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Effects of Artificial Sweat Formulation and Extraction Temperature on Estimation of the Dermal Bioaccessibility of Potentially Toxic Elements in a Contaminated Soil from an E-Waste Recycling Site

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Abstract: Informal recycling of electronic waste leads to soil contamination that can impact human health. To accurately assess exposure to potentially toxic elements (PTE) in soil it is necessary to consider their bioavailability through ingestion, inhalation and dermal contact. However, bioaccessibility tests that estimate dermal absorption following adhesion of contaminated soil particles to skin are not well established. In this study the concentrations of As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn were estimated in the <45 µm particle size fraction of a bulk composite soil from an e-waste recycling site using five different artificial sweat formulations. Extractions were performed at temperatures ranging from 17 to 47 °C to investigate the effect of ambient temperature on bioaccessibility. Results obtained using the different artificial sweats were not consistent with one another. In particular, the NIHS 96-10 formulation solubilized larger amounts of analytes (ranging from 6.3 times the next most effective extractant for Cu to 1700 times the next most effective for Pb). There was a general increase in release of PTE with increasing temperature, except for As. Although trends varied between analytes and formulations, this highlights the need to consider ambient temperature when estimating dermal bioaccessibility of PTE in soil.

Keywords: dermal bioaccessibility; potentially toxic elements; soil; e-waste; temperature

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1. Introduction

Volumes of electronic waste (e-waste) generated globally are increasing, and their recycling to recover valuable materials has had a significant impact on the environment and human health [1–5]. Of particular concern is the high proportion of recycling activities carried out in developing countries, often without personal protective equipment, and using hazardous procedures such as removal of components by hand, open-air burning and acid leaching [6,7]. There have been numerous reports worldwide of ill health amongst e-waste workers, their families, and communities, associated with exposure to potentially toxic elements (PTE) either directly from recycling activities or following contamination of the local environment [8–10].

The risk associated with exposure to contaminated soil relates not only to the concentrations of PTE present, but also their chemical speciation and availability [11]. This had prompted considerable research to develop and validate in vitro bioaccessibility tests to estimate the proportion of soil PTE content that is available for absorption into the human systemic circulation following oral ingestion, inhalation or dermal contact. Oral bioaccessibility tests such as the simple bioaccessibility extraction test [12], the physiologically-based extraction test [13] and the unified BARGE method [14] are now well established and widely used. Estimation of PTE bioaccessibility following inhalation of contaminated particles using variants on Gamble's solution [15], artificial lysosomal fluid [16] or other physiologically-relevant extractants [17,18] is also becoming more common. However, less studied is the dermal route in which absorption of PTE occurs following adhesion of contaminated soil particles to the skin.

A variety of artificial skin surface film liquids have been proposed to assess dissolution of chemical substances from consumer products (jewelry, watches, textiles and cosmetics), drugs and industrial chemicals [19]. As with oral and inhalation bioaccessibility test, formulations range widely in composition, from complex mixtures that seek accurately to mimic the chemical composition of human sweat, to simple (but less physiologically-representative) 'recipes', that nevertheless provide results sufficiently indicative of the degree of metal release to be useful [20].

A 2009 review of research on dermal absorption of chemical substances from soil and sediment [21] noted that the majority of studies to date had focused on organic substances—with As, Cd, Hg and Ni the only PTE represented—and that inconsistent methodology made inter-comparison between results produced by different laboratories difficult, even where the same analyte was determined. Only a few articles featuring use of artificial sweat solutions to estimate dermal absorption of PTE from soil have since appeared (although numerous publications estimate dermal exposure to PTE in soil, values are not based on bioaccessibility tests but calculated from total PTE concentrations using standard risk assessment models). Notably, Leal et al. [22] used two synthetic sweat formulations (EN 1811 and NIHS 96-10) to determine the dermal bioaccessibility of Cr, Ni, Pb and Zn in soils from an industrial site in France and mine tailings from Quebec. Khelifi et al. [23] applied NIHS 96-10 in their study of Cd, Cr, Cu, Pb and Zn in stream sediment, urban soil and mine tailings from a phosphate-mining area in Tunisia. While Villegas et al. [24] compared five artificial skin surface film liquids—three synthetic sweats and two synthetic sebum—for assessing dermal bioaccessibility of Cr, Ni, Pb and Zn using certified reference soils SQC001 and BGS 102 as test substrates. They found that significantly different results were obtained using different formulations.

