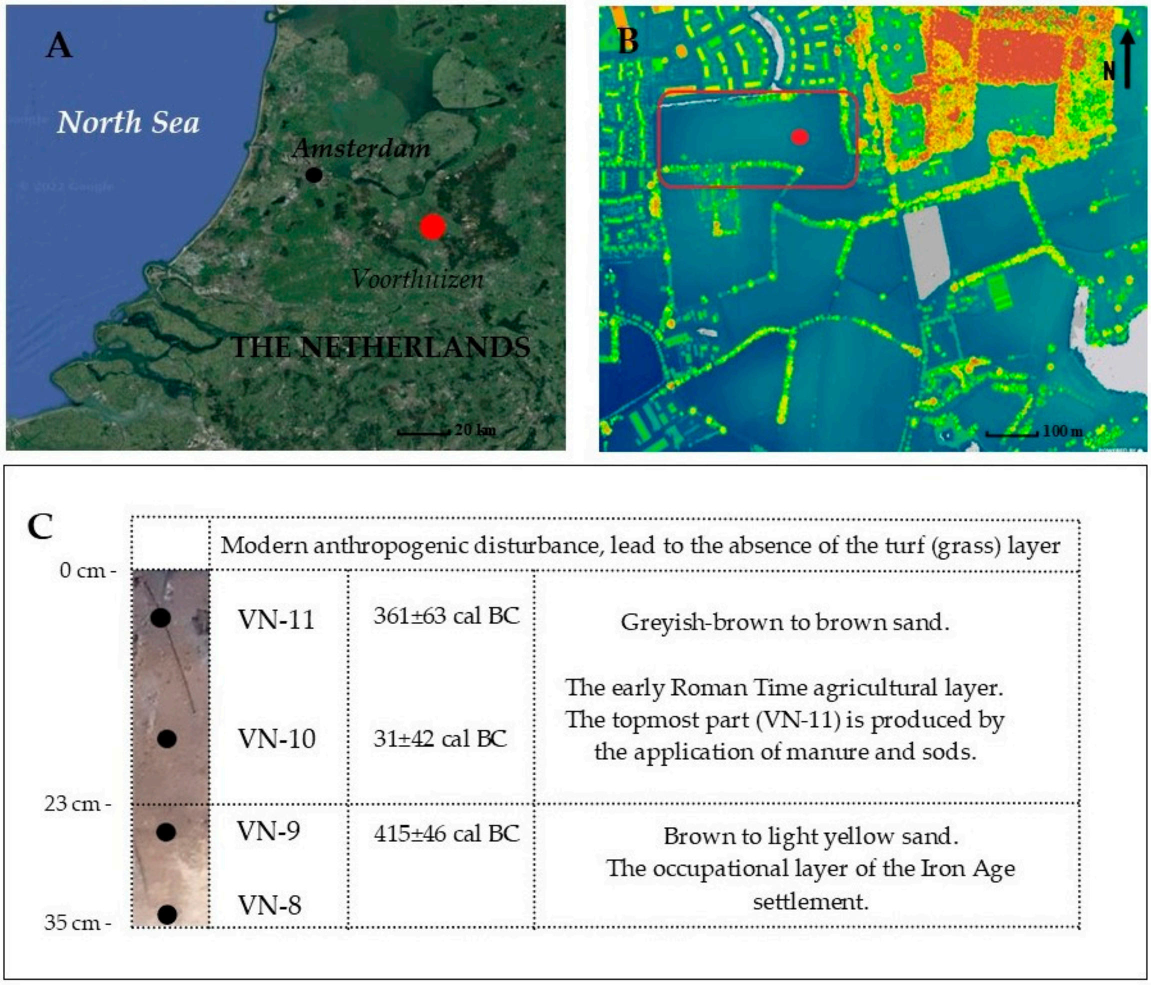

Figure 1. (**A**) Location of Voorthuizen in The Netherlands. (**B**) Northern part of the excavated area in Voorthuizen and the location of the profile, where samples VN-8–VN-11 were taken. (**C**) Profile of the Voorthuizen cultural layer and sampling sites.

2. Study Area and Archaeological Setting

Voorthuizen is situated on one of the coversand ridges in the transition zone of the ice-pushed Veluwe massif to the Geldese Vallei formed by ice tongue erosion. The modern vegetation around the Voorthuizen site is dominated by pine and mixed forest, heather land, and meadows on the various types of podzol soils. The study area has a temperate maritime climate. The annual average temperatures range between 5 °C and 14.4 °C and the average annual precipitation, evenly distributed over the year, varies from 750–850 mm.

2018–2019 excavations in Voorthuizen have revealed the remains of several settlements (or several phases in habitation) over an area of 3 ha [12]. The earliest date obtained for the area goes back to the (late) Bronze Age (1100–750 BC), though the majority of archaeological finds represent the Iron Age–Roman Time (750 BC–50 AD) periods of habitation.

The geochemical results reported in this paper were obtained for samples taken from soil layers at various depths in the northern part of the excavation terrain. The remains of the settlement found here are dated on the basis of archaeological finds and AMS ^{14}C dates.

The archaeological material is composed of ceramics. The ceramic finds consist mainly of hand-shaped pottery, which, based on technical aspects, such as fabric, leaning, and the diversity of shapes, can be dated at the Middle–Late Iron Age. Single fragments of wheel-thrown pottery from Roman Time are present, too [12].

