Insights on hazardous metal bioaccessibility, and groundwater impacted by Zn residues from a legacy mine and risk evaluation of adjacent soils.

Walubita Mufalo [a]*, Takahiko Arima [a], Toshifumi Igarashi [a], Mayumi Ito [a], Tsutomu Sato [a], Shingo Tomiyama [a], Imasiku Nyambe [b], Carlito Baltazar Tabelin [c], Hokuto Nakata [d], Shouta Nakayama [d, e] and Mayumi Ishizuka[d]

[a] Division of Sustainable Resources Engineering, Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan

[b] IWRM Centre/Geology Department, School of Mines, The University of Zambia, Lusaka 32379, Zambia

[c] Department of Materials and Resources Engineering Technology, Mindanao State University—Iligan Institute of Technology, Iligan City 9200, Philippines

[d] Faculty of Veterinary Medicine, Hokkaido University, Kita 18, Nishi 9, Kita-Ku, Sapporo 060-0818, Japan

[e] Biomedical Sciences Department, School of Veterinary Medicine, The University of Zambia, Lusaka P.O. Box 32379, Zambia

*Corresponding email: wmufalo@gmail.com

Supplementary information

Summary

This supplement contains 7 figures and 10 tables, which provides additional data on the following: (1) monitoring wells, (2) particle size distribution of < 30 μm particles, (3) chemical composition of simulated fluids, (4) sequential extraction procedure, (5) *QA/QC*, (6) SEM micrograph, (7) ORP and EC of groundwater, (8) Eh-pH stability diagrams, (9) thermodynamic calculations, (10) bioaccessible fractions of soils under simulated and gastric fluids, (11) changes of ORP and pH after extraction with simulated fluids, (12) bioaccessible fractions/phases of the total pb/Zn partitioning contents and (14) calculated hazard quotients

Monitoring well	Altitude (m)	Height above ground (m)	Monitory cable (m)	Drilling depth (m)
KA-01	1186.5	0.41	12.0	15.0
KA-02	1184.3	0.41	5.59	10.0
KA-03	1176.3	0.47	8.20	10.0

Fig. S1. Monitoring wells installed at the Kabwe mine site, with their respective depth and altitude.

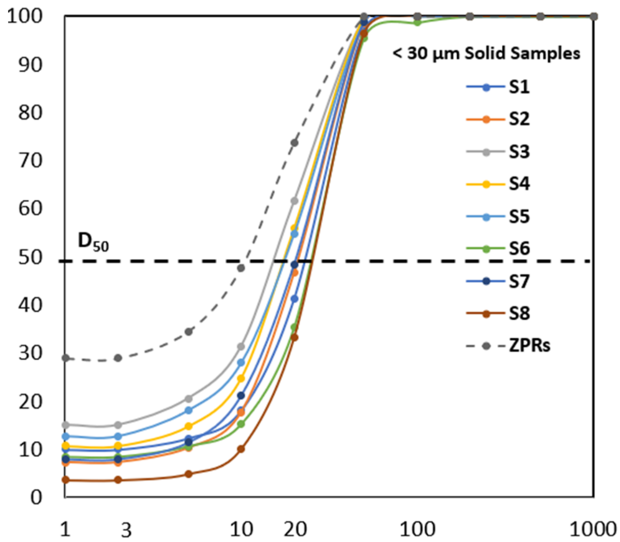

Fig. S2. Particle size distribution of < 30 μm solid samples. D_{50} represents 50% effective diameter.

Table. S1. Simulated fluids compositions for bioaccessibility tests in < 30 µm dust from ZPRs and soil samples; ALF- Artificial lysosomal fluid, GS- Gamble solution and PBS-Phosphate-buffered saline.

