Supplementary Materials

Table S1. The standards of the analyzed method for selected metals in the laboratory

Heavy metals	Analyses methods
Cr	HJ 491-2019 Soil and sediment—Determination of copper, zinc, lead, nickel and chromium—Flame atomic absorption spectrophotometry /USEPA-6020B-T
Ni	HJ 491-2019 Soil and sediment—Determination of copper, zinc, lead, nickel and chromium—Flame atomic absorption spectrophotometry /USEPA-6020B-T
Cu	HJ 491-2019 Soil and sediment—Determination of copper, zinc, lead, nickel and chromium—Flame atomic absorption spectrophotometry /USEPA-6020B-T
Zn	HJ 491-2019 Soil and sediment—Determination of copper, zinc, lead, nickel and chromium—Flame atomic absorption spectrophotometry /USEPA-6020B-T
As	GB/T 22105.2-2008 Soil quality-Analysis of total mercury, arsenic and lead contents-Atomic fluorescence spectrometry-Part2: Analysis of Total Arsenic contents in soil /USEPA-6020B-T/HJ 803-2016 Soil and sediment-Determination of aqua regia extracts of 12 metals elements- Inductively coupled plasma mass spectrometry
Cd	GB/T 17141-1997 Soil quality-Determination of lead, cadmium-Graphite furnace atomic absorption spectrophotometry/USEPA-6020B-T
Hg	GB/T 22105.2-2008 Soil quality-Analysis of total mercury, arsenic and lead contents-Atomic fluorescence spectrometry-Part1: Analysis of total mercury contents in soils /USEPA-6020B-T/GB/T 17136-1997 Soil quality-Determination of total mercury-Cold atomic absorption spectrometry
Pb	GB/T 17141-1997 Soil quality-Determination of lead, cadmium-Graphite furnace atomic absorption spectrophotometry /USEPA-6020B-T

Table S2. Statistics characteristics of pXRF and Lab analyzed result of samples from pXRF low-value dataset (mg kg^{-1})

Heavy metal	**pXRF-Cr**	**pXRF-Ni**	**pXRF-Cu**	**pXRF-Zn**	**pXRF-As**	**pXRF-Cd**	**pXRF-Hg**	**pXRF-Pb**
Counts	1144	1949	1843	1367	2071	151	456	2202
Mean	51.10	20.19	20.66	61.67	6.85	0.11	0.043	18.65
Std	18.89	8.11	8.52	16.76	3.33	0.060	0.032	7.59
Min	2.08	0.47	0.25	1.78	0.038	0.00030	0.00050	0.034
25%	38.17	14.26	15	52	4.31	0.062	0.018	13.65
50%	51	20	21.81	62	6.70	0.13	0.035	19
75%	65.12	26	27.58	73	9	0.17	0.059	24
Max	89.05	39.86	34.84	99.56	14.84	0.20	0.15	34.78
CV	0.37	0.40	0.41	0.27	0.49	0.53	0.76	0.41
Heavy metal	**Lab-Cr**	**Lab-Ni**	**Lab-Cu**	**Lab-Zn**	**Lab-As**	**Lab-Cd**	**Lab-Hg**	**Lab-Pb**
Counts	1144	1949	1843	1367	2071	151	456	2202
Mean	70.13	32.27	31.87	75.40	11.05	0.11	0.078	26.15
Std	29.32	10.19	50.25	83.10	5.38	0.12	0.32	29.60
Min	13.93	4.21	4	29	1.01	0.010	0.0030	7.30
25%	52	24	20	54	8.27	0.05	0.016	19.10
50%	64.28	33	26.46	63	10.50	0.072	0.024	23
75%	80	39	32	75	13.4	0.106	0.039	27.19
Max	337	104	1350	1680	86.30	0.76	5.99	1040
CV	0.42	0.32	1.58	1.10	0.49	1.14	4.14	1.13

Table S3. Statistics characteristics of pXRF and Lab analyzed result of samples from pXRF high-value dataset (mg kg^{-1})

