Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

Understanding the mobilisation of metal pollution associated with historical mining in a carboniferous upland catchment

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Supplementary Information

Table 1-SI. Mean, maxima and minima from water chemical analysis. Sites are indicated as reservoir (RS), main channel (MC), ephemeral tributaries (ET) and perennial tributaries (PT). Metal forms are denoted as Total (T) and dissolved (D). Concentrations are expressed in μg/l. Values below the detection limit are represented by (b/d).

Site			Pb_T	Pb_D	Ba_T	Ba_D	Cd_T	Cd_D	Sr_T	Sr_D	Zn_T	Zn_D	Cu_T	Cu_D	Fe_T	Fe_D	Mn_T	Mn_D	Al_T	Al_D
H15	RS	Ave	316.7	279.6	293.8	288.1	6.4	6.4	25.8	26.9	2058.8	2028.0	12.3	12.4	562.9	406.4	69.3	70.9	383.8	341.1
		Max	411.9	423.6	570.4	465.5	8.2	8.6	37.8	46.0	2542.4	2759.5	19.6	19.9	2473.1	1622.1	201.7	202.4	522.5	428.7
		Min	96.3	103.6	165.2	173.5	3.1	4.3	15.9	14.1	722.4	1080.7	3.8	1.3	185.8	94.5	39.5	24.2	132.1	102.2
H14	PT	Ave	178.3	157.6	687.8	651.8	3.6	3.9	63.9	60.1	1318.6	1397.9	6.2	7.7	288.1	203.4	24.0	26.3	270.6	249.9
		Max	292.3	375.5	1195.3	1135.2	4.5	7.5	103.1	99.0	1778.9	2193.1	10.4	15.0	626.6	337.0	48.5	53.9	574.0	462.1
		Min	106.9	75.7	408.3	241.4	3.1	2.9	40.5	21.2	864.7	900.3	b/d	1.4	114.2	103.6	9.0	9.5	101.1	123.6
H13	ET	Ave	227.1	205.9	200.2	201.2	0.9	0.9	13.7	13.8	260.4	207.4	2.6	2.3	967.6	833.8	74.3	74.3	613.3	552.2
		Max	331.3	283.4	501.2	513.5	4.1	3.7	47.2	49.7	1619.8	1435.5	9.0	8.3	1451.9	1515.1	95.5	112.6	972.1	752.5
		Min	141.2	138.0	139.3	135.2	0.4	0.4	8.1	7.5	b/d	b/d	0.9	b/d	483.4	187.2	36.0	30.0	371.2	284.0
H12	ET	Ave	686.4	284.2	285.5	198.6	29.1	27.7	391.5	340.2	5168.8	4252.3	14.0	9.5	528.4	205.8	73.7	70.5	312.0	147.5
		Max	2701.2	439.9	419.4	285.4	45.7	47.0	737.3	602.1	12619.3	7438.4	25.9	19.8	1635.4	988.7	171.6	180.0	1277.4	506.2
		Min	261.8	184.1	183.0	148.1	0.6	0.5	8.9	8.6	66.5	73.6	2.2	2.0	84.6	62.6	22.6	19.1	82.7	55.0
H11	PT	Ave	64.0	31.6	143.9	111.8	1.7	2.6	40.6	52.8	295.7	410.5	2.5	2.0	1282.9	1017.2	100.7	98.2	103.1	91.5
		Max	765.6	355.2	604.8	181.7	21.7	35.9	207.6	372.5	3493.9	5276.2	18.8	14.6	2894.7	2404.3	613.7	633.3	190.2	181.9
		Min	3.7	b/d	65.3	68.0	b/d	0.02	9.9	10.5	b/d	b/d	b/d	b/d	258.6	142.3	28.4	24.6	b/d	34.5
H10	ET	Ave	108.1	80.7	441.1	415.0	1.6	1.6	67.0	63.4	468.8	444.4	2.8	2.7	632.3	434.8	54.2	48.4	188.8	147.0
		Max	268.1	145.2	933.8	956.2	2.2	2.3	123.6	133.8	787.4	777.0	8.3	6.7	1942.8	815.9	116.6	77.5	385.2	249.2
		Min	11.8	3.1	97.8	79.5	0.1	0.1	17.5	15.2	b/d	b/d	b/d	b/d	260.8	163.8	29.2	28.7	63.1	62.0
H9	PT	Ave	28.5	20.8	131.0	122.3	0.7	0.7	32.3	33.0	125.2	95.7	1.1	1.4	1448.8	1097.9	69.0	64.9	158.1	136.9
		Max	171.9	94.3	412.3	282.7	2.2	1.9	83.0	88.1	572.2	518.6	5.1	5.3	3028.1	2045.1	145.2	155.7	366.7	254.7
		Min	12.7	2.0	66.7	68.4	0.42	0.5	11.4	10.5	b/d	b/d	b/d	b/d	584.1	379.2	35.5	29.6	44.0	36.7

Table 1-SI (continued). Mean, maxima and minima from water chemical analysis. Sites are indicated as reservoir (RS), main channel (MC), ephemeral tributaries (ET) and perennial tributaries (PT). Metal forms are denoted as Total (T) and dissolved (D). Concentrations are expressed in μg/l.Values below the detection limit are represented by (b/d).

