



Assessment of potentially toxic metal contents of clay bricks manufactured and utilized as structural building material in Türkiye

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Abstract

Building material waste stored for long periods near agricultural lands and water resources may pose a danger to the environment and human health due to the toxic chemicals and metals they contain. Clay bricks (CBs), generally produced by mixing clay and water, are formed by firing the air-dried mixture to make them durable and stable. During firing, the CB suffers some chemical and physical changes and turns into a new artificial material. CBs, known as masonry units, have been one of the most used building materials throughout the history of construction. CB may naturally contain PTMs depending on the geochemical structure of the clay used in the production phase. In this study, major and minor oxides and PTM distributions in 45 CB samples collected from 31 CB factories that provide approximately one-third of the CB utilized in buildings in Türkiye were determined for the first time using an energy-dispersive X-ray fluorescence spectrometer. The average contents (in %, dry weight) of major and minor oxides in CB samples are in order of SiO₂ (49.9) > Al₂O₃ (17.8) > CaO (9.5) > MgO (8.2) > Fe₂O₃ (7.5) > SO₃ (3.6) > Na₂O (3.3) > K₂O (1.8) > TiO₂ (0.9) > P₂O₅ (0.2) > MnO (0.1). The average contents (in mg/kg dw) of Fe, Ti, Mn, Cr, Sr, V, Ni, Zr, Zn, Cu, Co, Pb, and As in CB samples were analyzed as 52779, 5329, 736, 341, 233, 192, 190, 110, 85, 44, 39, 14, and 8, respectively. According to the enrichment factor results based on the Earth's crust average, it was revealed that Cr, Ni, and As were naturally moderately enriched.

Keywords Clay brick · Potentially toxic metal and metalloid · Major oxides · Enrichment factor · EDXRF

Introduction

The term potentially toxic metal(loid)s (PTMs) is used to collectively refer to a group of metals such as titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe),

cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), zirconium (Zr), mercury (Hg), and lead (Pb), and metalloids, such as germanium (Ge), arsenic (As), antimony (Sb), and tellurium (Te) (Tchounwou et al. 2012; Miletić et al. 2023). The source of PTM pollution, which threatens the environment and human health even at very low concentrations due to its bioaccumulative nature, toxicity, and persistence in the ecosystem, can be both natural (geogenic and lithogenic) and anthropogenic (Ali et al. 2019). An enhanced content of PTMs in the environment, such as rocks, soils, and waters, can take place in connection with natural processes such as volcanic eruptions, weathering of metal-bearing rocks, and acid drainage (Ali et al. 2019; Miletić et al. 2023). Global industrialization, mining, agricultural activities, and urbanization trends around the world have led to an increase in the anthropogenic share of PTMs in the environment (Alloway 2013; Edelstein and Ben-Hur 2018; Ali et al. 2019; Rezapour et al. 2022; Turhan et al. 2023). PTMs can be classified into two groups: essential metals (Cu, Co, Zn, Ni, Fe, Mn, Cr III, etc.), which are required, in trace level, for

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biological physiology and function, and non-essential metals (As, Hg, Pb, Cd, and Cr IV), whose biological functions are unknown (Tchounwou et al. 2012; Khaneghah et al. 2020; Apau et al. 2022; Ding et al. 2022; Kollander et al. 2023). Cr is found in the Earth's crust whose oxidation states range from Cr II to Cr VI, but Cr released into the environment as a result of anthropogenic activity occurs mainly in the Cr VI (Tchounwou et al. 2012). The health hazard associated with exposure to Cr depends on its oxidation state, which ranges from the low toxicity of the metal form to the high toxicity of the hexavalent form (Tchounwou et al. 2012). Accumulation of PTMs in organs causes various chronic and acute diseases affecting the entire system: immune, cardiovascular, endocrine, nervous, skeletal, etc. (Miletić et al. 2023).

The toxicity of these PTMs primarily depends on the concentration, exposure route, exposure frequency, metal form (elemental, ions, and chemical compound), duration, and dose (Tchounwou et al. 2012; Jaishankar et al. 2014; Fashola et al. 2016; Kaur et al. 2021; Ohiagu et al. 2022; Hong et al. 2020). PTMs can enter the human body from different contamination sources through ingestion, inhalation, or dermal absorption, and then bioaccumulate in various organs or target tissues over different periods (Fashola et al. 2016; Peng 2023; Miletić et al. 2023). Each route may have different effects in terms of exposure and health outcomes (Peng 2023). Various toxicological and biological effects of PTMs take place as a result of the different forms in which PTMs exist, and this is also relevant for compounds that vary widely in toxicity (Fashola et al. 2016). The ion forms of some PTMs (As^{3+} , Cd^{2+} , Pb^{2+} , etc.) interact with biological organisms to form relevant toxic compounds, while ligands and oxidized states play important roles in the bioavailability of PTMs (Hong et al. 2020).

The construction industry plays a vital role in the socioeconomic development of any country such as sustainable economy, urbanization, and population growth (Koroneos and Dompros 2007; Arianpour and Arianpour 2022). The construction sector utilizes more building and raw materials by weight than other industrial sectors (Koroneos and Dompros 2007). Nearly 50% of all materials extracted from the Earth's crust are converted into building materials (cement, concrete, gas concrete, clay brick, pumice brick, roofing tile, ceramics marble, granite, limestone, gypsum, etc.) (Koroneos and Dompros 2007). However, construction and demolition waste constitutes a large building material waste stream and poses significant environmental impacts because these wastes can contain high levels of natural radionuclides and heavy metals. Therefore, the disposal and recycling of these waste materials present great difficulties (Koroneos and Dompros 2007). There has been a sustainable increase in urbanization and population growth in Türkiye in the last decades. The Turkish construction sector is one of the most important industrial sectors and a crucial motivating