Heavy metal	pXRF-Cr	pXRF-Ni	pXRF-Cu	pXRF-Zn	pXRF-As	pXRF-Cd	pXRF-Hg	pXRF-Pb
Counts	219	159	389	240	650	954	90	300
Mean	367.97	63.43	171.41	193.34	22.77	2.67	2.11	89.11
Std	1028.73	16.65	622.74	267.91	12.45	2.62	3.09	73.34
Min	90.01	40.51	35.08	100.61	15.01	0.20	0.15	35.56
25%	103	49.32	38.86	117	17	0.39	0.30	41
50%	129.86	62	46.34	133.63	20	2	1	61
75%	239	75.5	86.27	184.5	24	4	2.75	124
Max	10845	106	7905	3044	201.58	13	25.62	670.80
CV	2.80	0.26	3.63	1.39	0.55	0.98	1.46	0.82
Heavy metal	**Lab-Cr**	**Lab-Ni**	**Lab-Cu**	**Lab-Zn**	**Lab-As**	**Lab-Cd**	**Lab-Hg**	**Lab-Pb**
Counts	219	159	389	240	650	954	90	300
Mean	383.96	38.55	181.64	408.80	14.51	0.12	0.43	109.10
Std	858.56	8.15	555.83	573.17	11.33	0.16	1.44	131.78
Min	48	20	17	56	5.85	0.017	0.011	20
25%	74	33	30	144.75	9.79	0.060	0.046	35.38
50%	112	38	45	308.38	11.8	0.090	0.13	87.75
75%	280	43	115.29	490.49	16.28	0.12	0.31	127.44
Max	7400	74	5000	5720	196.27	3.09	13.27	1380
CV	2.24	0.21	3.06	1.40	0.78	1.32	3.35	1.21

Table S4. Validation statistics for predictive results of heavy metals using LR model and MARS model

Heavy metals	LR			MARS		
	R^2	RMSE	RPD	R^2	RMSE	RPD
Cr	0.80	164.57	2.22	0.88	126.08	2.89
Cu	0.73	125.1	1.94	0.77	115.22	2.11
Pb	0.44	59.73	1.34	0.42	99.81	1.32
Zn	0.37	208.11	1.26	0.28	221.95	1.18
As	0.22	6.52	1.13	0.28	6.26	1.18
Hg	0.16	0.61	1.09	0.29	0.56	1.19
Ni	0.13	9.89	1.07	0.13	9.87	1.07
Cd	0.0011	0.15	1.00	-0.05	0.16	0.98

Table S5. Validation statistics for predictive results of heavy metals of samples in the pXRF low-value dataset using univariate LR model and MARS model

Heavy metal	Background value (mg/kg)	LR			MARS		
		R^2	RMSE	RPD	R^2	RMSE	RPD
Cr	90	0.051	28.54	1.03	0.05	28.54	1.03
Cu	35	0.0025	50.17	1.00	-0.0458	51.37	0.98
Pb	40	-0.0017	29.62	1.00	0.02	29.82	0.99
Ni	35	0.085	9.75	1.05	0.09	9.72	1.05
As	15	0.045	5.26	1.02	0.05	5.25	1.03

Heavy metal	Background value (mg/kg)	LR			MARS		
		R^2	RMSE	RPD	R^2	RMSE	RPD
Hg	0.15	-0.006	0.32	1.00	-0.0044	0.03	1
Cd	100	-0.026	0.12	0.99	-0.013	0.06	1
Zn	0.2	-0.005	83.30	1.00	-0.12	87.84	0.95

Table S6. Validation statistics for predictive results of heavy metals of sample in pXRF high-value dataset using univariate LR model and MARS model

Heavy metal	Background value (mg/kg)	LR			MARS		
		R^2	RMSE	RPD	R^2	RMSE	RPD
Cr	90	0.80	387.12	2.22	0.87	306.14	2.8
Cu	35	0.75	277.74	2.00	0.79	255.5	2.18
Ni	40	0.19	7.3	1.2	0.21	7.21	1.13
Pb	35	0.42	99.81	1.32	0.36	105.55	1.25
As	15	0.35	9.13	1.24	0.35	9.14	1.24
Hg	0.15	0.13	1.33	1.08	0.34	1.16	1.24
Zn	100	0.26	492.36	1.16	0.20	512.31	1.12
Cd	0.2	-0.0001	0.16	1.00	-0.059	0.16	0.97