Site			Pb_T	Pb_D	Ba_T	Ba_D	Cd_T	Cd_D	Sr_T	Sr_D	Zn_T	Zn_D	Cu_T	Cu_D	Fe_T	Fe_D	Mn_T	Mn_D	Al_T	Al_D
H8	ET	Ave	38.1	19.0	399.4	398.2	1.0	0.9	108.5	106.1	318.5	269.0	2.1	1.9	369.8	218.8	39.4	33.2	70.4	47.8
		Max	123.5	28.2	661.3	606.8	1.5	1.6	197.1	222.0	438.3	435.2	4.3	5.5	865.8	614.7	92.9	53.6	165.1	104.0
		Min	12.2	5.3	195.2	246.8	0.6	0.5	52.2	48.9	b/d	b/d	b/d	b/d	75.7	32.0	18.5	12.2	b/d	14.6
H7	PT	Ave	7.7	4.3	218.9	220.2	16.6	16.6	834.8	809.4	3440.2	3220.5	5.5	2.5	386.0	40.2	52.6	54.9	21.3	12.4
		Max	21.1	47.7	258.1	268.8	22.6	23.6	1391.3	1156.0	5425.8	4312.3	11.7	5.6	860.4	189.2	66.6	73.5	39.0	37.0
		Min	0.8	b/d	179.6	186.3	10.4	11.5	425.5	436.4	2062.0	1936.7	1.3	0.1	49.8	18.3	33.6	31.8	b/d	b/d
H6	MC	Ave	60.4	49.4	307.1	308.7	2.5	2.5	104.8	105.8	537.6	510.2	1.9	2.2	596.2	471.7	44.6	43.0	123.3	113.4
		Max	102.0	85.6	549.3	557.0	3.6	3.6	283.0	298.5	664.1	674.1	3.5	5.9	914.4	822.4	84.9	90.7	223.9	212.4
		Min	20.5	13.8	187.4	180.2	1.7	1.7	38.7	36.5	468.3	390.2	b/d	b/d	218.4	142.7	22.4	19.9	33.5	27.6
H5	PT	Ave	60.4	54.3	209.3	213.7	5.0	5.1	223.1	228.3	883.5	867.2	2.5	2.4	82.5	46.3	6.6	6.0	87.0	74.6
		Max	132.3	157.8	238.4	235.0	6.6	6.8	348.8	370.2	1216.5	1206.0	5.1	6.3	154.1	152.0	9.9	11.7	185.1	223.2
		Min	17.1	10.0	173.5	176.9	4.0	3.9	146.6	149.3	688.0	613.5	b/d	b/d	43.4	5.4	4.8	3.9	b/d	11.2
H4	ET	Ave	8.3	4.4	91.6	78.0	0.2	0.2	9.4	9.2	b/d	b/d	0.8	1.6	1320.0	635.3	136.9	135.8	416.9	277.2
		Max	26.7	6.6	228.4	99.4	0.2	0.3	15.0	12.2	68.6	68.6	3.0	10.2	5331.3	1006.0	164.6	179.1	822.2	389.0
		Min	3.2	b/d	57.4	60.0	0.1	0.1	6.8	6.5	b/d	b/d	b/d	b/d	455.9	336.9	95.4	31.8	248.7	189.7
H3	PT	Ave	2.8	0.2	200.1	200.0	0.6	0.6	373.5	381.4	b/d	b/d	0.2	0.3	37.4	3.7	16.7	5.3	37.7	9.6
		Max	10.6	0.7	251.6	217.8	0.7	0.6	405.4	420.6	98.6	84.7	1.3	1.6	152.9	18.5	54.3	26.3	153.0	47.0
		Min	0.05	b/d	157.9	160.7	0.5	0.5	324.6	292.0	b/d	b/d	b/d	b/d	2.4	b/d	1.7	1.5	b/d	b/d
H2	MC	Ave	46.7	39.4	239.6	246.7	2.6	2.7	164.9	169.8	515.0	485.9	2.1	1.6	314.0	248.0	28.3	27.8	101.2	93.5
		Max	93.5	87.4	318.0	306.1	3.6	3.5	333.0	356.4	765.4	606.9	5.9	4.5	733.6	657.2	62.5	67.6	207.1	187.8
		Min	17.0	4.2	171.1	180.1	1.2	2.0	70.9	67.9	194.5	360.5	b/d	b/d	103.3	7.6	13.7	5.3	37.9	24.2
H1P	PT	Ave	3.0	1.9	199.7	200.5	0.1	0.09	51.9	53.1	b/d	b/d	1.1	0.7	317.9	205.4	27.9	9.6	85.1	58.6
		Max	5.2	8.3	285.4	261.5	0.2	0.2	69.9	70.2	68.6	68.5	3.8	3.00	779.1	583.3	57.2	36.0	179.1	140.9
		Min	0.8	b/d	112.3	120.5	0.1	0.02	30.7	29.5	b/d	b/d	b/d	b/d	134.9	29.3	7.9	2.7	31.4	16.0
H1	MC	Ave	31.1	16.6	221.5	217.4	1.3	1.1	129.1	132.4	217.5	158.9	1.5	1.1	328.6	185.1	39.9	22.0	103.7	70.2
		Max	146.8	43.7	272.1	267.5	2.1	1.4	209.3	220.3	375.9	302.9	4.5	4.3	1252.7	405.4	169.7	66.6	358.6	137.3
		Min	5.1	b/d	153.1	145.8	0.8	0.7	62.2	57.7	77.9	67.8	b/d	b/d	122.5	50.1	19.3	10.9	b/d	19.9