supporter of these social developments. There is an increase in the building stock due to the increasing demands of the construction sector. In Türkiye, the number of apartments issued with building permits was 319,720 in 2019 and reached 695,804 in 2022 (TÜİK 2024). As it is known, Türkiye is a country prone to earthquakes. Türkiye's location on the border of the Eurasian and African plates makes it a seismically active region. On February 6, 2023, southeastern Türkiye was shaken by two major earthquakes that devastated 11 provinces (Mavroulis et al. 2023). Tens of thousands of buildings collapsed, including newly built apartment buildings, and many more were later demolished (Mavroulis et al. 2023). As a result of these demolitions, thousands of tons of building material wastes and debris containing toxic chemicals and PTMs were generated. Unfortunately, several earthquake debris disposal sites in these provinces operated in or near agricultural areas and surface water bodies (Mavroulis et al. 2023). Also, this pollution can be carried by water and wind and reach areas far from the pollution source or remain as waste. PTM contents in soil may be high at greater distances from the main source. This situation can pose serious threats to public health and the environment. Considering the possibility of earthquake debris consisting of broken, fragmented, and pulverized building materials stored near agricultural lands and water resources being left for years, the knowledge of the PTM contents in the building materials is important to obtain preliminary information about the potential risks that may arise from the spread of these clouds of dust to cultivated areas and water resources by wind and to raise awareness on this issue.

Brick, generally known as a clay-based masonry unit, is one of the most used building materials throughout the history of construction due to their durability and high compressive strength and is mainly used in the construction of external and internal walls of buildings (Mavroulis et al. 2023; Lachheb et al. 2023). Brick is manufactured by firing a mixture of soil-based raw materials such as clay, silt, and sand at 800–1200 °C. Approximately 340 billion tons of clay are utilized worldwide every year for brick production (Aakash 2014). The Turkish clay industry has been growing since 1990 due to the high demands of the domestic building markets (Arianpour and Arianpour 2022). A total of 28 billion CBs were produced between 2018 and 2022, and approximately 5.6 billion CBs are produced annually in Türkiye (İMSAD 2022). To date, many studies on the energy consumption, usage, and carbon emissions of brick production have been published in the literature (Darain et al. 2013; Kumbhar et al. 2014; Yüksek et al. 2020; Rehman et al. 2020; Xin et al. 2023). However, there is a lack of comprehensive studies on the determination of PTM contents in CB samples, whereas broken, fragmented, and powdered CB waste from brick factories and demolished buildings may contain high amounts of PTMs. The presence of elevated

PTM contents in the environment can pose a serious health problem due to their non-destructive nature, which makes them persistent and therefore can create long-term effects on the ecosystem. Therefore, it is important to investigate the PTM levels in CBs to (1) assess the potential risks that may arise from inhalation of brick dust by workers working in the brick production line, (2) establish awareness and regulations regarding the appropriate storage of earthquake debris or collapsed building wastes, and (3) determine the extent by the content of PTM that abandoned brick factories may produce. The purposes of this study are to (i) determine the contents of major and minor oxides and PTMs in CB samples collected from 31 CB factories using an energy dispersive X-ray fluorescence (EDXRF) spectrometry and (ii) calculate enrichment ratio (to clay average) and enrichment factor (to Earth's crustal average) of the PTMs. The novelty of this study is that it is the first attempt to raise awareness about the presence of PTMs accompanying CBs, one of the most used building materials, and to create a database on PTM distributions of brick kilns in the Western Black Sea Region of Türkiye.

Materials and methods

Collection, preparation, and analysis of sample

The CB factories where the samples within the scope of this study were collected are located in the Boyabat district of Sinop province and Tosya district of Kastamonu province in the Western Black Sea Region of Türkiye. Boyabat basin is located in the middle part of the Pontide tectonic belt, one of the tectonic units of Türkiye, and was established within the tertiary aged depression area (Ustaömer et al. 2007). Thick subduction-accretion complexes consisting of ocean floor sediments and basic magmatic rocks in this basin developed during the closure of the Paleo-tethys and Neotethys oceans (Ustaömer et al. 2007). In the basin, in addition to the alluviums formed by the Gökırmak depression, clayey limestone (marl) observed in the raw material area, there are also conglomerate, sandstone, and mudstone units deposited in different periods (Ustaömer et al. 2007). Tosya and its immediate surroundings are located in the North Anatolian Fault Zone, one of the important tectonic areas of Türkiye. There is Devrez depression (Devrez Stream) formed due to this fault. Alluviums at the bottom of the Devrez depression extend throughout the valley. The raw material area is within the Pliocene lacustrine storage area.

Forty-five CB samples and seven clay samples were collected from 31 CB plants and clay quarry, the locations of which are shown on the map in Fig. 1. Samples were brought to the sample preparation laboratory in plastic bags. Following the procedure for preparing the sample mentioned in the

references (Turhan et al. 2020, 2022; Altıkulaç et al. 2022; Altıkulaç and Turhan 2023), CBs were crushed and powdered to fit the calibrated powder geometry in the EDXRF spectrometer. Each CB sample was dried at 110 °C in an oven for 10 h. Analysis of major and minor oxides and PTMs in CB and clay samples was performed using an EDXRF spectrometer (Spectro Xepos, Ametek) with a thick binary Pd/Co alloy anode X-ray tube (50 kV, 60 W), the properties of which were detailed in previous studies (Turhan et al. 2020, 2022; Altıkulaç et al. 2022; Altıkulaç and Turhan 2023). NIST SRM 2709 reference material was utilized for quality assurance of the EDXRF spectrometer (Turhan et al. 2020). CB samples were placed in the automatic sampler and counted once for 2 h and then analysis processes were completed. The overall uncertainty (%) of Fe, Ti, Sr, Mn, Cr, Zn, Ni, Cu, Zr, V, Pb, As, and Co was found as 0.1, 0.2, 0.2, 0.3, 0.4, 0.6, 0.8, 1.2, 1.2, 2.1, 2.8, 3.3, and 9.8, respectively.