To accurately estimate dermal absorption of PTE from soil, it is recommended that a bioaccessibility test should mimic the actual exposure scenario as closely as possible. Factors typically considered include soil particle size, soil load, soil-to-sweat ratio and soil-skin contact time [21]. Since smaller soil particles adhere most readily to human skin, the use of the < 63 μm diameter fraction is recommended [25]. The soil load should be representative of monolayer coverage, which occurs in the range 0.28–6.9 mg per cm^2 of skin for particles of 0.002–0.05 mm diameter [26]. The soil-to-extractant ratio should be chosen based on realistic sweat volumes (the typical sweat layer thickness on skin is around 0.1 cm [27]). The bioaccessibility test duration should be appropriate, e.g., 8 h for a typical occupational exposure.

A further parameter that may be important, but is rarely considered, is skin temperature. While the core body temperature is generally regulated at 37 °C, the surface skin temperature is affected by ambient conditions and activity levels [28]. Values as low as 18 °C have been reported in individuals sledging in the Antarctic [29] and as high as 41 °C in subjects exercising at elevated temperatures in an environmental chamber [30]. Such differences may affect the dissolution of PTE from soil and their subsequent dermal absorption. Since informal e-waste recycling is often carried out in the Tropics, and global climate change is likely to lead to increased incidence of extreme temperatures, it is possible that e-waste workers may be exposed to ambient temperatures well in excess of the range currently used in estimation of dermal bioaccessibility (32–37 °C).

The aims of the current study were therefore to compare results obtained using five different artificial sweat formulations, and to investigate the effect of extraction temperature, on the dermal bioaccessibility of As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn, using as test substrate a bulk composite contaminated soil from an e-waste recycling site in Lagos, Nigeria.

2. Materials and Methods

All glassware and plastic vessels were soaked overnight in 5% (v/v) nitric acid then rinsed with distilled water before use. All reagents used were of analytical grade or higher purity, purchased from either Sigma-Aldrich or Fisher Chemical Company, Loughborough, UK.

2.1. Preparation of the Test Substrate

To compare the extraction methods and study the effect of temperature, a bulk composite sample of topsoil (0–5 cm) from the main recycling area of Alaba International Market in Lagos, Nigeria was prepared by mixing individual samples collected in 2016 and 2017 as part of an environmental survey. Founded in 1978, Alaba International Market is the largest site in West Africa for collection, dismantling, recycling and resale of used electronic products, receiving around five million individual items from Europe and Asia per day [31]. Activities carried out in the recycling area include manual disassembly and burning of e-waste. The soil was sieved to ≤45 µm particle size with a pre-cleaned 45 µm sieve (BS410/1986, Endecotts Ltd., London, UK).

2.2. Determination of pH and Organic Matter (OM)

Soil pH was determined using a British Standard International (BSI) method [32] at a solid to deionized water ratio of 1:5. The organic matter content was estimated by loss on ignition at 550 °C.

2.3. Determination of Pseudototal Element Concentration

The pseudototal PTE concentration in the soil was determined by microwave-assisted acid digestion using a MARS Xpress system (CEM, Buckingham, UK). Triplicate 0.5 g test portions were digested in 20 mL freshly prepared *aqua regia*. The operating conditions were: 800 W applied power; a ramp time from room temperature to 160 °C of 30 min; and a hold time at 160 °C of 20 min.

2.4. Assessment of Soil Contamination

Contamination factor (CF) values for the PTE were obtained using Equation (1).

$$\mathrm{CF} = \frac{\text{Pseudutotal PTE } \left(\mathrm{mgkg}^{-1}\right)}{\text{Soil background value } \left(\mathrm{mgkg}^{-1}\right)} \tag{1}$$

A CF < 1 indicates low contamination, 1 < CF < 3 moderate contamination, 3 < CF < 6 considerable contamination and CF > 6 very high contamination [33].

2.5. Dermal Bioaccessibility Tests

The test soil was extracted with deionized water (DIW) and with five different artificial sweat solutions (Table 1) based on.

- EN 1811:2011, the British Standards Institution artificial sweat formulation for the determination of Ni in body pierced parts [34] (referred to in tables and figures as BSI)
- NIHS 96-10, a quality standard used by the Federation of the Swiss Watch Industry to assess the gold alloy coverings of watch cases and accessories [35] (NIHS)
- A formulation used by Altkofer et al. [36] in their study of the release of nitrosamines from condoms (ALT)
- A formulation used by Ariza et al. [37] in their study of the corrosion resistance of colored ZrN_xO_y films that have potential applications as decorative coatings on, e.g., eyeglasses (ARI)
- A formulation used by Cheng et al. [38] in their study of the partitioning of volatile organic compounds into sweat (CHE).

