Potentially Toxic Elements and Pb Isotopes in Mine-Draining Meža River Catchment (NE Slovenia)

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Table S1. Operating conditions for the 7700x ICP-MS and Nu II MC ICP-MS.

ICP-MS	
Nebulizer	MiraMist
Spray chamber	Scott double-pass
RF Power	1550 W
Plasma gas flow	15 L/min
Carrier gas	1.05 L/min
Dilution gas	0.15 L/min
Sampling depth	7.5 mm
Sample uptake rate	0.3 mL/min
Sampling and skimmer cones	Nickel
Isotopes of internal standards	^{45}Sc, ^{72}Ge, ^{89}Y,^{103}Rh, ^{115}In, ^{193}Ir
MC ICP-MS	
RF power	1300 W
Plasma gas flow	13 L/min
Auxiliary gas flow	0.80 L/min
Nebuliser gas pressure	38 Psi
Sampler cone	Ni, aperture diameter 0.9 mm
Skimmer cone	Ni, aperture diameter 0.7 mm
Integration time	10 s
Number of cycles	25
Number of blocks	2
Mass assignment to Faraday cup detectors	H4 208
	H3 207
	H2 206
	H1 205
	Ax 204
	L1 203
	L2 202

Table S2. Concentrations of selected elements determined in certified reference material BCR 320R after microwave digestion and in SPS-SW1 by ICP-MS.

BCR 320R	certified (mg/kg)	determined (mg/kg)
Cr	59 ± 4	58 ± 3
Fe	25700 ± 1300	26000 ± 1000
Ni	27.1 ± 2.2	27.8 ± 2.0
Zn	319 ± 20	321 ± 15
As	21.7 ± 2.0	22.5 ± 1.8
Cd	2.64 ± 0.18	2.59 ± 0.16
Pb	85 ± 5	84 ± 3

SPS-SW1	certified (ng/mL)	determined (ng/mL)
Cr	2.00 ± 0.02	1.99 ± 0.02
Fe	20 ± 1	20.4 ± 0.2
Ni	10.0 ± 0.1	10.0 ± 0.1
Zn	20	19.9 ± 0.4
As	10.0 ± 0.1	10.1 ± 0.1
Cd	0.50 ± 0.01	0.50 ± 0.01
Pb	5.0 ± 0.1	5.0 ± 0.1

Table S3. Procedure for Pb separation from the matrix with Dowex® 1X8 resin.

An appropriate amount of sample was evaporated on a sand bath (T = 70-90 °C) and then re-dissolved in 0.6 mL of 0.5 M HBr by sonification for 3 h, and then applied to the resin.

Washing of the resin	0.5 mL of Milli-Q water 1 mL of 0.5 M HBr 0.2 mL of Milli-Q water 1 mL of 6 M HCl 0.2 mL of Milli-Q water
Conditioning of the resin	3 x 0.5 mL of 0.5 M HBr
Loading of the sample	0.6 mL of sample
Removal of the matrix	3 x 0.5 mL of 0.5 M HBr
Elution of Pb	6 x 1 mL of 6 M HCl

After Pb extraction chromatography, samples were evaporated on a sand bath (T = 70-90 °C) and re-dissolved in 6 mL of 2 % HNO_3 by sonification for 5 h.

Table S4. Total element concentrations (μg/L) in water samples determined by ICP-MS. Results are expressed with standard deviation.