Enrichment ratio and enrichment factor

The enrichment ratio (ER) for PTM analyzed in CB samples was calculated using the following formula:

$$ER = \frac{(C_{PTM})_{CB}}{(C_{PTM})_{Clay}} \quad (1)$$

where C_{PTM} is the content of PTM analyzed in CB and clay samples. The enrichment factor (EF) is an index used to assess the level of enrichment or pollution and to infer the distribution of metals of anthropogenic origin from locations determined by individual metals in environmental samples (Parvez et al. 2023). EF is calculated using the following formula (Kowalska et al. 2018; Turhan et al. 2020):

$$EF = \frac{(C_n/C_{Ref})_{CB}}{(C_n/C_{Ref})_{Earth}} \quad (2)$$

where C_n and C_{Ref} are the content of PTM and reference element in the CB sample and geochemical background (Earth's crustal), respectively. In the EF calculations, aluminum (Al) was taken as a reference element. Al has no important anthropogenic input compared to the major geogenic element, and Al's ion potential is close to target elements, reducing variation in comparison (Bourennane et al. 2010; Poh and Tahi 2017). EF values close to unity represent the crustal origin of the PTMs (comparable to Earth's crust); $EF < 1$ represents a possible mobilization or depletion of PTMs; $EF > 1$ represents that the PTM is of anthropogenic origin. Therefore, EF values of 1–2 are considered slightly enriched; conversely, $2 \leq EF < 5$ is moderately enriched, $5 \leq EF < 20$ is severely enriched, $20 \leq EF < 40$ is highly

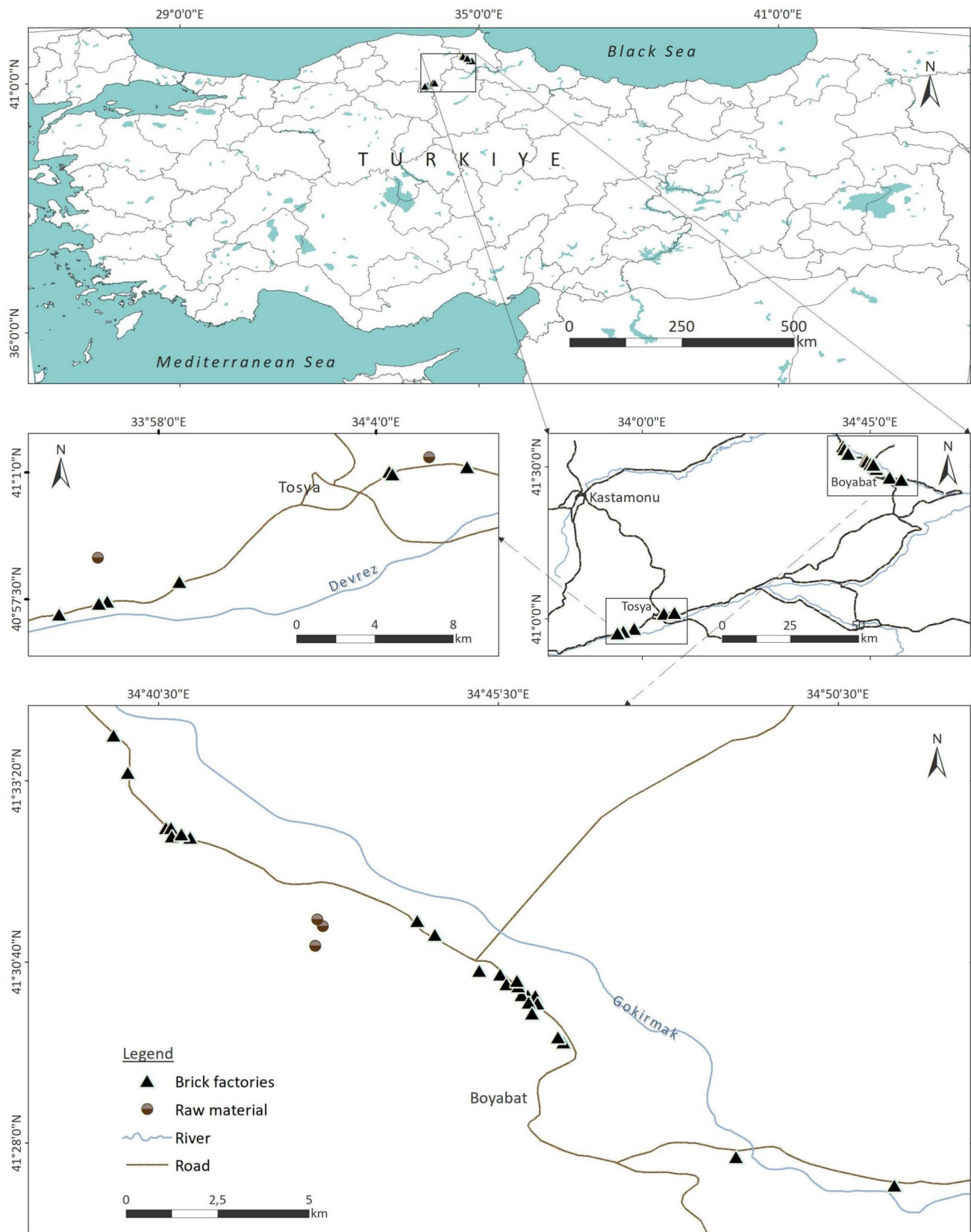


Fig. 1 Geological map of locations of CB factories and clay quarry

enriched, and $EF \geq 40$ is extremely highly enriched (Turhan et al. 2020; Parvez et al. 2023).

Statistical analysis

Statistical analysis was conducted to assess data distribution, variance homogeneity, and potential differences. The Shapiro–Wilk and Bartlett tests were used to confirm the data distribution and variance homogeneity, respectively. The results of these tests indicated that most of the data did not conform to the normal distribution and/or exhibit variance homogeneity. Thus, logarithmic transformation was applied to the dataset to address the challenges of non-normality and variance heterogeneity and to compare the data on the same scale.

After applying the logarithmic transformation, the data were re-assessed using the Shapiro–Wilk and Bartlett tests. However, some of the transformed data still exhibited deviations from normality or lacked homogeneity of variances. Therefore, the Kruskal–Wallis test was performed to investigate potential differences, and subsequent pairwise Wilcoxon rank-sum tests were conducted to identify significant differences. All statistical analyses were conducted using R studio version 2023.06 (R Core Team 2022).