For the bioaccessibility test, a soil to extractant (artificial sweat solution) ratio of 1:100 was used. This was based on a moderate soil loading of 1 mg per cm^2 skin and sweat volume of 0.1 mL per cm^2 skin. A 10 mL aliquot of deionized water or freshly prepared artificial sweat solution was added to 0.1 g of the sample in a flat-bottom HDPE tube. The resulting suspension was homogenized by manual shaking for 30 s and the tube then placed into an incubating shaker (Stuart® SI500 orbital incubator, Cole-Parmer, St Neots, UK). Extraction was carried out at 100 rpm, for 8 h, at temperatures of 17, 27, 32, 37 and 47 °C to cover the range of skin temperatures reported in literature (and a little beyond). The tubes were then removed from the incubator and centrifuged at 4200 g for 15 min. The supernatant was filtered through a 0.45 µm pore size Acrodisc® (Sigma Aldrich, Gillingham, UK) cellulose acetate membrane filter (25 mm diameter) attached to a disposable syringe. Syringes and cellulose acetate filters were pre-washed with 0.032 M HCl immediately before use to remove trace element contaminants, particularly Cu and Zn [39]. Filtrates were then diluted to 2% HNO_3 and stored in HDPE bottles at 4 °C prior to analysis. A flowchart summarizing the methodology used is presented in Figure 1.

Table 1. Composition of the artificial sweat solutions (grams of reagent used to prepare 100 mL of solution unless otherwise stated).

	BSI [34]	**NIHS [35]**	**ALT [36]**	**ARI [37]**	**CHE [38]**
Acetic acid	-	0.25	-	-	-
Ammonia	-	-	-	-	0.0343
Ammonium Chloride	-	1.75	0.04	-	-
Lactic acid	0.1	1.5	0.3	0.1 mL	-
Potassium chloride	-	-	0.03	0.12	-
Sodium chloride	0.5	2.0	0.45	0.75	0.468
Sodium lactate	-	-	-	-	0.6
Sodium sulfate	-	-	0.03	-	-
Urea	0.1	0.5	0.02	0.1	0.0516
pH	6.5	4.7	(5.3)*	4.5	6

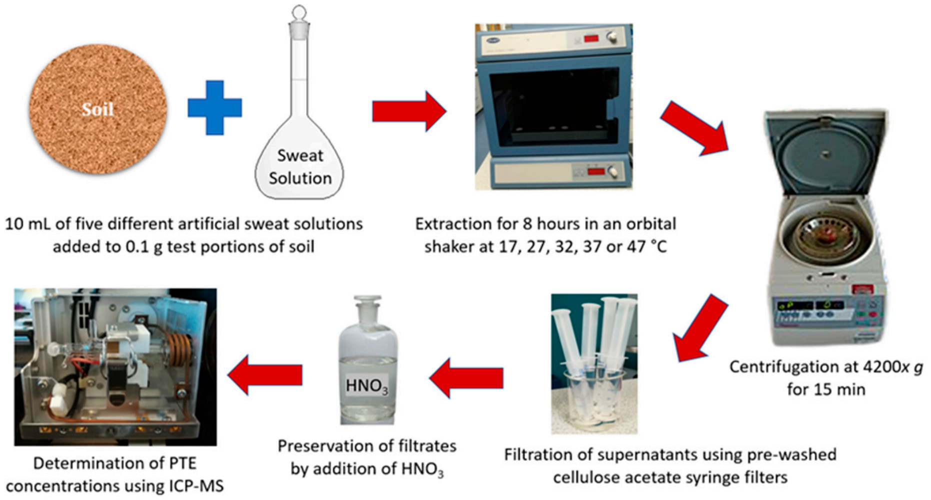

Figure 1. Flowchart illustrating the dermal bioaccessibility test methodology.

For the tests carried out at 27 °C, the pH of the extract was determined after centrifugation, but before filtration, and compared with the pH of the original artificial sweat solution to determine if the addition of soil altered the pH of the formulation.

2.6. Elemental Analysis and Quality Control

Digests and extracts were analyzed by ICP-MS using an Agilent 7700× instrument with ASX-500 autosampler (Agilent Technologies Ltd., Cheshire, UK) operated at 1550 W and 27 MHz. Calibrants were prepared in 2% nitric acid from commercial standard solutions (a 10 mg/L multi-element solution containing As, Cd, Cr, Cu, Mn, Ni, Pb and Zn and a

1000 mg/L Fe solution, both from Qmx laboratories, Thaxted, UK). Preliminary checks showed no difference in sensitivity between reagent-matched calibrants and those prepared in dilute nitric acid. Quantification was based on ^{75}As, ^{114}Cd, ^{53}Cr, ^{65}Cu, ^{57}Fe, ^{55}Mn, ^{60}Ni, ^{208}Pb and ^{66}Zn, cross-checked against results for a second isotope were available. The internal standard was ^{115}In.

A secondary reference material (GLA URM) prepared during the EU URBSOIL project (EVK4-CT-2001-00053) was used to assess the quality of the pseudototal digestion. This is an urban soil from a park in Glasgow [40]. Unfortunately, no reference soil certified for PTE extractable by the dermal bioaccessibility tests studied is available. Spike recovery tests were carried out on the sweat solutions (without soil) at 17, 27, and 32 °C. Spike concentrations were 10,000 µg/L for Fe and 250 µg/L for the other analytes.