Table 2-SI. Mean, maxima and minima of major ions, dissolved inorganic and organic carbons. Description of sites are indicated as reservoir (RS), main channel (MC), ephemeral tributaries (ET) and perennial tributaries (PT). Units are in mg/l.

Sites	Description		Cations				Anions				Dissolved carbons	
			Ca_T	Ca_D	Mg_T	Mg_D	SO_4^{2-}	NO_3^{2-}	PO_4^{2-}	Cl^-	DIC	DOC
H15	RS	Ave	7.9	8.3	0.6	0.6	3.5	1.3	0.003	7.2	3.8	12.4
		Max	12.0	14.7	0.9	0.9	7.5	2.9	0.01	13.8	9.3	21.2
		Min	5.0	5.1	0.5	0.5	1.3	0.001	0.0005	3.3	1.3	6.9
H14	PT	Ave	10.4	9.9	0.7	0.7	5.9	1.0	0.003	7.5	3.9	8.3
		Max	15.7	12.8	0.9	0.8	9.1	1.6	0.007	13.4	6.2	14.7
		Min	7.1	7.1	0.5	0.5	3.4	0.4	0.0005	4.5	2.1	4.2
H13	ET	Ave	2.9	3.0	0.5	0.5	3.6	1.1	0.02	7.9	0.9	16.8
		Max	8.7	9.1	0.7	0.7	6.2	2.1	0.03	13.0	2.0	26.5
		Min	1.8	1.9	0.4	0.3	1.3	0.2	0.0005	2.4	0.2	8.9
H12	ET	Ave	27.2	25.8	1.4	1.3	20.0	1.8	0.007	8.5	12.5	6.8
		Max	45.9	45.2	2.0	2.0	46.0	3.0	0.013	18.8	24.2	11.0
		Min	2.0	2.1	0.5	0.5	9.9	0.5	0.0005	3.4	4.9	2.0
H11	PT	Ave	7.4	8.5	1.2	1.2	3.0	1.5	0.02	7.5	4.0	16.3
		Max	13.7	25.4	2.3	2.2	8.4	6.4	0.05	11.8	10.6	31.2
		Min	2.3	2.2	0.5	0.6	1.3	0.001	0.01	3.8	0.8	6.4
H10	MC	Ave	13.5	15.0	0.94	1.0	4.9	1.6	0.01	7.8	8.2	10.3
		Max	28.5	30.1	1.9	1.9	9.6	4.0	0.05	12.9	18.9	20.9
		Min	4.5	4.2	0.5	0.6	3.1	0.01	0.0005	3.9	3.4	3.6
H9	PT	Ave	7.6	7.8	1.2	1.2	3.8	1.3	0.02	7.9	3.7	16.7
		Max	18.9	20.0	2.7	2.7	6.2	2.3	0.03	13.4	13.4	33.0
		Min	2.3	2.3	0.6	0.6	2.7	0.6	0.01	4.7	0.7	7.3
H8	ET	Ave	37.0	38.7	2.0	2.03	10.7	2.5	0.008	8.5	22.3	8.0
		Max	65.9	64.2	4.0	3.9	20.1	8.0	0.012	16.9	39.3	17.5
		Min	0.04	19.2	b/d	1.2	5.1	1.0	0.0005	2.9	10.2	3.8
H7	PT	Ave	41.5	41.5	5.4	5.4	24.9	2.3	0.002	7.5	27.2	1.2
		Max	55.1	55.0	6.9	6.9	31.0	4.6	0.01	11.0	36.1	3.1
		Min	25.0	24.6	3.6	3.6	16.9	1.0	0.0005	6.0	16.6	0.001
H6	MC	Ave	18.7	18.9	1.5	1.5	6.7	1.9	0.01	7.9	10.5	10.9
		Max	38.9	38.7	3.3	3.4	10.6	3.5	0.05	13.3	24.1	23.9
		Min	8.6	8.5	0.8	0.8	3.4	0.3	0.0005	4.8	3.7	3.3
H5	PT	Ave	46.2	45.8	4.1	4.0	12.8	12.3	0.01	7.6	27.8	3.1