Sample number	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
Sample location	Meža - Topla	Meža – Črna 1	Meža – Črna 2	Meža Žerjav 1	Meža – Žerjav 2	Meža - Mežica	Meža - Podklanc	Helena rivulet	Jazbina rivulet	Junčar rivulet
Coordinates	x: 146484 y: 484539	x: 147799 y: 488847	x: 148118 y: 489093	x: 148726 y: 490293	x: 149077 y: 490026	x: 152666 y: 489231	x: 158390 y: 501470	x: 147391 y: 486637	x: 149098 y: 490448	x: 151680 y: 489913
Li	1.27 ± 0.05	1.19 ± 0.03	1.22 ± 0.02	1.32 ± 0.06	1.70 ± 0.09	1.35 ± 0.05	1.80 ± 0.07	0.56 ± 0.02	0.86 ± 0.04	0.66 ± 0.05
Al	57.5 ± 0.8	10.7 ± 0.4	10.8 ± 0.4	10.3 ± 0.3	12.1 ± 0.5	9.16 ± 0.27	15.5 ± 0.2	3.35 ± 0.24	4.42 ± 0.12	6.20 ± 0.11
V	0.69 ± 0.01	0.58 ± 0.01	0.56 ± 0.01	0.51 ± 0.01	0.59 ± 0.01	0.47 ± 0.01	0.66 ± 0.01	0.35 ± 0.01	0.40 ± 0.01	1.78 ± 0.05
Cr	0.43 ± 0.01	0.35 ± 0.01	0.36 ± 0.01	0.37 ± 0.01	0.49 ± 0.01	0.43 ± 0.01	0.57 ± 0.01	0.30 ± 0.01	0.35 ± 0.01	0.32 ± 0.01
Mn	4.94 ± 0.16	0.85 ± 0.02	1.13 ± 0.05	1.74 ± 0.08	3.29 ± 0.11	2.74 ± 0.05	6.61 ± 0.09	0.21 ± 0.02	0.54 ± 0.04	0.87 ± 0.05
Fe	64.1 ± 1.3	8.56 ± 0.10	8.75 ± 0.04	9.05 ± 0.20	20.2 ± 0.3	16.1 ± 0.6	44.9 ± 0.8	3.06 ± 0.07	4.60 ± 0.09	5.28 ± 0.21
Co	0.082 ± 0.007	0.022 ± 0.005	0.023 ± 0.004	0.030 ± 0.004	0.077 ± 0.002	0.063 ± 0.006	0.102 ± 0.005	0.032 ± 0.002	0.022 ± 0.003	0.027 ± 0.003
Ni	0.24 ± 0.01	0.32 ± 0.01	0.25 ± 0.01	0.33 ± 0.01	1.38 ± 0.02	1.12 ± 0.02	1.09 ± 0.02	0.37 ± 0.01	0.37 ± 0.01	0.51 ± 0.01
Cu	0.39 ± 0.01	0.30 ± 0.01	0.29 ± 0.02	0.49 ± 0.02	0.82 ± 0.02	0.81 ± 0.03	1.00 ± 0.04	0.87 ± 0.05	0.34 ± 0.02	0.50 ± 0.02
Se	0.64 ± 0.02	0.82 ± 0.04	0.71 ± 0.03	0.95 ± 0.04	0.87 ± 0.03	0.92 ± 0.04	0.69 ± 0.03	0.64 ± 0.02	0.74 ± 0.02	0.59 ± 0.02
Rb	0.69 ± 0.03	0.59 ± 0.02	0.63 ± 0.02	0.92 ± 0.03	1.25 ± 0.02	0.70 ± 0.03	1.01 ± 0.03	0.48 ± 0.01	0.29 ± 0.01	0.41 ± 0.01
Sr	39.1 ± 0.8	98.2 ± 1.7	113 ± 2	143 ± 2	142 ± 4	108 ± 3	118 ± 1	106 ± 1	87.4 ± 0.7	85.4 ± 1.3
Mo	0.20 ± 0.03	0.24 ± 0.02	0.34 ± 0.01	0.74 ± 0.04	3.60 ± 0.13	1.76 ± 0.08	2.87 ± 0.10	0.21 ± 0.02	0.58 ± 0.03	0.35 ± 0.02
Ag	0.0020 ± 0.0004	0.0015 ± 0.0008	0.0016 ± 0.0006	0.0026 ± 0.0007	0.0038 ± 0.0008	0.0019 ± 0.0006	0.0023 ± 0.0014	0.0018 ± 0.0011	0.0026 ± 0.0015	0.0014 ± 0.0011
Sb	11.1 ± 0.9	17.4 ± 1.4	31.7 ± 1.4	101 ± 7	255 ± 6	246 ± 5	77.7 ± 2.4	39.5 ± 2.2	60.3 ± 2.1	65.4 ± 2.6
Ba	5.13 ± 0.23	9.99 ± 0.29	10.6 ± 0.1	12.1 ± 0.2	11.7 ± 0.3	19.3 ± 0.3	21.8 ± 0.4	8.33 ± 0.11	15.7 ± 0.1	15.1 ± 0.3
Tl	0.010 ± 0.002	0.012 ± 0.003	0.023 ± 0.002	0.035 ± 0.004	0.196 ± 0.012	0.096 ± 0.012	0.118 ± 0.003	0.045 ± 0.003	0.067 ± 0.003	0.103 ± 0.004
U	0.23 ± 0.01	0.25 ± 0.01	0.29 ± 0.01	0.21 ± 0.01	0.23 ± 0.01	0.60 ± 0.01	0.57 ± 0.02	0.68 ± 0.03	0.73 ± 0.02	0.93 ± 0.03

Table S5. Total element concentrations (mg/kg) in sediment samples determined by ICP-MS. Results are expressed with standard deviation.