2.7. Statistical Analysis

Statistical analysis was carried out using Minitab Version 18. ANOVA was used to determine the effects of temperature and artificial sweat solution formulation on the bioaccessible metal concentrations [41]. Where a significant difference was detected, the Tukey pairwise comparison test was used to identify the factor giving rise to the difference [42].

3. Results and Discussions

3.1. Quality Control

The result obtained for analysis of the GLA URM secondary reference material (Table 2) following aqua regia digestion were within two standard deviations of the target values, with precision <12%, n = 3. The overall average recoveries of PTE spiked into the artificial sweat solutions at 17, 27 and 32 °C were: As 92.6 ± 3.7; Cd 88.6 ± 4.2; Cr 86.2 ± 3.8; Cu 89.7 ± 5.9, Fe 89.7 ± 2.6, Mn 91.7 ± 4.0; Ni 81.2 ± 5.7; Pb 95.7 ± 5.7, and Zn 87.2 ± 10% (see Supplementary Table S1 for further details). As previously noted by Leal et al. [22] in their study of Cr, Ni, Pb and Zn in the EN 1811 and NIHS 96-10 formulations, the solubility of some of the analytes appeared to decrease slightly in the presence of the extraction reagents, with the most notable effect for Ni in NIHS 96-10.

Table 2. Analyte concentrations determined in the GLA URM secondary reference material (mg/kg dry weight).

	As	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
Found	17.2 ± 1.5	0.524 ± 0.060	41.2 ± 4.4	92.3 ± 9.9	29,500 ± 2800	407 ± 31	43.5 ± 4.7	380 ± 26	180 ± 19
Indicative [40]	17.7 ± 4	0.646 ± 0.184	43.2 ± 3	111 ± 5	30,600 ± 1200	442 ± 18	48.8 ± 7	389 ± 25	177 ± 11
Recovery (%)	97.2	81.1	95.4	83.2	96.4	92.1	89.1	97.7	102

Results are mean ± S.D (n = 3 for found values; n = 34 for indicative values).

3.2. Characterization of Bulk Composite Soil Sample

The pH of the soil was 7.98 and the OM 21.0%. Similar values have been reported previously within Alaba International Market [43,44]. As expected, the pseudototal PTE concentrations (Table 3) by far exceeded average values for world soils [45] and were substantially greater than the widely cited Dutch Target and Intervention Values [46] (except for As and Cr). Extremely high soil PTE concentrations have been reported previously at sites where informal e-waste recycling is practiced, not only in Nigeria, but also elsewhere in the world, e.g., [47–49]. The levels of PTE in the test substrate are therefore not untypical of those workers could encounter during their day-to-day activities.

Contamination factors were: As 2; Cd 90; Cr 2; Cu 806; Fe 4; Mn 34; Ni 27; Pb 209 and Zn 231, confirming that the soil was very highly contaminated with all the PTEs except As and Cd (where it was moderately contaminated) and Fe (where it was considerably contaminated). Enrichment of soil with Cd, Cu, Pb and Zn at e-waste processing sites results from the widespread use of these elements in electronic goods. Cadmium is associated with batteries, toners and plastics; copper with wiring (amongst other components); lead with solder, cathode ray tubes (CRT) and batteries; and zinc with CRT and printed circuit boards [50].

Table 3. Analyte concentrations in the bulk composite soil sample from the Alaba e-waste recycling site (mg/kg dry weight, n = 3) and comparison with reference and selected recent literature values.

	As	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
Found	10.1 ± 1.8	78.3 ± 5.4	88.6 ± 12.0	13,700 ± 843	73,500 ± 5260	1120 ± 92	355 ± 26	3340 ± 132	11,100 ± 618
World soil [45]	0.1	1.1	42	14	-	418	18	25	62
Background [†]	5.2	0.87	<37	17	18,000	330	13	16	48
Dutch target values [46]	29	0.8	100	36	-	-	35	85	140
Dutch intervention values [46]	55	12	380	190	-	-	210	530	720
Isimekhai et al. [43]	-	26.4 ± 2.6	35.4 ± 3.6	3280 ± 277	-	115 ± 9	40.8 ±4.9	2420 ± 289	2200 ± 180
Anselm et al. [44]	5.48 ± 0.38	34.9 ± 1.4	106 ± 4	13,300 ± 195	88,000 ± 2700	974 ± 38	240 ± 15	1690 ± 56	6600 ± 243
Liu et al. [47] (Zhejiang, China)	nr	0.2–6.2	56–172	30–1860	nr	nr	21–305	18–2060	15–2710
Cao et al. [48] (Accra, Ghana)	4.3–26.2	<LOD-28.5	nd	100–20,400	nr	nr	nr	51–12,500	nr
Chakraborty et al. [49] (Indian cites)	<LOD-111	<LOD-11	2–386	15–4900	nr	nr	4–872	2–706	nr

[†] Background values are from the Screening Quick Reference Tables for Inorganics in Soil [51] except Cd from [43], nr = not reported.

