Acta Geochim (2022) 41(1):132–146
https://doi.org/10.1007/s11631-021-00500-3

ORIGINAL ARTICLE

Geochemical analysis of multi-element in archaeological soils from Tappe Rivi in Northeast Iran

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Received: 14 June 2021 / Revised: 23 September 2021 / Accepted: 27 September 2021 / Published online: 23 October 2021

Abstract Multi-element analysis in historical sites is a major issue in archaeological studies; however, this approach is almost unknown among Iranian scholars. Geochemical multi-element analysis of soil is very important to evaluate anthropogenic activities. The aim of this study consists of assessing the potential usefulness of multi-elemental soil analysis, obtained by Analytical Jena atomic absorption spectrophotometer (AAS) and ICP-MS, to recognize ancient anthropogenic features on the territory of Tappe Rivi (North Khorasan, Iran). For that purpose, a total of 80 ancient soil samples were sampled from each soil horizon and cultural layer. The research involved Fe, Al, Cd, Cu, Ni, Co, Cr, Pb, and P which trace element samples were extracted according to the International Standard ISO 11466 and phosphorus samples by Olsen method. Besides, the contamination of the soils was assessed based on enrichment factors (EFs) by using Fe as a reference element. This geochemical/archaeological approach highlights that the content of most elements in the Parthian and Sassanid ages were significantly higher than the contents of the elements in other zones, which shows that by the development of the eras, the content of the elements has also increased. Also, the accumulation of metals in the Rivi site was significantly higher than in the control area. Among the sampled zones, enrichment factor (EF) indicated that the enrichment of Cu and phosphate at the Parthian and Sassanid had the highest content. This result is important because it shows that the amount of metals and human activities are directly related to each other during different ages.

Keywords Tappe Rivi · Multi-element · Phosphorus · Ancient human impact · Samalghan plain

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1 Introduction

Ancient soils may be highly polluted with heavy metals because of intensive anthropogenic activities over the centuries (Rouhani and Shahivand 2020). This has resulted in extended changes over a period of time in the chemical properties of soil. Soil chemical analysis in archaeological sites may cause the identification of areas impacted by various anthropogenic activities in ancient times (Salisbury 2013; Charzyński et al. 2015). Recent investigations show that an analysis of the geochemical and geophysical properties of sediments can help in the identification of human occupation beyond the archaeological remains. This is because human activities, such as preparation of food, fireplaces, midden, or craft-working, changed the natural sediments in easily identified ways, and made new soil characteristics that can be identified and assessed through multi-analytical methodologies. To date, raised amounts of Ca, P, Cu, Fe, Mg, K, Na, Zn, etc., have been generally found in archaeological soils and related to specific inputs (Dirix et al. 2013; Entwistle et al. 2000; Hjulstrom and Isaksson 2009; Linderholm 2007; Marwick 2005; Middleton 2004; Parnell et al. 2002; Wells 2004; Wilson et al. 2008). However, the relationships between soil properties and past anthropogenic activities are by no means understand. Ancient soil effects are site-specific and usually hard to describe because of the combined impact of natural variations in background geology, the complexity of site-use history, processes of formation, and methodological factors (Oonk et al. 2009a, b; Wilson et al. 2009; López Varela and Dore 2010).

Despite the rising interests in the multi-element analysis of archaeological soils (Fleisher and Sulas 2015), the determination of phosphorus accumulation remains an extremely important matter in many cases (Wilson et al. 2008; Oonk et al. 2009a). Because the elevated concentration of phosphorus (P) is one of the most archaeologically important anthropogenic changes of soil. Due to its ubiquity between living organisms, phosphorus is often considered to being the strongest and most important chemical marker of ancient human settlements (Save et al. 2020). Fixed forms of P are largely insoluble and renitent to chemical and physical procedures of reduction, leaching, and oxidation. Fixed P remains permanent in most occupation soil surfaces throughout the centuries (Holliday 2004). It has been revealed that the chemical signature of ancient settlement activities can be recognized even in the topsoil layer, despite the point that it may have been impacted by recent fertilizer application (Oonk et al. 2009b). Geochemistry has been not only a tool in characterization, but also an exploration one, and it could be an initial step in the development of an excavation strategy (Wilson et al. 2008). Investigation of soil chemical accumulations can clarify areas where anthropogenic activities are repeated and would have left increased levels related to byproducts of such activities (Holliday 2004).

Multi-element analytical approaches including ICP-AES, ICP-OES, ICP-MS, and XRF have made fast soil analysis which is available to archaeological studies (Terry et al. 2004; Wilson et al. 2008; Middleton et al. 2010; Misarti et al. 2011). In comparison with other geochemical approaches, inductively coupled plasma-mass spectrometry (ICP-MS) has more sensitive finding limits on many elements (Kennett et al. 2004). Several scholars have reported that various elements correlate to the various particular human activities (Homsey and Capo 2006; Barba 2007; Misarti et al. 2011). The multi-element analysis has been used in several ways in the analysis of sediments at open-air sites (Abrahams et al. 2010; Middleton et al. 2010; Misarti et al. 2011; Vyncke et al. 2011; Dirix et al. 2013).

There have been a number of sites where have applied geochemistry to respond to archaeological questions, more recently in the Vinča-Belo Brdo, Serbia (Veselinović et al. 2021) a multidisciplinary approach was used for a detailed characterization of sediments. This study reported that quartz was the most abundant mineral in paleosol, while the organic matter had a mixed origin, with a major input of microorganisms in the precursor biomass. Lisetskii and Stolba (2020) at the archaeological sites in the south of the East European Plain, by investigations of archaeological ashes, opened prospects for further research into archaeological ash deposits in varying cultural, temporal, and environmental conditions.

Also, the Thai site at Ban Non Wat and Nong Hua Raet (Kanthilatha et al. 2014), from at least 4000 BP, indicated that P, Ca, and K as crucial human-derived elements which manifest the occupation severity of ancient people in different floor surfaces. Moreover, the prehistoric archaeological sites at Cape Cod in America (Schlezinger and Howes 2000), where a thorough investigation of an anthrosol from the last glacial period reports the applying of organic P and elemental ratios in outlining human occupations in acidic and sandy soils. In Guatemala, two sites from the Maya period have been geochemically investigated. Las Pozas (Fernández et al. 2002), where elevated amounts of P, K, Mg, and pH were associated with the preparation of food areas, as well as high P accumulations and low pH with consumption of food areas. At Piedras Negras site (Parnell et al. 2002), where high amounts of Ba, P, and Mn were related to organic waste disposal areas whereas Hg, and Pb accumulations were related to craft production areas. Geochemical studies in ancient periods, mainly concerned with Pb, Hg, and other metal-related smelting activities (Kawahata et al. 2014), pigments (Emslie et al. 2015), or agricultural activities that can be identified by Ca, Sr, P, Zn and Cu accumulation patterns associated with charcoal and bone mediated for late 1800s farms (Wilson et al. 2008). Pîrnăua et al. (2020) studied the potential efficiency of multi-elemental soil analysis to identify ancient anthropogenic features, in comparison with the natural context on the territory of Roman-Byzantine Ibida city (Dobrogea, SE Romania). Their results indicated that particular elements including Ca, P, and K show higher concentrations in the Ibida fortress area. They found that the understanding of the multi-elemental composition of the topsoil only is not enough for precise identification of the ancient characteristics which can be associated with the Roman-Byzantine period.