Sample number	(2a)		(3a)		(5a)		(7a)		(10a)	
Sample location	Meža – Črna 1		Meža – Črna 2		Meža – Žerjav 2		Meža - Podklanc		Junčar rivulet	
Fraction (mm)	<0.063	<0.150	<0.150	<0.250	<0.063	<0.150	<0.063	<0.150	<0.063	<0.150
Li	43.1 ± 0.1	ND	42.3 ± 0.1	ND	30.1 ± 0.1	ND	35.0 ± 0.1	ND	7.69 ± 0.01	ND
Al	61717 ± 45	86442 ± 376	54120 ± 23	80931 ± 920	41092 ± 66	59489 ± 379	51249 ± 50	64469 ± 985	11910 ± 12	8700 ± 53
V	160 ± 1	ND	90.2 ± 0.1	ND	174 ± 1	ND	292 ± 1	ND	54.1 ± 0.1	ND
Cr	206 ± 1	148 ± 5	55.6 ± 0.1	58.0 ± 0.6	342 ± 1	115 ± 1	3900 ± 21	2482 ± 45	24.4 ± 0.1	18.4 ± 0.3
Mn	1170 ± 1	ND	606 ± 1	ND	1433 ± 1	ND	1463 ± 2	ND	387 ± 1	ND
Fe	56008 ± 490	79386 ± 1511	33962 ± 213	49373 ± 107	81431 ± 866	53946 ± 215	90157 ± 383	166545 ± 1148	11297 ± 115	9583 ± 39
Co	19.9 ± 0.1	ND	12.7 ± 0.1	ND	20.8 ± 0.1	ND	38.8 ± 0.1	ND	3.00 ± 0.1	ND
Ni	51.8 ± 0.1	44.8 ± 0.4	33.2 ± 0.1	28.3 ± 0.3	73.4 ± 0.1	42.6 ± 1.0	482 ± 1	355 ± 7	12.2 ± 0.1	8.80 ± 0.06
Cu	33.3 ± 0.1	ND	28.0 ± 0.1	ND	81.5 ± 0.1	ND	168 ± 0.1	ND	13.0 ± 0.1	ND
Se	2.83 ± 1.07	ND	2.10 ± 1.09	ND	5.77 ± 2.47	ND	5.75 ± 1.71	ND	1.87 ± 1.42	ND
Rb	77.1 ± 0.1	ND	73.6 ± 0.1	ND	39.9 ± 0.1	ND	59.2 ± 0.1	ND	15.5 ± 0.1	ND
Sr	229 ± 1	ND	201 ± 1	ND	229 ± 1	ND	199 ± 1	ND	160 ± 1	ND
Mo	32.8 ± 0.1	25.6 ± 0.5	2.52 ± 0.01	1.08 ± 0.04	130 ± 1	19.4 ± 0.1	344 ± 1	191 ± 3	68.4 ± 0.1	27.1 ± 0.3
Ag	0.43 ± 0.01	< DL	0.22 ± 0.01	< DL	2.02 ± 0.01	< DL	0.66 ± 0.01	< DL	0.50 ± 0.01	< DL
Sb	1184 ± 3	ND	239 ± 1	ND	23482 ± 26	ND	4672 ± 4	ND	751 ± 3	ND
Ba	628 ± 1	ND	277 ± 1	ND	754 ± 1	ND	926 ± 1	ND	1199 ± 1	ND
Tl	0.62 ± 0.01	ND	0.46 ± 0.01	ND	0.73 ± 0.01	ND	2.26 ± 0.01	ND	1.12 ± 0.01	ND
U	6.17 ± 0.01	ND	2.39 ± 0.01	ND	7.80 ± 0.01	ND	5.96 ± 0.01	ND	10.8 ± 0.01	ND

ND – not determined

Table S6. A) Pearson correlation matrix for metal concentrations in water samples from Meža river [µg/L]. B) Pearson correlation matrix for metal concentrations in sediment samples from Meža river, fraction <0.063 mm [mg/kg]. C) Pearson correlation matrix for metal concentrations in sediment samples from Meža river, fraction <0.150 mm [mg/kg].