		Max	58.4	57.0	5.3	5.5	18.0	40.2	0.01	9.7	35.1	7.7
		Min	37.6	36.3	3.1	3.1	7.4	6.3	0.0005	5.9	20.9	0.2
H4	ET	Ave	2.6	2.6	0.7	0.7	4.7	4.9	0.05	8.3	0.9	8.8
		Max	3.8	3.8	0.9	0.9	9.7	15.2	0.1	12.6	2.3	12.9
		Min	1.5	1.7	0.6	0.6	2.0	0.8	0.03	4.6	0.1	6.5
H3	PT	Ave	55.1	54.9	9.0	8.9	12.7	5.1	0.005	7.6	42.7	1.2
		Max	60.2	58.1	9.8	9.8	14.9	9.9	0.01	12.0	46.5	4.7
		Min	47.3	44.7	7.9	7.6	8.7	2.1	0.0005	5.3	36.3	0.001
H2	MC	Ave	32.0	31.9	3.5	3.4	9.4	9.5	0.007	8.0	18.8	7.5
		Max	53.6	54.9	6.3	6.6	15.2	17.7	0.01	12.3	33.2	22.3
		Min	16.2	16.3	1.6	1.6	4.5	1.9	0.0005	5.6	6.3	1.4
H1P	PT	Ave	28.1	27.8	1.9	1.9	7.2	17.8	0.1	10.1	13.6	9.2
		Max	37.8	36.3	2.4	2.4	14.5	36.7	0.1	17.9	19.3	24.6
		Min	16.7	16.4	1.3	1.3	3.0	0.001	0.05	7.0	5.9	3.1
H1	MC	Ave	32.8	34.5	4.1	4.3	8.3	3.3	0.05	10.5	22.7	7.7
		Max	48.5	48.4	7.7	8.0	10.7	5.5	0.2	17.2	34.9	19.6
		Min	20.7	19.9	1.8	1.8	4.5	1.7	0.0005	7.6	11.1	3.1

Table 3-SI. Monthly averages of in situ parameters in the catchment.

Months	Temp (°C)	DO (mg/l)	pH	EC (μs/cm)	Flow (l/s)
Nov.13	7.6 (±0.8)	11.4 (±0.4)	5.6 (±0.8)	94.0 (±58.8)	NM
Dec.13	9.0 (±0.6	10.2 (±0.3)	6.0 (±1.0)	99.9 (±68.8)	310.5 (±638.8)
Jan.14	5.0 (±1.4)	12.1 (±0.8)	6.1 (±1.1)	87.9 (±57.0)	250.2 (±422.8)
Feb.14	3.6 (±1.2)	12.5 (±0.9)	5.9 (±1.1)	78.0 (±43.1)	699.4 (±1365.1)
Mar.14	7.3 (±0.8)	12.3 (±1.1)	6.5 (±0.9)	120.4 (±65.7)	129.4 (±343.0)
Apr.14	8.5 (±1.7)	11.9 (±1.0)	6.6 (±1.1)	123.5 (±64.3)	62.9 (±146.8)
May.14	8.9 (±1.3)	12.6 (±0.9)	6.6 (±1.0)	137.3 (±70.8)	79.2 (±206.1)
Jun.14	13.7 (±2.8)	10.9 (±0.7)	6.6 (±1.1)	138.7 (±75.4)	98.9 (±233.9)
Jul.14	15.6 (±2.6)	10.3 (±0.6)	7.0 (±1.0)	209.0 (±82.3)	54.0 (±114.3)
Aug.14	13.0 (±1.8)	11.7 (±0.8)	6.4 (±1.4)	123.8 (±85.0)	389.8 (±954.3)
Sep.14	12.4 (±1.9)	14.0 (±1.2)	7.1 (±1.0)	154.3 (±71.0)	71.1 (±157.6)
Oct.14	9.7 (±1.1)	10.4 (±0.5)	6.6 (±1.0)	119.5 (±66.8)	107.3 (±183.4)
Nov.14	9.2 (±0.4)	10.4 (±0.5)	6.6 (±1.0)	99.9 (±59.0)	2666.1 (±10243.7)
Dec.14	4.2 (±1.2)	12.6 (±1.1)	6.8 (±0.8)	93.2 (±54.0)	292.1 (±568.8)