The location, where samples are taken, is situated at the northern edge zone of the ancient settlement discovered. The edge zone as such contains few finds and features. Close to the sampling point, some structures used for storing the crops harvest were present. The structures can be split in so-called spiekers, built as four-posted square structures, and a large multi-posted, almost hangar-like, storage for crops or grain, a so-called horreum. Such types of structures are common on the margins of the settlements. The soil profile studied during the excavation visually consists of a brown, nearly homogeneous ~35 cm thick sand horizon overlying light yellow coversand (Figure 1).

The number of samples taken and the choice of research methods were dependent on the project budget. Samples were taken from the brown layer and the transitional layer as deep as the coversand mother material, where remains of archaeological features (mostly postholes) were found. The study has revealed three interlayers in the brown horizon dated at Iron Age–early Roman Time.

According to geoarchaeological interpretation of the soil built-up at the Voorthuizen site, the layers in the lower part of the profile were the living surface (sample VN-9) of the Iron Age settlement and the underlying horizon (sample VN-8) with traces of former structures in it. During the next habitation phase, in Roman Time, the settlement shifted several hundred metres to the south, while the study territory was involved in agricultural activities (samples VN-10, VN-11). The Roman Time agricultural layer is an early historical example of man-made arable horizon produced by the application of manure and sods, which were cut in the surrounding and brought to the field.

3. Methods

3.1. Radiocarbon Analysis

Terrestrial soil samples from anthropogenic layers were analyzed by AMS ^{14}C survey after acid-base-acid pre-treatment. The analysis was performed at the Centre for Physical Sciences and Technology, Mass Spectrometry Laboratory, Vilnius, Lithuania. The calibrated data (calAD) were obtained with OxCal v. 4.4.2. [13].

3.2. Geochemical Analysis

One sample from each sublayer was taken for geochemical analysis. The samples were prepared at the Open Access Centre of the Nature Research Centre in Vilnius using the standard procedures described previously in [14]. Dried samples were powdered and 20 mm tablets pressed previously were added to each specimen Licowax binder (Fluxana). The tablets were analyzed on EDXRF equipment Spectro Xepos using the Turboquant for a pressed pellet calibration procedure [6] elaborated by the manufacturers at Klaipeda University, Marine Research Institute. The equipment was used to identify 31 elements (Si, Al, Fe, K, Na, Ti, Ba, Ca, Mg, Mn, P, Zr, Br, Cr, Cu, Cl, Y, S, Rb, Sr, Zn, As, Co, Ga, Nb, Ni, Pb, Sn, Th, V, and Tl) in each subsample.

Loss-on-ignition analysis was carried out on four samples. Organic content (LOI 550 °C) was measured using the basic loss-on-ignition methodology [15] at the Nature Research Centre (Vilnius) and heating the sample at 550 °C and carbonates (LOI 900 °C) at 900 °C, respectively.

Since 2007, quality control has been performed by participation in the "International Soil-Analytical Exchange" (ISE) programme organised by Wageningen University [16]. More than 50 ISE reference samples and other certified reference materials were used for the recalibration of geochemical results.

Energy-dispersive X-ray fluorescence (EDXRF) equipment Spectro Xepos HE (Kleve, Germany) uses the TurboQuant (TQ) II calibration method elaborated by the manufacturers for samples with various matrices. The TQ method combines different procedures: calculation of the mass attenuation coefficient, using the extended Compton model, and final calibration based on fundamental parameters method. Calibration for major, minor and trace elements performed by measuring a series of international geological and mineral reference materials (e.g., GSR-01–GSR-10, AC-E, AL-I, AN-G, BE-N, BX-N, DR-N, DT-N, FK-N, GA, GH, GS.N, IF-G, MA-N, MICA-Fe, MICA-Mg, PM-S, UB-N, WS-E, ZW-C, SARM-18–SARM-20, NIST-2709, NIST-2711, NIST-2780–NIST-282, BCR-142–BCR-146, TB, GnA, SY-3, NOD-P1, GXR-03, G303-06, NCSDC-86306, NCSDC-86315, NIST-120C, GSS-5, AMIS-84, AMIS-0118, AMIS-0122, AMIS-0185, and AMIS-0191).

The Spearman correlation coefficients between the content of each element and other variables (the amount of organic matter, carbonates, mineral matter, MS, and geochemical elements) were calculated for each soil sample using StatSoft Statistica 8 MR-3. Significance levels (P values) for the correlations were calculated as well.

3.3. Magnetic Susceptibility (MS)

Four samples were analyzed at the Palaeomagnetic Laboratory of the Nature Research Centre in Vilnius, Lithuania, using the MFK1-B kappa bridge (AGICO) static specimen method with a manual holder facility. The data obtained were analyzed using the SAFYR software, and MS values were expressed in SI units (10^{-8} m^3 kg^{-1}).

4. Results

4.1. Radiocarbon Analysis

All the samples contained a sufficient amount of carbon for accurate measurement and produced a sufficient ion beam during AMS ^{14}C measurement. The δ ^{13}C values are within the normal range for organic samples, confirming the significant reliability of the results.