For decades, the chemical analysis of multi-element on archeological soils has not received much attention from

Iranian scholars. In this context, the use of multi-element analysis on an ancient site in the northeast of Iran presented a relatively recent method to these types of researches. Chemical studies on ancient soils had a major role in learning more about life and human activities with the environment in a specific archaeological community. The present study aimed to describe the changes in the concentration of some multi-elements in different ages in an Iranian prehistoric site, utilizing soil chemical analysis. It was assumed that comparison in the content of these elements should show that are there any differences in the samples of soils taken from the ancient site. To our knowledge, in Iran and particularly in Rivi, there were not any studies regarding the topic of multi-element analysis of soil for collecting data so far. Therefore, it was important to assess the advantages and limitations of this method for Iranian sites.

1.1 The archaeological context of the study area

This ethnoarchaeological investigation at the archaeological site of Rivi, Iran, tried to refine the interpretation of the relationship between soil chemical signatures and anthropogenic activities for archaeological applications. "Tappe Rivi" or "Riba Tappe" (meaning "hill of the weasel") was first presented by E. Neghaban, who reported three settlement mounds during his investigation in the Samalghan Plain. The Samalghan Plain and adjacent valleys in North-Khorasan Province were visited on several occasions by archaeologists and other researchers from 1968 onwards. In 2012 and 2014, J. Jafari conducted the initial systematic archaeological studies on the Rivi site and also attempted to set up a comprehensive protection program for the ancient area. More data was collected through many expeditions into the Atrak Valley, particularly along the Upper and Middle Atrak in the region among Kushan, Faruj, and Shirvan, and the area around Darreh Gāz, where many clusters of Iron Age and ancient sites were recorded (Jafari et al. 2019). These studies lead to a territorial distribution pattern of the Late Bronze and Iron Age Namazga/Yazmaterial along the Middle Atrak until Mashad and Nishapour in the south; while the Hissar-Gorgan/Dehistan material of NE-Iran and SW-Turkmenistan which it seems did not spread intensively into the Atrak region and further south (Jafari 2015).

1.2 Geological setting and environmental condition

There has not been any study about the physical and geological characteristics of the study area. The only investigation was in the 2017 autumn season, in which a team of geo-archaeologists from Humboldt University/Berlin under the direction of J. Lentschke sampled at least two large profiles in the Samalghan plain. Their result showed that the samples in individual profile-section are composed of different types of sediments in different ratios. Every sample had a significant sand portion in the fine and middle categories. Numerous samples were composed of more than 30% sand. Other samples had also a significant sand content, which means, it was not a Loess-Profile or at least the profile does not contain pure loess. Also, there were significant variations in the "red-values" graphic, approximately between 6.0 and 7.0 m. By correlating the "red-values" graphic with the segment and the "grain-size" graphic it is unusual, that the portion of coarse-silt is considerably low as compared to other areas of the profile. The lack of coarse-silt is manifest to be replaced for a greater portion of fine-silt in that area, where the "red-values" evidence variable levels. In conclusion, they reported that the first profile is not a pure loess profile and consequently, the profile should be specified elsewhere (Jafari et al. 2019).

2 Materials and methods

2.1 Study area

The archeological site of Rivi is located in the Northeastern of Iran, and it lies between latitudes 37°27' N and 37°37' N and longitudes 56°32' E 56°49' E. Tappe Rivi is located in the Samalghan plain (10 km south of the Atrak valley) in North-Khorasan province, Iran (Fig. 1) (Rouhani and Shahivand 2020). This plain is a major and densely populated human settlement, particularly, Ashkhaneh, the center of Maneh and Samalghan County. As regards lithology, the majority of the heights of this plain are composed of Tirgan limestone formations (Rouhani 2020).

Tappe Rivi A (approx. 8 m in height) is situated in the south of the ancient site area, while Tappe Rivi B with a height of approx. 5 m is situated 600 m to the north. In among lays the greatly diminished mound of Tappe Rivi C with only 2 m preserved height. Tappe Rivi D with a high of approx. 4 m is located between Rivi A and Rivi C. Finally, E-Rivi D is located next to Rivi D, which the first meter belonged to Achaemenid age while lower layers were natural soil. According to the earlier investigations a possible horizontal stratigraphy with an (a) Iron Age occupation in the South around Tappe Rivi A, (b) a possible Achaemenid-Parthian occupation takes the form of Rivi D and (c) Rivi C mounds, and (d) a Parthian to Sassanid occupation in Rivi B in the northern part have been observed (Jafari 2015).