		Pb	Zn	As	Cd
A)					
	Pb	1			
	Zn	0.22	1		
	As	**0.98**	0.18	1	
	Cd	**0.95**	0.48	**0.95**	1
B)					
	Pb	1			
	Zn	0.47	1		
	As	**1.00**	0.41	1	
	Cd	0.45	**1.00**	0.39	1
C)					
	Pb	1			
	Zn	**0.96**	1		
	As	**0.99**	**0.98**	1	
	Cd	**0.96**	**1.00**	**0.98**	1

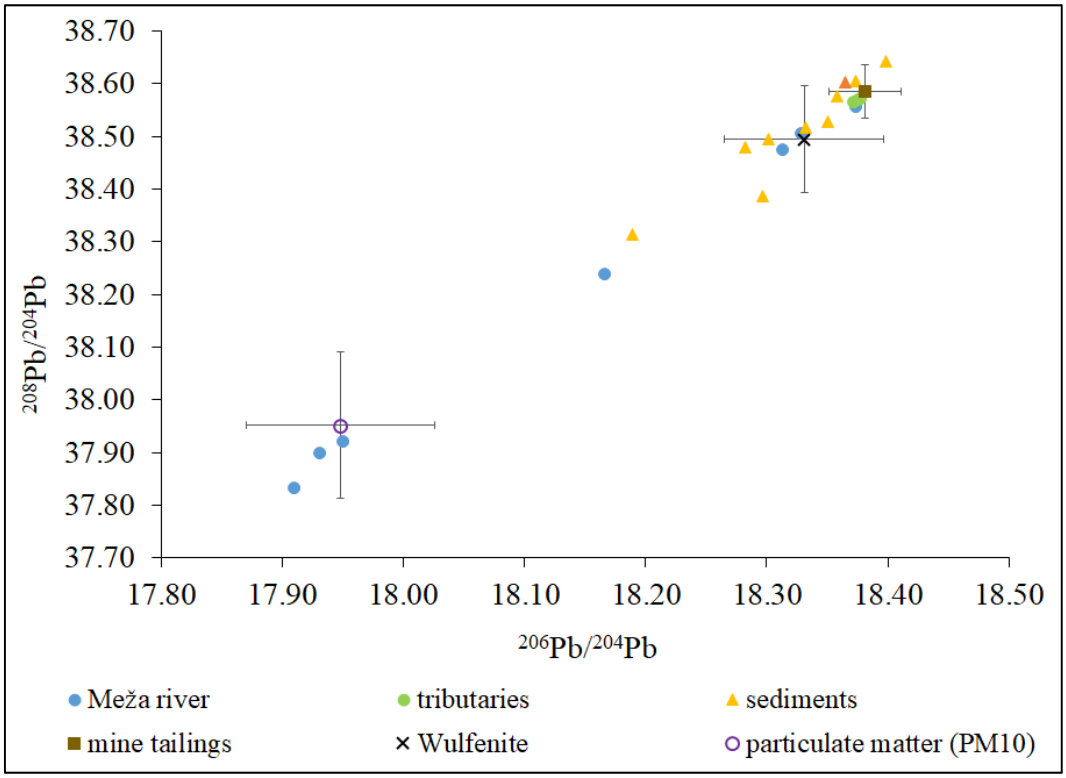


Figure S1. Pb isotopic composition of water and sediment samples from Meža river and its tributaries shown on a biplot of $^{208}Pb/^{204}Pb$ with $^{206}Pb/^{204}Pb$. Triangle marker for sediments with orange colour represents sample from Črna 2, with fraction <0.250 mm. Values for mine tailings, particulate matter PM_{10} and wulfenite are from our unpublished data.

