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Geophagic Materials Characterization and Potential Impact on Human Health: The Case Study of Maputo City (Mozambique)

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Abstract: This study aims to characterize and estimate risk assessment associated with geophagic materials consumption in Maputo city (Mozambique). Samples were collected in extraction mines, unprepared and prepared ones, and in Maputo markets. Fractions < 2 mm (total consumed material) and <63 μm were analyzed to determine pH, EC, OM, chemical composition (XRF), and mineral phases present (XRD). The results revealed pH from slightly acidic to slightly alkaline, and electrical conductivity ranging from 13 to 47 μS/cm in mine unprepared and prepared samples, while 264–465 μS/cm in sampled sold in markets. Organic matter content was <2.76%, except in one sample (8.14%), suggesting a potential risk of containing bacteria. Textural analysis revealed that sand-size particles were more representative in all samples (57.2–93.02%). Mineralogical phases identified in the consumed sample were ranked quartz (>60%) > Fe oxides/hidroxides > phyllosilicates (micas and kaolinite) > feldspars, suggesting a risk of dental enamel damage and perforation of the sigmoid colon. The chemical concentration of some elements was higher than recommended daily dose, suggesting a potential risk. However, geophagic materials' chemical composition does not pose a carcinogenic risk.

Keywords: geophagy; geochemistry; mineralogy; risk assessment; Maputo city

1. Introduction

The intake of minerals and chemical elements for food, water, soil (through geophagy), or dust can be accomplished by ingestion, inhalation, and/or dermal absorption [1]. Geophagy is a practice characterized by the consumption of earthy materials, particularly soils and clays, both by humans and animals [2,3]. The practice is as old as mankind and was commonly regarded as magical and superstitious, hence the desire for its prevention and therapy for those indulged in its habit [4]. Geophagists' motivations are diverse, e.g., cultural/social, medicinal, nutritional, spiritual, religious, and physiological [5]. Although associated with pregnant and lactating women, the practice is also reported in children, adolescents, and young people, transversal to religious beliefs, culture, and socioeconomic classes [6,7]. Geophagy can also occur by involuntary ingestion, mostly associated with children and their deliberate hand-to-mouth activities, but can also occur by pica behavior, i.e., voluntary ingestion of soil materials [8,9]. Pica behavior has been reported worldwide, e.g., in Indonesia [10] and Turkey [11], although the highest prevalence occurs in African and tropical latitudes countries [12–14]. Childhood and pregnancy, especially early pregnancy, which is the critical period of organogenesis [15], are the periods when pica behavior would most likely occur [16].

In diverse African countries, there are societal-cultural groups that consider the practice of geophagy by pregnant women a promoting factor for the dark skin pigment in infants [17]. The Chaggas people (Tanzania) consider geophagy sacred for women [18];

in South Africa, it is common for women to associate soil ingestion with aesthetic benefits [19]. Several studies reported that geophagic practices are prevalent in pregnant women (e.g., Refs. [8,9]), especially in African countries such as Kenya, Ghana, Rwanda, Nigeria, Tanzania, and South Africa. Studies suggested that the portion of geophagic materials consumed daily by pregnant women is variable according to regional and cultural heritage, e.g., in western Kenya, the daily amount is ~40 g [20]. In Ghana, daily consumption of ~70 g was estimated [21]. In South Africa, pregnant women consume ~90 g per day, and non-pregnant women consume 40–60 g [22].

The practice of geophagy can induce adverse health effects, varying not only with the amount of material consumed but also their physical, chemical, mineralogical, and morphological properties [18,23]. Geophagic materials can be a source of potentially toxic elements (PTEs), such as As, Pb, and Hg; bacteria; fungus; and parasites that can induce infections and other health outcomes [24]. Many studies suggested that geophagic material PTEs contamination sources can be diverse [20], e.g., in African markets, usually open-air, anthropogenic activities such as industry [25] and traffic-related emissions [26,27], have been associated with PTEs enrichment of geophagic materials [23]. This occurs especially in dry and relatively high temperatures environments, with PTEs suspension and deposition [28,29]. High concentrations of PTEs can induce neurotoxic effects, which are critical in prenatal, neurodegenerative diseases, and cancer [2,9]. Red clays are considered to have properties that might prevent iron deficiency anemia due to their high iron content. Previous studies suggested ingestion of red soils to alleviate symptoms of Fe deficiency, anemia, and nausea in pregnant women [30,31]. A study conducted in Guatemala suggested that geophagic materials have been used to provide 17–55% of pregnancy supplements, such as Ca, Mg, Zn, Fe, Cu, Mn, Se, K, Ni, and Co [32]. Studies conducted by [2,24] described that the presence of minerals with coarse and angular morphology could cause damage to tooth enamel and the gastrointestinal tract, including perforation of the sigmoid colon. Different natural, earthy materials were used for the practice of geophagy, varying in their physical, mineralogical, and chemical characteristics [33]. Among the different earthy materials consumed, clay materials are the most consumed owing the fine particle size and the presence of mineral aggregates [34,35].

Geophagic practices in Mozambique are common among pregnant women and young people. It is believed that the consumption of these materials shows that women are indeed pregnant. A study reported by the newspaper Savana in 2010 and published on 11 June 2022 states that geophagy is practiced by people of all ages in the city of Maputo, and the causes of this practice are not consensual among the practicing population (consumption by taste, imitation, uncontrollable desire) [36]. The same study showed that the practice of geophagy leads to gastrointestinal diseases, diarrhea, and urinary infections due to high rates of contamination of the materials by fecal coliforms. Informal conversations with geophagic materials vendors and consumers revealed that geophagic materials trading in Maputo markets is widespread, with characteristic material preferences clearly identified. A preference for red clays is related to anemia prevention, a custom outcome during pregnancy. According to [37] reported that in Mozambique, geophagic practices are a problem that can cause chronic origin malnutrition in pregnant women and children, including gastrointestinal diseases and anemia. In Maputo City, studies suggested that up to 25% of women of reproductive age and children suffer from malnutrition associated with the consumption of non-nutritional substances, such as soils, and charcoal, often contaminated with parasites that cause intestinal diseases, e.g., *G. duodenales, Shigella*/EIECE [38]. The present study aims to analyze and characterize geophagic materials extracted from Bobole/Maputo mines and materials sold in the main markets of Maputo city (Zimpeto, Xipamanine, and Xiquelene), regarding the geochemical, mineralogical, and granulometric characteristics, as well as to estimate human health risk assessment.