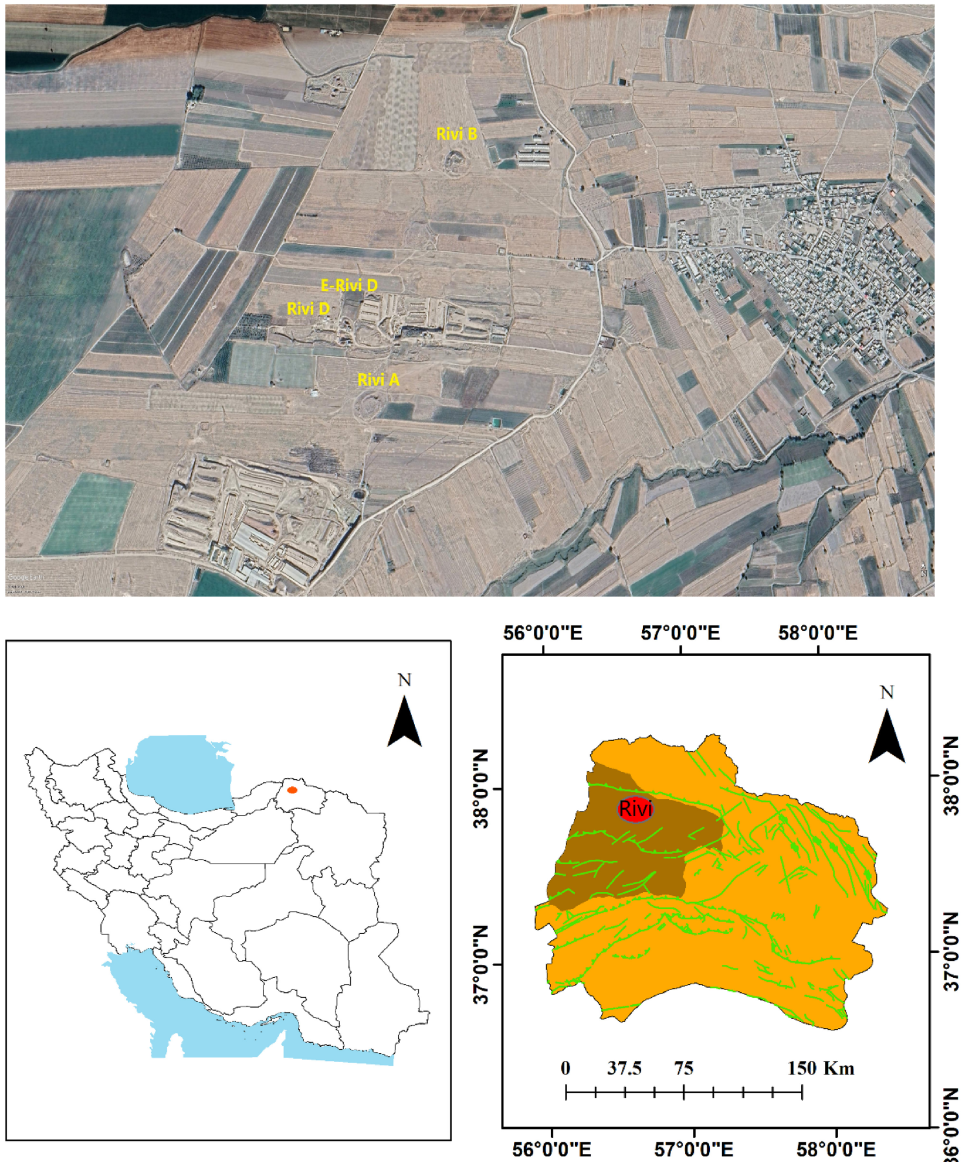

Fig. 1 The location of the study area

2.2 Soil sampling

The ancient soil samples of different soil layers were carefully collected from four ancient zones belonging to four historic mounds in Rivi by hand-driven stainless steel. Depending on the site conditions, soil sampling was carried out in-depth. The distribution of the sampling sites was as follows: (i) In Rivi A, nine samples were taken (1–3 m) from the Achaemenid zone, and ten samples were taken (3–8 m) from the Iron Age zone. (ii) In Rivi B, seventeen soil samples were collected (0–5 m) from the Sassanid zone and nine soil samples were taken (5–7 m) from the Parthian zone. (iii) Thirteen soil samples were collected from Rivi D mound (0–4 m) which was related to Achaemenid age. (iv) and seven soil samples were collected from a Great pit near the Rivi D (E-Rivi D) which was located on-site and related to the Achaemenid age. In addition to the samples of anthrosoils which were collected on-site, 15 samples were taken as control (0–400 cm) from off-site being located outside the ancient site with soil without ancient texture. The objective of collecting control samples was to compare the variations of the elements in the anthrosoils samples with the control and to measure the elemental changes outside and inside the ancient site.

It was essential to measure the 'natural' background characteristics of the soil properties area (Entwistle et al. 2000), to determine if there were these 'on-site' soils at Rivi affected by human activity. This background signature was derived from control samples taken from a zone lying outside the area of the Rivi site. No documentary evidence was found to illustrate that this area was previously cultivated, nor are there any remains of cultivation traces. The soil samples were placed in clean polypropylene tubes and transferred to the laboratory. All the samples were air-dried and passed through a 2 mm stainless steel sieve. The chemical digestion of the samples was performed using the standard ISO_11466, 1995 method. After screening, the samples were extracted using HCL and HNO3 acid to determine the contamination of heavy metals. In addition, the total contamination of Al, Cd, Cu, Ni, Co, Cr, Pb, and Fe of the soil samples was tested using an Atomic absorption spectroscopy (AAS) model Analytical Jena-350 Germany. Various methods have been used to analyze phosphorus in archaeological soil, however, general recommendations for the adequate choice of the research method yet need to be formulated. The search for a reliable and efficient method for phosphorus assessment of anthropogenic sources in soil was important from the applied point of view, particularly in the case of a large series of samples. The method of phosphorus analysis used in this study was based on the Mehlich II extraction solution and Hach reagents (Terry et al. 2000). Two grams of air-dried, sieved (< 2 mm) floor or soil sample was placed in one of six 50 ml jars attached to a board that facilitated shaking and processing of multiple samples. Each soil sample was extracted with 20 ml of the Mehlich II solution for 5 min. Then, the samples were filtered and the filtrate was collected in clean 50 ml jars. One ml of the extract was dispensed to a vial, diluted to 10 ml, and the contents of a Phosphate 3 powder pillow were added to the vial. The samples were shaken by shaker for exactly 1 min and allowed to stand an additional 4 min for color development. The concentration of phosphorus in the samples was determined on a Hach DR 700 spectrophotometer at a wavelength of 810 nm. A control sample was analyzed with each run. The results were compared with a standard curve of known P accumulation and percent transmittance. A more detailed explanation of the process can be found in Terry et al. (2000). The concentrations of each element in the soil were calculated in mg/kg weight of soil.

2.2.1 Enrichment factor (EF)

The enrichment factor is an index that is used as a proxy to determine the heavy metals' pollution level in soil by estimating the differential of heavy metal accumulations against the uncontaminated background or reference levels (Dragović et al. 2018). It has been recently reported that the EF is a suitable measure of geochemical trends and can be applied for contemplating on lithogenic or anthropogenic provenance of heavy metals (Ye et al. 2011). Fe was used as a reference element to compute anthropogenic metal enrichments by using the following equation. An enrichment factor can be defined as in Eq. (1):

$$\mathrm{EFi} = \frac{(\mathrm{C/R})\mathrm{sample}}{(\mathrm{C/R})\mathrm{background}} \tag{1}$$

where (C/R) sample represents the ratio of the concentration of elements of interest (C) to reference element (R) in the sediment samples, and (C/R) background represents the ratio of the concentration of elements of interest (C) to reference element (R) in the geochemical background. Zhang and Liu (2002) proposed using EF = 1.5 as an estimation criterion, i.e., EF values between 0.5 and 1.5 (i.e., $0.5 \leq \mathrm{EF} \leq 1.5$) proposed that the trace metals might have been totally from crustal substances or natural weathering processes while EF values greater than 1.5 (i.e., $\mathrm{EF} > 1.5$) suggests that a significant section of trace metal is delivered from non-crustal materials. Thus, this study used the local background values as reference values, 10.25 mg/kg for Cu, 72.46 mg/kg for Ni, 19.36 mg/kg for Pb, 16.91 for Co, and 15.66 mg/kg for Cr. The reference value of Fe was 11,353.33 mg/kg.

