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Phosphorus in archaeological soil: comparison of different extraction methods

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Phosphorus is one of the most widely studied chemical elements to identify paleoanthropogenic activity. Various methods have been used to analyse phosphorus in archaeological soil, however, general recomendations for the adequate choice of the research method are yet to be formulated. The search for a reliable and efficient method to estimate phosphorus of anthropogenic origin in soil is important from the applied point of view, especially in the case of a large series of samples.

The aim of these studies was to test different P extraction methods with samples of the known archaelogical context. The sample texture, elemental composition (XRF), pH, loss on ignition at temperatures of 550 and 1000 °C have been determined. The P extraction methods using aqua regia, 1 and 5M HCl, citric acid, Mehlich 2 and Mehlich 3 extractants, as well as sample ignition at 550 ir 800 °C have been tested. It has been determined that the proportion of total P (XRF) extracted by nearly all the methods was higher and in a better agreement with the total P in sand soil samples than that in loamy sand samples. The extraction of sieved/unmilled and ignited at 550 °C soil with 1M HCl appeared to be a reliable and sustainable method and therefore was best suited for the samples of the series studied.

Keywords: soil phosphorus, extraction methods, archaeology

INTRODUCTION

Measurements of P content as the marker of paleoanthropogenic activity are widely used in the studies of archaeological soil [1]. When combined with traditional archaeological methods, the measurements of P quantities can help determine excavation priorities, specify the outlines of archaeological settlements, intervals of different intensity of anthropogenic activity. Along with other elements, the variations in P amount in soil help interpret archaeological data, localize different functional zones and the function of various archaeological features.

The amount, form and compounds of P penetrated into the soil and retaining up till now depend not only on the character and intensity of the anthropogenic activity, but also on the soil mineralogy, texture, pH, organic matter, humidity, microbial activity, landscape position, time, weathering, post-occupational land use and other factors [1, 2]. Thus, the same activity in different locations may leave greatly varying traces, whose elucidation sometimes needs employing of particular methods.

A comprehensive overview to determine the P amount in soil employed in archaeology was presented by Holliday and Gartner [1]. The authors report that over 50 methods have been published in general soil chemistry, and of these over 30 are applied in archaeology. In the last decade researchers still argue over which P form better accounts for anthropogenic P and still employ different methods.

The following digestion and extraction methods have been in use: digestion with different strong concentrated acids or their mixtures [3–16], mild extraction procedures with diluted strong acids [6, 17–24], extraction with 1 or

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2% citric acid [25, 26], extractants Mehlich 2 [27, 28] and Mehlich 3 [29, 30] or P extraction after soil ignition [7, 14, 31, 32]. After analysing the same samples employing different methods it emerges that not always they give similar tendencies of P distribution in soil [1, 26, 33]. On the whole, there are a lot of successful works, based on the measurement of P quantity in soil, however, there is yet no standardized test protocol to determine anthropogenic phosphorus in the archaeological soil [34].

It was not until fairly recently that chemical studies of archaeological soil began in Lithuania and not many of them have been performed so far – the "spot" test and a couple of P extraction methods (mild extraction with 1M HCl with a small sample series and microwave digestion with aqua regia with several samples) have been tried [35, 36], there are also several works presenting results of investigation of archaeological soil by using the XRF method [37–39]. XRF studies of archaeological soil are very informative, making it possible to explain and interpret archaeological soil features. While performing surveying research in order to locate and delineate archaeological sites and human activity areas it is needed to investigate a considerable series of samples. Determination of P amount by the extraction methods could be a simpler and cheaper way to achieve these purposes. However, it remains unclear which of the methods presented in literature are best fitted to evaluate the P amount in the archaeological soil.

In this work we investigated the elemental composition and properties of soil samples of various archaeological context and tried various P extraction methods in order to select an optimal economical and reliable method to determine anthropogenically increased phosphorus.

EXPERIMENTAL

Archaeological sites and sampling pattern

25 bulk soil samples were collected from 5 excavated archeological sites (Fig. 1). The samples were taken from different contexts, which were grouped into 3 groups: 1) an archaeological layer or sunken features with artefacts; 2) a cultural layer or sunken features holding no artefacts; 3) a subsoil layer with no traces of anthropogenic activity (Table 1).