AMS ^{14}C measurements yielded the following results (Table 1):

Table 1. Results of the geochronological study of the Voorthuizen archaeological site.

Sample Designation	Lab. Code	Radiocarbon Age, BP	Calibrated Date (cal BC)	Median, cal BC	Av, cal BC
VN-11	FTMC-BJ24-1	2278 ± 26	68.3% probability 395–359 calBC (48.1%) 276–261 calBC (11.9%) 244–234 calBC (8.3%) 95.4% probability 400–351 calBC (54.2%) 291–209 calBC (41.2%)	361 ± 63	323
VN-10	FTMC-BJ24-2	2041 ± 26	68.3% probability 89–81 calBC (5.4%) 53 calBC-10 calAD (62.8%) 95.4% probability 150–135 calBC (1.9%) 114 calBC- 29 calAD (91.3%) 43–59 calAD (2.2%)	31 ± 42	34
VN-9	FTMC-BJ24-3	2360 ± 27	68.3% probability 465–437 calBC (18.4%) 421–391 calBC (49.8%) 95.4% probability 516–387 calBC (95.4%)	415 ± 46	434
V-14-sp363	FTMC-LY85-1	2549 ± 27	68.3% probability 794–754 calBC (47.4%) 682–669 calBC (9.6%) 610–593 calBC (11.3%) 95.4% probability 800–747calBC (49.8%) 689–664calBC (12.9%) 644–551calBC (32.7%)	750 ± 80	701

Samples VN-9–VN-11 represent soil profile horizons, while sample V-14-sp363 shows the date obtained for the remains of the structure found in the northern part of excavation.

4.2. Geochemical Analysis

As the differences in the values obtained were considerable, the elements were divided into macro (>100 mg/kg) and micro (<100 mg/kg) types for a better visual comparison (Figure 2). The results of geochemical multi-element analysis are shown below:

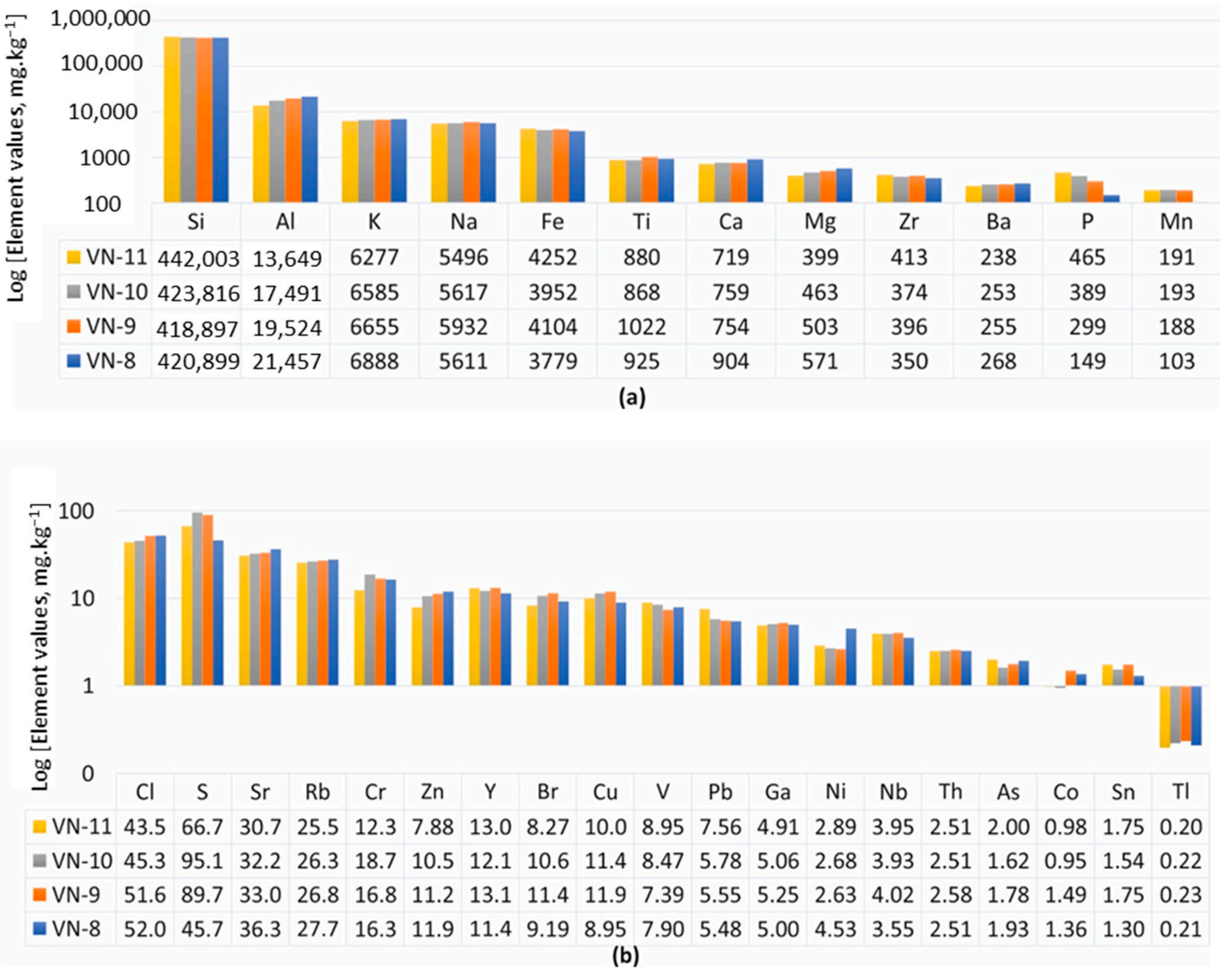

Figure 2. Comparison of element values (mg kg^{-1}) in the soils samples (VN-8–VN-11) of the Voorthuizen archaeological site: (**a**) Macro-elements (Si, Al, K, Na, Fe, Ti, Ca, Mg, Zr, Ba, P, and Mn) values; (**b**) Micro-elements (Cl, S, Sr, Rb, Cr, Zn, Y, Br, Cu, V, Pb, Ga, Ni, Nb, Th, As, Co, Sn, and Tl). Values are expressed in logarithmic scales, for visual expression.

Sample VN-11, the upper part of the soil profile studied, is enriched in Si and Zr, as well as in Fe, P, V, Pb, As, and Sn. Al, K, Na, Ca, Mg, Ba, Cl, Sr, Rb, Cr, Zn, Br, Ga, Th, and Tl display the lowest values in this part of the profile. Sample VN-8, on the contrary, exhibits the highest Al, K, Ca, Mg, Ba, Sr, and Rb values accompanied by low to the lowest Si, Zr, Ti, and Th values. In comparison to this, sample VN-10 shows the highest Mn, S, and Cr values.

The dynamics of individual chemical elements, commonly regarded as indicators of anthropogenic activity, does not show a uniform pattern. For example, P value displays a well-defined trend decreasing towards the lower part of the profile, with the amount of P (149 mg kg^{-1}) in sample VN-8 two to three times as low as that in other samples. The K value increases slightly from sample VN-11 (6277 mg kg^{-1}) to a maximum (6888 mg kg^{-1})

in sample VN-8. A similar trend is observed for N, but the difference is that maximum Na value (5932 mg kg^{-1}) is in sample VN-9.

Based on increasing Zn and Mg dynamics with a maximum of 11.9 mg kg^{-1} and 571 mg kg^{-1}, respectively, in sample VN-8, the Cu and Mn distribution displays a more complicated pattern: elevated values are characteristic of samples VN-10 and VN-9, while the lowest part of the profile exhibits minimum Cu and Mn values (8.95 mg kg^{-1} and 103 mg kg^{-1}, respectively).

Sr, Ba, and Rb share the same profile distribution trend. The values of these elements grow towards the lower part of the profile, reaching a maximum in sample VN-8: Sr (36.3 mg kg^{-1}), Ba (268 mg kg^{-1}), and Rb (27.7 mg kg^{-1}). Th displays a more stable dynamics throughout the profile, except for sample VN-9, where its amount shows a maximum value of 2.58 mg kg^{-1}. A significant increase in the Ca value (904 mg kg^{-1}) in sample VN-8 is remarkable.

The soil-sediments consist of terrigenous material with a small admixture of organic matter in the bottom layer, which increases towards the topmost layer from 3.03% to 6.61%, respectively. LOI 900 °C is very insignificant and was revealed only in VN-8 and VN-10 layers. VN-8 consists 0.32% and VN-10 0.25% of LOI 900 °C (Table 2).

Table 2. Results of the LOI and microcharcoal analyses at the Voorthuizen archaeological site.

	VN-8	VN-9	VN-10	VN-11
Microcharcoal	803	1855	1800	1300
LOI 550 °C, %	3.03	4.82	5.46	6.61
LOI 900 °C, %	0.32	0	0.25	0
LOI residue, %	96.65	95.36	94.29	93.39

The amount of microcharcoal is significant in all samples; the highest concentration is in sample VN-9 (Table 2).

4.3. Magnetic Susceptibility (MS)

The MS values are comparably high, following LOI 550 °C trends. They increase upwards from 1.9 to 5.3×10^{-8} m^3 kg^{-1}. The biggest change is fixed between VN-8 and VN-9 samples (Table 3).

Table 3. Results of the MS measurements at the Voorthuizen archaeological site.

	VN-8	VN-9	VN-10	VN-11
MS ($\times10^{-8}$ m^3 kg^{-1})	1.9	3.8809	4.43993	5.2832

5. Discussion

The case study of the Voorthuizen archaeological site provides the opportunity to compare the geochemical composition of two important archaeological phenomena: the settlement occupational surface and the ancient agricultural horizon. We can thus understand whether there are chemical elements that better indicate particular anthropogenic activities related to the settlement itself, as well as agricultural activities per se.