Composition (g/L)	ALF (pH 4.5±0.1)	GS (pH 7.3±0.1)	PBS (pH 7.3±0.1)
NaCl	3.21	6.779	8.77
Na_2HPO_4	0.071	-	1.28
$NaHCO_3$	-	2.268	-
Trisodium citrate dihydrate	0.077	0.055	-
NH4Cl	-	0.535	-
Glycine	0.059	0.375	-
NaH_2PO_4	-	1.872	-
L-cysteine	-	0.121	-
NaOH	6	-	-
Citric acid	20.8	-	-
$CaCl_2$·2H2O	0.128	0.026	-
Na_2SO_4	0.039	-	-
$MgCl_2·6H_2O$	0.05	-	-
Disodium tartrate	0.09	-	-
Sodium lactate	0.085	-	-
Sodium pyruvate	0.172	-	-
KH_2PO_4	-	-	1.36
Ionic strength (mol/L)	0.34	0.17	0.19

Table. S2. Sequential extraction for cationic element speciation.

Step	Extractant	pH	Liquid to solid ratio (mL/g)	Temperature (°C)	Duration (h)	Mixing speed (rpm)	Extracted phase
1	1 M $MgCl_2$	7	20/1	25	1	120	Exchangeable
2	1 M CH_3COONa	5	20/1	25	5	120	Carbonates
3	0.04 M $NH_2OH·HCl$ in 25% acetic acid		20/1	50	5	120	Reducible
4	0.04 M $NH_2OH·HCl$ in 25% acetic acid; 30% H_2O_2; 0.02 M HNO_3		36/1	85	5	120	Oxidizable
5	60% HNO_3		20/1	60	1	-	Residual

Table. S3. Quality assurance (*QA*) and quality control (*QC*).

Calibration standard for ICP-AES											
Elements	Mass concentration (w/v) ± expanded measurement uncertainty										
	Certified value (mg/L)	Uncertainty	Measured value								Traceable to SRM
			Multi Standard				SO_4^{2-} Standard				
			Std 1	Std 5	Std 10	Std 20	Std 1	Std 5	Std 10		
Ca	1009	±10	999	1015	1000	1001					SRM 3109a
Fe	998	±10	1006	997	1007	1004					SRM 3126a
Mg	999	±10	990	992	990	995					SRM 3131a
Na	1001	±10	1005	997	1003	995					SRM 3152a
K	1002	±10	1010	1004	1000	1005					SRM 3141a
Pb	999	±10	993	1006	995	991					SRM 3128
Zn	997	±10	989	988	990	995					SRM 3168a
SO_4^{2-}	1000						1010	994	996		
	0.8% (coverage factor *k*=2 level of confidence approximately 95% (Sulfate Ion Standard solution SO_4^{2-} 1,000) (ISO/IEC 17025:2017 and ISO 17034:2018)										

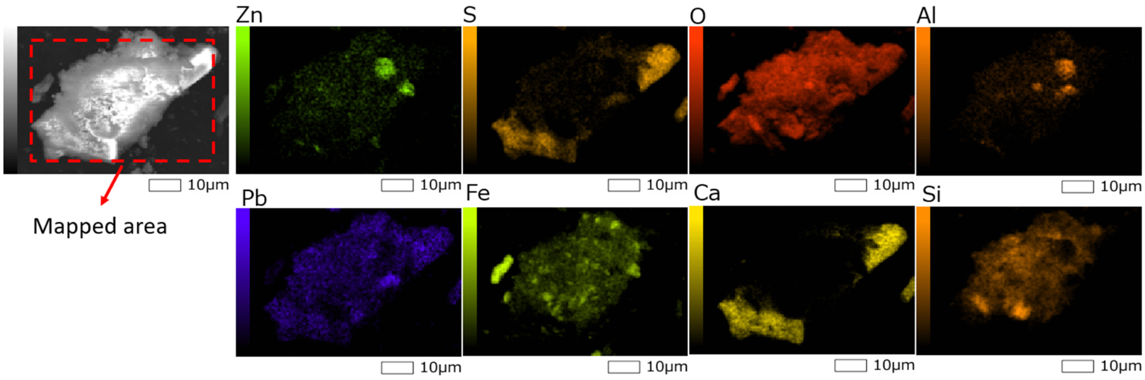

Fig. S3. SEM elemental photomicrograph of the corresponding elemental maps (Zn, S, O, Al, Pb, Fe, Ca and Si).