Results and discussion

The distribution of major and minor oxides analyzed in the CB samples is shown in Fig. 2. The contents (in dry weight, dw) of SiO_2 , Al_2O_3 , CaO , MgO , Fe_2O_3 , SO_3 , Na_2O , K_2O , TiO_2 , P_2O_5 , and MnO varied from 46.7 to 52.9%, 14.9 to

20.3%, 7.0 to 12.8%, 6.7 to 18.0%, 5.4 to 11.1%, 0.5 to 6.7%, 2.4 to 4.0%, 1.0 to 2.1%, 0.6 to 1.7%, 0.1 to 0.3%, and 0.1 to 0.2%, respectively. The average contents of Al_2O_3 , CaO , MgO , Fe_2O_3 , SO_3 , Na_2O , and K_2O are higher than the average contents of 15.9%, 9.4%, 5.4%, 1.1%, 0.1%, 2.7%, and 1.1% in Earth's crust, respectively (Yaroshevsky 2006).

PTM content (in mg/kg dw) of each CB sample and some descriptive statistical data of PTMs analyzed in all CB samples are given in Table 1. The frequency distribution of the content of PTMs is shown in Fig. 3. From Table 1, the average PTM contents are ranked in descending order as follows: $Fe > Ti > Mn > Cr > Sr > V > Ni > Zr > Zn > Cu > Co > Pb > As$. Both from Fig. 3 and the results of the Shapiro–Wilk test, it can be proposed that the content distributions of V, Cr, Co, Ni, Zn, Sr, Zr, and Pb in all clay bricks exhibit a normal distribution ($p > 0.05$), while Ti, Mn, Fe, Cu, and As have a non-normal distribution ($p < 0.05$). According to the Bartlett test, most data did not present variance heterogeneity. Thus, a logarithmic transformation was applied to the data. The difference between PTMs in the CB samples is given in Fig. 4. The result of the Kruskal–Wallis test showed that the content of at least one PTM found in samples was different than others ($p < 2.2 \times 10^{-16}$). Wilcoxon rank-sum tests presented that the Co–Cu and V–Ni contents were similar in all CB samples ($p > 0.05$), while the rest of the PTMs differed ($p < 0.05$).

Fe is an abundant metal on Earth and a biologically essential micronutrient for every living organism. Fe overload can increase the risk of liver and heart diseases (Turhan et al. 2023). The contents of Fe in the CB samples varied from 37,510 (CB27) to 77,420 (CB43) mg/kg with an average value of 52,779 mg/kg, which is higher than the Earth's crust average of 46,500 mg/kg (Yaroshevsky 2006). The average values of ER and EF calculated for Fe are 1.10 and 0.98, respectively. The average ER value shows that Fe in CB is 10% more enriched than in clay, while the average EF value indicates that Fe is comparable to the Earth's crust. Ti has low toxicity, and inhalation of dust with Ti may cause chest tightness and pain, cough, and difficulty breathing. Contact with skin or eyes may irritate. The contents of Ti in the CB samples varied from 3639 (CB19) to 10,220 (CB43) mg/kg with an average value of 5329 mg/kg. The average Ti content is higher than the Earth's crust average of 4500 mg/kg (Yaroshevsky 2006). The average values of ER and EF calculated for Ti are 0.90 and 1.03, respectively. The average EF value indicates that Ti is comparable to the Earth's crust. Mn is classified as Group 4—probably not carcinogenic by the International Agency for Research on Cancer (IARC) (Briffa et al. 2020). Mn is both essential and toxic. Adverse health effects can result from inadequate intake or excessive exposure (Turhan et al. 2023). Mn compounds occur naturally in the environment as solids in soils and small particles in water. Industrial activities increase Mn concentrations in

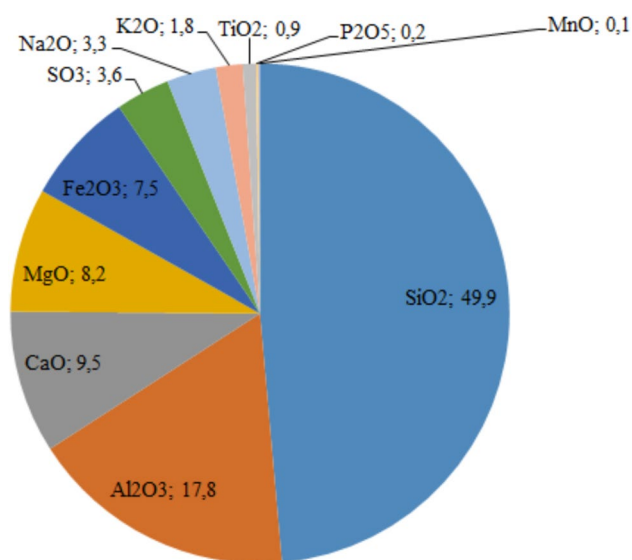


Fig. 2 Major and mineral oxides of CB samples in percentage

Table 1 The content and some descriptive statistics data of potentially toxic metals in clay brick samples