3.3. Comparison of Artificial Sweat Solutions

The bioaccessible analyte concentrations obtained using the five different artificial sweat formulations, at a fixed temperature of 37 °C, are shown in Table 4, together with percent bioaccessibility values calculated using Equation (2).

$$\%\text{bioaccessibility} = \frac{\text{Measured PTE concentration (mg/kg)}}{\text{Pseudototal concentration of PTE (mg/kg)}} \tag{2}$$

The analyte with highest bioaccessible concentration in all of the artificial sweat solutions was Cu. This is perhaps to be expected since the element is usually relatively mobile in soil [11]. Although not traditionally considered important in terms of dermal exposure, Cu has been reported as an emerging cause of skin hypersensitivity [52]. High concentrations of zinc were also bioaccessible. In contrast, bioaccessible concentrations of As, Cd, Cr, Ni and Pb were low (<5 mg/kg) except for Cd, Ni and Pb in the NIHS formulation.

Comparison with previous studies is limited by the paucity of research featuring the use of extraction methods to estimate dermal bioaccessibility of PTE in soil and the fact that different workers have studied different substrates. However, Leal et al. [22] found Zn generally to have higher dermal bioaccessibility than Cr, Ni or Pb (though not for all samples studied) whilst Khelifi et al. [23] reported substantially higher bioaccessibility for Cd than for Cr, Cu, Pb or Zn, in particular for mine tailings. Villegas et al. [24] observed a marked difference in behavior between reference soils SQC001 (where Zn was more bioaccessible than Cr, Ni or Pb) and BGS 102 (where Zn was the least bioaccessible element) which they attributed to differences in soil properties such as cation exchange capacity and organic carbon content. This lack of consensus highlights the need for more research to improve the understanding of links between soil physicochemical properties and PTE bioaccessibility [53].

The deionized water extracted smaller amounts of analytes than any of the artificial sweat solutions. The presence of solutes, which increases the ionic strength of the extractant, and complexing agents such as chloride, promotes the desorption of PTEs and aids their retention in solution once released. The NIHS 96-10 solubilized substantially higher amounts of all the analytes than the other formulations. A major factor that influences PTE solubility is pH. Although NIHS does not have the lowest pH of the extractants when freshly prepared, analysis of soil extracts shows that its pH was less affected by addition of the (slightly alkaline) soil than the other formulation (Table 5) meaning analytes were less likely to precipitate out of solution. This greater buffering capacity is probably due to the higher concentrations of acetic and lactic acids present. Although the order of extraction varied between analytes, the second most efficient formulation overall appeared to be that of Cheng et al. (CHE) [38] and the second least efficient EN 1811 (the BSI method [34]). This is consistent with the findings of Leal et al. [22] and Villegas et al. [24] both of whom found higher bioaccessible concentrations of PTE when their samples were extracted using method NIHS 96-10 than method EN 1811.

The difference in extraction performance of the five formulations markedly affected the % BA values obtained, which—except for As and Cu—were at least an order of magnitude larger for NIHS 96-10 than for any other extractant. This was particularly noticeable for Pb, where 17% BA was indicated by NIHS 96-10 but <0.011% by all other methods.

Table 4. Bioaccessible analyte concentrations obtained using five artificial sweat formulations at 37 °C, together with % bioaccessibility values.