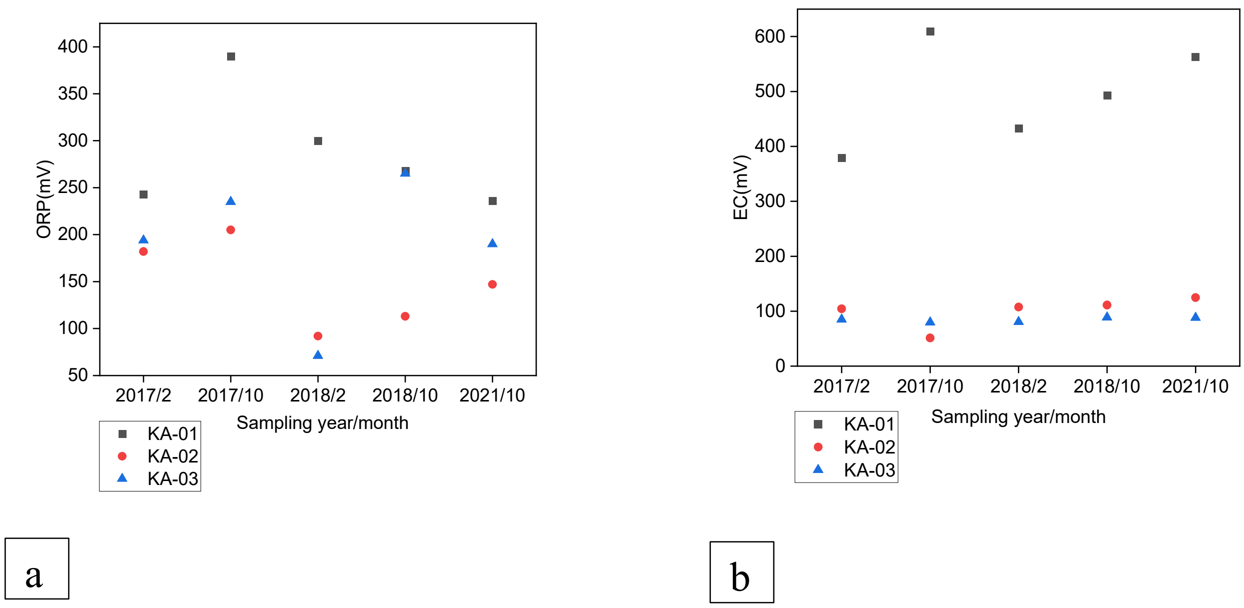

Fig. S4. Groundwater parameters of the monitoring wells KA-01 to 03, including their oxidation reduction potential (ORP) (a) and Electrical conductivities (EC) (b) for sampling years between 2017 to 2021.