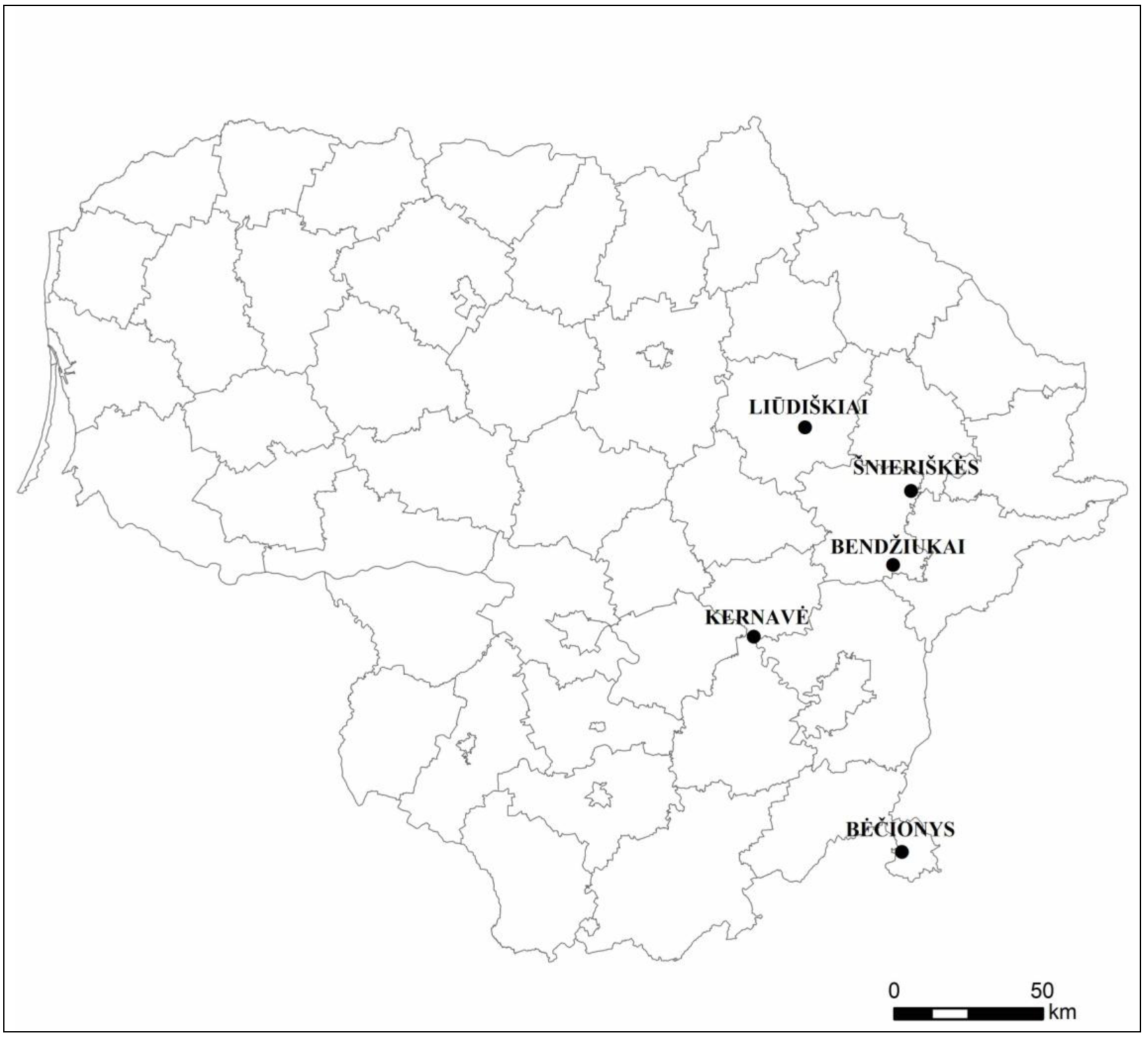

Fig. 1. Archaeological soil sampling sites

Table 1. **Soil samples retrieved in the archaeological sites**

Sample ID	Groups of context	Sampled context (feature/statigraphy)	Depth interval from original terrain level or object's recorded top, cm
BE-14	2	feature	40–47
BE-20	2	feature	50–84
BE-21	3	subsoil (on-site)	70
BE-34	2	feature	25–47
BE-40	1	feature	25–40
BE-of	3	subsoil (off-site)	30
KE-42	1	feature 32	7
KE-45	1	feature 52	10
KE-46	2	feature 52	20
KE-47	2	feature 52	30
KE-48	1	feature 53	25
KE-49	2	feature 53	45
KE-51	1	feature 92	upper layer
KE-44	1	feature 92	lower layer
BEND-05	1	archaeological layer	25–65
BEND-19	2	cultural layer	60–70
BEND-20	3	subsoil	70–80
LIU-05	1	disturbed archaeological layer	55–60
LIU-11	1	archaeological layer	85–90
LIU-14	3	subsoil	95–100
LIU-15	2	feature 66 (posthole 57)	–
ŠNR-36	3	subsoil	20–30
ŠNR-39	1	mixed zone	7–15
ŠNR-40	1	mixed zone	18–30
ŠNR-41	1	mixed zone	30–60
ŠNR-35	1	mixed zone	10–20

Background information: BE, Bėčionys; KE, Kernavė; BEND, Bendžiukai; LIU, Liūdiškiai; ŠNR, Šnieriškės. Groups of context: 1 is features/horizon with artefacts; 2 is features/horizon holding no artefacts; 3 is subsoil with no artefacts.

Bėčionys, hilltop settlement in Šalčininkai District Municipality

A hilltop settlement is situated on the hill of a marginal glaciofluvial formation rising 4 to 8 meters on the right bank of the Gauja River. A total area of 300 m^2 was uncovered on the hilltop in 2012 [39, 40]. As a result, almost the entire "hillfort" plateau was excavated and findings characteristic of the 1st–2nd centuries AD – hand-made pottery, predominantly – were detected. At the subsoil level contours of pit-shaped subsurface features were revealed. Their fillings consisted of grey or brown sandy soil with small bits of charcoals. In some of them artefacts were found (mostly hand-made pottery shards), however, the major part of them held no artefacts. Some of these features might have been postholes, while others represent kitchen midden or traces of animal burrowing pits with a cultural layer accumulated within them.

One sample was taken from the archaeological feature with artefacts (BE-40) and three samples were collected from pit-shaped features without artefacts (BE-14, 20, 34). One on-site control sample was taken from the substratum level (BE-21) and one off-site control sample was taken from the subsoil outside the site (BE-of).

Bendžiukai, a settlement site in Molėtai District Municipality

The Bendžiukai settlement is a new archaeological site discovered in 2015 [41]. The location of the settlement is on the heights promontory between Liminas Lake and Kamanis Lake. On the promontory several hills were separated by a footslope, where one trench (10 m^2) was excavated. Under a ploughzone, up to a 40 cm thick black archaeological layer bearing traces of human activity (pottery shards, slag, wattle daub) was detected. The bottom part of the layer was somewhat lighter of brown colour and held no artefacts. At a depth of 70 to 80 cm subsoil was reached.

Three samples were selected from the profile. One sample was taken from the archaeological layer (BEND-5), one sample was taken from the cultural layer holding no artefacts (BEND-19) and one sample was taken from the subsoil level (BEND-20).

Kernavė, a settlement site in Širvintos District Municipality

The Kernavė settlement is located in the Neris River valley, in the so-called Pajauta, on the elevation of fluvioglacial origin. Here investigations have been carried out with interruptions for many years since 1983, an area of more than 16500 m^2 has been investigated and an intensive cultural layer bearing artefacts and subsurface objects from different periods has been detected. In 2013 during investigations soil samples were taken from four objects (obj. 32, 52, 53 and 92). These were pits 1 × 0.8 m to nearly 5 × 3 m in diameter and 0.2 to 0.6 m in depth of a circular or irregular shape filled with grey or blackish sandy soil. In the filling of some pits several layers were distinguished. In the pits numerous artefacts were found: pottery shards, flint, wattle daub, slag, somewhat animal bones. The artefacts were distributed unevenly, here they were found in the whole mass of filling, elsewhere – in separate layers of the pit filling (obj. 52, 53). According to the dominating pottery three objects may be dated back to the 5–7th century, one to the middle of the 2nd millennium BC [42].

