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Effect of episodic rainfall on aqueous metal mobility from historical mine sites

Magaly Valencia-Avellan[1], Rebecca Slack[2], Anthony Stockdale[3], Robert John George Mortimer[4]

[1]water@leeds, School of Geography, University of Leeds, Leeds LS2 9JZ, UK.

[2]The Royal Horticultural Society, Harlow Carr, Crag Lane, Beckwithshaw, Harrogate, North Yorkshire, HG3 1QB.

[3]School of Earth & Environment, University of Leeds, Leeds LS2 9JZ, UK.

[4]School of Animal, Rural and Environmental Sciences, Nottingham Trent University, Brackenhurst Campus, Southwell, Nottinghamshire, NG25 0QF, UK.

E-mail contact: magyvalencia80@gmail.com

Supplementary Material

This document contains supplementary data as referred to in the main manuscript.

SI. Methods

Study area

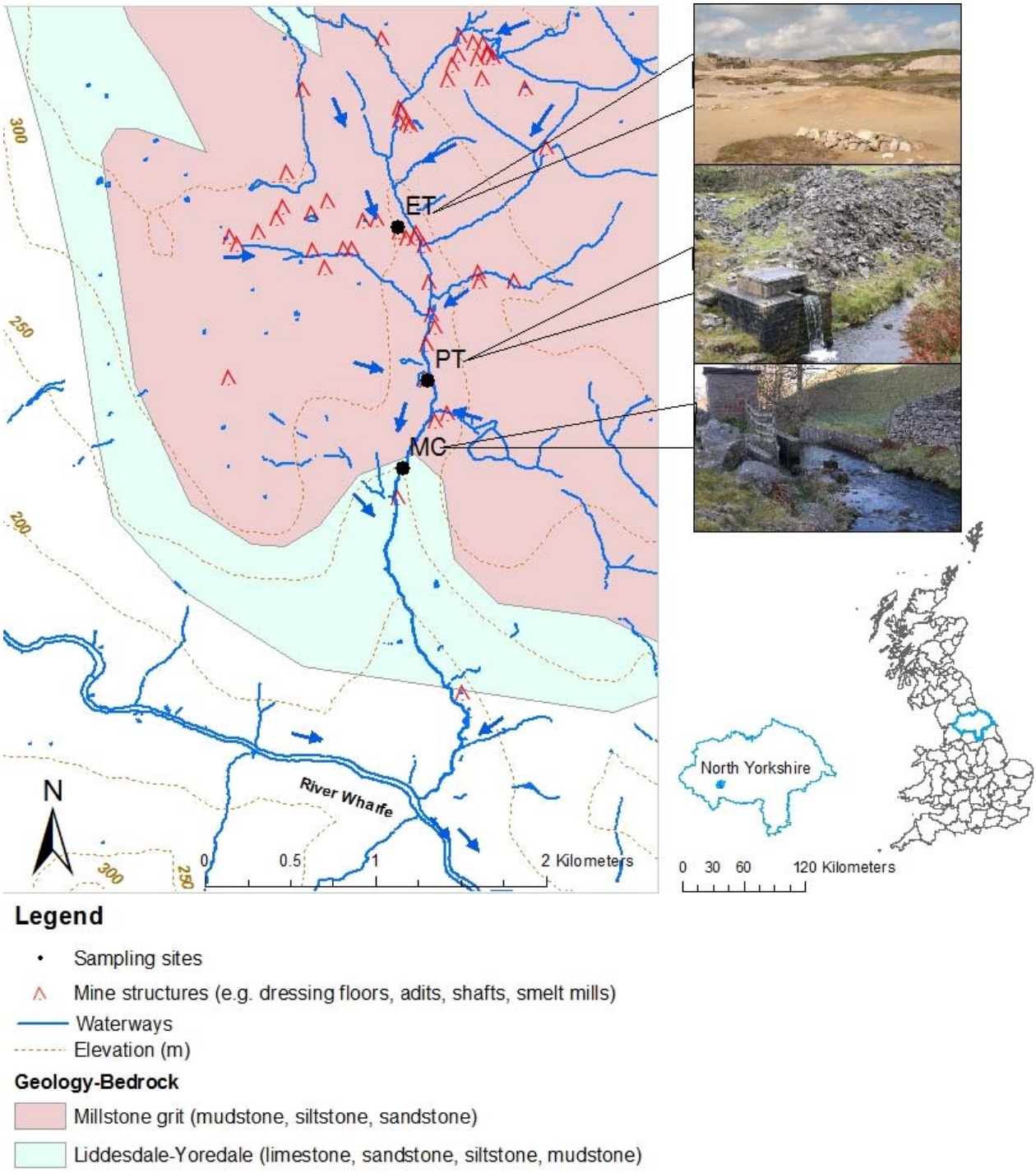

Figure S1. Sampling sites at Hebden Beck showing the underlying geology comprised by the Millstone grit and Liddesdale-Yoredale bedrock. Hydrological and Geological base maps contain OS data © Crown copyright and database right (2016).