2.3 Statistical analyses

This study computed the background control concentrations by averaging the five samples of the lowest accumulation for each element (Wells et al. 2000). The background accumulation for extractable phosphate was comparable to those found by Wells et al. (2000). Statistical analysis and one-way ANOVA were performed by using IBM SPSS Statistics version 20. The Kolmogorov–Smirnov test was applied on the control and the on-site data to check for normality of each of the 9 elements considered in our study. The Duncan test was performed, to establish whether there was a significant divergence between ages and the control data (Tallarida and Murray 1987).

2.4 Chronology

Radiocarbon dating of the selected samples at the Rivi site in North-Khorasan indicates very convincing demonstrations to determine a long period of time and large-scale project (Table 1). Over near 2000 years of occupation from the Iron Age to the Sassanid era can be explored at Rivi,

Table 1 Chronology of the site

Mounds	Height (m)	Age
Rivi A	1–3	Achaemenid (2500 years ago)
	3–8	Iron age (2900 years ago)
Rivi B	0–5	Sassanid (1400 to 1800 years ago)
	5–7	Parthian (1800 to 2000 years ago)
Rivi D	0–4	Achaemenid (2500 years ago)
E-Rivi D	0–1	Achaemenid (2500 years ago)

Table 2 Descriptive statistics of element concentrations in Tappe Rivi

Sampling zone		Element (mg/kg)								
		Cd	Cu	Ni	Pb	Co	Cr	Fe	Al	P
Iron age	Minimum value	4.11	15.09	106.73	28.49	20.79	25.28	13,583.33	8590.00	133.33
	Maximum value	5.60	19.02	140.57	35.10	27.38	30.78	18,310.00	14,710.00	266.67
	Mean	4.71	17.22	126.51	31.56	25.38	27.09	15,650.00	11,862.33	191.66
	SD	0.40	1.28	11.14	2.26	1.86	1.71	1630.45	1779.07	42.72
Achaemenid	Minimum value	4.32	14.59	18.07	27.50	19.65	23.01	13,150.00	11,746.67	40.00
	Maximum value	6.98	23.96	145.30	47.16	26.20	35.00	18,750.00	12,200.00	133.33
	Mean	5.57	20.24	114.53	38.37	23.16	29.03	15,941.76	11,894.16	81.75
	SD	.97	2.21	23.76	5.00	2.02	3.01	1598.34	211.24	44.62
Parthian	Minimum value	4.75	24.32	95.78	52.57	21.89	27.81	15,950.00	11,725.00	333.33
	Maximum value	5.14	28.91	135.38	54.47	24.96	30.87	17,036.67	16,950.00	533.33
	Mean	4.97	26.81	108.60	53.70	23.24	29.53	16,722.50	13,440.66	416.66
	SD	0.19361	1.94	9.61	0.85	1.27	1.34	518.74	1435.85	100.00
Sasanian	Minimum value	4.19	19.58	78.17	44.07	20.52	29.21	13,836.67	8976.67	266.67
	Maximum value	5.47	26.76	115.60	52.77	29.67	37.10	17,833.33	16,363.33	466.67
	Mean	5.01	23.72	94.82	48.97	25.96	33.67	15,878.62	12,541.37	316.66
	SD	0.31639	2.13	12.22	2.60	2.45	1.99	1128.05	2708.09	100.00
Control	Minimum value	5.01	10.25	69.40	19.37	18.03	16.20	11,623.33	6210.00	40.00
	Maximum value	7.08	14.26	92.40	23.40	21.53	27.95	18,183.33	13,503.33	100.00
	Mean	5.69	12.66	79.04	21.33	18.81	22.27	13,155.44	9956.20	68.92
	SD	.48	1.17	9.81	1.35	0.90	3.82	1520.42	1842.88	28.53

Table 3 Average enrichment factor and contamination levels of the soil in Tappe Rivi

Area	Cd	Cu	Ni	Pb	Co	Cr	P
Iron age	0.84	1.23	1.28	1.19	1.10	1.27	6.37
Achaemenid	1.26	1.41	1.12	1.41	0.75	1.32	2.80
Parthian	0.82	1.77	0.74	1.88	0.93	1.28	15.28
Sassanid	0.87	1.66	0.94	1.81	1.10	1.54	11
Control	1.20	1.06	1.30	0.94	0.97	1.14	1.70

such as a local sequence for North-Khorasan Province which can be assumed for the wider region. Rivi manifests at least 1500 years of occupation history, from ca. 1200 BC to 500 AD (Jafari et al. 2019).

The mean concentrations of Fe, Al, Cd, Cu, Ni, Co, Cr, Pb, and P in the ancient soils of Tappe Rivi are presented in Table 2. The results reveal clear differences in element concentrations in on-site compared to the off-site (control) samples. The on-site geochemical data were expressed as enrichment factors relative to the mean value of the control samples. Thus, the enrichment factor of each element for each sample was calculated (Table 3).

It was obvious that the higher concentrations of heavy metals were detected at the Parthian and Sassanid ages which were located in Rivi B while the lower concentrations of heavy metals were detected at the control area being located on the north and outside the Rivi site. The highest concentrations of Cu (26.81 mg/kg), Pb (53.70 mg/kg), Fe (16,722.50 mg/kg), Al (13,440.66 mg/kg), and P (416.66 mg/kg) were found in soil samples collected from Parthian zone, whereas the highest concentrations of Ni (126.51 and 114.53 mg/kg) in soil samples collected from the Iron Age and Achaemenid zones, the highest concentrations of Cd (5.57 mg/kg) in the Achaemenid zone and the highest concentrations of Co (25.96 and 25.38 mg/kg) in the Sassanid were observed (Table 2). It was found that the concentration of phosphorus is in elevated level at Parthian, Sassanid, and Iron Age zones (416.66, 316.66, and 191.66 mg/kg, respectively). Low phosphorus concentrations were found in the Achaemenid zone (Table 2). We notice that the majority of elements (Cu, Pb, Fe, Al, and P) present a rise of accumulation in the Parthian zone.