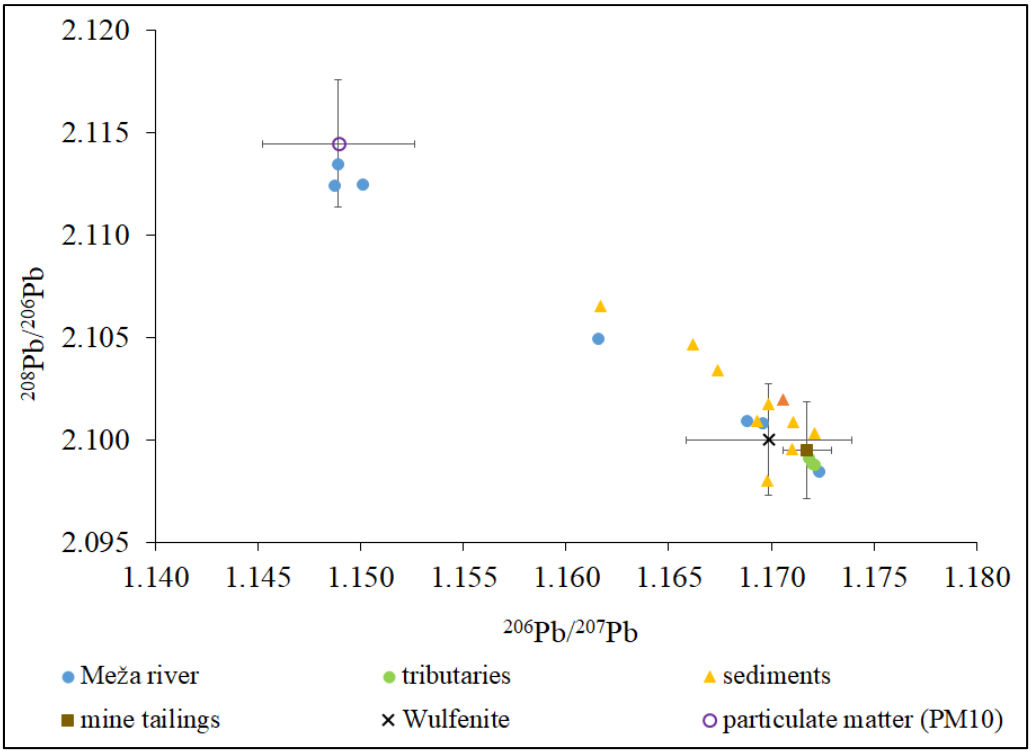


Figure S2. Pb isotopic composition of water and sediment samples from Meža river and its tributaries shown on a biplot of $^{208}Pb/^{206}Pb$ with $^{206}Pb/^{207}Pb$. Triangle marker for sediments with orange colour represents sample from Črna 2, with fraction <0.250 mm. Values for mine tailings, particulate matter PM_{10} and wulfenite are from our unpublished data.