2. Materials and Methods

For the present study, geophagic samples were collected in three different contexts: (i) mines, the source of the geophagic material; (ii) materials prepared in the mines surrounding area; and (iii) geophagic materials sold in Maputo markets.

2.1. Geophagic Material Sources Characterization

Geophagic materials sold in Maputo city have their origin in mines located in the north section of Marracuene city, in Maputo province, Bobole administrative area, and in the locality of Nhomgonhana (Figure 1). The history of local geophagic materials extraction for commercialization dates to the 1990s. The exploration occurs in erratically located open pits, mainly by the local population (Figure 2). The on-site observation allowed testifying that the pits are explored laterally and may have extensions of up to 150 m. Some risks related to the extraction were reported, e.g., the death of about 20 people caused by landslides in the last 10 years.
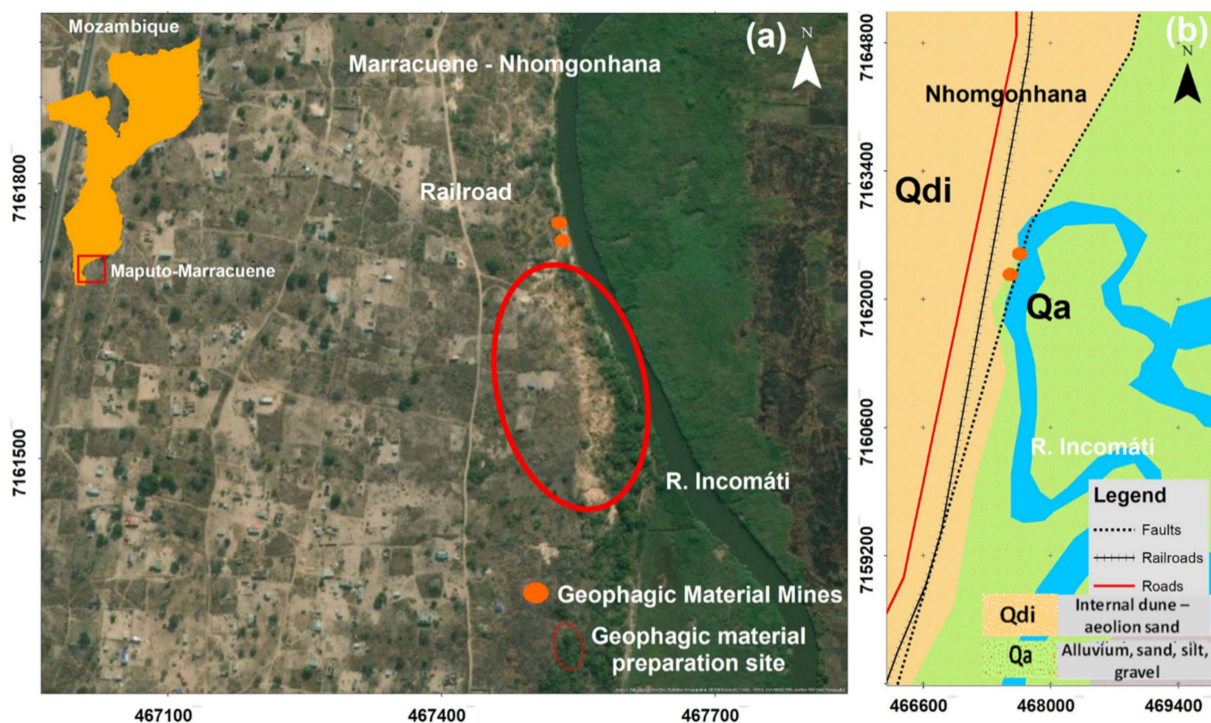
Figure 1. (**a**) Location of the Geophagic Materials Mines; (**b**) Geology.

Figure 2. Extraction and preparation of geophagic materials: (**a**) open pits; (**b**) crushing; (**c**) sieving; and (**d**) final product.

Geophagic materials are prepared near their source, consisting of: (a) materials that are open-air dried and, if necessary, dried in small handmade fire ovens; (b) ground with a pestle; and (c) sieved (Figure 2). Salt (NaCl) can be added. The final product is stored

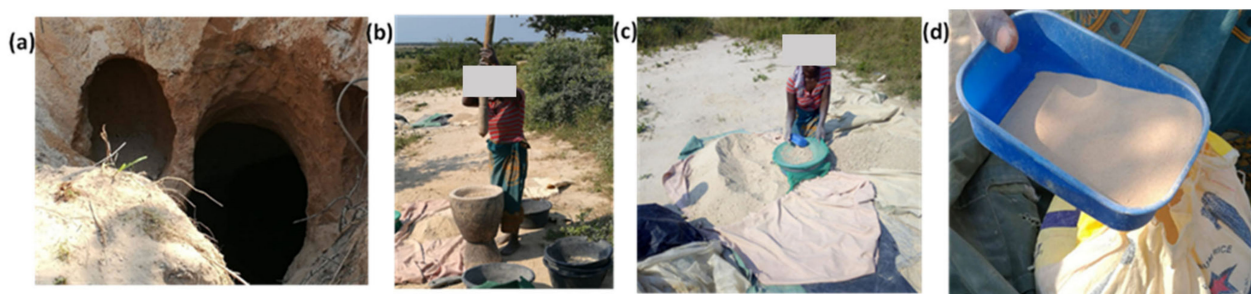in ~400 g plastic bags and transported to Maputo markets. For the present study, two unprepared samples and two locally prepared samples were collected between March and May 2021.