EF values varied based on the background used (Table 2). Given the local background, EF values showed the deficiency in the enrichment of Cd, Co, and Ni in all zones. Also, it was found that calculated EF shows a deficiency in the enrichment of Cu (1.5 > EF) in the Iron

Age (1.23), and Achaemenid (1.41) areas, while it was higher than 1.5 in Parthian (1.77) and Sassanid (1.66) zones. The EF analysis for Cr showed values lower than 1.5 in all areas except for the Sassanid area (1.54). The EF values for Pb ranged from 0.94 to 1.88. Similar to Cu, the mean EF values of Pb showed the minimal enrichment of this element were in the Iron Age (1.19) and Achaemenid (1.41) zones, while the enrichment value of Pb was higher than 1.5 in Parthian (1.88) and Sassanid (1.81) zones. According to Entwistle et al. (1998 and 2000), the enrichment factor of P was obtained. The results of the enrichment factor showed that the EF values for P range from 1.70 to 15.28. All the on-site topsoils were enriched in P, with the majority having enrichment values greater than 6.0, except the Achaemenid zone which was 2.80. The mean EF values of P showed the minimal enrichment of this element in the soil samples taken from the Achaemenid zone (Table 3).

Areas of human occupation at Tappe Rivi indicate variation from the controls for most elements. Contents of phosphorus are significantly lower in the control samples (68.92), compared to anthropogenic zones in the archaeological samples. For several elements (Cu, Pb, Cr, and P), the samples of the control area are low enriched than the archaeological samples.

Correlation among different elements was calculated with the purpose of groups of inter-correlated variables (elements). The Pearson correlation matrix (Table 4) indicates that the correlation between elements was often statistically significant. Pb stands out by having significant correlations with Cu (0.942**), Fe (0.608**), P (0.661**) and with Cr (0.807**), and no significant correlation with the other elements. Moreover, there are significant correlations of P with Cr (0.470**), Co (0.536**), Cu (0.596**). The variation indices that Cu with Cr (0.775**), P (0.596**), Cu (0.605**) and Co with Cr (0.402**), Al (0.332**), P (0.536**) have significant correlations. Cd showed differently behaves, indicating no significant positive correlation with any of the elements. It has significant negative correlations with Co (**−0.801****), Al (−0.447**) and P (−0.309**). Also, there are significant negative correlations between Pb-Ni (−0.355**) and P-Ni (−0.392**).

Many archaeological sites were gradually abandoned and artifacts were transferred or taken from their locations of utilization, either in ancient or modern times. Archaeological evaluation is challenging when artifacts are dislocated or altogether missing. Investigation of ancient human activities at historical sites can be assisted by assessing particular elemental residues that remain in the soils and floors. Chemical residues of ancient anthropogenic activities depict invisible yet crucial artifacts of ancient human lives (Terry and Brown 2020). The discussion of natural opposed to anthropogenic factors associated with past and present environment, erosion, and soil formation processes have recently become more and more popular investigation topic (Smejda et al. 2017; Hafez et al. 2017; Mikołajczyk and Milek 2016; Monge et al. 2016; Pîrnăua et al. 2020). Our study based on multi-element analysis of ancient soil showed its potential to contribute to the discussion from another perspective.

Ancient people mostly have been looking for rocks and minerals for the construction of lithic tools, paints, and pigments. Increased levels of these elements in activity areas can present us with a greater awareness of what different areas may have been applied for (Terry and Brown 2020). The descriptive statistics and EF of the 80 ancient soil elements (Tables 2 and 3) demonstrate that soils from the study area are rich in P in all zones, Cu, and Pb in Parthian and Sassanid areas, and Cr in the Sassanid zone due to the ancient human activities, but also to the parent material, in the case of Cd, Ni, and Co.

Phosphorous (P) is the most extensively used human-derived indicator in archaeological sites (Oonk et al. 2009b). P is usually prevalent in plant and animal tissue, urine, bones, ashes, and faeces, thus it is a crucial element

Table 4 Correlations matrix for the elements in ancient soils of Tappe Rivi

Metals	Cd	Cu	Fe	Ni	Pb	Co	Cr	Al	P
Cd	1	0.129	0.109	−0.061	0.126	**−0.801****	−0.016	−0.447**	−0.309**
Cu		1	0.605**	−0.244*	**0.942****	0.203	0.775**	−0.172	0.596**
Fe			1	0.138	0.608**	0.169	0.629**	−0.059	0.201
Ni				1	−0.355**	0.108	−0.005	0.032	−0.392**
Pb					1	0.218	**0.807****	−0.205	0.661**
Co						1	0.402**	0.332**	0.536**
Cr							1	−0.072	0.470**
Al								1	0.144
P									1

**$P < 0.01$; *$P < 0.05$

in occupation waste and manure (Bethell and Mate 1989). Moreover, P is relatively stable in the majority of soils (Robinson et al. 1995) and sediments. The general agreement is that most human-derived P in soils becomes immobilized in a short time after deposition (Oonk et al. 2009b). A high concentration of P was found in the Parthian, Sassanid, and Iron Age zones (Fig. 2). The elevated levels of P in the Parthian and Sassanid zones are probably related to deposits, such as the high proportions of food waste. It can be said that the samples having an enrichment factor of higher than 1.5 demonstrated strong human impact (Rashed 2010; Zhang and Liu 2002). Thus, the P of Parthian, Sassanid, and Iron Age zones having EF values higher than 2, indicating that P might have been enriched as a result of anthropogenic inputs. High content of P has been recorded at the Bronze Age Settlement in Central Russia (Voronin 2020). Save et al. (2020) in their study of the early Medieval mountain settlement of Brison-Saint-Innocent Chemin de Pompierre (France), recorded enrichment of P which was associated with a hearth and a work surface made of arranged flat stone fragments. Janovský et al. (2020a, b) also, recorded high contents of P in the built-up area in the front garden, close to the house, and on the village square at an ancient abandoned mountain village in the Czech Republic. They claimed that this high accumulation of P can be associated with the deposition of biomass ashes also.