Indicators of human activities. The range of the elements that have been reported to be indicative of human occupation consists of two main groups: elements with generally elevated values as compared to their concentrations in natural soils, and those which can also decrease during the transformation of the soil horizon into a cultural layer. The frequently used indicators of anthropogenic activities are phosphorus (P), calcium (Ca), potassium (K), sodium (Na), and magnesium (Mg), as well as trace metals such as manganese (Mn), copper (Cu), lead (Pb), and zinc (Zn) [8,10,17,18]. P is associated with general organic (both human and animal) refuse, including kitchen and residential waste, animal pens, and agricultural activity. Animal bones, shells, and building or agricultural activities with lime application enrich cultural layers in Ca. High Ca concentrations at metal working sites are due to the use of ashes of calcined bones in this process [7]. Ca, K, and Mg may indicate the presence of ash in intense burning zones, and K is also prevalent in plant tissues. Therefore, higher K value indicate the existence of settlements and agricultural activities. While Cu and Pb enrichment have been reported as an indicator of mining, smelting and fuel combustion at a wide range of archaeological sites [10,19], according to [20], the considerable elevation of Pb and Zn was observed in ancient arable soils in Scotland. Pb isotope signatures and analysis of waste streams have shown that the pollution was caused by peat and turf ash (Pb and Zn), and by bird carcasses (Zn). Strontium (Sr), thorium (Th), barium (Ba), and rubidium (Rb) are present in household waste material [10,17,21].

However, the transformation of natural soil into a cultural layer can be accompanied by a decrease in Cu, Zn, Co, Fe, and Mn concentrations [22]. In addition, site effects appear to influence elements such as Ti, Ni, and Fe [10], though these elements are successfully used for functional area interpretation on archaeological sites by [23].

It has been noted that similar associations related to anthropogenic activities, such as P–Mg–Ca–Sr–Ba–Cl–Mn–Zn–Cu [24], have been revealed even in other areas and sedimentary environments. This association is well-defined (maybe, except Mn) in the lower part of the Voorthuizen archaeological site profile (samples VN-8 and VN-9), representing the cultural occupational surface of the Iron Age settlement. Simultaneously, the values of all the above elements besides Mn and P, decrease in the upper—ancient agricultural—part of the profile, while manganese and phosphorus concentrations grow.

Fe and Mn depletion revealed in [22] during the study of Bronze Age and Roman Time cultural layers at three archaeological sites in The Netherlands has also been reported for the Iron Age settlement layer in Voorthuizen. Simultaneously, this layer is enriched in a group of household waste indicators, such as Sr, Ba, Rb, and Th [21]. The latter shows slightly lowered values in the agricultural layer of Roman Time.

Charcoal and bone are essential for geochemical elements, such as Ca, Ba, Cu, Sr, Zn, P, and Pb, in the loading and post depositional retention of soils [10,18] and, thus, may be significant for the formation of soil element concentration patterns. Both the occupational surface and agricultural horizon in Voorthuizen are enriched in microcharcoal, and the relationship between microcharcoal finds and the geochemical composition of the soil layers in this case is expressed through a positive correlation with Cu and S (Table 4).

Table 4. Correlation matrix of chosen (Cu, P, S, MS, and microcharcoal) elements. Marked correlations are significant at $p < 0.05000$, $n = 4$.

	Cu	P	S	MS	Charcoal
Cu	1.0000 p = -				
P	0.4121 p = 0.588	1.0000 p = -			
S	0.9664 p = 0.034	0.5304 p = 0.470	1.0000 p = -		
MS	0.4975 p = 0.502	0.9915 p = 0.009	0.5877 p = 0.412	1.0000 p = -	
Charcoal	0.9895 p = 0.011	0.5239 p = 0.476	0.9892 p = 0.011	0.5964 p = 0.404	1.0000 p = -

-: absence of data.

No significant enhancement of Pb in arable fields, as compared to that in farmyards, was observed by [10]. This pattern is also true for the Voorthuizen archaeological site, though the soil profile still displays a slight increase of Pb upwards with the highest concentration in the Roman Time agricultural layer (7.56 mg/kg). This value is comparable with the values obtained for the Nistelrode Roman Time settlement, which is located on sandy soils in the south-eastern Netherlands (7.66 and 6.22 mg/kg on-site and off-site, respectively [22]). A broader comparison of the geochemical composition of Voorthuizen and Nistelrode shows a relative similarity in the values of major anthropogenic indicators with the exception of Cu and Zn, whose concentrations are remarkably higher at Nistelrode, and Ba and Sr with significantly higher values at Voorthuizen (Table 5). Other factors, in addition to possible differences in lithology, could be to a different range of activities carried out on these two locations and imprinted to the soil: geochemical measurements at Nistelrode are indicative of a dwelling house with its functional zones, while the situation at Voorthuizen is related to the study of the occupational surface close to but outside the structure, which was located at the edge of the settlement and seems to have been used as a crop storage.

Table 5. Major anthropogenic geochemical indicators at Voorthuizen (samples VN 8-11) and Nistelrode (samples NS46) archaeological sites, The Netherlands. Unmarked element values expressed in mg/kg, * marked element oxides values expressed in %.