Sample code	PTM contents (mg/kg dw)												
	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Sr	Zr	Pb
CB1	4412.0	184.1	296.9	634.2	49,810.0	29.7	171.5	39.7	77.3	5.1	233.3	92.1	12.8
CB2	4770.0	172.2	324.4	687.8	49,240.0	36.7	186.1	39.4	85.4	8.7	265.5	114.7	15.8
CB3	3747.0	141.0	243.6	576.6	38,230.0	28.5	135.9	28.9	62.5	4.8	193.4	80.0	12.5
CB4	4717.0	176.9	341.8	600.3	47,350.0	33.9	165.1	34.5	76.5	8.2	199.1	117.0	12.2
CB5	3842.0	144.3	295.4	557.7	38,910.0	21.3	147.6	26.8	62.4	6.8	171.6	78.8	12.8
CB6	4784.0	201.2	377.0	655.8	54,570.0	33.1	212.0	41.3	105.8	7.3	249.4	100.2	14.0
CB7	4682.0	180.3	313.5	688.5	49,460.0	42.0	194.8	40.7	84.9	7.5	259.7	106.5	15.7
CB8	3942.0	157.3	260.2	554.9	41,000.0	25.5	137.3	31.4	63.2	5.2	153.1	80.1	12.3
CB9	5062.0	202.0	351.3	687.8	54,170.0	37.4	206.4	42.6	92.7	6.6	263.5	117.8	17.7
CB10	4918.0	193.4	357.6	655.5	50,420.0	37.7	187.9	40.2	87.4	11.2	201.5	122.4	15.2
CB11	4925.0	219.5	360.1	682.0	55,550.0	36.7	214.3	42.8	90.6	10.4	257.8	101.2	13.9
CB12	5213.0	230.8	350.8	754.0	58,780.0	37.2	208.2	49.8	93.7	7.0	323.7	105.7	15.9
CB13	5053.0	199.7	355.5	670.6	52,910.0	43.1	201.0	45.0	90.3	5.9	218.5	123.7	17.3
CB14	4780.0	166.4	386.2	795.2	48,780.0	50.4	212.2	40.6	90.0	11.9	290.8	124.0	17.4
CB15	5233.0	216.0	382.9	682.8	56,690.0	38.9	216.4	43.0	92.3	6.4	281.0	115.6	14.9
CB16	4766.0	207.2	337.4	653.4	54,260.0	35.5	200.6	41.4	88.9	6.1	234.8	94.8	14.6
CB17	5210.0	197.8	382.4	694.7	54,480.0	45.7	201.9	46.5	96.1	7.9	229.7	128.2	17.2
CB18	5558.0	237.3	413.4	742.6	60,500.0	56.4	244.7	50.3	104.5	6.8	267.9	128.5	19.5
CB19	3639.0	146.5	308.5	556.5	39,900.0	29.4	159.3	31.9	59.0	14.9	170.9	78.5	11.1
CB20	4646.0	181.5	418.8	663.1	48,170.0	40.6	206.5	38.6	81.0	9.7	207.8	114.0	15.0
CB21	5173.0	203.0	361.6	698.8	54,810.0	43.8	212.5	45.5	93.1	6.2	257.7	116.0	17.9
CB22	5158.0	227.1	359.9	720.2	58,320.0	39.5	225.6	45.7	96.9	8.1	264.6	105.9	15.5
CB23	4328.0	178.9	308.0	551.4	46,980.0	31.2	169.3	34.1	73.0	5.8	212.1	95.4	12.4
CB24	3949.0	160.1	305.3	528.5	42,130.0	34.3	146.1	31.0	64.6	7.4	148.7	81.2	10.9
CB25	4732.0	207.5	365.5	682.5	53,300.0	39.7	195.0	44.2	83.9	4.8	283.5	100.7	13.7
CB26	4673.0	185.9	310.3	661.6	48,310.0	35.9	168.4	38.6	82.3	7.4	224.9	113.5	14.7
CB27	3719.0	152.8	252.3	498.3	37,510.0	27.8	128.7	28.5	59.1	4.3	149.8	83.8	11.3
CB28	5578.0	227.4	352.5	742.5	60,620.0	45.0	220.3	51.2	101.7	6.2	249.7	132.3	17.9
CB29	4925.0	213.3	342.6	652.9	54,430.0	39.9	202.6	44.6	91.3	6.6	222.4	108.6	17.0
CB30	5183.0	203.5	385.9	708.7	53,760.0	38.7	203.9	46.6	93.2	9.8	196.7	135.5	16.9
CB31	4629.0	180.6	361.6	594.9	47,270.0	43.3	180.0	37.7	76.6	6.2	186.3	115.1	13.4
CB32	4950.0	197.0	325.8	654.6	50,670.0	34.2	173.1	39.1	86.5	7.5	214.5	119.5	15.2
CB33	4902.0	193.6	405.7	637.8	51,030.0	35.8	201.4	43.1	87.2	13.5	201.4	119.1	14.8
CB34	4942.0	203.4	341.2	599.0	52,510.0	44.8	186.7	40.6	84.2	6.1	253.6	107.5	14.6
CB35	3842.0	162.1	270.5	511.8	40,790.0	26.7	140.8	28.6	62.8	3.5	166.5	75.1	11.8
CB36	4444.0	166.0	323.5	693.7	44,940.0	35.2	182.1	37.0	84.1	8.5	283.0	113.6	16.9
CB37	5082.0	211.1	350.4	662.8	54,160.0	36.1	194.4	41.3	88.2	6.5	256.3	115.7	15.3
CB38	5053.0	199.7	355.5	670.6	52,910.0	43.1	201.0	45.0	90.3	5.9	218.5	123.7	17.3
CB39	8028.0	206.9	324.4	1166.0	64,850.0	43.5	188.2	65.5	93.3	10.4	286.1	137.7	14.5
CB40	9235.0	214.7	289.8	1236.0	68,890.0	45.2	175.8	72.2	97.9	7.5	302.7	125.4	11.8
CB41	8933.0	184.8	304.0	1049.0	60,830.0	44.0	159.2	58.8	75.5	5.7	231.3	93.7	7.7
CB42	9231.0	220.7	439.6	1438.0	75,940.0	58.5	270.4	81.6	109.8	8.5	265.6	155.3	16.8
CB43	10,220.0	216.7	299.1	1319.0	77,420.0	55.4	201.7	80.2	117.5	13.2	305.3	166.4	14.7
CB44	8421.0	191.0	381.5	1207.0	65,070.0	46.4	216.1	65.7	85.3	7.6	219.7	120.6	10.9
CB45	6571.0	173.5	358.0	1037.0	54,430.0	41.0	187.8	50.4	68.3	3.5	193.5	86.9	9.5
Average	5328.9	191.9	340.7	735.9	52,779.1	38.9	189.8	44.3	85.1	7.5	232.6	110.5	14.5
Median	4925.0	197.0	350.4	670.6	52,910.0	38.7	194.8	41.4	87.2	7.0	231.3	114.0	14.7
SD	1580.1	24.4	43.7	220.8	8861.4	7.9	29.1	12.4	13.7	2.5	43.9	20.1	2.5

Table 1 (continued)