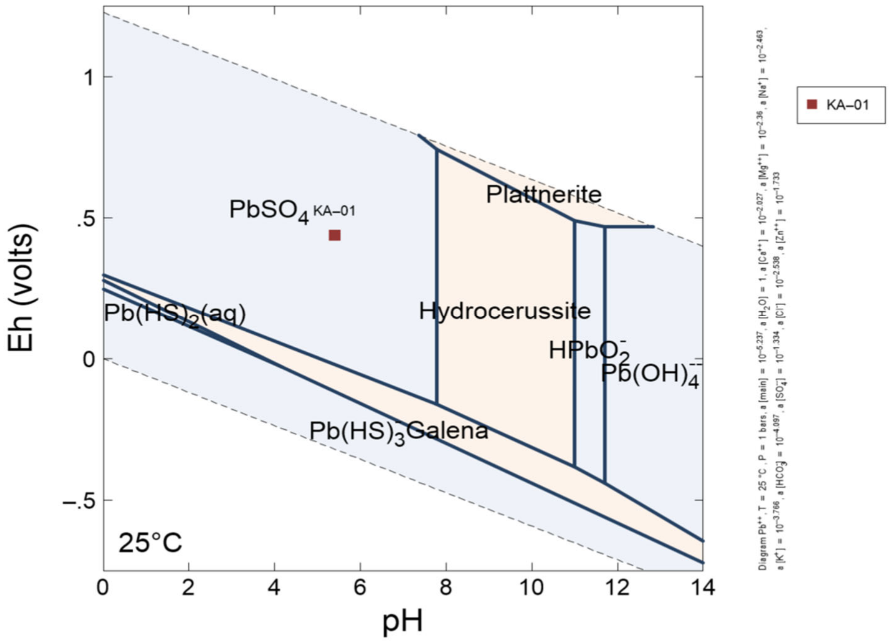

Fig. S5. Eh-pH predominance diagram of Pb for groundwater in KA-01 at 25 °C, 1.013 bars and their actual activities.

Table S4. Species distribution in groundwater samples.

KA-01	%	KA-02	%	KA-03	%
Pb^{2+}	30.16	Zn^{2+}	56.24	Zn^{2+}	64.26
$PbOH^{+}$	0.09	$ZnOH^{+}$	1.05	$ZnOH^{+}$	0.78
$PbSO_{4\,(aq)}$	58.24	$Zn(OH)_{2\,(aq)}$	0.32	$Zn(OH)_{2\,(aq)}$	0.15
$Pb(SO_4)_{2\text{-}2}$	10.15	$ZnSO_{4\,(aq)}$	6.36	$ZnCl^{+}$	0.14
$PbCO_{3\,(aq)}$	0.05	$Zn(SO_4)_{2\text{-}2}$	0.08	$ZnSO_{4\,(aq)}$	6.55
$PbHCO_3^{+}$	1.29	$ZnCO_{3\,(aq)}$	24.03	$Zn(SO_4)_{2\text{-}2}$	0.07
Zn^{2+}	48.04	$ZnHCO_3^{+}$	11.73	$ZnCO_{3\,(aq)}$	15.87
$ZnSO_{4\,(aq)}$	41.43	$Zn(CO_3)_{2\text{-}2}$	0.18	$ZnHCO_3^{+}$	12.08
$Zn(SO_4)_{2\text{-}2}$	10.44	-	-	$Zn(CO_3)_{2\text{-}2}$	0.06
$ZnHCO_3^{+}$	0.08	-	-	-	-

Table S5. Saturation indices (*SI*s) for the groundwater samples (±0.5 apparent equilibrium).

Speciation/monitoring well	KA-01	KA-02	KA-03
Anglesite	-0.362	N/A	N/A
Cerrusite	-1.85	N/A	N/A
Gypsum	-0.094	-1.505	-1.667
Hydrocerrusite	-6.703	N/A	N/A
Smithsonite	-0.444	-0.147	-0.394
Zincite	-2.886	-2.501	-2.883
Anhydrite	-0.341	-1.755	N/A
Aragonite	-3.262	0.378	0.024
Calcite	-3.118	0.522	0.167
Vaterite	-3.685	-0.044	-0.399