Eight samples were selected from pits filling or separate filling layers with or without artefacts.

Liūdiškiai, a hillfort foot settlement in Anykščiai District Municipality

The hillfort is situated on the highest hill of the moraine hills massif on the right bank of the Šaltupis rivulet. To the N, E and SE from the hillfort there is a settlement occupying the area of 1 ha. In 2009–2010 and 2015 the part of the foot settlement was investigated, the area of 518 m^2 was uncovered and an archaeological layer up to 1.25 m in thickness was detected. Its upper part up to 65 cm in depth was somewhat disturbed, while the bottom horizon (at a depth of 65–95 cm) was well preserved and at a depth of 95 cm subsoil was reached. During the investigation numerous findings were detected (shards, slag, animal bones, etc.) and various features indicative of human activity (postholes, fireplaces, iron smelting furnaces) which are dated back to the beginning of the 2nd millennium [43] were discovered.

Four samples were collected: one sample was taken from the posthole 57 (LIU-15) and three were selected from the profile: one sample was taken from the disturbed upper part of the the archaeological layer (LIU-5), one sample was taken from a well preserved part of the archaeological layer (LIU-11), and one sample was taken from the "sterile" non-antropogenic horizon (LIU-14).

Šnieriškės, a prehistoric site on an island in Lake Aisetas in Molėtai District Municipality

Traces of prehistoric anthropogenic activity were discovered on one of the small islands in Aisetas Lake in 2015 [44]. The island is a moraine hillock approximately 200 × 40–50 m in size elevating up to 3 m above the waters of Aisetas Lake. In the highest hillock part a trench of 10 m^2 was investigated. An occupation layer escaped detection, under a sandy loam horizon at a depth of 15 to 30 cm moraine subsoil was reached and it looked as if dug out in pits, which were filled up with a whitish fine sand. In this filling artefacts from various periods from the Mesolithic period to the Late Iron Age were found. The majority of them were artefacts related to metallurgy. More than 135 kg of iron slag and furnace shaft fragments were found and attributed to the 10–12th centuries by C14 dating of the charcoal found in the filling layer. The data obtained suggest that at the beginning of the second millennium AD on this island iron was smelted, right here clay to built furnaces was quarried, and while digging for clay the level of earlier periods was destroyed.

Five samples were selected from the profile. Four samples were taken from sediments having filled the depressions in the subsoil (ŠNR 35, 39–41), and one sample was taken from the loamy subsoil (ŠNR-36).

Sample analysis

Samples were air-dried and sieved using a 2 mm polypropylene sieve. A part of soil (30 g) was milled with a ball mill. The milled soil was used for XRF analysis and for some extraction experiments. The samples for XRF and LOI analyses were dried for 12 h at 105 °C.

Soil pH

Soil pH measurements were conducted in a 1:5 sediment to a deionized water solution (5 ml soil and 25 ml water, shaken for 1 h using a mechanical shaker, stored for 2 h and filtered) with a pH meter Orion 3 Star (Thermo Electron Corporation, USA), calibrated using buffer solutions of pH 4.01, 7 and 10.04.

Loss on ignition

To estimate the amount of organic matter (OM) and the amount of carbonates in the samples the loss on ignition in the temperature ranges 105–550 °C and 550–1000 °C was determined. 5 g of soil was placed in a heated and weighed ceramic crucible, and subsequently heated for 12, 4 and 2 h at temperatures of 105, 550 and 1000 °C, respectively. After each heating procedure the sample was cooled in the oven down to a temperature of 100 °C, following which the sample was capped and placed in an exicator until cooled down to room temperature. After that it was weighed and the loss on ignition data was calculated.

Particle-size analysis

20–40 g of the samples were dispersed for 4 h in the shaker (200 rpm) in 100 ml of a 20 g/l sodium pyrophosphate solution. Thereafter, the sand-size particles were separated from the suspensions by wet sieving through a 63 µm sieve. The fraction retained by the sieve was dried and then weighed. The clay fraction (<2 µm) was determined using the pipette method as prescribed by [45]. The silt fraction was determined by difference. Soil textural classes were determined in compliance with the German Bodenartendiagramm soil texture classification [46].

X-ray fluorescence

For multi-element analysis of soil samples an X-ray spectrometer with a wavelength dispersive detector Axios mAX (PANalytical Netherlands. 2010) was used. Soil samples were prepared according to the references [47, 48]: 5 g of each milled sample was mixed with 1 g Hoechst wax C micropowder. The soil/binder mixtures were compressed into tablets using a hydraulic press applying the pressure of 150 kN/cm^2 for 3 min. The accuracy was determined using the external standards N 139 (Czech Republic), NCS DC60105 (China), and IMZ-267 (Poland). The paper presents the results of the major elements (Si, Al, Fe, Mg, Ca, Na, K, Mn, P, Ti, Ba). The relative standard deviations of measurements of two tablets were lower than 10%.

Extraction methods

The extraction methods applied in this research may be divided into five groups as follows:

1) Aqua regia digestion (Table 2, No. 1) was chosen as a technique to determine $P_{\text{near total}}$ (or $P_{\text{aqua regia extractable}}$); the procedure was performed according to the recommendations of [49];

2) Mild extraction with diluted solutions of strong acids – as a technique to obtain $P_{\text{acid extractable}}$; along with this, the dependence of the extracted P quantity on the acid