The mine's surrounding area has a population of about 4010 inhabitants, with the predominant activities being agriculture, fishing, and commerce [39]. The climate of the Marracuene district is subtropical, with two distinct climatic seasons, a rainy and humid (September to March) and a dry and cool (April to September). The average annual rainfall in Marracuene is 768 mm, and the mean annual temperature is 22.9 °C, with a relatively low annual temperature semi-range of around 3.5 °C. February is the hottest month (~26.0 °C), and July is the coldest (~19 °C) [40]. Southern winds are predominant throughout the year [41].

Geologically, the studied mines are located in the southern Mozambique Mesocenozoic sedimentary basin. Locally the mines lie on the boundary of inland interdunal deposits consisting of eolian sands (Qdi) and alluvial deposits (Qa), consisting of sands, silts, and gravels [37]. These two units are separated by a tectonic fault, and from the base level of the floodplain to the top of the fault is about 10 m (Figure 1) [42]. The mine entrances are profiled on the fault scarp that separates the interdune formation of aeolian (Qdi) and alluvial (Qa) deposits (Figure 1) [43]. The eolian deposits (Holocene) are composed of fine, white- to red-colored highly calibrated sands. The origin of these sands is unclear and may have resulted either from remobilization of the surrounding poorly consolidated sands or from strong Holocene wind transport. The mineralogical composition of this deposit was described with a constitution in addition to quartz (SiO_2), ilmenite ($Fe^{2+}TiO_3$), monazite ($REE(PO_4)$), leucoxene (mixture of Fe-Ti oxides), zircon ($Zr(SiO_4)$), and rutile (TiO_2). In a previous study, the chemical analyses of samples from this area revealed a composition with SiO_2 89.3%, Fe_2O_3 5.7%, Al_2O_3 2.4%, CaO 0.26%, MgO 0.19%, K_2O 0.92%, Na_2O 0.64%, SO_3 0.53% [43]. The alluvial deposits (Qa; Holocene) consist of centimetric alternations of well-calibrated sands, dark clays and carbonate, and saline levels.

2.2. Geophagic Material Sold in Markets

Five geophagic material samples were acquired in the three main markets of Maputo city: (a) one sample in the Xipamanine market, (b) one sample in the Xiquelene market, and (c) three samples Zimpeto market (Figure 3). Xipamanine market is a historical market in Maputo city, renowned for the existence of traditional supplements, including geophagic materials, locally associated with the treatment of different diseases. The Xiquelene market, one of the busiest in the city of Maputo, serves populations from various parts of the peripheral area of the city due to its geographical location. Zimpeto market, located in the northern part of the city, is the largest and the one that offers a larger variety of geophagic materials.

Figure 3. Geophagic material markets in Maputo City: (**a**) Xipamanine; (**b**) Xiquelene; and (**c**) Zimpeto markets.

2.3. Samples Preparation and Physical Parameters

All samples collected were coded and stored in plastic bags. Samples were coded according to sampling characteristics: MI for mine samples, R for samples prepared near the mines, and M for samples collected in markets samples (MX—Xiquelene, MZ—Zimpeto, and ME—Ximpanine). Additional code was added according to the color: W—whitish, R—reddish, and Y—yellowish. The samples' color was determined using the Munsell Soil Color chart [44]. In the Pedagogical University of Maputo (Mozambique) laboratory, samples were dried in an oven at 40 °C and prepared for further analysis at the GeoBioTec Research Centre, University of Aveiro (Portugal) laboratories.

Samples (<2 mm; sand) were subjected to wet sieving to obtain the <63 μm (silt) fraction. Granulometric distribution of <63 μm fraction was determined using an X-ray grain size analyzer (Micromeritics® SediGraph III Plus, Norcross, GA, USA), based on Stokes' law and absorption of X-radiation (Beer-Lambert law). The pH was determined in the sand and silt fractions with a 1:2.5 soil/water solution using a pH meter, and the classes defined were: extremely acid (3.5–4.4), very strongly acid (4.5–5.0), highly acid (5.1–5.5), moderately acid (5.6–6.0), slightly acid (6.1–6.5), neutral (6.6–7.3), slightly alkaline (7.4–7.8), moderately alkaline (7.9–8.4), and highly alkaline (8.5–9.0) [45]. Electrical conductivity (EC) was measured under the same conditions as pH in the two fractions, using a high-resolution conductivimeter, where untreated samples' EC ($\leq$25 μS/cm) was considered as a base for classification. Organic matter (OM) content was determined on sand fraction, which required to be placed in a muffle furnace at 105 °C/24 h for moisture determination and, after, at 430 °C/24 h for OM quantification [46]. Untreated samples' OM content ($\leq$1.45%) was used as a base. The color of the soil was determined using the Munsell color soil chart [44].

2.4. Mineralogical, Chemical, and Morphological Analysis

Mineralogical analysis of all fractions was determined by powder X-ray diffraction (XRD) using a Phillips/Panalytical powder diffractometer, model X'Pert-Pro MPD, equipped with an automatic slit (UA, Aveiro, Portugal). A Cu-X-ray tube was operated at 50 kV and 30 mA. Data were collected from 2 to 70° 2θ with a step size of 1° and a counting interval of 0.02°/s. The geochemical composition was obtained by an X-ray fluorescence spectrometer (XRF) using an Axios PW4400/40 X-ray, Malvern Panalytical (UA, Aveiro, Portugal) dispersive wavelength fluorescence spectrometer using the Omnian Helium technique. Results were within the 95% confidence limits. Precision and accuracy of analyses and digestion procedures were monitored using internal standards, certified reference material, and quality control blanks. Results were within the 95% confidence limits. The Relative Standard Deviation was between 5% and 10%.

3. Results and Discussion

The studied geophagic samples RW and RR, prepared in mines, presented whitish and reddish colors (Table 1), which are associated with geological processes from which the mine materials originated (sediments of coastal dunes (whitish) and continental dunes (reddish) eolian origin). According to previous studies, reddish and yellowish materials are probably enriched in iron oxides and have been the most preferred by consumers in Swaziland and South Africa [47]. Samples sold in Maputo markets presented three color categories: the MXR, MZR, and MER market samples showed a reddish color, and MZW and MZY samples were whitish and yellowish, respectively. Whitish materials suggest a link to clay minerals [48]. Yellowish samples found in the Zimpeto market may have an origin in different mines or be the result of a mixture of whitish and reddish geophagic materials and/or other additives. Supplement additives to geophagic materials are a common practice in many African markets to provide multiple choices for consumers [49].