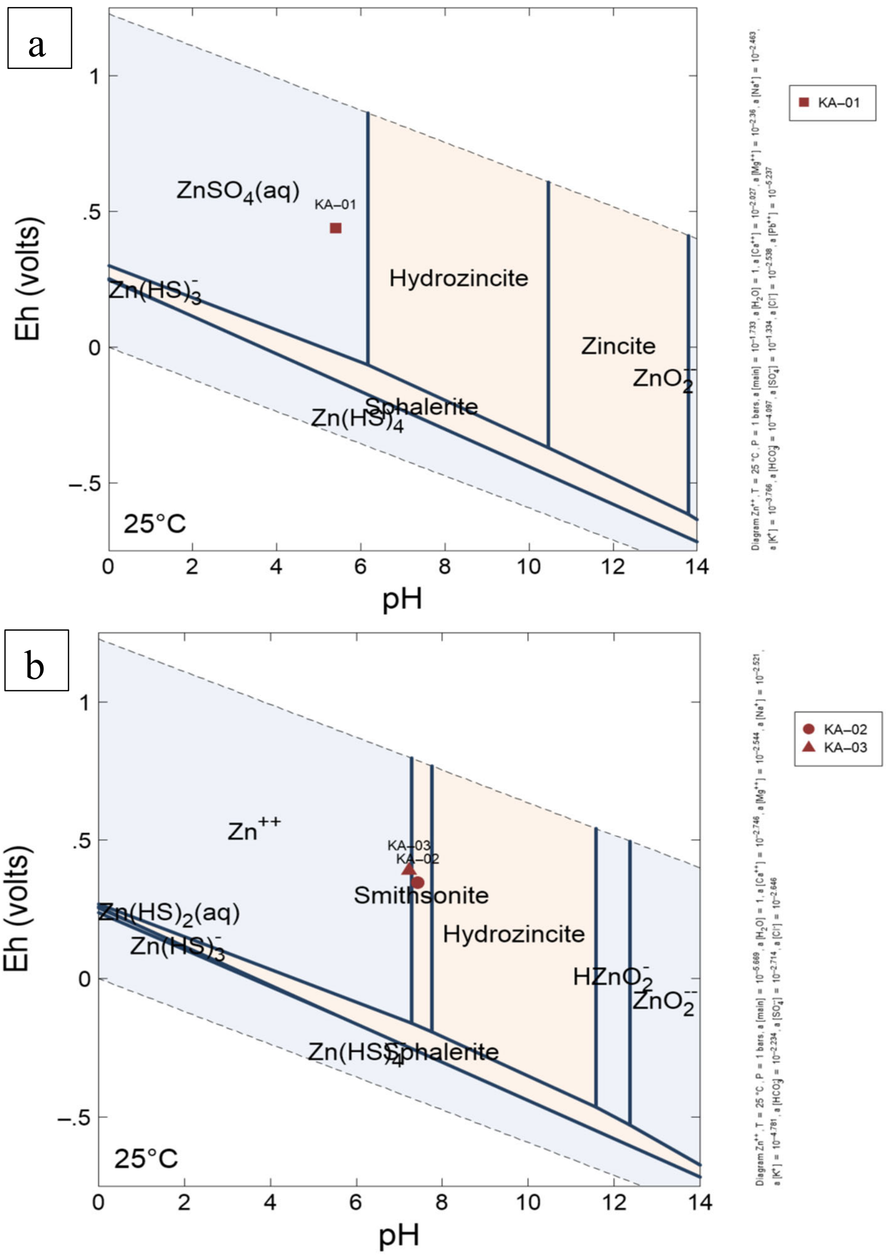

Fig. S6. Eh-pH predominance diagram of Zn in groundwater (a) KA-01 and (b) KA- 02 and KA-03 at 25 °C, 1.013 bars and their actual activities.