Table 2. **Analytic parameters of extraction methods**

No.	Method	Sample treatment after sieving (<2 mm)	Extractant	Sample amount, g	Amount of extactant, ml	Soil and extractant weight ratio	Duration of storage at room temperature, shaking (150 rpm) at room temperature or boiling
1.	AR-m	Milled	Aqua regia (HNO_3 conc + HCl conc, 1:3)	1	10	~1:10 → ~1:00	16 h stored, 2 h boiled
2.	1M-HCl-2h-m	Milled	1M HCl	0.3	30	~1:100	2 h shaken
3.	1M-HCl-2h-s		1M HCl	0.3	30	~1:100	2 h shaken
4.	5M-HCl-2h-m	Milled	5M HCl	0.3	30	~1:100	2 h shaken
5.	1M-HCl-2w-m	Milled	1M HCl	0.3	30	~1:100	30 s shaken, 1 week stored, 30 s shaken, 1 week stored, 30 s shaken
6.	1M-HCl-2w-s		1M HCl	0.3	30	~1:100	30 s shaken, 1 week stored, 30 s shaken, 1 week stored, 30 s shaken
7.	1M-HCl-2h-550-m	Milled, ignited at 550 °C 1 h	1M HCl	0.3	30	~1:100	2 h shaken
8.	1M-HCl-2h-550-s	Ignited at 550 °C 1 h	1M HCl	0.3	30	~1:100	2 h shaken
9.	1M-HCl-2h-800-m	Milled, ignited at 800 °C 1 h	1M HCl	0.3	30	~1:100	2 h shaken
10.	1M-HCl-2h-800-s	Ignited at 800 °C 1 h	1M HCl	0.3	30	~1:100	2 h shaken
11.	1%-Cit-2h-1:10-m	Milled	1% citric acid	1	10	~1:10	2 h shaken
12.	1%-Cit-2h-1:100-m	Milled	1% citric acid	0.1	10	~1:100	2 h shaken
13.	M2-5m-s		Mehlich 2: 0.2 M acetic acid + 0.015 M ammonium fluoride + 0.2 M ammonium chloride + 0.012 M hydrochloric acid	1	10	~1:10	5 min shaken
14.	M3-5m-s		Mehlich 3: 0.2 M acetic acid + 0.25 M ammonium nitrate + 0.015 M ammonium fluoride + 0.013 M nitric acid + 0.001 M EDTA	1	10	~1:10	5 min shaken

concentration, extraction time and sample fineness (sieved/unmilled or sieved/milled) (Table 2, No. 2–6) was examined; the procedure (No. 5–6) was performed according to [50,51];

3) Extraction of the ignited samples was chosen as an alternative approach to obtain $P_{\text{near total}}$; along with this, the dependence of the quantity of extracted P on the ignition temperature and sample fineness (sieved/unmilled or sieved/milled) (Table 2, No. 7–10) was examined; the ignition temperature of 550 °C was chosen as the one most often used by other authors [7, 14, 31, 32], 800 °C was the maximum temperature presented in the literature sources [52];

4) Along with the studies of extraction with weak citric acid – in an effort to obtain $P_{\text{citric acid extractable}}$ (Table 2, No. 11–12), the dependence of the quantity of the extracted P on the ratio of soil and reagent amounts was checked;

5) The methods to analyse plant available P (Table 2, No. 13–14): Mehlich 2 [53, 54] and Mehlich 3 [55, 56] extractants were chosen as the ones sucessively used in archaeology by other authors [27–30].

The composition of extraction solutions and other analytic parameters are shown in Table 2. Subsequent to the extraction all the solutions were filtered. The P quantity in the filtrates obtained was measured by using the inductively coupled plasma optical emission spectrometry (ICP-OES) method (Optima7000DV, Perkin Elmer, USA). The P quantity was measured at $\lambda_p = 213{,}617$ nm. Three probes of every sample were taken for the analysis. The relative standard deviations of the measurements of three milled and three unmilled samples were <1% and <10%, respectively.

RESULTS AND DISCUSSION

Soil properties and composition

In order to obtain the most complete information on testing samples, their elemental composition, pH, loss on ignition at temperatures of 550 and 1000 °C as well as soil texture were determined (Table 3).

The soil from the Bėčionys hilltop settlement is the most alkaline (pH 7.9–9.0), most likely due to a higher quantity of carbonates as compared to that of the other sites. This is confirmed by higher quantities of Ca and Mg as well as $LOI_{550-1000}$. The subsoil sample BE-21, which contains about 12% carbonates (calculated as $CaCO_3$), testifies that the subsoil of the hill is a slightly calcareous sand. The soil of other on-site samples was sand. In these anthropogenic sediments the amount of carbonates was found to be less possibly due to decalcification processes; they contained a higher amount of organic matter (0.53–1.47%). The soil from the remote surroundings (BE-of) was more acidic (pH 6.1), non-calcareous.

The soil of Kernavė, similar to that in Bėčionys, is sand, however, of different acidity: from acidic (pH 4.8) to neutral (pH 7.1). The amount of OM was detected to be higher (0.4–3.15%) as compared to that in Bėčionys, meanwhile the values of $LOI_{550-1000}$ were lower (0.09–0.37%), which testifies that the soil is non-calcareous.

The soil of Bendžiukai is close to neutral (pH 6.8–7.6). As compared to the Kernavė and Bėčionys soil, it was found to contain more clay and silt fractions. The samples of the archaeological and cultural layers are loamy sand, while the subsoil sample is sandy loam. Clearly Al, Fe, K, Ti elements impurities reflecting clay and other often found minerals (illite, mica, feldspar, etc. [57]) were among the highest ones, especially in the subsoil sample. The highest OM amount (6.95%) of all the samples under investigation was detected in the sample from the archaeological layer (BEND-05). Somewhat higher $LOI_{550-1000}$ values of the samples BEND-05 and BEND-20 may be related not only to a possibly minor carbonate amount, but also to the removal of the structural water from minerals.

The soil from Liūdiškiai, as does the soil from Bendžiukai, is close to neutral (pH 7.2–7.3). All the samples are loamy sand. The highest OM quantities were present in the samples from the archaeological context (2.59–4.68%), while the lowest ones in the subsoil sample LIU-14 (0.56%).

The soil of Šnieriškės from the layer with archaeological artefacts is a weakly acidic (pH 5.2–6.6) sandy loam. The subsoil sample ŠNR-36 distinguishes itself by its composition and properties. This soil is a more alkaline (pH 7.8), sandy clay loam. The highest $LOI_{550-1000}$ values of this sample may be related to both carbonates decomposition (this sample was found to contain the highest Ca and Mg quantities at this site), and to the removal of structural water from clay minerals (the highest quantity of both clayey fraction and Al). The Šnieriškės sediments with artefacts were found to contain relatively minor OM amounts (0.81–2.65%), the deeper the sample was, the less it contained OM.