Table 1. Samples physical parameters.

Var	Unprepared Samples		Prepared Samples			Markets Samples				
	MIW	MIR	RW	RR	MZW	MZY	MZR	MER	MXR
Color	Pinkish white 7.5YR 8/2	Pale red 2.5YR 7/4	White 2.5YR 8/1	Pale red 2.5YR 7/4	White 2.5YR 8/1	Pale yellow 5Y 8/2	Pale red 7/4 2.5YR	Pale red 7/4 2.5YR	Pale red 7/4 2.5YR
pH	7.22	6.98	7.52	7.18	7.18	7.51	6.2	6.09	6.17
EC	13	25	47	28	301	465	264	401	269
OM	1.35	1.45	8.14	1.53	1.21	1.35	2.7	2	2.76

EC—electrical conductivity (µS/cm); OM—organic matter (%).

Samples MZR, MER, and MXR revealed a slightly acidic pH (6.09 to 6.17), samples MIW, MIR, RR, and MZW presented a neutral pH, ranging from 6.98 to 7.18, while samples RW and MZY showed a slightly alkaline pH of 7.52 and 7.51, respectively. The reddish-colored samples from the markets showed a tendency to acidity. Ref. [50] reported that acidic geophagic materials are more preferred by pregnant women in Kenya, Malawi, South Africa, and Nigeria. The preference for acidic materials is traditionally accepted as capable of preventing excess saliva secretion and reducing nausea during pregnancy [51,52]. According to [53] slightly acidic geophagic materials aid in gastric juice neutralization. Electrical Conductivity (EC) showed a clear distinction between unprepared (13 and 25 µS/cm) and prepared in mines (28 and 47 µS/cm) materials and samples from markets (264–465 µS/cm). The slight EC difference between unprepared and prepared near the mine samples may be associated with sieving once fine fractions are more conductive [54], while higher EC results in market samples may be the result of additives (e.g., NaCl) added to geophagic materials, to improve flavor. Other studies reported high EC values in geophagic materials with salt added, and that can be linked to diarrhea-causing enterotoxins absorption and to gastrointestinal epithelium protection [55].

Unprepared samples MIR and MIW showed similar OM content. Prepared sample MIV had the higher OM content (8.14%) of all samples, suggesting additives. OM-rich geophagic materials are likely to have more bacteria added, some of which can be pathogens, including *E. coli*, *E. histolytica S. typhi,* and intestinal helminth infections such as *A. lumbricoides*, *T. trichiura,* and *S. stercoralis* [47]. Materials sold in markets OM ranged from 1.21 to 2.76%, similar to other studied geophagic materials, e.g., in Zaire, Thailand, and Uganda, 0.2 to 1.5% [51]; Cameroon, 2.32 and 3.02% [56]; and South Africa and Swaziland, <1.7% [47], which is considered with a low risk of bacterial aggregation.

Textural analysis of studied samples revealed that sand-size particles are the most representative (Figure 4). Unprepared mine sample MIW is the one with higher sand content (93.02%), while samples MER and MXR presented lower sand content, with 57.02 and 61.34%, respectively. As expected, samples with higher clay content were the ones prepared for geophagic consumption. The prevalence of sand fraction in prepared samples contradicts the belief that soils deliberately ingested are of clayey texture. The same sandy trend was reported in South Africa, Swaziland, and the Democratic Republic of Congo [57].