Sample code	PTM contents (mg/kg dw)												
	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Sr	Zr	Pb
SE	235.5	3.6	6.5	32.9	1321.0	1.2	4.3	1.9	2.0	0.4	6.6	3.0	0.4
Kurtosis	1.8	−0.3	−0.1	1.8	0.7	0.3	0.0	1.4	−0.2	1.1	−0.1	0.3	−0.4
Skewness	2.6	−0.6	−0.1	2.7	1.0	0.5	0.5	2.3	−0.1	1.2	−0.7	0.4	−0.1
Min	3639.0	141.0	243.6	498.3	37,510.0	21.3	128.7	26.8	59.0	3.5	148.7	75.1	7.7
Max	10,220.0	237.3	439.6	1438.0	77,420.0	58.5	270.4	81.6	117.5	14.9	323.7	166.4	19.5

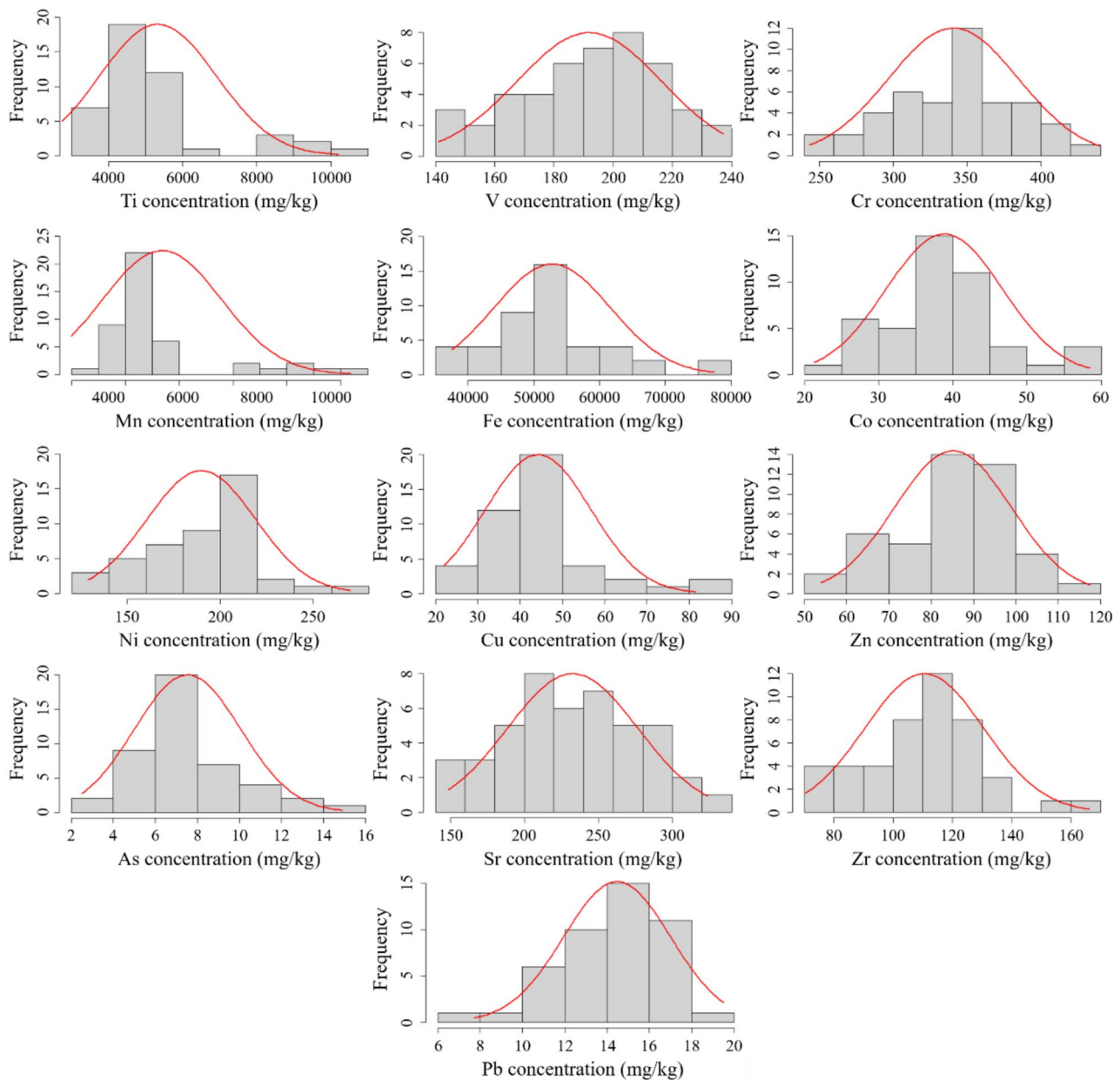
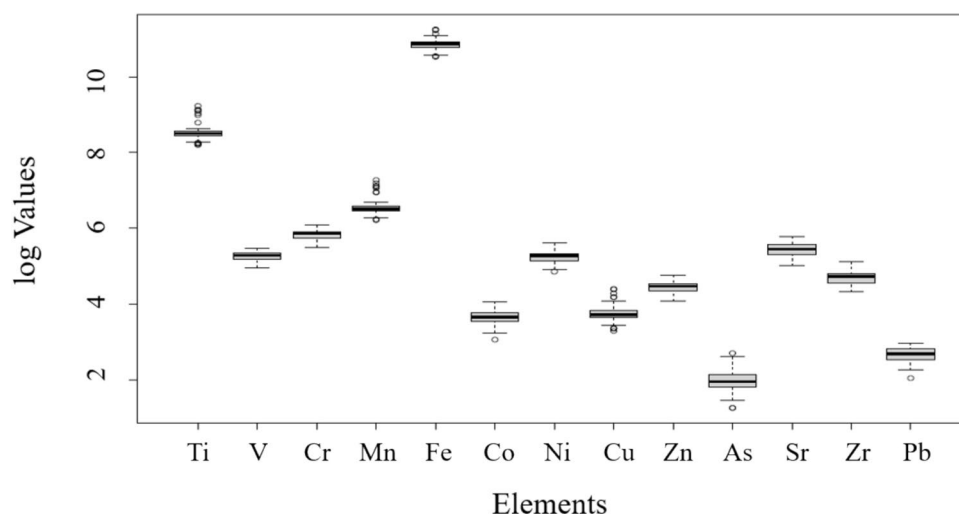
**Fig. 3** Frequency distributions of PTM contents in CB samples