NM: No measured

Table 4-SI. Averages, maxima and minima of in situ parameters. Description of sites are indicated as reservoir (RS), main channel (MC), ephemeral tributaries (ET) and perennial tributaries (PT).

Sites	Description		pH	EC (µs/cm)	Temperature (°C)	DO (mg/l)	Flow (l/s)
H15	RS	Ave	6.3	52.4	9.7	11.1	NM
		Max	7.1	95.4	18.5	13.2	NM
		Min	4.6	35.3	1.4	9.2	NM
H14	PT	Ave	6.6	59.4	10.0	11.5	128.5
		Max	7.6	99.9	18.3	13.1	761.7
		Min	5.3	41.1	3.0	9.5	2.6
H13	ET	Ave	4.5	48.9	8.4	11.0	57.0
		Max	5.0	65.2	15.7	13.1	134.4
		Min	4.0	35.6	3.7	9.1	0.0
H12	ET	Ave	6.9	123.7	8.9	11.5	9.0
		Max	7.4	199.7	18.0	13.2	31.9
		Min	5.6	64.9	2.8	10.0	0.0
H11	PT	Ave	6.2	47.8	6.9	11.8	57.4
		Max	7.6	100.4	11.0	13.3	123.6
		Min	5.4	30.0	2.0	9.5	3.1
H10	MC	Ave	6.8	76.0	9.7	12.2	200.2
		Max	7.7	160.3	18.8	14.2	684.4
		Min	5.6	46.8	4.1	10.0	5.1
H9	PT	Ave	5.9	52.3	9.2	12.0	118.8
		Max	7.4	107.5	17.9	14.8	315.0
		Min	4.4	36.7	3.7	10.0	12.8
H8	ET	Ave	7.4	152.1	9.1	12.1	51.3
		Max	8.2	303.0	16.9	15.7	149.3
		Min	6.2	75.8	2.2	9.8	0.0
H7	PT	Ave	6.9	192.4	9.1	10.9	3.0
		Max	7.3	292.0	11.9	13.9	7.3
		Min	6.0	112.0	5.1	9.5	0.6
H6	MC	Ave	6.9	94.7	8.7	12.4	265.0
		Max	7.4	253.0	16.9	15.4	1087.3
		Min	5.9	48.4	3.6	10.4	36.3
H5	PT	Ave	6.8	185.1	8.5	10.7	83.1
		Max	7.2	269.0	12.8	13.9	243.2
		Min	5.9	138.4	4.8	9.5	10.3
H4	ET	Ave	3.9	121.1	8.0	12.2	14.3
		Max	5.0	342.0	14.5	14.6	54.3
		Min	3.3	50.8	2.1	10.2	0.0
H3	PT	Ave	7.0	248.2	8.6	10.9	12.4
		Max	7.5	295.0	11.5	14.0	20.1
		Min	5.5	186.9	5.7	9.6	6.9
H2	MC	Ave	6.6	146.2	8.1	12.2	386.1
		Max	7.2	288.0	12.8	15.1	1147.0
		Min	5.4	76.0	3.2	10.0	106.6
H1P	PT	Ave	6.3	133.0	8.8	12.2	192.7
		Max	6.8	218.3	14.5	14.2	1162.2
		Min	4.3	71.9	3.5	10.0	3.8
H1	MC	Ave	7.5	159.8	10.6	11.5	4804.9
		Max	8.0	264.0	16.9	12.8	41076.0
		Min	6.2	90.9	4.5	10.1	432.0