King (2008) carried out a geochemical analysis of residues in Post-classic floors and waste deposits to obtain data on food-sharing, commensality, and household social organization in the coastal Oaxaca zone of Oaxaca in Mexico. In the same way, Parnell et al. (2001) declared a considerable positive correlation between sherd density in test pits and P concentrations in surface soil. Also, Parnell et al. (2002) claimed that phosphorus at or near background levels is descriptive of non-food-related activities including patio sweeping, high-traffic pathways, and sleeping areas. Besides, Knudsona et al. (2004) reported hearths as a reason for the elevated levels of P in the soil. They also

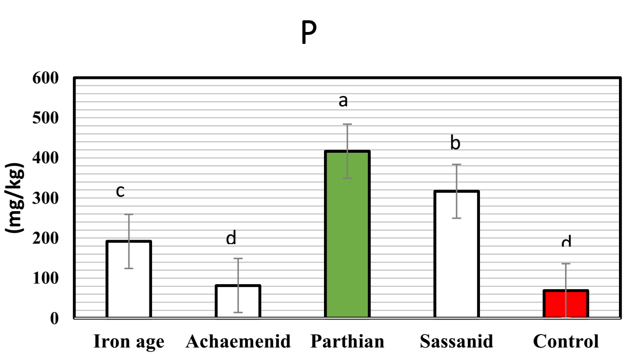

Fig. 2 Mean P concentrations for selected areas

demonstrate that animal droppings could dramatically change the chemical signature of soils by increasing P accumulations. P enrichment in the Achaemenid zone is not too surprising. Thus, if the enrichment of P in archaeological sites is considered to be a trace of ancient human activities, then decreased concentrations could be considered for a weaker human footprint. Asare et al. (2020) also recorded decreased value of P in their study at the Corded Ware Culture graveyard in the Czech Republic; leaching of P was their one possible explanation for this matter. Based on Wells et al. (2000) decreased concentrations have been indicated to correlate with walkways, under beds, entrances, in workshops where organics were not utilized, recently leveled terrain, and harvested agricultural fields.

Lead (Pb) has been an essential raw material for humans (Patterson 1972; Nriagu and Pacyna 1988). It has been used extensively since ancient times in processes intended for the recovery of silver from ores with the low silver amount (Rothemberg et al. 1989) and related to other metal-ore outcrops and applied in different metal alloys (García-Alix et al. 2013). The addition of Pb to raw materials was very common over the Early Iron Age, even where the outcrops had adequate Pb content (Anguilano et al. 2010). The content of Pb in Parthian and Sassanid areas was higher than other zones, while the Iron Age had lower content of this element (Fig. 4a). These data are in agreement with previous studies in Copper Age sediments from the Sierra Nevada, which indicates that contents are barely distinguishable from a natural background (García-Alix et al. 2013). Thus, it does not register the deep anthropogenic environmental effect proposed by Nocete et al. (2005, 2008) in Southwestern Spain. In agreement, another study at the Zoñar Lake (Cordoba) in Southeastern Iberia (Martín-Puertas et al. 2010) did not indicate enrichment of lead. Also, Hong et al., (1996) reported that anthropogenic pre-industrial Pb enrichment was usually a result of mining and smelting. Moreover, Weiss et al. (1998) claimed that soil erosion associated with intense deforestation and intensive agriculture could slightly elevate the Pb content before the development of mining activities.

Copper (Cu) is a microelement existing in plant and animal biomass, and also it stores up resulting from deposition of organic materials including faeces, cadavers, plant biomass, and biomass ashes (Hejcman et al. 2011). Oonk et al. (2009b) demonstrate that Cu is one of the most potential anthropogenic indicators, due to its relative stability in soils and sediments (Fontes and Gomes 2003). Metallurgy over the Copper and Bronze Age was usually relying on Cu, and the smelting processes needed significant content of the fuel (wood) (Constantinou 1982, 1992; Stöllner 2003). Weisgerber (1982) regarded that intensification of this activity could result in vegetal cover loss, deforestation, triggering erosion and desertification of the landscape, and also the impact of intensive agriculture and pasturing cannot be ignored.

The distribution patterns of Cu and Pb were similar. The higher contents of these two elements were observed around the Parthian and Sassanid areas, whereas lower contents were observed mainly around the Iron Age, Achaemenid, and Control areas of the region (Fig. 3). In addition, the Pearson analysis showed that Cu and Pb had a strong spatial correlation. The average contents of Cu and Pb were below or near the heavy metal background value of ancient soils in the Achaemenid, Iron Age, and Control areas. Based on the results of the enrichment factor, we think that Cu and Pb in these areas may be controlled by the background value of the parent materials, but the Parthian and the Sassanid zones having an enrichment factor of higher than 1.5 indicated human impacts on the soils. Souza et al. (2016) claimed that Cu accumulates in locations of a high density of pottery fragments in archaeological localities. Similar to many archaeological sites, we can find many pottery fragments at the Rivi. Maybe this matter is one of the reasons for the accumulation of Cu in these areas. Voronin (2020) recorded high content of Cu associated with the metalworking process in the Bronze Age settlements in the central part of Russia. Cu and Pb appear to be the best palaeonutritional indicators in both the Parthian and the Sassanid zones. Asare and Afriyie (2020) also showed that the highest total content of Cu in the soil from their study area related to the longevity and intensity of the past human activities, and it was well reflected the past human activities from different geographical regions. Moreover, Wilson et al. (2008) and Monge et al. (2015) in their studies have detected Cu as an enriched element in ashes from fires in terms of other background soil geochemical information.

The earliest study on anthropogenic chemical pollution was conducted by Nocete et al. (2011) in Gorham's Cave and Vanguard Cave in Gibraltar, where sediments from Palaeolithic hearths contain values of heavy metals enough to meet present-day standards for enriched soil. This enrichment is associated with fires and is manifest in increased levels of Pb and Cu.

Salisbury (2017) regarded that the enrichment of Cu and Pb do not assist in finding metal workshops, but we can predict that smelting and metalworking will elevate contents of Pb, Cu, and other metals. Bintliff et al. (1990) reported that increased contents of Pb and Cu are associated with metalworking and related industries. They also predicted that accumulations of human and animal waste during a long period may contain "abnormal concentrations" of these elements. Cook et al. (2006) found evidence for Roman metalworking areas at Silchester in terms of