Silt fraction granulometric distribution revealed that clay size presented the higher content (67.5 to 88.1%), except in sample MIW (27.9%), which is ranked MXR > MZR > MER > MIR > MZW > RR > MZY > RW > MIW (Figure 5). The higher clay size content in the market and prepared samples can be associated with preparation processes, which involve crushing and sieving (Figure 2). The samples' color presented a link to samples' clay content, with whitish and yellowish samples exhibiting a relatively lower clay size content (27.9 to 80.3%) than reddish samples (81.0 to 88.1%).
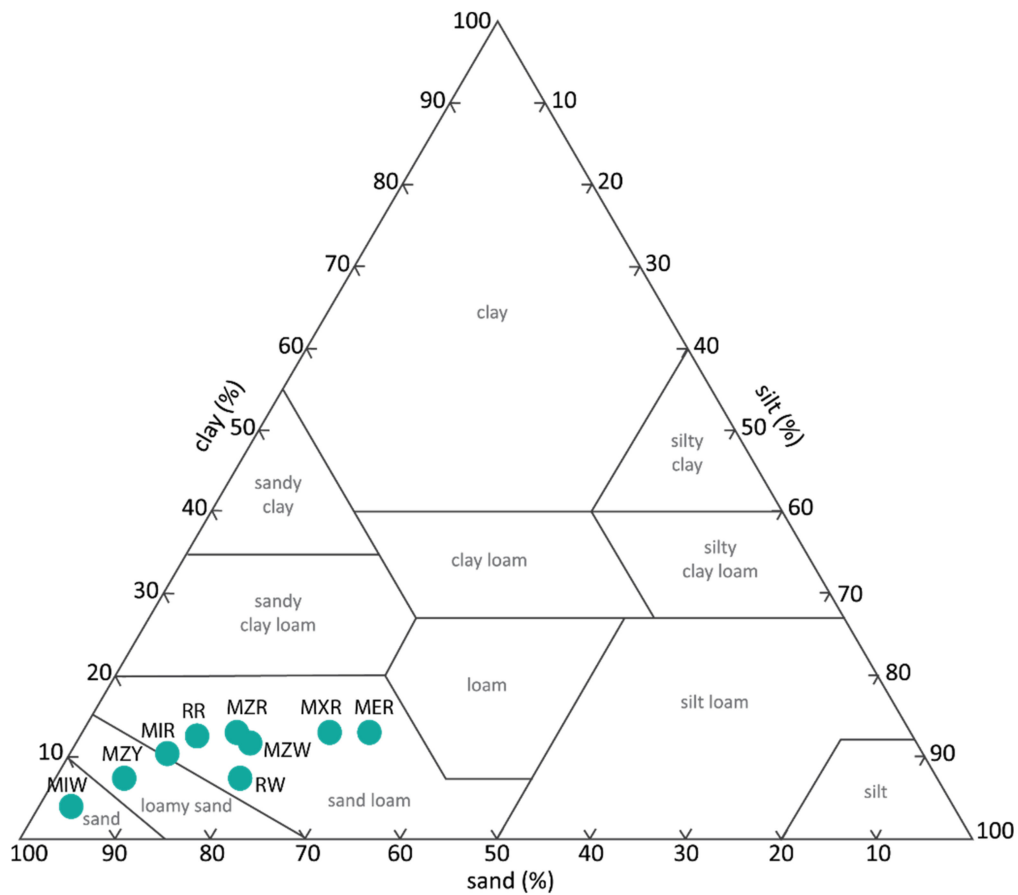
Figure 4. Granulometric classification of studied samples.
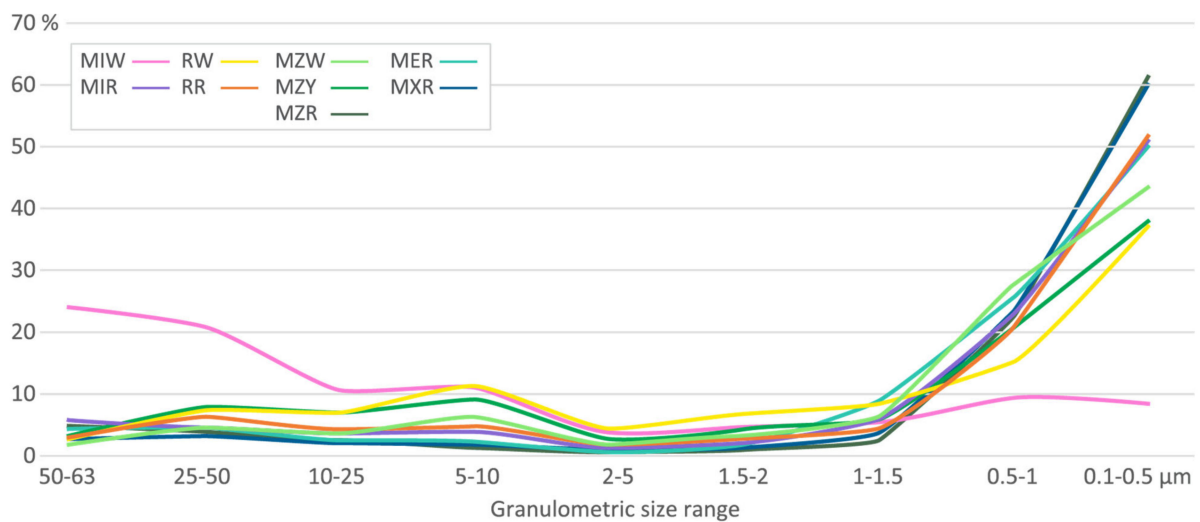
Figure 5. Relative granulometric distribution of silt fraction particles (in %).

Mineralogical analysis showed that quartz (SiO_2) is the prevalent mineral (>60%) identified in consumed materials (sand fraction) in all samples (Figure 6). Moreover, Fe oxides/hydroxides, feldspars, and phyllosilicates were identified. A similar mineralogical composition was described in [43] in this area. The presence of quartz, K-feldspar, and plagioclase in geophagic material was associated with the risk of tooth enamel damage,

given that the main inorganic component of human teeth is dominated by hydroxyapatite $(Ca_5(PO_4)_3(OH)$, a calcium phosphate mineral, which is softer than quartz [23].
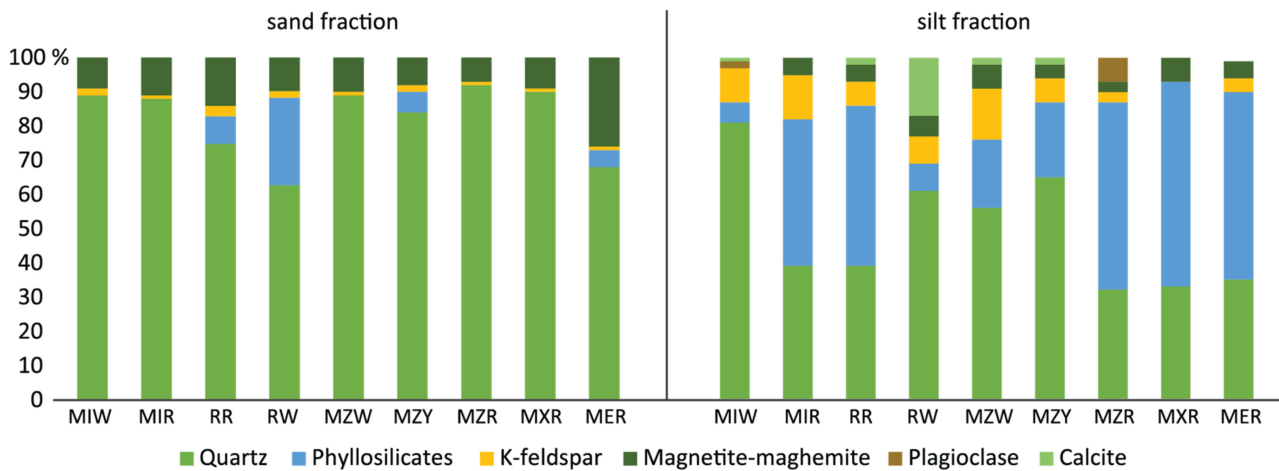

Figure 6. Relative mineralogical composition of sand and silt fractions of studied samples.

Silt fraction revealed that quartz and phyllosilicates (mainly micas and kaolinite) are predominant in all samples. Quartz content decreased in all samples, except MIW, which is still very high (81%). Phyllosilicates content increased significantly in three of the four samples from the local markets (MZR, MXR, and MER), in which phyllosilicates amount is higher than quartz. Plagioclase $[(Na,Ca)[(Si,Al)AlSi_2]O_8]$ was identified in MIW and MZR samples. Calcite $[CaCO_3]$ presented variable content, which is more abundant in whitish samples. Magnetite–maghemite was identified in all samples and fractions (except in the MIW sample) and was more abundant in reddish ones.