NM: No measured

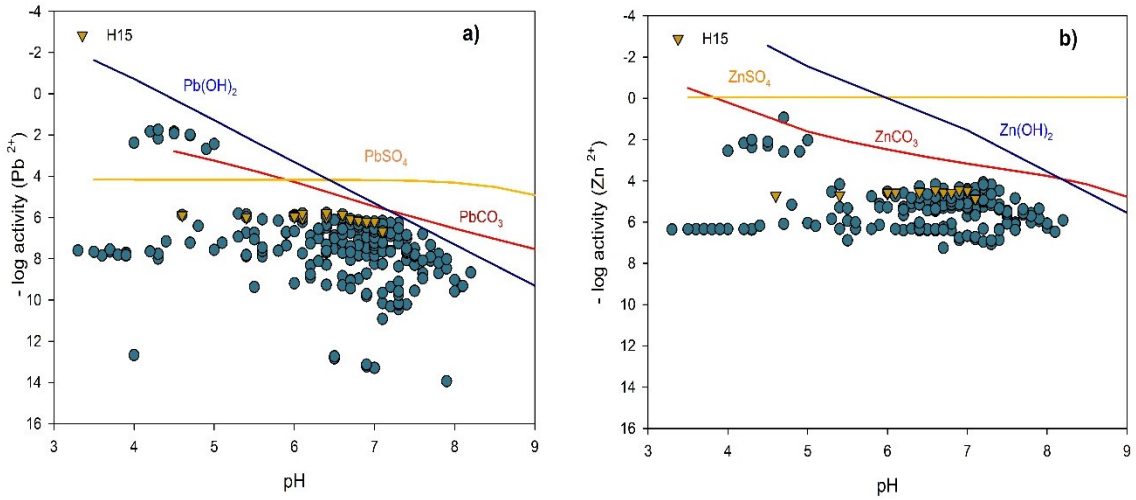

Figure 1-SI. Lead and Zn activity as a function of pH, SO_4^{2-} (13592 μg/l), Cl (7730 μg/l) and pCO_2 = 0.0012 atm. Theoretical saturation of mineral forms are represented by solid lines and calculated metal free ion activity of experimental data by dots. Data from a source pond (H15) is shown separately as an example of how longer water residence times may result in free ion activities closer to saturation.

Table 5-SI. Correlation coefficients showing positive and negative relationships between metal forms (T: total, D: dissolved) and pH, EC, DIC, SO_4^{2-}, and DOC.