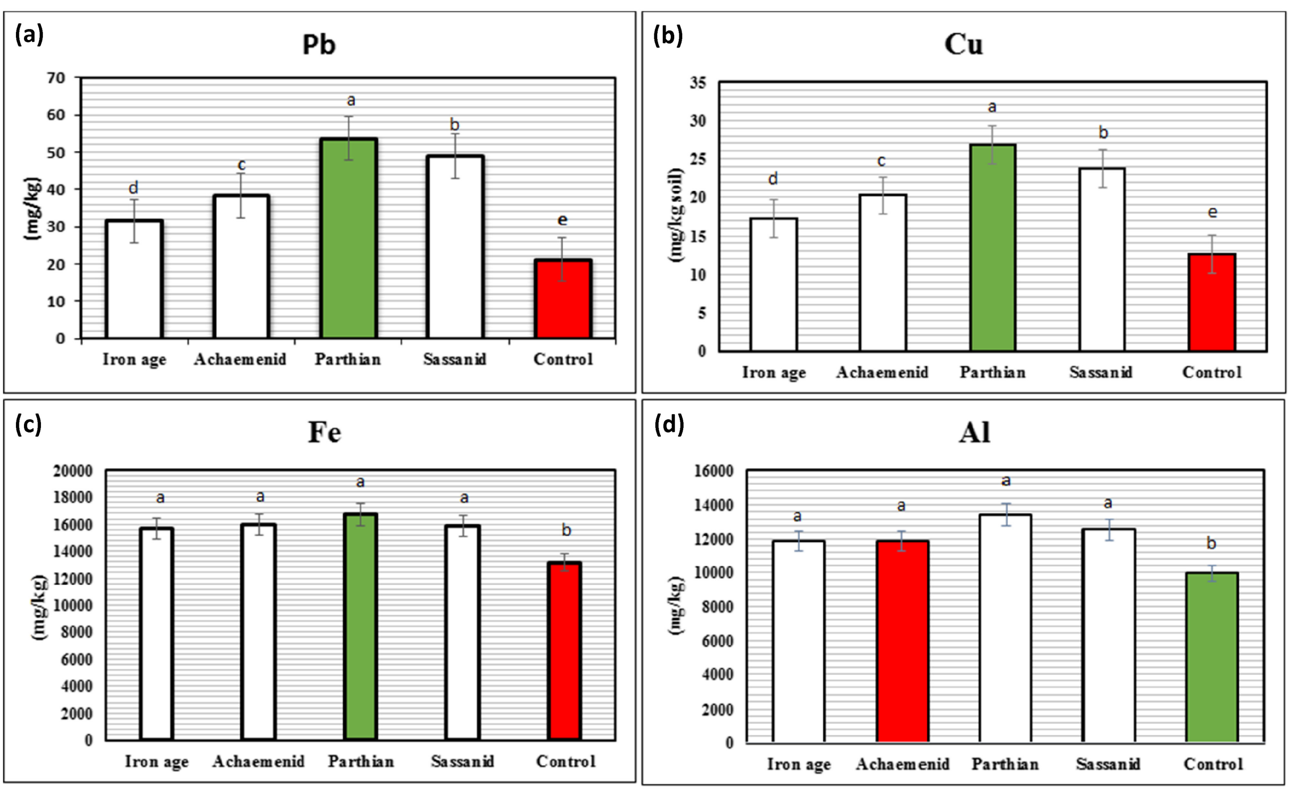

Fig. 3 Mean Pb, Cu, Fe, and Al concentrations for selected areas

accumulations of Pb and Cu, with a distribution of Sn that correlates closely with the distribution of Cu and Pb. Scott (2020) declared that a high concentration of Cu and Pb may indicate the presence of a metalworking installation nearby. She also mentioned Cu can deposit through organic material accumulation. Jenkins (1989) carried out trace element analysis on charcoal, rather than sediments, applying Atomic Emission Spectroscopy on samples from archaeological sites in North Wales. His study showed increased levels of Cu, Pb, and Sn, which suggested that charcoal absorbs trace metals from metalworking (Maskall and Thornton 1998; Monna et al. 2004, 2000). As earlier investigations have reported anomalous concentrations of P and Cu, as the most frequent elements identified in archaeological soils (Ottaway and Matthews 1988; Middleton and Price 1996; Haslam and Tibbett 2004).

The concentrations of Fe were almost the same in all areas; however, the Parthian area was slightly higher than others and the control area had the lowest content (Fig. 3c). Pîrnăua et al. (2020) in their study at the ancient city of Ibida (Dobrogea, SE Romania), showed enrichment of Fe in soils from the study area, due to the calcareous bedrock. Manzanilla (1996) recorded an elevated level of Fe in soils in areas related to animal butchering or agave processing, as well as kitchen areas. Fernández et al. (2002) claim that Fe levels in the floors may be impacted by utilizing metallic cooking utensils and by different cooking methods. Also, a smithy at the Lethra Iron Age village at the Lejre Experimental Centre in Denmark was described by an increased level of Pb and low content of Fe (Hjulström and Isaksson 2009). Sulas et al. (2019) in a study at the Unguja Ukuu, Zanzibar recorded enrichment in Fe and Pb commonly associated with anthropogenic activities. Terry et al. (2004) have also, showed that increased concentrations of Fe, Pb, and Cu related to the use of pigments (ochre, hematite) inside Maya classic-period houses.

The concentration of Al was found in the following order, Parthian > Sassanid > Iron Age > Achaemenid > Control. Accordingly, the concentration of this element in the Parthian area was higher than others, while the Achaemenid had the lowest value (Fig. 3d). Scott (2020) recorded a high concentration of Al in her study at Kaymakçı, a Bronze Age site located in the Gediz (ancient Hermus) River valley in western Turkey. Knudsona et al. (2004) reported an elevated level of Al at an activity area in contemporary Yup'ik fish camps, which indicates a high mineral content of the soil but not an anthropogenic signature.

Cu and Ni are redox-sensitive elements (Tribovillard et al. 2006), and their mobility in soils is associated with element speciation, organic matter content, water content among others (Kiikkilä et al. 2002). The Iron Age had higher values of Ni and Co rather than other areas, in contrast to that the Sassanid area had the lowest content of Ni, and Achaemenid and Parthian areas had the lowest value of Co (Fig. 4). The enrichment of Co and Pb in the sandy surfaces could be related to the use of metal-bearing resources (or metalworking), and wood ash (Sulas et al. 2019).

The EF for Cd in all sample areas was lower than 1.5 which is in agreement with the finding of Fernández et al. (2002). They reported that no consistent patterns were indicating the effect of anthropogenic activities on the accumulation of Cd in their study area (Fernández et al. 2002). The concentrations of Cd, Ni, and Co in all samples were the minimal values of enrichment (EF < 1.5). This study suggested that these element concentrations may come entirely from natural weathering processes (Fig. 4). The highest concentration of Cr was in the Sassanid area, whereas the lowest content of this metal was measured in the Iron Age area (Fig. 4b). The results of the enrichment factor shared no associated patterns with the archaeological evidence of human activity in most of the areas. Accordingly, only samples were related to the Sassanid zone had enrichment higher than 1.5, which was enriched by human actions in the ancient periods.