Element/Site mg/kg, * oxide %	VN-8, XRF	VN-9, XRF	VN-10, XRF	VN-11, XRF	Element	NS46 On-Site, XRF	NS46 Off-Site, XRF	Element	NS46 On-Site, ICP-OES	NS46 Off-Site, ICP-OES
Ca	904	754	759	719	CaO	* 0.06%	* 0.08%	Ca	119.89	82.28
Cu	8.95	11.92	11.40	10.01	Cu	17.75	13.51	Cu	2.77	2.40
Mn	103	188	193	191	MnO	* 0.02%	* 0.01%	Mn	185.71	150.31
P	149	299	389	465	P_2O_5	* 0.06%	* 0.03%	P	285.96	240.86
Pb	5.48	5.55	5.78	7.56	Pb	7.66	6.22	Pb	-	-
Ti	925	1022	868	880	TiO_2	* 0.17%	* 0.14%	Ti	21.04	15.84
Sr	36.34	33.07	32.29	30.74	Sr	27.82	31.55	Sr	-	-
Ba	268	255	253	238	Ba	171.97	179.97	Ba	4.94	3.18
Th	2.51	2.58	2.51	2.51	Th	2.70	1.85	Th	-	-
Rb	27.71	26.87	26.32	25.57	Rb	26.54	27.00	Rb	-	-
Ni	4.53	2.63	2.68	2.89	Ni	3.93	2.20	Ni	-	-
Sn	1.30	1.75	1.54	1.75	Sn	2.34	1.04	Sn	-	-
Zn	11.94	11.24	10.57	7.88	Zn	17.90	12.03	Zn	8.12	7.07
MS ($\times 10^{-8}$ m^3 kg^{-1})	1.9	3.8809	4.43993	5.2832						
Microcharcoal	803	1855	1800	1300						

Phosphorus. It has been noted in [8] that P is unique as a sensitive and persistent indicator of human activity. This conclusion is based on (1) a long list of the anthropogenic sources of phosphorus: human waste refuse; ash; manure—guano, dung; animal husbandry, etc.; (2) accumulation of anthropogenic P at the site of deposition directly connected to the duration of occupation; and (3) relative P stability in the soil in terms of biochemical weathering. Though some natural and cultural factors, such as "certain parent materials and organic amendments, redoxymorphic conditions … geomorphic forces, soil formation, and disturbance … , may redistribute or remove particles that host P compounds" [8], (p. 325), the majority of cases of soil enrichment in phosphorus remains a useful geochemical indicator of human presence and activities. Numerous studies have clearly shown that the highest phosphorus concentration within a settlement is found in byres, as well as in middens and hearths, while in arable fields manure (dung and waste) provokes elevated P values [4,8,9,25–28]. In The Netherlands, studies of P as an indicator of human activity have been carried out at several ancient settlements and on the Celtic Fields, which represent an ancient system of agricultural activity dating back to the late Bronze Age up to the Roman Time (1100 BC–200 AD) and widespread throughout north-west Europe [14,22].

The geochemical study of Voorthuizen has revealed a remarkable difference in P values between the Iron Age settlement occupational surface and the Roman Time agricultural horizon. The P value of the latter is 2–3 times as high, reaching 465 mg/kg. Comparison of Voorthuizen has yielded P values for natural sandy heathland soils (Noordseveld, Zeijen, The Netherlands), prehistoric Celtic Fields soils (Zeijen, The Netherlands) and the Nistelrode Roman Time settlement (Table 5), showing that P values of the agricultural layer of Voorthuizen are the highest and are comparable to values obtained for the banks (high ridges) of the Celtic Fields [14,22]. This seems to reflect the similarity of the agricultural (manure) technique applied in both cases. Simultaneously, the lower values of the household waste indicators in the Voorthuizen agricultural layer seem to indicate that litter was not used as a fertilizer in this case, though this type of manure is known to occur on Celtic Fields in Zeijen [14].

Comparative analysis of living layers in two settlements, Voorthuizen and Nistelrode, has revealed that P values are relatively similar as well (299 mg/kg and 285.96 mg/kg, respectively; Table 6). These values can serve as a first P reference number for the occupational layers of the "sandy" prehistoric settlements in The Netherlands Further research is expected to provide more data to make this reference more accurate.

Table 6. Comparison of P values: (i) Voorthuizen archaeological site cultural layer (VN-8–VN-11) (mg P kg^{-1} dry soil, XRF, and real total); (ii) Natural heathland soils and Celtic Field soils at Noordseveld (Zeijen, The Netherlands) (mg P kg^{-1} of dry soil, detected spectrophotometrically using molybdene blue, [14]); and (iii) Nistelrode (NS46) (mg P kg^{-1}, detected using ICP-OES [22]).

Object	Mean	Standard Deviation	Spread
Voorthuizen, The Netherlands			
VN-8	149	79	-
VN-9	299	5	-
VN-10	389	20	-
VN-11	465	29	-
Natural heathland soils at Noordseveld, Zeijen, The Netherlands			
Ah-horizon podzol	131	62	48–231
Celtic Field soils at Zeijen, The Netherlands			
Field plots	235	64	153–371
Basic layer ridges	211	42	135–275
Top layer ridges	323	94	170–498
Nistelrode (NS46), The Netherlands			
On site	285.96	-	-
Of site	240.86	-	-

Indicators of extra mineral matter input. The Voorthuizen samples have Si values most similar to other sandy soil locations in The Netherlands, for which Si values are available in ISE reports [16]. However, soil sample VN-11 has the highest Si value (442,003 mg/kg), as compared to the data reported and other samples from Voorthuizen. A similar phenomenon, consisting of unusually high concentrations of Si in the layers with anthropogenic contexts, was observed by [29] at an Iron Age *Viereckschanze* type of site in Bohemia. The authors concluded that this may have been due to a particular type or intensity of human activity that required the use of additional amounts of sand. Sample VN-11 also displays "mobile" Fe, Mn, V, Pb, As, and Sn values that are higher than those in the lower part of the profile and the highest organic matter concentration (up to 6.61%). In addition, carbonate matter (LOI 900 °C and, i.e., Ca) in soil samples VN-8 and VN-10 increases slightly. This, along with high Si value, seems to be due to the manure technique, when "a new portion" of elements with sods and dung was brought in, distorting natural podzolization processes, which lead to the replacement of mobile elements from the upper parts of the soil profile and their deposition in deeper horizons.