	pH	EC	DIC	SO_4^{2-}	DOC
Pb_T	r= -0.02 p= .736 CI [-0.162 0.115]	r= -0.2 p= .003 CI [-0.341 -0.076]	r= -0.2 p= .003 CI [-0.338 -0.072]	r= 0.1 p= .438 CI [-0.084 0.192]	r= 0.1 p= .145 CI [-0.035 0.239]
Pb_D	r= -0.1 p= .084 CI [-0.257 0.016]	r= -0.4 p< .001 CI [-0.523 -0.291]	r= -0.4 p< .001 CI [-0.517 -0.284]	r= -0.1 p= .194 CI [-0.228 0.047]	r= 0.3 p< .001 CI [0.135 0.393]
Ba_T	r= 0.39 p<0.001 CI [0.265 0.502]	r= -0.01 p= 0.915 CI [-0.146 0.131]	r= 0.01 p= 0.879 CI[-0.128 0.149]	r= 0.02 p= 0.829 CI[-0.123 0.154]	r=-0.06 p= 0.439 CI[-0.192 0.084]
Ba_D	r= 0.43 p<0.001 CI[0.308 0.535]	r= 0.02 p= 0.739 CI[-0.115 0.162]	r= 0.05 p= 0.460 CI [-0.087 0.190]	r= 0.02 p= 0.826 CI [-0.123 0.154]	r= -0.11 p= 0.116 CI[-0.247 0.027]
Cd_T	r= 0.2 p= 0.021 CI [0.025 0.296]	r= 0.2 p= 0.037 CI [0.009 0.281]	r= 0.1 p= 0.134 CI [-0.032 0.242]	r= 0.7 p< 0.001 CI [0.614 0.759]	r= -0.2 p= 0.016 CI [-0.302 -0.032]
Cd_D	r= 0.2 p= 0.015 CI [0.034 0.304]	r= 0.1 p= 0.081 CI [-0.015 0.258]	r= 0.1 p= 0.195 CI [-0.047 0.228]	r= 0.7 p< 0.001 CI [0.561 0.723]	r= -0.2 p= 0.010 CI [-0.312 -0.043]
Sr_T	r= 0.3 p<0.001 CI [0.207 0.454]	r= 0.6 p<0.001 CI [0.506 0.684]	r= 0.6 p<0.001 CI [0.531 0.702]	r= 0.9 p<0.001 CI [0.833 0.901]	r= -0.5 p<0.001 CI [-0.590 -0.378]
Sr_D	r= 0.4 p<0.001 CI [0.235 0.478]	r= 0.6 p<0.001 CI [0.547 0.713]	r= 0.7 p<0.001 CI [0.568 0.728]	r= 0.9 p<0.001 CI [0.826 0.897]	r= -0.5 p<0.001 CI [-0.600 -0.391]
Zn_T	r= 0.2 p= 0.040 CI [0.006 0.278]	r= 0.1 p= 0.405 CI [-0.080 0.196]	r= 0.04 p= 0.586 CI [-0.100 0.176]	r= 0.6 p< 0.001 CI [0.503 0.682]	r= -0.2 p= 0.039 CI [-0.279 -0.007]
Zn_D	r= 0.2 p= 0.008 CI [0.051 0.319]	r= 0.1 p= 0.381 CI [-0.077 0.199]	r=0.04 p= 0.588 CI [-0.101 0.176]	r= 0.6 p<0.001 CI [0.517 0.692]	r= -0.2 p= 0.022 CI [-0.295 -0.024]
Cu_T	r= 0.03 p= 0.715 CI [-0.113 0.164]	r= -0.3 p< 0.001 CI [-0.389 -0.130]	r= -0.3 p< 0.001 CI [-0.408 -0.152]	r= 0.2 p= 0.027 CI [0.018 0.289]	r= 0.2 p= 0.001 CI [0.105 0.368]
Cu_D	r= 0.04 p= .622 CI [-0.104 0.173]	r= -0.3 p< .001 CI [-0.381 -0.121]	r=-0.3 p< .001 CI [-0.422 -0.169]	r=0.04 p= .602 CI [-0.102 0.175]	r= 0.2 p= .003 CI [0.073 0.339]
Fe_T	r= -0.3 p<0.001 CI [-0.440 -0.189]	r= -0.3 p<0.001 CI [-0.429 -0.177]	r= -0.4 p<0.001 CI [-0.549 -0.325]	r= -0.3 p<0.001 CI [-0.441 -0.191]	r= 0.5 p<0.001 CI [0.358 0.575]
Fe_D	r= -0.3 p< 0.001 CI [-0.432 -0.180]	r= -0.5 p< 0.001 CI [-0.576 -0.360]	r= -0.5 p< 0.001 CI [-0.621 -0.420]	r= -0.5 p< 0.001 CI [-0.574 -0.358]	r= 0.7 p< 0.001 CI [0.638 0.776]
Mn_T	r= -0.3 p<0.001 CI [-0.420 -0.167]	r= -0.2 p= 0.007 CI [-0.319 -0.050]	r= -0.3 p<0.001 CI [-0.449 -0.201]	r= -0.2 p= 0.011 CI [-0.312 -0.042]	r= 0.2 p= 0.001 CI [0.102 0.365]
Mn_D	r= -0.3 p<0.001 CI [-0.437 -0.187]	r= -0.2 p= 0.003 CI [-0.337 -0.071]	r= -0.4 p<0.001 CI [-0.464 -0.219]	r=-0.2 p= 0.028 CI [-0.288 -0.016]	r= 0.2 p= 0.001 CI [0.106 0.368]
Ca_T	r= 0.6 p<0.001 CI [0.493 0.675]	r= 0.9 p<0.001 CI [0.838 0.904]	r= 0.9 p<0.001 CI [0.951 0.972]	r= 0.7 p<0.001 CI [0.583 0.738]	r= -0.6 p<0.001 CI [-0.698 -0.525]
Ca_D	r= 0.6 p<0.001 CI [0.526 0.698]	r= 0.9 p<0.001 CI [0.845 0.908]	r= 0.9 p<0.001 CI [0.963 0.978]	r= 0.7 p<0.001 CI [0.571 0.730]	r= -0.6 p<0.001 CI [-0.701 -0.529]

r: Pearson correlation coefficient; p: p-value; CI: Confidence interval at 95%

Table 5-SI (continued). Correlation coefficients showing positive and negative relationships between metal forms (T: total, D: dissolved) and pH, EC, DIC, SO_4^{2-}, and DOC.

	pH	EC	DIC	SO_4^{2-}	DOC
Al_T	r= -0.6	r= -0.4	r= -0.6	r=-0.4	r= 0.4
	p<0.001	p<0.001	p<0.001	p<0.001	p<0.001
	CI [-0.644 -0.451]	CI [-0.545 -0.320]	CI [-0.658 -0.470]	CI [-0.465 -0.220]	CI [0.226 0.470]
Al_D	r=-0.6	r= -0.6	r= -0.7	r= -0.4	r= 0.5
	p<0.001	p<0.001	p<0.001	p<0.001	p<0.001
	CI [-0.690 -0.515]	CI [-0.646 -0.454]	CI [-0.731 -0.572]	CI [-0.542 -0.316]	CI [0.417 0.619
Mg_T	r= 0.4	r= 0.8	r= 0.9	r= 0.6	r= -0.6
	p<0.001	p<0.001	p<0.001	p<0.001	p<0.001
	CI [0.315 0.542]	CI [0.782 0.869]	CI [0.899 0.941]	CI [0.472 0.660]	CI [-0.657 -0.469]
Mg_D	r= 0.4	r= 0.8	r= 0.9	r= 0.6	r= -0.6
	p<0.001	p<0.001	p<0.001	p<0.001	p<0.001
	CI [0.322 0.547]	CI [0.787 0.872]	CI [0.897 0.939]	CI [0.463 0.653]	CI [-0.651 -0.461]