		As	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
Concentration (mg/kg)	DIW	0.0419 ± 0.0361	0.000924 ± 0.001401	0.0379 ± 0.0298	8.77 ± 6.52	4.37 ± 3.35	0.545 ± 0.413	0.0749 ± 0.0568	0.0580 ± 0.0372	0.0478 ± 1.3222
	BSI	0.0939 ± 0.0016	0.479 ± 0.036	0.0763 ± 0.0108	87.4 ± 1.8	12.5 ± 0.4	8.61 ± 0.30	0.711 ± 0.0223	0.155 ± 0.019	9.98 ± 6.21
	NIHS	1.17 ± 0.06	19.7 ± 0.8	2.59 ± 0.08	4540 ± 62	859 ± 7	242 ± 0	42.1 ± 0.5	579 ± 3	3190 ± 19
	ALT	0.134 ± 0.013	1.36 ± 0.05	0.114 ± 0.011	405 ± 28	31.2 ± 1.6	24.2 ± 1.1	2.74 ± 0.11	0.343 ± 0.162	157 ± 18
	ARI	0.0930 ± 0.0107	1.32 ± 0.06	0.0321 ± 0.0122	132 ± 3	21.5 ± 0.4	20.0 ± 0.5	1.86 ± 0.05	0.185 ± 0.157	69.3 ± 5.8
	CHE	0.140 ± 0.001	0.779 ± 0.013	0.229 ± 0.009	717 ± 11	38.6 ± 3.8	15.8 ± 0.1	2.26 ± 0.03	0.109 ± 0.010	34.2 ± 0.3
% BA	DIW	0.415	0.00118	0.0428	0.0640	0.00595	0.0486	0.0211	0.00173	0.000431
	BSI	0.929	0.611	0.0860	0.638	0.0170	0.769	0.200	0.00466	0.0900
	NIHS	11.5	25.1	2.93	33.1	1.17	21.6	11.9	17.3	28.7
	ALT	1.32	1.74	0.128	2.95	0.0425	2.16	0.773	0.0103	1.41
	ARI	0.920	1.69	0.0362	0.962	0.0293	1.79	0.524	0.00553	0.625
	CHE	1.39	0.995	0.259	5.23	0.0525	1.41	0.637	0.00327	0.309

Table 5. Comparison between pH of freshly prepared sweat solutions and pH of soil extracts.

	pH Before Use	Extract pH
DIW	5.00	7.96
BSI	6.48	7.67
NIHS	4.68	5.41
ALT	5.30	7.43
ARI	4.49	7.34
CHE	6.00	8.00

Since the test substrate is a bulk composite sample, containing topsoil from several locations and prepared specifically for the purpose of analytical method comparison, limited conclusions can be drawn concerning risk or potential human health impact of the PTE it contains (environmental studies at Alaba International Market are already available in literature [43,44]). However, it is noticeable that analytes with highest soil contamination factors also had highest bioaccessibility. The fact that the dermal bioaccessible concentrations alone of Cd (19.7 ± 0.8 mg/kg), Cu (4540 ± 62 mg/kg), Pb (579 ± 3 mg/kg) and Zn (3190 ± 19 mg/kg) estimated by NIHS 96-10 exceeded Dutch Intervention Values for total soil PTE concentrations [46] suggests further investigation of bioaccessibility at this site is urgently needed.

3.4. Variation in Bioaccessible Analyte Concentrations with Extraction Temperatures

The bioaccessible PTE concentrations found using the five artificial sweat formulations at different temperatures are shown in Figures 2 and 3 (results for NIHS are plotted on a secondary axis because of the substantially larger amounts of PTE released by this extractant). Visual inspection suggests that amounts of Cd and Mn released by almost all of the artificial sweats increased with temperature, especially above 32 °C. Extraction of Cu, Fe and Ni was less affected, with only the ALT and NIHS formulations showing a strong upward trend. For Cr, the CHE formulation released considerably more analyte at 47 °C than at other temperatures. This was also the case for Pb using the ALT formulation. Although several formulations extracted more Zn as temperature increased, the effect was again most marked for ALT. The behavior of As was different from that of the other PTE, with largest amounts released at 17 °C and similar extraction, for a particular formulation, between 27 and 47 °C.

Statistical analysis indicated that there was no overall statistically significant increase in Cr, Cu, Fe, Ni or Zn extraction with temperature ($p > 0.05$). For As, Cd, Mn and Pb, while extractable concentrations at lower temperatures were generally statistically similar to one another, there was significant difference between measured values at the lowest (17 or 27 °C) and highest (47 °C) temperatures. ($p < 0.05$) indicating the importance of considering ambient (and hence skin) temperature in the application of dermal bioaccessibility tests. There was no statistically significant difference between results obtained at 32 °C and 37 °C, for any analyte or formulation.

Monthly average air temperatures in the City of Lagos range from 29–34 °C [54] but values as high as 38 °C have been reported and are likely to increase due to global climate change. Dermal bioaccessibility tests carried out in the 32–37 °C range may therefore underestimate the actual exposure to soil PTE experienced by individuals who live or work in Alaba International Market, and other metal processing sites in warm climates, in particular given that skin permeability is also greater at higher temperatures [55].