The results of the MS analysis also seem to indicate an input of an additional mineral component into the ancient agricultural layer. This assumption is based on the fact that magnetic susceptibility can be used as a tracer of mineral matter in sediment: higher MS values show higher enrichment in a mineral component. The Voorthuizen MS results show an increasing trend of mineral content in soil samples VN-8-11, respectfully, with the highest value 5283×10^{-8} m^3 kg^{-1} in the topmost layer.

6. Conclusions

The geochemical survey of anthropogenic horizons at the Voorthuizen archaeological site has led us to conclude that:

Comparison of the geochemical composition of the occupational surface of the Iron Age settlement and the early Roman Time agricultural horizon shows that the former is enriched in geochemical indicators such as Ba, Sr, Rb, Th, Cl, and Mg, while the agricultural horizon has elevated P, Pb, Ni, Mn, and V values.

The occupational surface of the settlement displays the higher values of household waste geochemical indicators than those of the agricultural horizon studied. It is assumed that waste as a fertilizer was not used in this case, while household garbage was used as a component of agricultural technology in the Celtic Fields. At the same time, P value in the Voorthuizen agricultural layer is comparable to that of the Celtic Fields, suggesting similar P sources in both manure techniques.

Elevated Si and "mobile" Fe, Mn, V, Pb, As, and Sn values, along with higher MS results, seem to be indicative of extra mineral matter input during fertilization of the ancient arable field at Voorthuizen.

Author Contributions: Conceptualization, O.D., K.v.d.B. and L.G.; methodology, L.G.; formal analysis, L.G.; data curation, L.G.; writing—original draft preparation, O.D.; writing—review and editing, O.D., K.v.d.B. and L.G.; visualization, L.G.; supervision, O.D.; project administration, K.v.d.B. All authors have read and agreed to the published version of the manuscript.

Funding: The geochemical research was carried out with the support of State Assignment no. FSZN-2020-0016.

Data Availability Statement: Raw data are available upon request, please contact the corresponding author.

Acknowledgments: The authors would like to thank the reviewers and editors for their valuable suggestions.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Cuenca-García, C. Inorganic Geochemical Methods in Archaeological Prospection. In *Best Practices of GeoInformatic Technologies for the Mapping of Archaeolandscapes*; Sarris, A., Ed.; Archaeopress: Oxford, UK, 2015; pp. 219–231.
2. Entwistle, J.A.; Abrahams, P.W. Multi-element analysis of soils and sediments from Scottish historical sites. The potential of inductively coupled plasma-mass spectrometry for rapid site investigation. *J. Archaeol. Sci.* **1997**, *24*, 407–416. [CrossRef]
3. Entwistle, J.A.; McCaffrey, K.J.W.; Dodgshon, R.A. Geostatistical and multielemental analysis of soils to interpret land-use history in the Hebrides, Scotland. *Geoarchaeology* **2007**, *22*, 391–415. [CrossRef]
4. Middleton, W.D. Identifying chemical activity residues on prehistoric house floors: A methodology and rationale for multi-elemental characterization of a mild extract of anthropogenic sediments. *Archaeometry* **2004**, *46*, 47–65. [CrossRef]
5. Save, S.; Issenmann, R.; Kovacik, J.; Poirier, S.; Demarly-cresp, F.; Sedlbauer, S.; Teyssonneyre, Y. Large-scale geochemical survey by pXRF spectrometry of archaeological settlements and features: New perspectives on the method. *Archaeol. Prospect.* **2020**, *27*, 1–16. [CrossRef]
6. Schramm, R.; Heckel, J. Fast analysis of traces and major elements with ED (P) XRF using polarized X-rays: TURBOQUANT. *J. Phys.* **1998**, *8*, 335–342. [CrossRef]
7. Cook, S.F.; Heizer, R.F. Studies on the Chemical Analysis of Archaeological Sites. In *University of California Publications in Anthropology 2*; University of California Press: Berkeley, CA, USA, 1965.
8. Holliday, V.T.; Gartner, W.G. Methods of soil P analysis in archaeology. *J. Archaeol. Sci.* **2007**, *34*, 301–333. [CrossRef]
9. Schlezinger, D.R.; Howes, B.L. Organic Phosphorus and Elemental Ratios as Indicators of Prehistoric Human Occupation. *J. Archaeol. Sci.* **2000**, *27*, 479–492. [CrossRef]
10. Wilson, C.A.; Davidson, D.A.; Cresser, M.S. Multi-element soil analysis: An assessment of its potential as an aid to archaeological interpretation. *J. Archaeol. Sci.* **2008**, *35*, 412–424. [CrossRef]
11. Druzhinina, O.A.; van den Berghe, K.J.; Golyeva, A.A.; Gedminienė, L.; Karpińska-Kołaczek, M. The results of the geoarchaeological study of the Voorthuizen archaeological site (The Netherlands) (in prep.). In Proceedings of the vEGU21: The 23rd EGU General Assembly, Online, 19–23 April 2021.
12. van den Berghe, K.J. *Evaluatierapport Proefsleuven en Opgraving Kromme Akker Zuid te Voorthuizen, Gemeente Barneveld*; Econsultancy Rapport 7241.003; Econsultancy: Zwolle, The Netherlands, 2020.