r: Pearson correlation coefficient; p: p-value; CI: Confidence interval at 95%

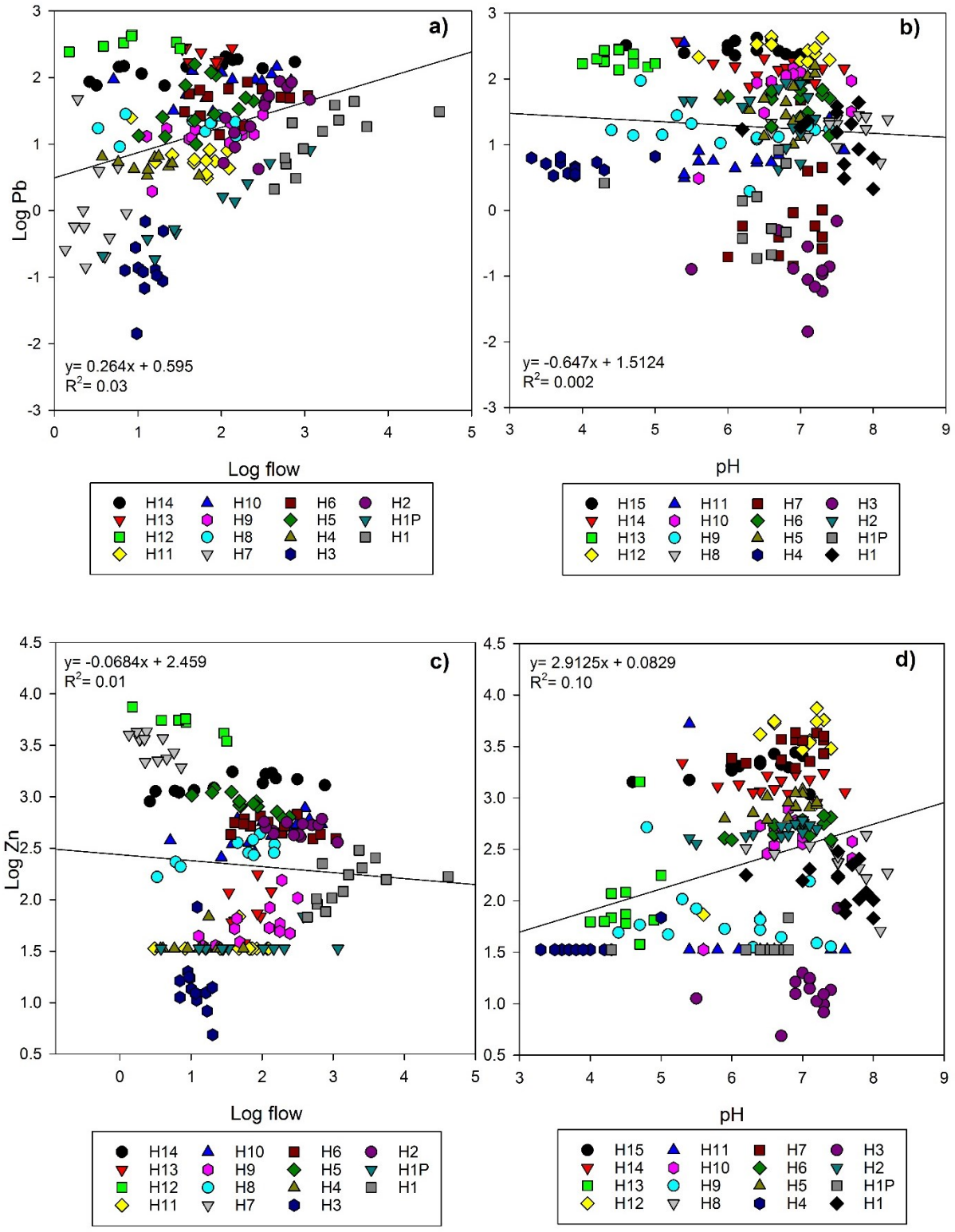

Figure 2-SI. Trends of metals in function of flow and pH in all sampling sites. Panel a and b show trends of Pb and panel c and d indicate Zn trends. Flow data from H15 (reservoir) were not measured. Solid lines represent regression lines.