Concerning clay fractions, mineralogical analysis by XRD (Table 2) showed that kaolinite $[Al_2Si_2O_5(OH)_4]$ was the predominant clay mineral, with the exception of the MIW sample, in which illite $[K_{0.65}Al_{2.0}(Al_{0.65}Si_{3.35}O_{10})(OH)_2]$ was predominant. Illite was also present in samples RW, RR, and MZW. Smectite $[(Na,Ca)_{0.33}(Al,Fe,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O]$ was present in discrete amounts (tr) in several samples.

Table 2. Mineralogical composition of clay fraction of studied samples.

ID	Kaolinite	Illite	Smectite	Corrensite	Halloysite
MIW	tr	+++			
MIR	+++			tr	
RW	+++	+	tr		
RR	+++	+	tr		
MZW	+++	+	tr		
MZY	+++				tr
MZR	+++		tr		
MXR	+++				
MER	+++		tr		

+/+++ relative amount; tr—trace.

This clay mineralogical composition is quite similar to geophagic clays from Cameroon and Nigeria [42], as well as in a similar study of geophagic materials from South Africa, Swaziland, and DRC, in which kaolinite was found to be the predominant mineral, followed by smectite and illite [47]. Kaolinitic clays are commonly consumed for the containment of stomach disorders [58]. Subject to sodium carbonate treatment, affordable and effective

kaolinitic clays could be used as antacids [59]. Thus, kaolinite is a gastrointestinal protector [60,61]. Their therapeutic action is based on their high specific area and adsorption capacity [62]; they adhere to the gastric and intestinal mucosa and protect them, and can absorb toxins, bacteria, and even viruses [63]. However, consumption and prolonged exposure can lead to health complications, and their toxicity is generally related to the presence of quartz [64,65], which was the predominant mineral in the sandy fraction. Illite and smectite reduce mucus destruction by bacteria and improves nutrient absorption [66]. It is also reported a great capacity of adsorption of *S. enteritidis, E. coli, V. cholerae, C. jejuni, C. difficile, Shigella sonnei*, eliminating up to 90% of their viral particles [67], as well as on the cure of acute diarrhea [68]. However, prolonged consumption of these clays can trigger health problems, as previously described by [34,68–70].

The chemical composition statistical summary of sand and silt fractions is presented in Table 3. A 1-way ANOVA test was performed to assess significant differences between the two fractions. The chemical composition presented significant differences between sand and silt fractions on variables Al, Ba, Cr, Fe, Mg, Mn, Ni, P, Pb, Rb, Si, Sr, Ti, V, and Zn ($p < 0.01$, except for Mn with $p < 0.02$). In general, the silt fraction revealed the highest concentration of most essential and potentially toxic elements, except for Na and P.

Table 3. Statistical chemical composition summary of studied samples sand and silt fractions.

Var	Sand					Silt				
	Min	Max	Mean	SD	Sk	Min	Max	Mean	SD	Sk
Al	14,632	120,889	77,615	32,160	−0.626	57,111	191,537	164,576	41,851	−2.591
Ba	3.5	339	66.5	128	1.795	3.5	946	491	314	−0.584
Br	0.4	21.3	7.5	8.7	0.534	0.4	35.5	16.5	13.1	0.189
Ca	2145	3032	2414	269	1.64	1979	2795	2235	249	1.469
Cr	48.4	139.5	110.0	28.6	−1.304	172	269	230	29.2	−0.756
Cu	1.5	87.0	33.2	31.8	1.17	26.6	96.9	44.7	21.1	2.245
Fe	1541	12,717	7877	3085	−0.725	10,333	33,040	27,633	6800	−2.497
K	9701	16,517	12,436	2278	0.499	10,321	31,934	15,122	6544	2.591
Mg	766	2429	1744	460	−0.974	1228	3782	2837	876	−0.833
Mn	3.0	164.1	86.8	51.8	−0.357	114	410	186	103	1.654
Na	100	7116.9	3675	2912	−0.302	100	5263	3238	1553	−1.089
Ni	1.0	46.1	31.2	14.0	−1.279	41.3	92.3	69.1	18.5	−0.243
P	1907	3969	2503	630	1.704	1409	1912	1583	141	1.645
Pb	1.0	42.1	9.6	17.1	1.641	30.8	53.5	45.4	7.7	−0.675
S	100	343	221	85.0	−0.161	170	1887	395	561	2.977
Si	227,241	526,562	456,435	94,067	−2.201	281,203	439,925	318,063	48,084	2.468
Sr	14.2	32.8	22.6	6.5	0.796	32.8	75.3	47.4	12.8	1.425
Ti	1920	7711	4091	1926	1.199	5845	8050	6642	634	1.336
V	1.5	104	37.2	38.3	0.556	50.2	255	195	59.1	−2.12
Zn	9.1	23.3	15.9	4.5	0.149	27.9	66.0	53.2	12.3	−1.215
Zr	101	440	209	121	1.108	176	531	258	108	2.477

Min—minimum; max—maximum; SD—standard deviation; Sk—skewness.