P_{total} (XRF) and its connection with the archaeological context

Consistent dependence of phosphorus quantities on the locality was not observed. P amounts in some samples up to fourfold exceeded the average P quantity in the Lithuanian soil – 574 mg/kg [58]. It was just anthropogenic sediments which exhibited the largest anomalies (>1000 mg/kg), which in turn confirmed the importance of P as the indicator of anthropogenic activity. True enough, high amounts of P (829–1131 mg/kg) were determined in the series of samples from natural background containing a considerable proportion of fine fractions (BEND-20, LIU-14, ŠNR-36). This can be related to soil formation processes, P elution from the upper part of the soil and/or the soil texture, as finer fraction soil has a greater specific surface area and is able to bind more P than coarse soil [2].

Furthermore, in some anthropogenic sediments no P enhancement was detected. The sample BE-14 from Bėčionys from a pit morphologically indistinguishable from the others at this site was detected to contain the same amount of P as in the subsoil sample BE-21 (493 and 487 mg/kg, respectively). In Kernavė different P amounts were determined in different layers of the filling of the same pit – the upper layer contained more P (KE-51, 743 mg/kg), while the underneath one contained less (KE-44, 495 mg/kg). In the Šnieriškės series the subsoil sample ŠNR-36 contained 2 to 4 times more P as compared to that in the sediments with artefacts. A minor P amount in the Šnieriškės archaeological context may be associated with the character of the archaelogical site – it was not a residential place, but a production site where primary production of iron was carried out.

Comparison of the P extraction methods

The analysis of the data obtained suggests that the amount of extracted P as compared to P_{total} (determined by XRF) depends on the texture of soil. The extracted proportion of total P was considerably higher for sandy samples of Kernavė and Bėčionys (group I) than those from the loamy sand, sandy loam and sandy clay loam samples of Liūdiškiai, Bendžiukai, and Šnieriškės (group II) (Table 4). Therefore, the results are further discussed for each group separately.

The results of group I testify that the amount of P extracted by the AR-m method correlates well with the P_{total} amount, however, only 76% of the total P on the average was extracted,

Table 3. **Elemental composition (by XRF) and properties of the samples**

Sample ID	Groups of context	Wt. %							mg/kg				pH	LOI$_{105–550}$, %	LOI$_{550–1000}$, %	Particle-size distribution, %			Soil textural classes
		Si	Al	Fe	Ca	Mg	K	Na	Ti	Ba	P	Mn				2000–63 µm	63–2 µm	<2 µm	
BE-40	1	38.9	2.91	1.44	1.57	0.31	1.41	0.54	831	792	1680	843	7.9	1.47	1.18	92.9	4.4	2.7	sand
BE-20	2	39.7	2.56	1.12	1.38	0.36	1.31	0.51	852	664	**1392**	832	8.9	1.37	1.37	92.3	4.7	3.0	sand
BE-34	2	39.7	2.88	1.16	1.04	0.41	1.41	0.61	830	767	**1233**	914	8.0	1.42	0.86	91.5	5.3	3.2	sand
BE-14	2	38.9	3.08	1.39	1.69	0.49	1.30	0.80	815	625	**493**	428	8.6	0.53	1.76	94.1	3.1	2.8	sand
BE-21	3	36.1	2.54	0.81	4.45	0.94	1.35	0.88	643	565	**487**	247	9.0	0.42	5.68	97.5	1.4	1.1	sand
BEof-1	3	41.6	2.89	1.11	0.19	0.16	1.09	0.49	841	135	**349**	162	6.1	0.75	0.12	92.9	4.1	3.0	sand
KE-48	1	40.6	2.18	1.10	0.64	0.15	1.13	0.38	810	513	**914**	685	6.6	2.87	0.35	87.2	8.0	4.8	sand
KE-51	1	41.1	2.11	0.98	0.56	0.13	1.11	0.38	763	688	**743**	538	7.1	2.65	0.31	88.5	7.1	4.3	sand
KE-45	1	40.8	2.13	0.96	0.57	0.11	1.08	0.38	732	739	**631**	573	6.2	3.15	0.37	87.4	7.6	4.9	sand
KE-44	1	42.3	2.23	0.80	0.28	0.10	1.14	0.40	631	173	**495**	465	6.2	0.98	0.12	92.7	4.5	2.8	sand
KE-42	1	43.1	1.91	0.75	0.18	0.08	1.08	0.38	794	560	**284**	200	4.8	0.40	0.09	92.2	5.4	2.3	sand
KE-47	2	40.6	2.22	1.05	0.55	0.16	1.16	0.38	701	744	**647**	616	5.4	2.97	0.37	87.7	7.0	5.3	sand
KE-46	2	42.5	2.13	0.80	0.24	0.10	1.12	0.39	653	586	**426**	374	6.1	0.86	0.11	92.0	5.1	2.9	sand
KE-49	2	42.7	2.16	0.77	0.24	0.11	1.08	0.44	650	225	**406**	324	6.2	0.56	0.09	93.7	4.5	1.9	sand
BEND-05	1	35.3	3.25	1.54	1.20	0.55	1.49	0.88	1387	845	**2259**	804	6.9	6.95	0.68	73.7	17.0	9.3	loamy sand
BEND-19	2	39.6	3.29	1.32	0.35	0.44	1.57	0.85	1382	624	**884**	425	6.8	1.34	0.21	74.6	19.8	5.6	loamy sand
BEND-20	3	36.2	4.49	2.84	0.70	1.26	2.01	0.63	2162	568	**1131**	514	7.6	1.39	0.72	59.7	24.3	16.0	sandy loam
LIU-11	1	39.0	2.73	0.99	0.60	0.32	1.45	0.57	1450	807	**1484**	1293	7.3	4.68	0.46	71.7	21.1	7.1	loamy sand
LIU-05	1	39.4	2.83	1.17	0.46	0.39	1.47	0.59	1436	847	**1136**	948	7.2	3.55	0.37	74.2	19.4	6.4	loamy sand
LIU-15	2	40.4	2.50	0.85	0.40	0.30	1.44	0.56	1476	873	**1227**	1050	7.2	2.59	0.24	75.0	20.9	4.1	loamy sand
LIU-14	3	41.4	2.85	0.74	0.19	0.23	1.67	0.60	1539	705	**993**	603	7.2	0.56	0.14	75.3	21.6	3.1	loamy sand
ŠNR-39	1	39.0	3.18	2.19	0.25	0.34	1.52	0.78	1725	174	**384**	310	5.3	2.51	0.16	72.3	22.2	5.5	loamy sand
ŠNR-40	1	39.4	3.27	2.00	0.23	0.34	1.46	0.99	1792	617	**269**	286	5.2	1.60	0.16	74.0	21.3	4.6	loamy sand
ŠNR-41	1	39.4	3.73	1.82	0.26	0.46	1.64	0.94	1853	710	**206**	297	5.5	0.81	0.12	71.8	24.9	3.3	loamy sand
ŠNR-35	1	38.0	3.63	2.21	0.35	0.58	1.66	0.80	1853	595	**409**	440	6.6	2.65	0.20	66.5	24.7	8.8	loamy sand
ŠNR-36	3	31.2	5.99	4.52	1.35	2.20	2.56	0.39	3163	738	**829**	549	7.8	2.49	1.95	49.9	24.4	25.8	sandy clay loam