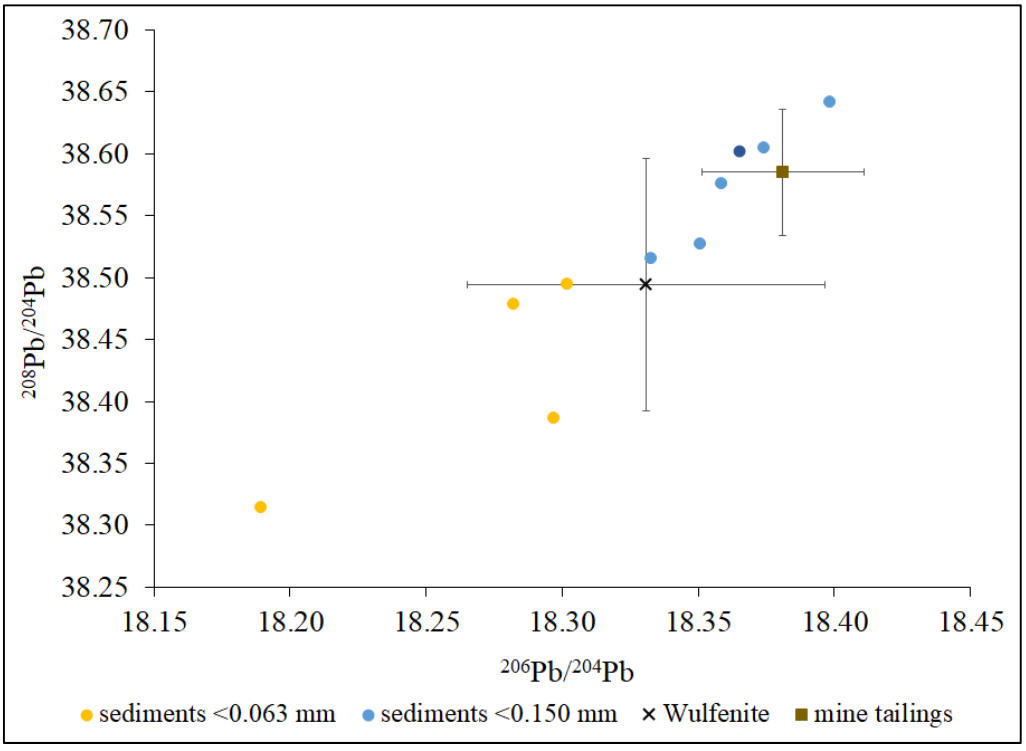


Figure S3. Pb isotopic composition of two different fractions of sediment samples from Meža river and its tributaries shown on a biplot of $^{208}Pb/^{204}Pb$ with $^{206}Pb/^{204}Pb$. Circle marker for sediments <0.150 mm with dark blue colour represents sample from Črna 2, with fraction <0.250 mm. Values for mine tailings and wulfenite are from our unpublished data

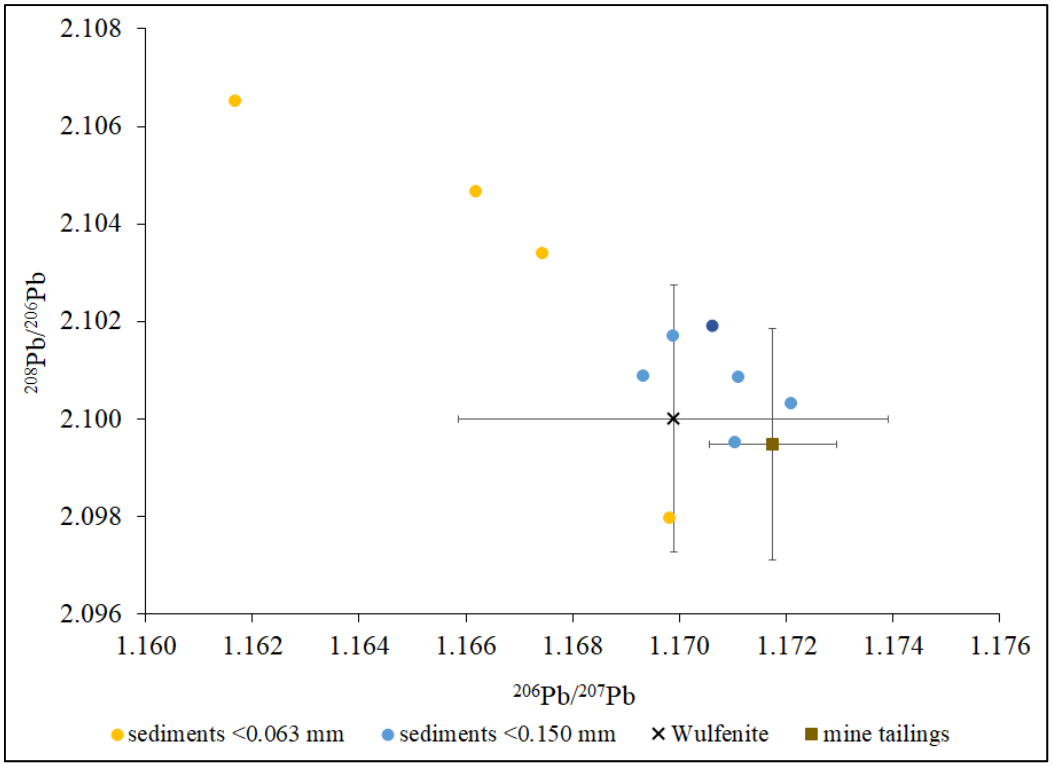


Figure S4. Pb isotopic composition of two different fractions of sediment samples from Meža river and its tributaries shown on a biplot of $^{208}Pb/^{206}Pb$ with $^{206}Pb/^{207}Pb$. Circle marker for sediments <0.150 mm with dark blue colour represents sample from Črna 2, with fraction <0.250 mm. Values for mine tailings and wulfenite are from our unpublished data