Fig. 4 Boxplot for PTMs in CB samples



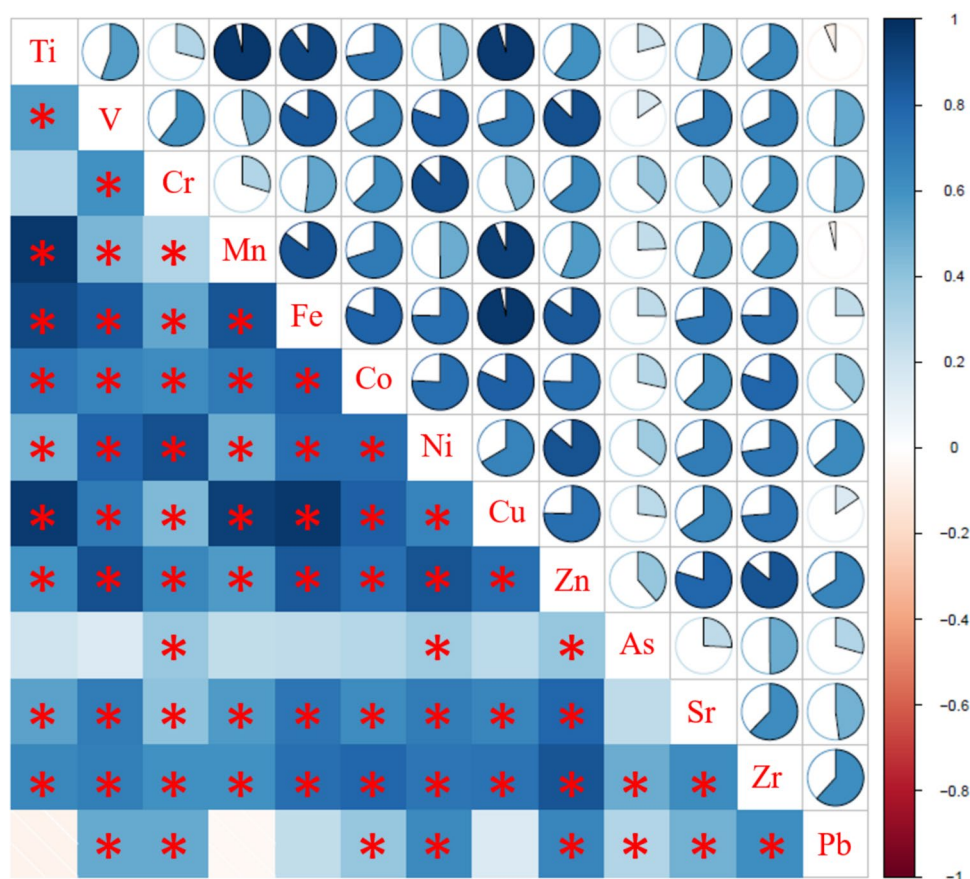
surface water, groundwater, and air. The contents of Mn in the CB samples varied from 498 (CB27) to 1438 (CB42) mg/kg with an average value of 736 mg/kg. The average Mn content is lower than the Earth's crust average of 1000 mg/kg (Yaroshevsky 2006). The average values of ER and EF calculated for Mn are 0.86 and 0.64, respectively. The average EF value indicates possible mobilization or depletion of Mn. Cr VI compounds are classified as Group 1—human carcinogen by the IARC and can damage biological regularities (Briffa et al. 2020; Turhan et al. 2023). The contents of Cr in the CB samples varied from 244 (CB3) to 440 (CB42) mg/kg with an average value of 341 mg/kg. The average Cr content is 4 times higher than the Earth's crust average of 83 mg/kg (Yaroshevsky 2006). The average values of ER and EF calculated for Cr are 0.78 and 3.55, respectively. The average EF value indicates moderate enrichment of Cr. The contents of Sr in the CB samples varied from 149 (CB24) to 324 (CB12) mg/kg with an average value of 233 mg/kg, which is lower than the Earth's crust average of 340 mg/kg (Yaroshevsky 2006). The average values of ER and EF calculated for Sr are 1.17 and 0.59, respectively. The average ER value shows that Sr in CB is approximately 20% more enriched than in clay, while the average EF value indicates possible mobilization or depletion of Sr. V compounds have low toxicity and are not carcinogenic (Briffa et al. 2020). While V compounds that can be dissolved in the lungs are well absorbed, V salts are not easily absorbed in the stomach and intestines (Briffa et al. 2020). If V is taken in large amounts, it can have many effects on human health. If V is taken in by air, it can cause bronchitis and pneumonia. Irritation in the lungs, throat, eyes, and nasal cavity is the most severe effect of V (Briffa et al. 2020). The contents of V in the CB samples varied from 141 (CB3) to 237 (CB18) mg/kg with an average value of 192 mg/kg, which is 2 times higher than the Earth's crust average of 90 mg/kg (Yaroshevsky 2006). The average values of ER and EF calculated

for V are 1.19 and 1.84, respectively. The average ER value shows that V in CB is 20% more enriched than in clay, while the average EF value indicates a slight enrichment of V. Ni is a compound that is found only at very low levels in the environment. The majority of all Ni compounds released into the environment will be adsorbed to soil and sediment and will eventually become immobile. However, in acidic soils, Ni will inevitably become more mobile and will generally leach into groundwater. The contents of Ni in the CB samples varied from 129 (CB27) to 270 (CB42) mg/kg with an average value of 190 mg/kg, which is approximately 3 times higher than the Earth's crust average of 58 mg/kg (Yaroshevsky 2006). The average values of ER and EF calculated for Ni are 1.11 and 2.83, respectively. The average ER value shows that Ni in CB is 10% more enriched than in clay, while the average EF value indicates moderate enrichment of Ni. Zr and its salts generally have low systemic toxicity. The contents of Zr in the CB samples varied from 75 (CB35) to 166 (CB43) mg/kg with an average value of 110 mg/kg, which is lower than the Earth's crust average of 170 mg/kg (Yaroshevsky 2006). The average values of ER and EF calculated for Zr are 1.14 and 0.56, respectively. The average ER value shows that Zr in CB is approximately 10% more enriched than in clay, while the average EF value indicates possible mobilization or depletion of Zr. Zn is classified as Group 4—probably not carcinogenic (Briffa et al. 2020). Zn occurs naturally in soil, air, and water, but Zn concentrations are increasing unnaturally due to industrial activities such as mining, coal and waste burning, and steel processing. The contents of Zn in the CB samples varied from 59 (CB27) to 118 (CB43) mg/kg with an average value of 85 mg/kg, which is slightly higher than the Earth's crust average of 83 mg/kg (Yaroshevsky 2006). The average values of ER and EF calculated for Zn are 1.17 and 0.89, respectively. The average ER value shows that Zn in CB is approximately 20% more enriched than in clay, while the