13. Bronk Ramsey, C. *OxCal Project*; Research Lab for Archaeology: Oxford, UK, 2020. Available online: https://c14.arch.ox.ac.uk (accessed on 1 February 2021).
14. Spek, T.; Groenman-van Waateringe, W.; Kooistra, M.; Bakker, L. Formation and land-use history of Celtic fields in north-west Europe–an interdisciplinary case study at Zeijen, The Netherlands. *Eur. J. Archaeol.* **2003**, *6*, 141–173. [CrossRef]
15. Dean, W.E. Determination of carbonate and organic matter in calcareous sediments and sedimentary rocks by loss on ignition: Comparison with other methods. *J. Sediment. Res.* **1974**, *44*, 242–248.
16. Dijk, D.V. Wageningen evaluating programmes for analytical laboratories (WEPAL): A world of experience. *Commun. Soil Sci. Plant Anal.* **2002**, *33*, 2457–2465. [CrossRef]
17. Wilson, C.A.; Davidson, D.A.; Cresser, M.S. An evaluation of multielement analysis of historic soil contamination to differentiate space use and former function in and around abandoned farms. *Holocene* **2005**, *15*, 1094–1099. [CrossRef]
18. Wilson, C.A.; Davidson, D.A.; Cresser, M.S. An evaluation of the site specificity of soil elemental signatures for identifying and interpreting former functional areas. *J. Archaeol. Sci.* **2009**, *36*, 2327–2334. [CrossRef]
19. Monna, F.; Hamer, K.; Lévêque, J.; Sauer, M. Pb isotopes as a reliable marker of early mining and smelting in the northern Harz province (Lower Saxony, Germany). *J. Geochem. Explor.* **2000**, *68*, 201–210. [CrossRef]
20. Meharg, A.A.; Deacon, C.; Edwards, K.J.; Donaldson, M.; Davidson, D.A.; Spring, C.; Scrimgeour, C.M.; Feldmann, J.; Rabb, A. Ancient manuring practices pollute arable soils at the St Kilda World Heritage site, Scottish North Atlantic. *Chemosphere* **2006**, *64*, 1818–1828. [CrossRef] [PubMed]
21. Horák, J.; Janovský, M.; Hejcman, M.; Šmejda, L.; Klír, T. Soil geochemistry of medieval arable fields in Lovětín near Třešť, Czech Republic. *Catena* **2018**, *162*, 14–22. [CrossRef]
22. Oonk, S.; Slomp, C.P.; Huisman, D.J.; Vriend, S.P. Effects of site lithology on geochemical signatures of human occupation in archaeological house plans in the Netherlands. *J. Archaeol. Sci.* **2009**, *36*, 1215–1228. [CrossRef]
23. Janovský, M.P.; Karlík, P.; Horák, J.; Šmejda, L.; Asare Opare, M.; Beneš, J.; Hejcman, M. Historical land-use in an abandoned mountain village in the Czech Republic is reflected by the Mg, P, K, Ca, V, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Zr, and Sr content in contemporary soils. *Catena* **2020**, *187*, 104347. [CrossRef]
24. Taraškevičius, R.; Stančikaitė, M.; Bliujienė, A.; Stakėnienė, R.; Zinkutė, R.; Kusiak, J. Search for geochemical indicators of pre-urban habitation sites: Case study from the Skomantai hill-fort and settlement, western Lithuania. *Geochem. Explor. Environ. Anal.* **2012**, *12*, 265–275. [CrossRef]
25. Roos, C.I.; Nolan, K.C. Phosphates, plowzones, and plazas: A minimally invasive approach to settlement structure of plowed village sites. *J. Archaeol. Sci.* **2012**, *39*, 23–32. [CrossRef]
26. Salisbury, R.B. Interpolating geochemical patterning of activity zones at Late Neolithic and Early Copper Age settlements in eastern Hungary. *J. Archaeol. Sci.* **2013**, *40*, 926–934. [CrossRef]
27. Šmejda, L.; Hejcman, M.; Horák, J.; Shai, I. Ancient settlement activities as important sources of nutrients (P, K, S, Zn and Cu) in Eastern Mediterranean ecosystems—The case of biblical Tel Burna, Israel. *Catena* **2017**, *156*, 63–72. [CrossRef]
28. Wells, E.C.; Terry, R.E.; Parnell, J.J.; Hardin, P.J.; Jackson, M.W.; Houston, S.D. Chemical analyses of ancient anthrosols in residential areas at Piedras Negras, Guatemala. *J. Archaeol. Sci.* **2000**, *27*, 449–462. [CrossRef]
29. Danielisová, A.; Horák, J.; Janovský, M.; Strouhalová, B.; Bursák, D. Geochemical approach to determine the anthropogenic signal at non-intensively settled archaeological sites—The case of an Iron Age enclosure in Bohemia. *Catena* **2022**, *210*, 105895. [CrossRef]