Multiple benefits for the body are ascribed to Ca; however, high intakes (Recommended daily dose (RDD) 1200 mg/kg) can cause renal failure, vascular and soft tissue calcification in fetuses, hypercalciuria, heart disease, and kidney stones [71,72]. Studied samples presented mean concentrations of 2414 and 2235 mg/kg in sand and silt fractions, respectively. The function K in humans is closely related to Na, an essential nutrient involved in fluid, acid, and electrolyte balance and is required for normal cellular function [73,74]. Gastrointestinal effects (e.g., discomfort, mucosal lesions, and sometimes ulceration) and heart failure can be linked to high K (RDD 5000 mg/kg) [74] and Na (2000 mg/kg) [75,76] ingestion. In this study, high concentrations of K and Na were found in both fractions (Table 3). One of the known key factors for geophagic materials consumption is Fe content [57]. Studies by [13,19] reported Fe supplementation has a motivation for pregnant women to practice geophagy in Namibia and in other African countries and

that moderate consumption of Fe-rich geophagic materials is indicated as a supplement. In this study, geophagic materials showed higher contents than RDD (30–60 mg/kg) [73] for women and adolescents. Studies showed similar results [2], suggesting that Fe toxicity depends on bioavailability, which can be reduced in geophagic materials [13]. For protein synthesis, muscle and nerve functions, blood glucose control, and the regulation of blood pressure, Mg is essential, and toxicity is linked to nausea and abdominal pain [77], with an RDD of 360 mg/kg in adults [78]. Studied samples presented mean = 1744 mg/kg in sand, and 2837 mg/kg in silty fractions. Zinc is described as beneficial in several physiological activities, including synthesis and degradation of carbohydrates, proteins, lipids, and nucleic acids, as well as testicular maturation and wound healing [52]. Excessive and prolonged Zn intake can cause anemia and affect the immune system [79]. In this study, Zn content in total consumed fraction was within RDD (40 mg/kg) [80]. Sulphur (S) is the seventh most abundant and essential element in the human body [81].

Copper is a component in enzymes involved in Fe transport, as well as glucose and cholesterol metabolism. Chronic Cu consumption may result in gastrointestinal irritation, diarrhea, and liver failure, with an RDD of 10 mg/kg [74,81]. In this study, mean concentrations were 33.2 and 44.7 mg/kg, in sand and silt fractions, respectively, with 1.5 mg/kg in market samples MZW and MXR. Another essential trace element for the organism is Mn [82], with a defined RDD of 3 mg/kg. Toxicity is linked to memory problems, hallucinations, and Parkinson's disease [83]. Studied samples showed means of 86.8 (sand) and 186 (silt), representing a potential risk.

In bone formation, Si represents a role. Si toxicity is linked to erosive gastritis promotion, which can lead to internal bleeding and ulcers [84,85]. The RDD is 19 mg/kg for women and 40 mg/kg for men [86]. Geophagic presented mean values of 456,435 (sand) and 318,063 (silt) mg/kg. No physiological function in the human body is attributed to Al, which is considered non-essential [87]. Samples revealed a higher concentration high than RDD for adults of 1 mg/kg [75], with a mean of 77,615 mg/kg on the total fraction (sand) and 164,576 mg/kg in silt fraction. In general, Al is removed by the kidneys; however, prolonged consumption can lead to toxicity [88]. Bone and neurological disorders and learning and memory disturbances associated with Al were also reported [88].

Barium is a non-essential element and is potentially toxic [89], with RDD of 0.02 mg/kg [90]. Toxic effects include breathing difficulties; increased blood pressure; changes in heart rate; stomach irritation; muscle weakness; changes in nerve reflexes; swelling of the brain; and damage to the liver, kidneys, and heart [91]. Geophagic samples' mean concentration was 66.5 and 491 mg/kg in sand and silt fractions, respectively. WHO established an RDD of 1 mg/kg for Br, with concentrations in this study ranging from 0.5 to 21.3 mg/kg in sand fraction and 0.4 to 35.5 mg/kg in silt fraction, with some samples posing a potential toxicity risk for consumers [82]. Cr toxicity in humans has been linked to damaged blood cells, livers, nervous systems, and kidneys. In this study, the mean concentration was 110 and 230 mg/kg in sand and silt fractions, respectively, posing a potential risk. Nickel is necessary for the absorption of Fe by the human body, with toxicity related to miscarriages and foot deformities, with RDD = 1.1 mg/kg [92]. The silt fraction revealed a Ni mean of 69.1 mg/kg and a sand fraction of 31.2 mg/kg, representing a potential risk. Vanadium can cause distress, with toxicity directly proportional to the increase in valances states, instigating depressed growth, diarrhea, and depressed food intake [93]. The average concentration in the sand fraction was 37.2 mg/kg and in the silt fraction 195 mg/kg, higher than an RDD of 0.002 mg/kg [94].

Spearman's correlation of sand and silt fraction is presented in Table 4. In sand fraction, pairs Na/Ca, S/Cl, Fe/Mn, K/Mn, and Zn/S, and silt fraction Ca/Cu, Cl/Na, Fe/S, and Mg/S showed a significant positive correlation, suggesting a common source, possibly of geogenic nature. Pairs P/Fe, K/P, and P/Mn, in sand fraction and K/Zn in silt fraction presented a significant negative correlation, which may indicate different sources. Previous studies in dry environments with relatively high temperatures reported geophagic materials enriched in Pb, Mn, and Cu and established a link with anthropogenic sources,

such as industry, traffic, and asphalt emissions resuspension, associated with higher PTEs adsorption and deposition in environments with temperatures > 20 °C [23,94,95]. Sources applicable to the climatic season and markets studied. Silt fraction correlation analysis, associated pairs, with significant positive correlation.

Table 4. Spearman's correlation of essential macronutrient elements of sand (in blue) and silt (in black) fractions.

	Ca	Cl	Cu	Fe	K	Mg	Mn	Na	P	S	Zn
Ca	1	0.6	**0.750 ***	0.117	0.117	0.067	0.234	0.627	−0.350	−0.059	−0.100
Cl	0.167	1	0.350	0.583	−0.117	0.450	−0.142	**0.780 ***	−0.167	0.326	−0.167
Cu	0.281	0.434	1	0.017	−0.033	0.100	0.276	0.254	−0.383	−0.109	0.017
Fe	−0.267	0.517	−0.136	1	−0.450	0.517	−0.251	0.441	−0.417	**0.686 ***	0.383
K	−0.283	−0.133	−0.443	0.483	1	−0.167	0.385	0.051	−0.283	0.033	**−0.833 ****
Mg	−0.350	0.133	−0.196	0.2	0.650	1	−0.092	**0.678 ***	0.133	**0.820 ****	−0.117
Mn	−0.267	0.117	−0.170	**0.700 ***	**0.883 ****	0.650	1	0.043	−0.226	−0.084	−0.075
Na	**0.792 ***	0.366	0.548	−0.034	−0.460	−0.366	−0.187	1	0.017	0.562	−0.288
P	0.600	−0.083	0.366	**−0.817 ****	**−0.717 ***	−0.417	**−0.783 ***	0.468	1	−0.226	−0.050
S	0.367	**0.817 ****	0.068	0.367	0.117	0.317	0.167	0.221	−0.033	1	−0.151
Zn	0.237	0.627	0.199	0.373	0.390	0.339	0.356	0.009	−0.254	**0.797 ***	1

In bold, ** $p < 0.01$, and * $p < 0.05$.