Abbreviations: BE, Bėčionys; KE, Kernavė; BEND, Bendžiukai; LIU, Liūdiškiai; ŠNR, Šnieriškės.

Groups of context: 1 is features/horizon with artefacts; 2 is features/horizon holding no artefacts; 3 is subsoil.

Table 4. **The average percentage of P extracted by different exctraction methods as compared to the total P (XRF) and correlation coefficients between extracted and total P**

No.	Method	Group I (Kernavė, Bėčionys)		Group II (Liūdiškiai, Bendžiukai, Šnieriškės)	
		Averaged extracted proportion of P_{total}, %	Pearson's r	Averaged extracted proportion of P_{total}, %	Pearson's r
		Aqua regia digestion			
1.	AR-m	76	0.99**	46	0.94**
		Mild extraction with diluted solutions of strong acids			
2.	1M-HCl-2h-m	77	0.99**	43	0.93**
3.	1M-HCl-2h-s	75	0.97**	42	0.94**
4.	5M-HCl-2h-m	78	0.99**	46	0.96**
5.	1M-HCl-2w-m	85	0.98**	58	0.88**
6.	1M-HCl-2w-s	88	0.97**	55	0.92**
		Extraction after ignition			
7.	1M-HCl-2h-550-m	91	0.99**	52	0.97**
8.	1M-HCl-2h-550-s	83	0.98**	53	0.97**
9.	1M-HCl-2h-800-m	81	0.99**	47	0.97**
10.	1M-HCl-2h-800-s	75	0.96**	43	0.96**
		Extraction with citric acid			
11.	1%-C-2h-1:10-m	47	0.96**	21	0.94**
12.	1%-C-2h-1:100-m	79	0.99**	40	0.90**
		Extraction with methods for plant available P			
13.	M2-5m-s	16	0.36	4	0.78*
14.	M3-5m-s	25	0.79**	9	0.75*

** $p < 0.001$; * $0.001 < p < 0.01$.

which is close to that extracted by the mild extraction method 1M-HCl-2h-m (77%). This evidences that in the case of AR the $P_{near\ total}$ value was not reached.

The amount of P extracted by mild extraction at room temperature hardly depended on the acid concentration (1M HCl and 5M HCl, 77 and 78%). However, a dependence on the extraction time has been observed: after agitating for 2 h with 1M HCl 77% of the total P was extracted, while after keeping for 2 weeks 85% P was extracted. From unmilled samples agitated for 2 h with 1M HCl somewhat less P (75%) was extracted as compared to that extracted from the milled ones, while from the unmilled samples kept for 2 weeks 88% of the total P was extracted. The correlation between the extracted and total P by mild extraction methods is very high for both milled and unmilled samples.

The greatest proportion of the total P was extracted from the samples exposed to 1M HCl which were ignited at a temperature of 550 °C – on the average 91% from the milled and 81% from the unmilled samples. The P amount extracted from the samples ignited at 800 °C, as compared to those ignited at 550 °C, was less (81% from milled and 75% from unmilled). The results could have been influenced by the sintering processes occurring at higher temperatures which impeded P extraction. It is reasonable that lower amounts of P were extracted from the unmilled samples as compared to those of milled ones due to lower surface areas of the soil particles in the former samples, and also the correlation coefficients in the case of the unmilled samples are slightly lower than those of the milled ones.

The extraction with weak citric acid (1%) showed that at the soil/reagent ratio equal to 1:100 on the average 79% of the total P was extracted during 2 h, i.e. even more than that extracted with 1M HCl (77%), and the correlation with P_{total} was also very high. At the soil/extractant ratio 1:10 a lower amount of P was extracted, i.e. 47%, the correlation coefficient was slightly lower as well.

The amount of P determined by the M2-5m-s and M3-5m-s methods was significantly lower – 16 and 25%, respectively, and the correlation coefficients were also the lowest ones.

The tendencies of P distribution in the samples of group I determined using the methods from No. 1 to No. 12 (Table 4) completely coincided with those shown by P_{total} (XRF). While methods No.13 and No.14 presumably extract another P form and present different information on the soil, for instance, by the P content determined by the M2-5m-s method, the Kernavė samples from different layers of the same pit (KE-51 and KE-44) differ from the samples from the other pits with the artefacts (KE-48, KE-45 and KE-49) (Fig. 2). In the case of Bėčionys the M2-5m-s method shows a considerable difference between the sample from the pit with artefacts BE-40 and the samples from the pits holding no artefacts BE-20 and BE-34; the sample BE-21, which was determined to contain the least P amount clearly stands out as subsoil, however, in the sample BE-of the P amount was not the least one, as may be inferred from the XRF data. In the case of BE-of lower pH of this sample could contribute to differences in the outcomes. The M3-5m-s method yields results close to those determined by M2-5m-s.