There have been significant correlations between elements [such as: Pb-Cu (0.942**), Pb-Cr (0.807**), Fe-Cr (0.629**) etc.]. Pîrnăua et al. (2020), also showed strong correlations between Fe and Cr which indicate a common link, possibly of natural origin. These correlations at Rivi demonstrated that they might have taken from common origins, likely from ancient human activities. It must be noted that the maximum values of most elements recorded in the control samples were remarkably lower than values commonly obtained in the territory of Tappe Rivi. This is in agreement with the findings of (Scott 2020; Janovský et al. 2020a, b; King 2008; Oonk et al. 2009a, 2009b; Kanthilatha et al. 2014; Monge et al. 2016; Pîrnăua et al. 2020).

3 Conclusion

Although there is a wide range of instances of using geochemical multi-element analysis of ancient soils worldwide, there have not been examples of applying this approach in an archaeological context in Iran. In this study, we attempted to describe the application of soil chemical analysis for multi-element on an archaeological site in Iran. Nine different elements were (Cu, Pb, Cd, Cr, Co, Ni, Fe, Al, and P) considered which may be relevant to particular occupational periods including, Iron Age, Achaemenid, Parthian, and Sassanid. The enrichment factor shows that the four heavy metals (Cd, Co, Ni, and Cr) in the study area appear to be the result of natural background. The other

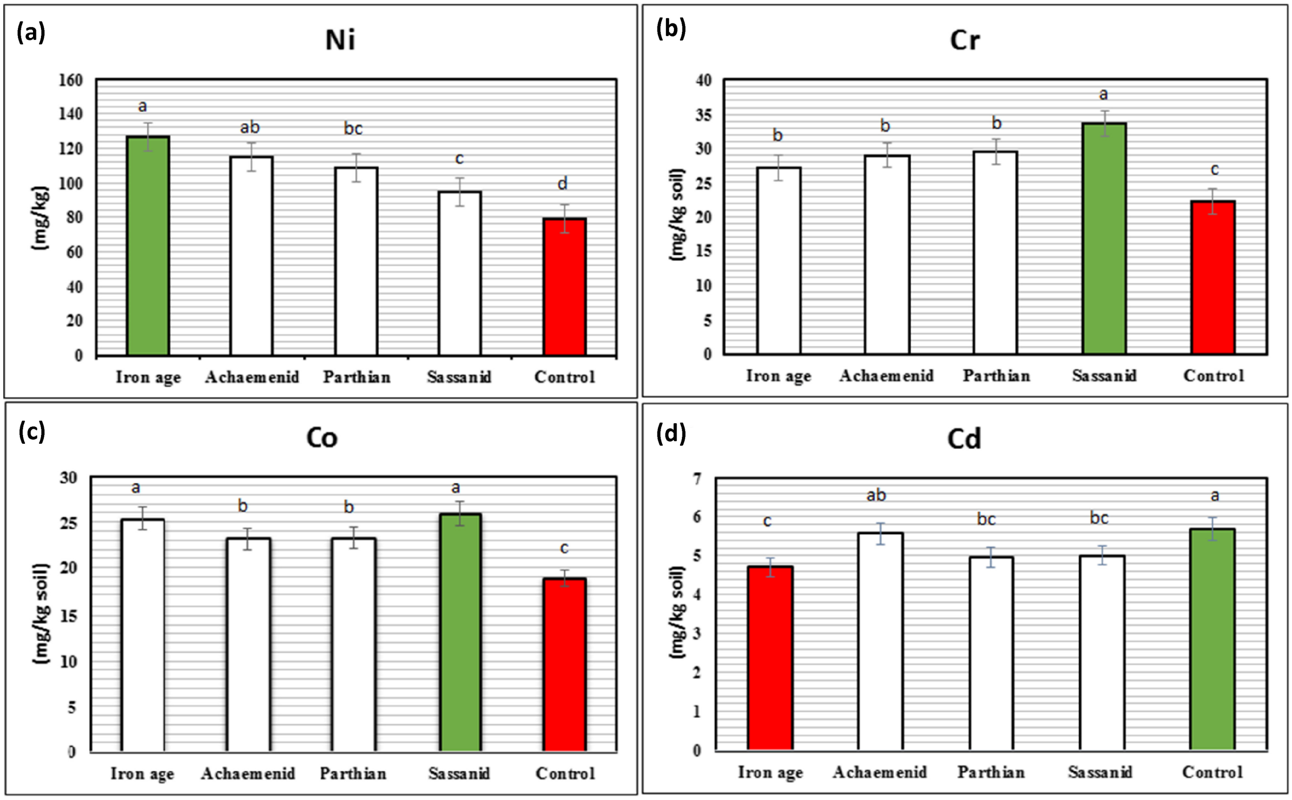

Fig. 4 Mean Ni, Cr, Co, and Cd concentrations for selected areas

five elements (Cu, Pb, Fe, Al, and P) were more likely to be sourced from ancient anthropogenic activities. The sampled soils over the Parthian and Sassanid areas indicated high levels of some elements compared with other soils in the study area. The Pearson analysis showed that Pb had a strong spatial correlation with Cu and Cr. The content of most elements on-site was higher than off-site, which can be attributed to anthropogenic activity. In conclusion, the result of this study demonstrates that the chemical analysis of ancient soils has great applicability in recognizing and understanding ancient anthropogenic activities. While our study demonstrates that the concentration of selected elements is associated with the ancient anthropogenic soil signatures, more research on the relationship between the ancient occupation of Tappe Rivi and soil chemical signature by applying different approaches and also, the complex geologic and anthropogenic processes involved in soil formation is necessary. In addition, a comparative study of various archeological areas in Iran by mapping the distribution of soil elements concentration would further demonstrate the potential use of this approach to identify ancient patterns of human occupation.

In conclusion, as Salisbury (2017) claims, soils are crucial in and around cultural material, and by considering cultural soils and sediments as artifacts, we enable answers to a wide range of new questions about people, production of craft, households, and regional interactions over time. Cultural soil chemistry, alone or in association with geophysical prospection, enables us to undertake studies on the empty areas in sites, where we cannot find any traditional artifacts or visible features. Thus, this could be the same in our study area at the Tappe Rivi, where we can move from empty spaces to cultural spaces.

Acknowledgements We wish to express our gratitude to Dr. Javad Jafari (ICHTO Shiraz & Bojnurd) and Dr. Jan Lentschke (Humboldt Universität Berlin), whose thoughts and comments on the early stages of this work contributed to the development of this manuscript, and Dr. Bahman Kiani for the statistical support.

Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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