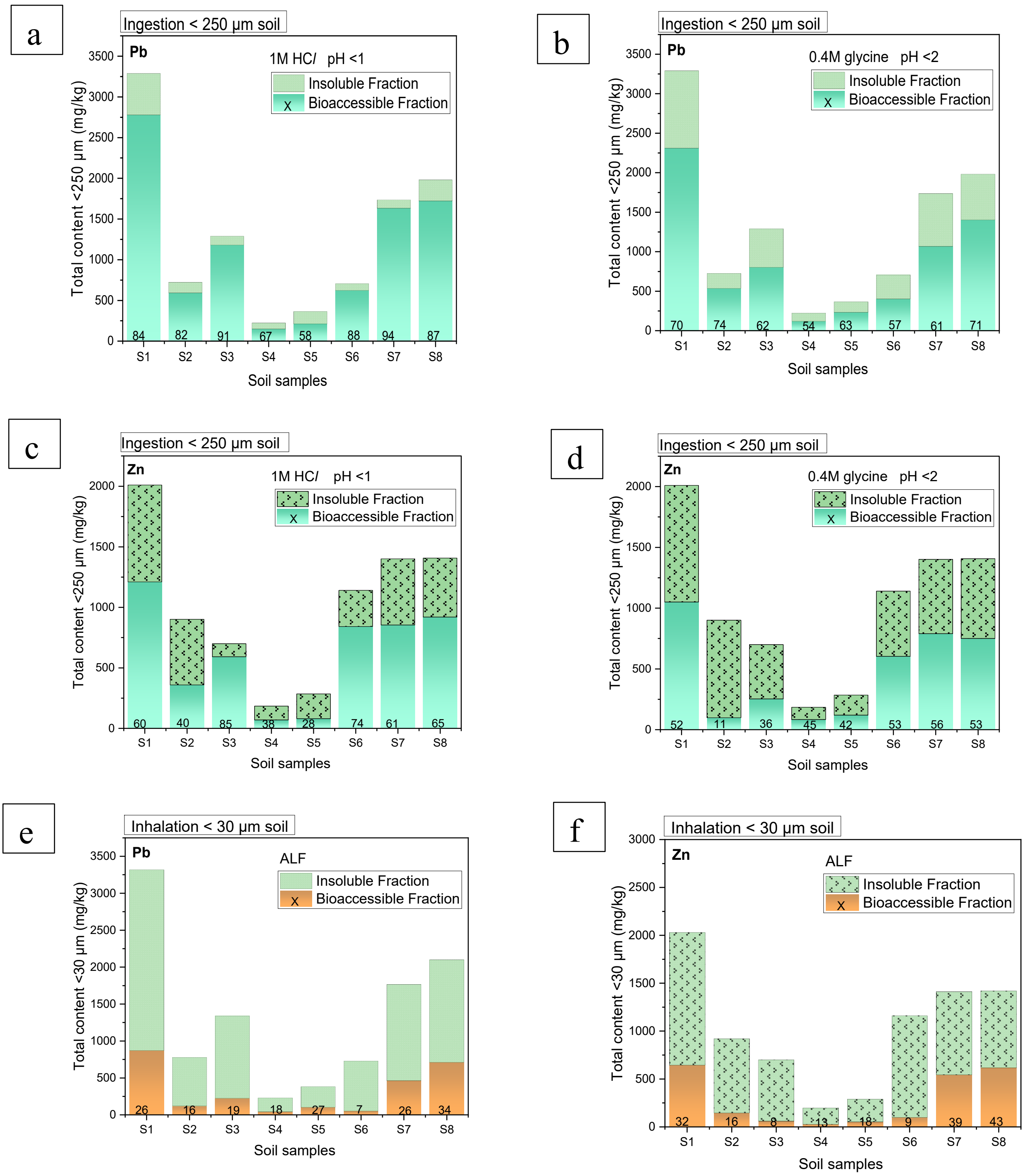

Fig. S7. Bioaccessible fractions of Pb and Zn from ingestible soil < 250 μm and inhalable dust < 30 μm in gastric and simulated fluids: (a) Pb; 1M HCI pH<1 (b)Pb; 0.4M glycine pH<2 (c) Zn; 1M HCI pH<1 (d) Zn; 0.4M glycine pH<2 (e) Pb; ALF- artificial lysosomal fluid pH 4.5 and (f) Zn; ALF- artificial lysosomal fluid pH 4.5