average EF value indicates possible mobilization or depletion of Zn. Cu is one of the essential trace elements required for the proper functioning of organs and metabolic parts (Turhan et al. 2023). However, very high intakes of Cu have adverse effects on the major organs such as the heart, brain, and kidneys (Turhan et al. 2023). Cu is often found near mines, industrial environments, water disposal, and landfills (Briffa et al. 2020). Most Cu compounds precipitate and bind to water sediment or soil particles. Soluble Cu compounds pose the greatest threat to human health. Water-soluble Cu compounds typically form in the environment after release through agricultural applications (Briffa et al. 2020). The contents of Cu in the CB samples varied from 27 (CB5) to 82 (CB42) mg/kg with an average value of 44 mg/kg, which is slightly lower than the Earth's crust average of 47 mg/kg (Yaroshevsky 2006). The average values of ER and EF calculated for Cu are 1.19 and 0.82, respectively. The average ER value shows that Cu in CB is approximately 20% more enriched than in clay, while the average EF value indicates possible mobilization or depletion of Cu. Co is classified as Group 2B—possibly carcinogenic (Briffa et al. 2020). Co is a naturally occurring element in soil, water, air, rocks, plants, and animals. It can also enter the air and water, settle on land via windblown dust, and become contaminated with surface water when rainwater passes through soil and rock

containing Co. Human activities such as mining, coal burning, processing Co-containing ores, and the production and use of Co chemicals increase the amount of Co in the atmosphere. The contents of Co in the CB samples varied from 21 (CB5) to 59 (CB42) mg/kg with an average value of 39 mg/kg, which is approximately 2 times higher than the Earth's crust average of 18 mg/kg (Yaroshevsky 2006). The average values of ER and EF calculated for Co are 1.09 and 1.87, respectively. The average ER value shows that Co in CB is approximately 10% more enriched than in clay, while the average EF value indicates slight enrichment of Co. Pb is classified as Group 2B—possibly carcinogenic by the IARC—and is a frequently encountered heavy metal in the environment (Briffa et al. 2020). During mining, smelting, refining, production processes, and the use of Pb, including commodities, lead may remain in the atmosphere. Bioaccumulation of Pb in the human body can cause serious diseases throughout life (Turhan et al. 2023). The contents of Pb in the CB samples varied from 8 (CB41) to 20 (CB18) mg/kg with an average value of 14 mg/kg, which is slightly lower than the Earth's crust average of 16 mg/kg (Yaroshevsky 2006). The average values of ER and EF calculated for Pb are 1.16 and 0.78, respectively. The average ER value shows that Pb in CB is approximately 20% more enriched than in clay, while the average EF value indicates possible

Fig. 5 Correlogram plot on PTMs in CB samples. Asterisk (*) denotes a statistically significant correlation ($p < 0.05$)



mobilization or depletion of Pb. As and inorganic As compounds are classified as Group 1—human carcinogens by the IARC (Briffa et al. 2020). Humans can be exposed to arsenic through dermal contact with As-containing soil or water, or the air and food chain. The contents of As in the CB samples varied from 4 (CB45) to 15 (CB19) mg/kg with an average value of 8 mg/kg, which is approximately 5 times higher than the Earth's crust average of 1.7 mg/kg (Yaroshovsky 2006). The average values of ER and EF calculated for As are 1.43 and 3.83, respectively. The average ER value shows that As in CB is approximately 40% more enriched than in clay, while the average EF value indicates moderate enrichment of As.

In addition, the correlation coefficients were calculated for PTM contents in CB samples to investigate potential relationships. The results are presented in the correlogram given in Fig. 5. The correlogram shows some significant correlations between PTM contents in CB samples. The correlation test reveals significant correlations between most PTM contents in CB samples, with one remarkable exception of As content in CB samples. This could mean that As contamination may have different sources or causes of contamination compared to others, leading to weaker correlations.

Conclusion

In this study, the PTM (Fe, Ti, Mn, Cr, Sr, V, Ni, Zr, Zn, Cu, Co, Pb, and As) contents of the CB samples manufactured and utilized as a building material in Türkiye were studied for the first time in detail. As a result of the study, it was observed that (i) almost all PTMs analyzed in CB samples, except Ti, Mn, and Cr, were naturally enriched according to the clay raw material used in CB production, and (ii) Cr, As, and Ni analyzed in CB samples were found to be at moderate levels compared to the Earth's crust average. However, this study is a preliminary study that creates awareness about the potential contribution of building materials to environmental pollution. To fully evaluate the possible risks of PTMs analyzed in the CB samples, leakage tests should be carried out, and the content of the released samples should be analyzed in depth.

The PTM content values in CBs obtained in this study will constitute a guiding information and database for the future, both for earthquake waste management and for regulations to be prepared regarding the production, transportation, and use of these materials. To eliminate situations that may threaten the health of workers, it must be mandatory to take necessary precautions, such as preventing workers from breathing brick dust.

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Author contribution Turhan was leading the research project on the assessment of potentially toxic metal of clay brick samples. Turhan, Duran, Bakır, Haçerlioğulları, Kurnaz, and Ünal collected the samples and made them ready for analysis. Turhan and Altuner performed the statistical analyses. Turhan evaluated the data and wrote the manuscript. All authors read and finalized the manuscript.

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