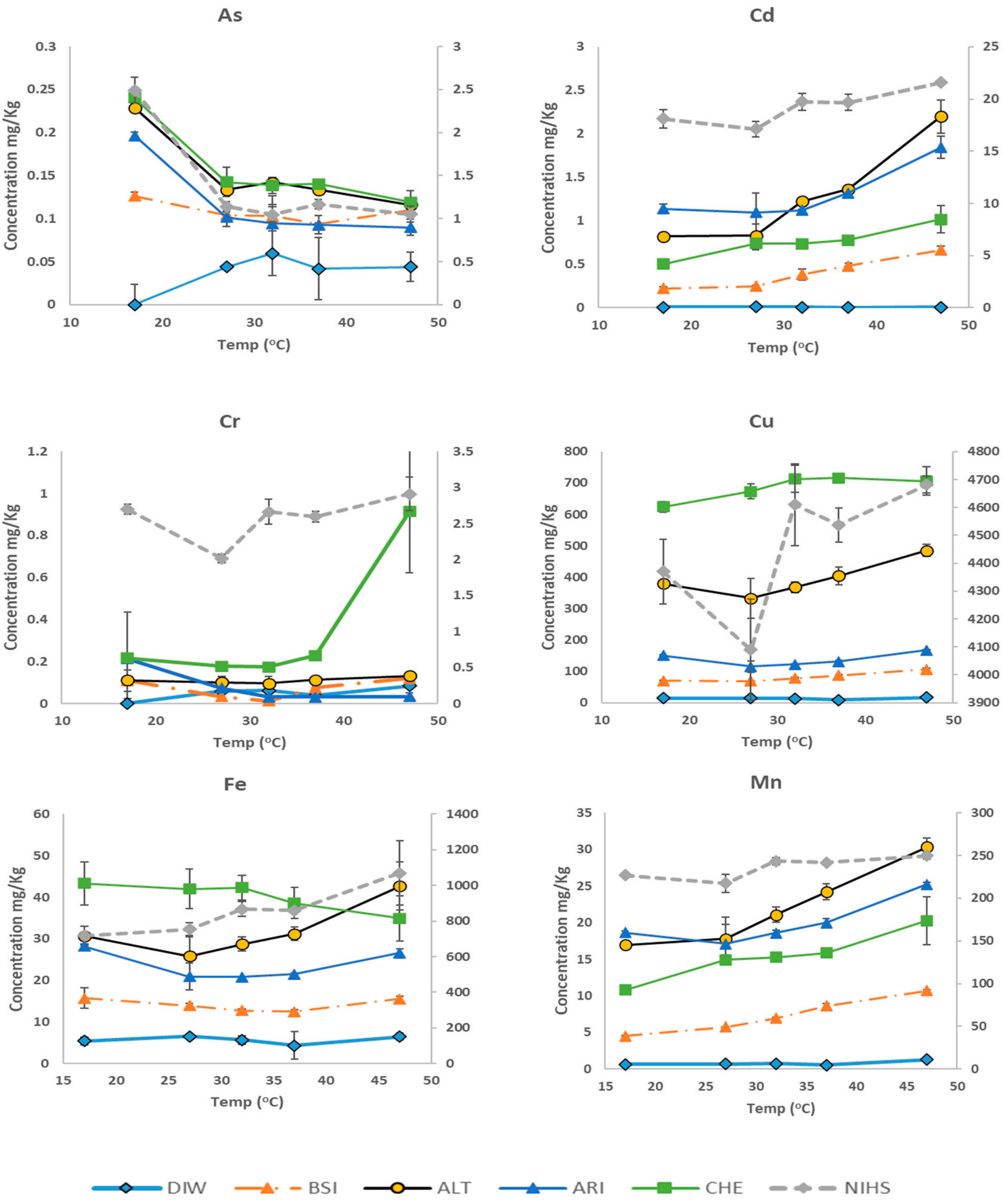

Figure 2. Dermal bioaccessible concentrations of As, Cd, Cr, Cu, Fe and Mn in bulk composite soil sample using different artificial sweat solutions and extraction temperatures. Results are plotted against the primary (**left-hand**) axis except NIHS, which is plotted against the secondary (**right-hand**) axis.