In group II in comparison to group I the extracted proportion of total P was considerably lower in all cases and the correlation coefficients between the extracted and total P in almost all cases were somewhat lower (except for the M2-5m-s method). The amount of P extracted by the AR-m method is only 46%. An increase in the HCl concentration from 1 to 5M increased the amount of extracted P moderately (from 43 to 46%). A dependence on the extraction duration has been observed: agitating 1M HCl for 2 h 43% of total P was extracted, while keeping for 2 weeks 58%, this being the greatest amount of P extracted as compared to the other methods (in contrast to that of the samples of group I). However, the correlation with the total P in this case is slightly lower. When extracting P from the unmilled samples for 2 h and 2 weeks, the amounts of P obtained were only slightly lower – 42 and 55%, respectively.

When extracting the ignited milled samples, similarly to group I samples, greater amounts of P were obtained from the samples ignited at a temperature of 550 °C as compared to those ignited at 800 °C (on the average 52 and 47%, respectively). The P amount extracted from the unmilled samples ignited at the mentioned temperatures was close to or slightly lower than that of the milled ones (53 and 43%). When extracting the ignited milled and unmilled samples, the P amount obtained most closely correlated with the total P. The results obtained are somewhat surprising, as keeping the samples of group II in 1M HCl for 2 weeks (in the expectation of P_{in}), the amount of P extracted was higher than that extracted from the samples ignited at 550 °C (in expectation of $P_{near\ total}$). This is possibly due to the fact that the ignited samples were exposed to acid at room temperature only for 2 h.

When exposing the samples of group II to 1% citric acid for 2 h at the soil and extractant ratio 1:100, as in the case of the samples of group I, the amount of P extracted was almost the same (40%) as it was extracted with 1M HCl (43%). When the soil and extractant ratio was 1:10, the amount of P extracted was lower – only 21%.

The amount of P extracted by the M2-5m-s and M3-5m-s methods was quite small (4–9%) and the correlation coefficients for the samples of this group, as they are in the case of the samples of group I, are the lowest ones.

In the case of the samples of group II the tendencies of P distribution in soil, obtained by the XRF method for all

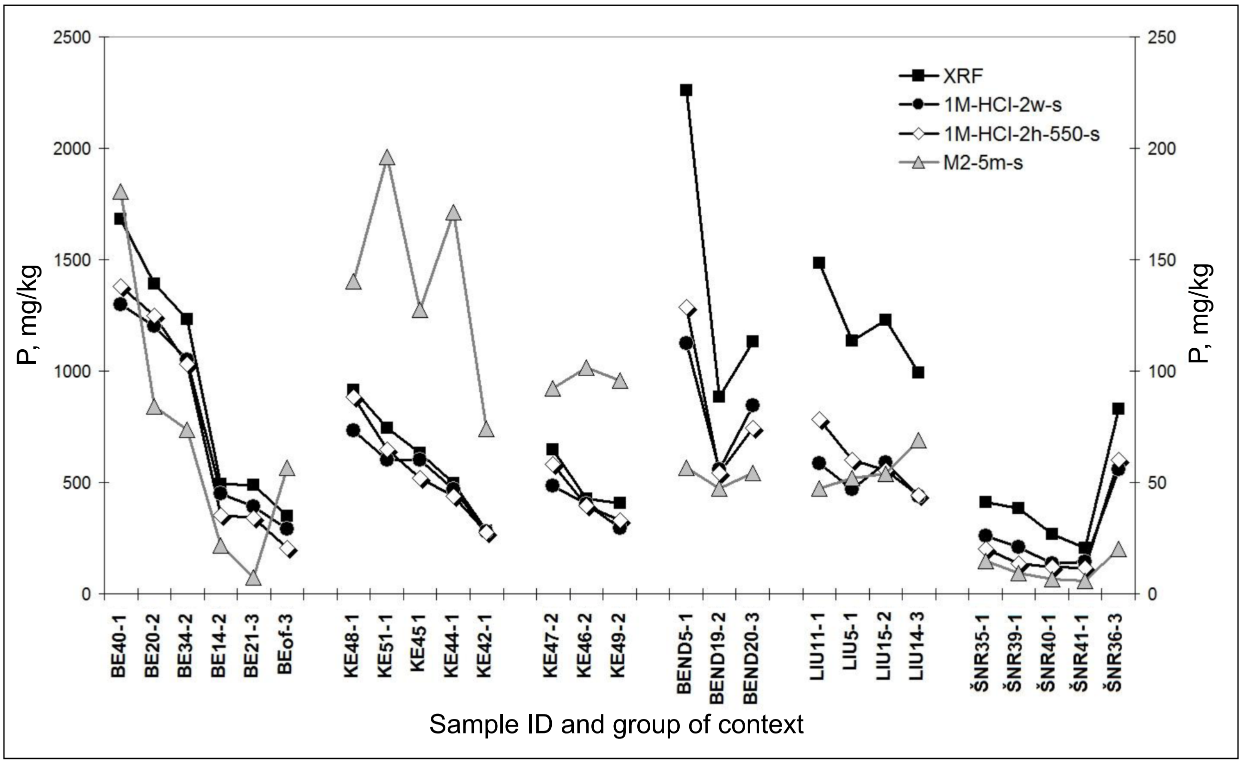

Fig. 2. P amounts in samples determined by the XRF, 1M-HCl-2h-550-s, 1M-HCl-2w-s (scale on the left) and M2-5m-s (scale on the right) methods. The group of context is given next to the sample number: 1 is features/horizon with artefacts; 2 is features/horizon holding no artefacts; 3 is subsoil

three localities, are completely replicated by no more than five methods: the AR and extraction method of the samples ignited at temperatures of 550 and 800 °C (Table 4, No. 1, 7–10). The results obtained by mild extraction or by citric acid methods depended on a particular site: in Bendžiukai and Šnieriškės these methods showed the same tendencies of P distribution in soil as in the case of P_{total} (XRF), however, in the case of Liūdiškiai the difference in P amounts in subsoil and archaeological sediments was not clear enough. The M2-5m-s and M3-5m-s methods, as in the case of the samples of group I, provided P distribution different from P_{total} (XRF), yet this gave no more clarity in separation of different sampling contexts, for instance, the subsoil sample from Liūdiškiai contained more $P_{Mehlich\text{-}2\ extractable}$ than those from the sediments with or without artefacts. In Bendžiukai the differences between the samples of all three different contexts were minimal and the layer with artefacts BEND-05 did not distinguish itself for its highest P amount as it was in the case of XRF studies (Fig. 2). Meanwhile in Šnieriškės the tendency remains the same, though the difference in P amounts between the samples of the subsoil and the archaeological layer is not that distinct as in the case of XRF.