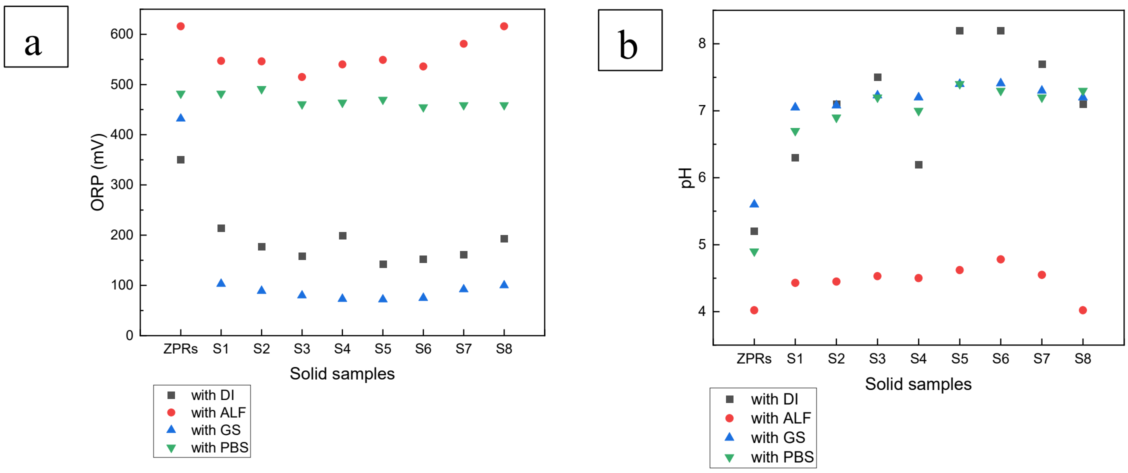

Fig. S8. Changes in ORP (a) and pH (b) of ZPRs and soil (for <30 µm dust particles) extracted in simulated fluids; ALF- artificial lysosomal fluid, GS-Gamble solution, PBS-phosphate-buffered saline in comparison to neutral conditions when leached in deionized water (DI).

Table S6. Total Pb/Zn partitioning phase contents obtained through sequential extraction (SE-Pb and SE-Zn) and the extracted Pb in gastric conditions of pH<1 using 1 M HC*l* with the associated bioaccessible fractions (*BF*s) of the total Pb/Zn bound phases.

Size µm	SE-Pb (mg/kg)	Extracted Pb (mg/kg)	*BF*s pH<1 %	SE-Zn (mg/kg)	Extracted Zn (mg/kg)	*BF*s pH<1 %
<30	63,900	22,000±8	34	23,670	12,300±4	52
30-75	53,500	19,600±3	37	19,625	9,800±3	50
75-150	63,750	22,400±4	35	21,280	10,700±8	50
150-250	72,150	22,700±9	31	22,375	11,400±9	51

Table S7. Total Zn partitioning phase contents obtained through sequential extraction (SE-Pb and SE-Zn) and the Extracted Pb in gastric conditions of pH<2 using 0.4 M glycine with the associated bioaccessible fractions (*BF*s) of the total Pb/Zn bound phases.

Size µm	SE-Pb (mg/kg)	Extracted Pb (mg/kg)	*BF*s pH<2	SE-Zn (mg/kg)	Extracted Zn (mg/kg)	*BF*s pH<2 %
<30	63,900	6,990±10	11	23,670	7,010±15	30
30-75	53,500	6,070±6	11	19,625	7,090±9	36
75-150	63,750	6,910±9	11	21,280	8,110±8	38
150-250	72,150	7,670±11	11	22,375	9,490±9	42

Table S8. Saturation indices (*SI*s) of potentially solubility controlling phases as calculated by PHREEQC code for the extracts obtained from ZPRs in 1 M HC*l*.

Phase/size	<30 µm	30-75 µm	75-150 µm	150-250 µm
Galena	-75.94	-74.24	-75.76	-73.4
Sphalerite	-78.38	-76.68	-78.26	-75.88
Quartz	0.69	0.55	0.54	0.58
Zincosite	-10.47	-10.27	-10.35	-10.37
Litharge	-15.76	-15.61	-15.58	-15.57
Anglesite	1.32	1.51	1.51	1.47
Lepidocrocite	-4.68	-4.58	-4.51	-4.49
Larnakite	-8.98	-8.66	-8.62	-8.65
Ferrihydrite	-6.77	-6.62	-6.6	-6.58
Goethite	-4.01	-3.88	-3.85	-3.82
Hematite	-5.65	-5.37	-5.31	-5.27
Zincite	-14.22	-14.1	-14.11	-14.08

Table S9 Hazard Quotients (*HQ*) of Pb and Zn for both children and adults. The data is derived from ingestible particles < 250 μm from Zinc plant residues (ZPRs) and soil S1 to S8 in Kabwe, Zambia