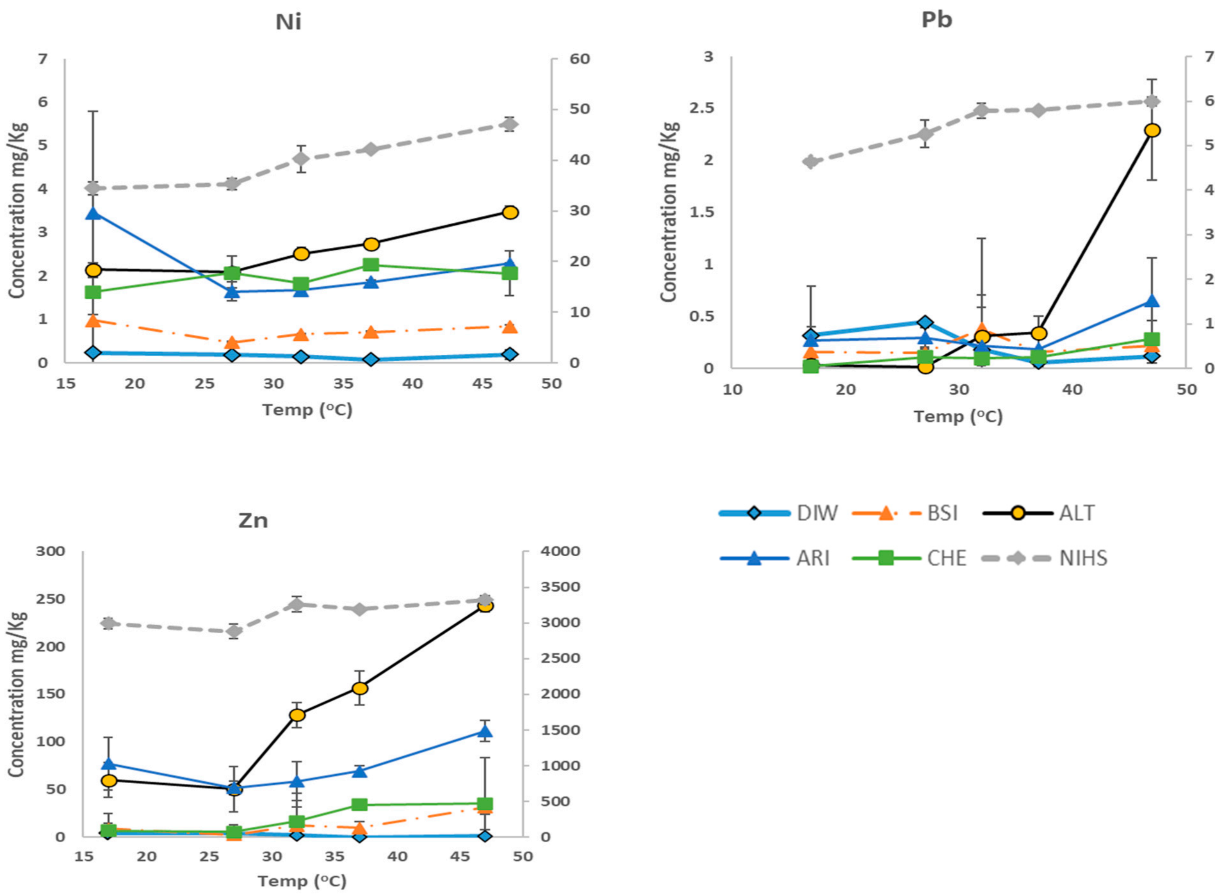

Figure 3. Dermal bioaccessible concentrations of Ni, Pb and Zn in bulk composite soil sample using different artificial sweat solutions and extraction temperatures. Results are plotted against the primary (**left-hand**) axis except NIHS, which is plotted against the secondary (**right-hand**) axis.

4. Conclusions

When five different artificial sweat formulations were used to estimate the dermal bioaccessibility of PTE in a bulk composite soil sample from an e-waste recycling site the results obtained differed between elements and extractants. Copper and Zn were the most bioaccessible elements, whereas the bioaccessibilities of As, Cd, Cr, Ni and Pb were low. In general, the amounts of PTE released were in the order: NIHS 96-10 > CHE > ALT > ARI > BSI > DIW. The NIHS 96-10 formulation gave a substantially higher estimation of bioaccessible PTE concentrations than any of the other extractants, due not only to its relatively low pH but also to its greater buffering capacity. Visually, there was a general increase in amounts of PTE extracted at higher temperatures for all formulations, with the exception of As. Whilst this trend was not statistically significant for all analytes and artificial sweat formulations, measured concentrations at the highest temperature studied (47 °C) were generally higher than those at the lowest temperatures studied (17 and 27 °C), while results at 32 and 37 °C were comparable.

This work highlights the need for further research on dermal bioaccessibility of PTE in soil to improve understanding of the complex interrelationships between soil properties, PTE speciation, and the performance of different simulated skin fluids. In terms of analytical science, there is a need to investigate the performance of different bioaccessibility tests and formulations when applied to different soil types (particularly soils of different pH, organic matter content and cation exchange capacity); to develop harmonized methodology that will produce comparable results in different laboratories; and to create associated (certified) reference materials for quality control. Better understanding is needed of the relationship between ambient temperature, skin temperature, and dermal bioaccessibility to establish whether extractions should sometime be carried out at >37 °C. Studies are also required to compare and validate results obtained against real dermal uptake. In terms of medical geology, dermal bioaccessibility tests should be applied more widely alongside procedures that estimate bioavailability of PTE following oral ingestion or inhalation. This will provide a more holistic understanding of PTE exposure and risk in situations where individuals live or work in proximity to soil impacted by high levels of metals/metalloids.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/geosciences12010031/s1, Table S1: Analyte recoveries from spiked sweat solutions without geological material (mean ± SD, n = 3).

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