To perform an archaeological large-scale survey it is important to choose the simplest possible method, i.e. cheap, fast and, undoubtedly, reliable. For sandy soils the choice of methods is wider – according to the amount of extracted P as compared to P_{total} (XRF), the correlation with P_{total}, and the relation to the sampling context, the AR, mild extraction, extraction with citric acid and extraction of ignited samples methods are suited for this purpose. Digestion with AR is a labour-consuming method associated with solution heating, moreover, from the P distribution point of view it did not show anything special in sandy soil experiments (other elements were not measured), therefore this method for fast research measuring one element (only P) seems to be too expensive. The employment of 5M HCl, as compared to 1M HCl, did not lead to improvement in the accuracy of the results obtained, thus, there is no point in increasing the concentration of acid for extraction at room temperature. 1% citric acid could be used as an environment-friendly extractant for sandy soil at the ratio 1:100. However, in this work only milled soil was investigated employing citric acid, while the effectiveness of the method for unmilled soils was not assessed.

With 1M HCl employed both 2 h extraction and 2 week extraction justified our efforts, though, of course during 2 weeks the extracted proportion of total P was higher. The best results for sandy soil were achieved when extracting the samples ignited at a temperature of 550 °C, while the ignition of the samples studied at a temperature of 800 °C appeared to be inexpedient. The analysis becomes simpler and shorter when the sieved unmilled samples rather than the milled ones are chosen for investigations. The studies employing four methods (1M-HCl-2h, 1M-HCl-2w, 1M-HCl-2h-550, 1M-HCl-2h-800) have shown that the correlation coefficient for the unmilled sandy soil samples diminishes only slightly as compared to that of the milled ones. Thus, the milling procedure in order to determine the differences in P amounts rapidly (at least employing the mentioned methods) for sandy soils can be omitted. The Mehlich 2 and Mehlich 3 extractants should not be totally rejected, they possibly could be used as supplementary methods providing information of different kind on the soil.

The studies have shown that the AR and extraction of the samples ignited at 550 and 800 °C were the most reliable for loamy sand soil. As in the case of sandy samples, the milling procedure and ignition at 800 °C appeared to be inexpedient, thus only the AR-m and 1M-HCl-2h-550-s methods remain. The laboratory staff should decide on the basis of the equipment and facilities available which of them will be the best option. It could depend on the goals of the investigations, as well: AR-m is mostly used not only to measure the amounts of P but also other elements [8–10, 13, 16], while 1M-HCl-2h-550-s is mostly used to determine only P [14, 31, 32]. When employing the latter method $LOI_{105–550}$ can be determined, moreover, combining it with the investigation of not ignited samples allows evaluating the approximate amount of P_{org} [1]. Although this work pursued to review essentially the methods not employing solution boiling/heating, however, while choosing the method for loamy sand soil it is worth trying more digestion methods with stronger acids, as well as boiling or microwave digestion procedures, which would allow to transfer more P to the solution. The mild extraction methods must not be ruled out (since they suited for the samples from two sites out of the three studied), however, while choosing them for loamy sand samples or for samples of some finer soil it is worth trying their effectiveness with a small series of samples. The Mehlich 2 and Mehlich 3 methods did not suit for the loamy sand soil samples studied for a rapid search of soil with anthropogenic features, because it did not show the existing differences in the P content among the samples of different context.

CONCLUSIONS

The studies have shown that the percentage of P extracted by different exctraction methods as compared to total P (determined by XRF) and correlation coefficients between the extracted and total P depended on the texture of soil: these indexes were higher for sandy soils as compared to those of loamy sand soils.

The digestion with aqua regia, mild extraction, extraction with citric acid and extraction after ignition suited to determine phosphorus in sandy soils as an indicator of anthropogenic activity. For loamy sand samples only the aqua regia and extraction after ignition were reliable, while the mild extraction and extraction with citric acid failed for one of the three series of samples.The amount of P determined using the Mehlich 2 and Mehlich 3 extractants was in a rather poor agreement or did not correlate with the total P (XRF) and showed different tendencies of P distribution in soil; for sandy samples this information was more closely associated with the soil archaeological context as compared to loamy sand samples.

Sieved/unmilled and ignited at 550 °C soil extraction with 1M HCl was considered to be a quite reliable and reasonable method for large-scale archaeological survey investigations for the sites both with sand and loamy sand soils.

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FOSFORAS ARCHEOLOGINIAME GRUNTE: SKIRTINGŲ EKSTRAHAVIMO METODŲ PALYGINIMAS

Santrauka

Vienas plačiausiai tiriamų cheminių elementų paleoantropogeninei veiklai atpažinti yra fosforas. Naudojama daug įvairių metodų fosforui archeologiniame grunte analizuoti, tačiau iki šiol bendrų metodo pasirinkimo rekomendacijų nėra. Patikimo ir ekonomiško metodo antropogeninės kilmės fosforui grunte įvertinti paieškos yra svarbios taikomąja prasme, ypač esant didelėms bandinių serijoms.

Šių tyrimų tikslas – išbandyti skirtingus P ekstrahavimo metodus su žinomo archeologinio konteksto bandiniais. Eksperimento metu buvo nustatyta bandinių tekstūra, elementinė sudėtis (RFA), pH, kaitinimo nuostoliai 550 ir 1 000 °C temperatūrose. Išbandyti P ekstrahavimo metodai naudojant karališkąjį vandenį, 1M ir 5M druskos rūgštį, citrinų rūgštį, ekstrahentus Mehlich 2 ir Mehlich 3, taip pat bandinių kaitinimo 550 ir 800 °C temperatūrose procedūrą. Nustatyta, kad beveik visais metodais ekstrahuota visuminio P (RFA) dalis buvo didesnė ir geriau koreliavo su visuminiu P smėlio grunto bandiniuose nei dulkingo smėlio. Tirtos serijos bandiniams kaip patikimas ir racionalus metodas labiausiai tiko sijoto / nemalto kaitinto 550 °C temperatūroje grunto ekstrahavimas 1M HCl.