Pb	Child			Adult			Zn	Child			Adult		
Ingestion < 250 μm	HQ	HQ_h	HQ_g	HQ_t	HQ_h	HQ_g	Ingestion <250 μm	HQ	HQ_h	HQ_g	HQ	HQ_h	HQ_g
ZPRs	230	83.3	28.	24.6	8.92	3.00	ZPRs	6.95E-01	4.86E-01	3.51E-01	7.44E-02	5.21E-02	3.76E-02
S1	12	10.2	8.44	1.29	1.09	0.90	S1	8.57E-02	5.16E-02	4.47E-02	9.18E-03	5.53E-03	4.79E-03
S2	2.64	2.17	1.96	0.28	0.23	0.21	S2	3.84E-02	1.53E-02	4.21E-03	4.11E-03	1.64E-03	4.51E-04
S3	4.71	4.31	2.93	0.50	0.46	0.31	S3	2.98E-02	2.52E-02	1.08E-02	3.20E-03	2.70E-03	1.16E-03
S4	0.81	0.55	0.44	0.09	0.06	0.05	S4	7.88E-03	2.98E-03	4.30E-03	8.45E-04	3.20E-04	4.61E-04
S5	1.33	0.77	0.84	0.14	0.08	0.09	S5	1.21E-02	3.45E-03	5.11E-03	1.30E-03	3.70E-04	5.48E-04
S6	2.58	2.28	1.47	0.28	0.24	0.16	S6	4.86E-02	3.58E-02	2.57E-02	5.21E-03	3.84E-03	2.75E-03
S7	6.34	5.96	3.89	0.68	0.64	0.42	S7	5.97E-02	3.64E-02	3.37E-02	6.40E-03	3.90E-03	3.61E-03
S8	7.24	6.29	5.13	0.78	0.67	0.55	S8	6.00E-02	3.92E-02	3.20E-02	6.42E-03	4.20E-03	3.42E-03

- *HQ*-Hazard quotient
- HQ_h-Hazard quotient from correction coefficient under pH<1
- HQ_g-Hazard quotient from correction coefficient under pH<2
- *HQ*>1 Risk of non-carcinogenic effects
- *HQ*<1 No risk of non-carcinogenic effects

Table S10 Hazard Quotients (*HQ*) of Pb and Zn for both children and adults. The data is derived from inhalable particles < 30 μm from Zinc plant residues (ZPRs) and soil S1 to S8 in Kabwe, Zambia

Pb	Child		Adult		Zn	Children		Adult	
Inhalation < 30 μm	*HQ*	HQ_{alf}	*HQ*	HQ_{alf}	inhalation <30 μm	*HQ*	HQ_{alf}	*HQ*	HQ_{alf}
ZPRs	1.64E-02	4.57E-04	3.52E-03	9.78E-05	ZPRs	5.05E-05	2.03E-05	1.08E-05	4.34E-06
S1	8.91E-04	2.34E-04	1.91E-04	5.01E-05	S1	6.36E-06	2.02E-06	1.36E-06	4.34E-07
S2	2.10E-04	3.28E-05	4.49E-05	7.02E-06	S2	2.89E-06	4.61E-07	6.18E-07	9.87E-08
S3	3.60E-04	6.07E-05	7.71E-05	1.30E-05	S3	2.20E-06	1.85E-07	4.71E-07	3.96E-08
S4	6.20E-05	1.13E-05	1.01E-05	1.84E-06	S4	6.20E-07	8.15E-08	1.01E-07	1.33E-08
S5	1.03E-04	2.74E-05	1.67E-05	4.46E-06	S5	9.06E-07	1.66E-07	1.47E-07	2.70E-08
S6	1.96E-04	1.37E-05	3.20E-05	2.23E-06	S6	3.64E-06	3.10E-07	5.92E-07	5.05E-08
S7	4.74E-04	1.24E-04	7.73E-05	2.02E-05	S7	4.43E-06	1.71E-06	7.21E-07	2.78E-07
S8	5.64E-04	1.90E-04	9.19E-05	3.10E-05	S8	4.45E-06	1.93E-06	7.25E-07	3.15E-07

- *HQ*- Hazard quotient
- HQ_{alf}-Hazard quotient from correction coefficient of artificial lysosomal fluid (ALF)
- *HQ*>1 Risk of non-carcinogenic effects
- *HQ*<1 No risk of non-carcinogenic effects