Risk Assessment

The adjusted hazard index for both children and adults ($HI_{adjusted}$) and the individual children and adults hazard index (HI_{child} and HI_{adult}), considering all selected variables of the silt and sand fractions of the geophagic materials, are presented in Figure 7. The dermal contact and inhalation hazard quotient (HQ) were considered negligible, only being considered the ingestion route ($HI \approx HQ_{ingestion}$). Children, due to body development, are more sensitive, which is reflected in the higher risk of systemic toxicity (non-carcinogenic HI). All samples revealed HI > 1 (threshold) in both sand and silt fractions, ranked MZY > MZW > MER > MXR > RW > MIR > RR > MIW > MZR and MIW > MER > MZY > MZR > MIR > MXR > MZW > RR > RW for sand and silt fractions, respectively. The results suggested that non-carcinogenic health outcomes might occur since exposure to elements is higher than the reference dose. The variable that most impacted children, adults, and adjusted HI was Zr, with mean contributions of 93.2 (sand) and 85.1% (silt) (Figure 8). Chronic Zr exposure can cause respiratory tract irritation, dermatitis, and pulmonary fibrosis [96]. Samples Br, Ca, Cr, Pb, Mg, P, K, Si, Na, S, and Ti concentration do not pose a non-carcinogenic risk to humans. Additionally, Ba, Cu, Fe, Sr, and Zn HI contribution was considered negligible (<1%) for the total HI in both fractions. Variable V presented a maximum contribution of 7.7 (sand; MZR sample) and 12.1% (silt; RW sample), followed by Al with 7.6 (sand; RR sample) and 6.4% (silt; RR sample). Studied geophagic samples do not present a carcinogenic risk, ranging from 1.22E-08 to 5.14E-07 and 3.79E-07 to 6.48E-07 on sand and silt fractions, respectively. Pb is the only variable contributing to the risk result, with other variables being negligible. Pb toxicity can cause several neurological outcomes such as reduced cognitive development and behavioral changes, which are mostly manifested in children, as well as renal tumors and high blood pressure in adults [23,97].
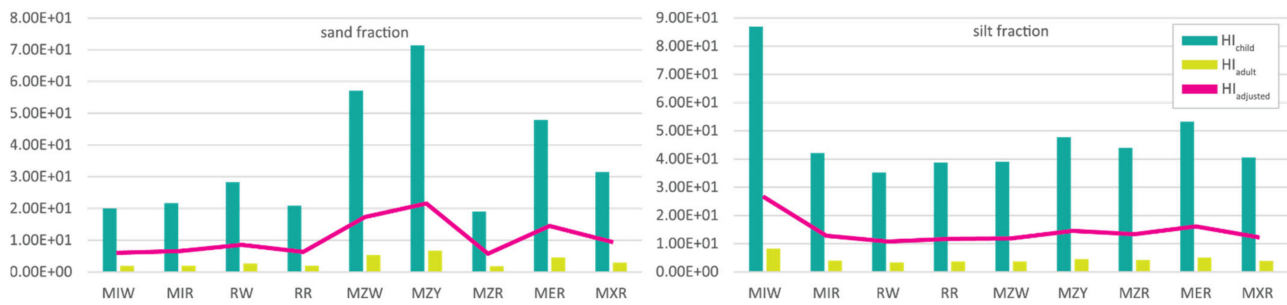
Figure 7. Geophagic material sand and silt fractions HI_{child}, HI_{adult}, and $HI_{adjusted}$.

Figure 8. Individual variable relative contribution for the $HI_{adjusted}$ in the samples sand and silt fractions (in %).

4. Conclusions

The study of Maputo geophagic materials revealed different physical, chemical, and mineralogical characteristics between unprepared and prepared ones. The results showed pH from slightly acidic to slightly alkaline, with markets reddish samples showing a tendency for acidity, typical of kaolinitic clayey materials. Materials collected in mines were reddish and whitish, with a yellowish one collected in a market. Organic matter content was <2.76% in all samples except one (8.14%), suggesting a potential risk of containing bacteria. Electrical conductivity tanged 13–47 µS/cm in mine and near mine prepared samples, and higher values in all market samples (264–465 µS/cm), pointing to the introduction of additives. Textural analysis revealed that sand-size particles were the most representative in all samples (57.20 to 93.02%) but decreased in market ones. Dominant mineral phases in the consumed fraction were ranked quartz (>60%) > > Fe oxides/hydroxides > phyllosilicates > feldspars, suggesting a risk of dental enamel damage and perforation of sigmoid colon, given minerals hardness (6 to 7). Kaolinite, illite, and smectite, predominant in clay fractions, have multiple benefits for the organism, given their potential to absorb toxins, bacteria, and viruses. Elements Al, Ba, Cr, Fe, Mg, Mn, Ni, P, Pb, Rb, Si, Sr, Ti, V, and Zn revealed concentrations higher than recommended daily dose. The risk assessment of all samples represents a hazard of developing non-carcinogenic outcomes in children. However, geophagic samples do not pose a carcinogenic risk, with Pb concentration being the only contributing for risk results, with others being considered negligible.

This research requires further studies to understand the specific dose consumed by geophagists in order to estimate specific risks. Bioaccessibility of potentially toxic elements is being undertaken. Nevertheless, results suggest the need to integrate education on good practices in the preparation, conservation, and selling of geophagic materials.

Abbreviations

EC	Electrical conductivity
HI	hazard index
HQ	hazard quotient
OM	organic matter
PTEs	potential toxic elements
Qa	alluvial deposits
Qdi	eolian sands
RDD	Recommended daily dose
XRD	X-ray diffraction
XRF	X-ray fluorescence

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