Table S1. Sampling sites along Hebden Beck. Three locations were adopted from Valencia-Avellan *et al.* (2017a)[1] Table indicates site elevation, coordinates, and distance from River Wharfe. Sites are listed from upstream to downstream.

Sites ID	Sites ID from (Valencia-Avellan et al. (2017a)	Sites description	Elev. (m)	Coordinates		From R. Wharfe (m)
				East	North	
ET	**H12**	Ephemeral tributary running through Beaver spoil wastes (Yarnbury mine)	285	402451	465822	3921
PT	**H5**	Perennial tributary flowing through mine channels (Duke's adit)	256	402638	464793	2836
MC	**H2(*)**	Main river channel	235	402488	464275	2271

(*) Gauging station (code F1960). Environment Agency, United Kingdom.

Sampling conditions

Conditions of local seasonality and episodic rainfall in August 2016 were characterised. Daily rainfall data were obtained for Pateley Bridge Ravens Nest (54°04'01.2"N 1°46'01.2"W) in order to present local seasonal drought and rainfall events for the month of August 2016 (> 12 mm during high rainfall days) (Figure S3).

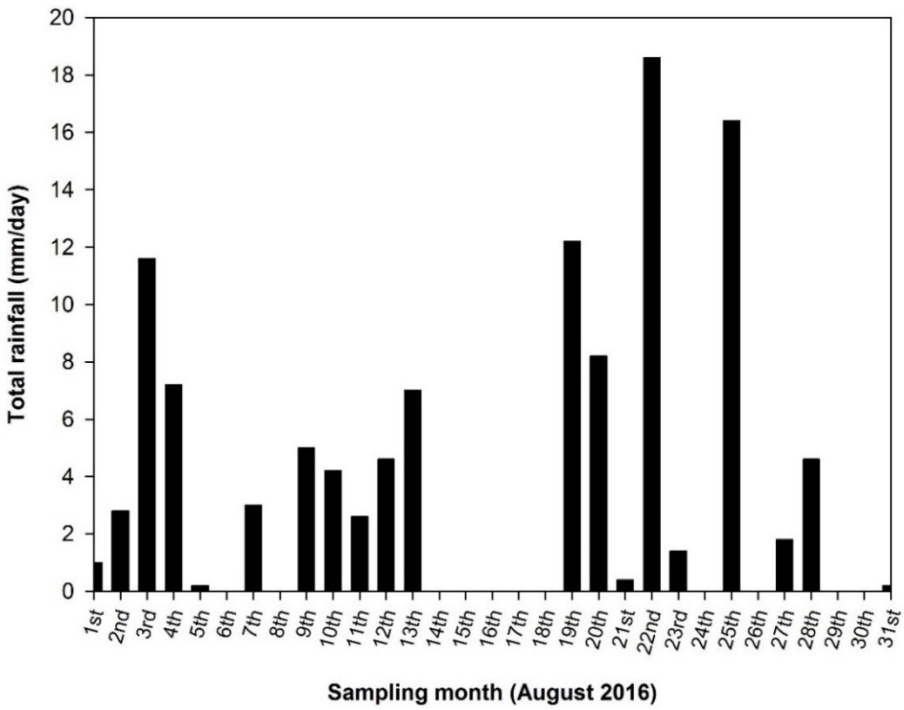

Figure S2. Daily rainfall records from Pateley Bridge Ravens Nest (54°04'01.2"N 1°46'01.2"W) during August 2016.

Three rainfall events (≥ 5 mm/hour) occurred during the sampling campaigns (Figure S 3). A low flow period (LF: 0.05 m^3/s) was measured for 0-6 hours. The first rainfall episode (5 mm/hour) produced little change in flow (0.07 m^3/s), insufficient to identify flow stages.

Subsequent episodes (>5 mm/hour) allowed the characterisation of three stages; base flow (BF), peak flow (PF) and post peak flow (PPF). The second event (9 mm/hour), BF corresponded to 7-28 hours, with flow values ranging from 0.07 to 0.14 m^3/s, PF corresponded to 29-34 hours, with flow ranging from 0.22 to 1.45 m^3/s, and PPF was between 35-52 hours, with flow ranging from 1.33 to 0.30 m^3/s. In the third event (5.8 mm/hour), unexpected problems (sampler malfunctioned or swept-away) restricted the sampling duration in sites PT and MC. During this last event, flow stages were characterised as BF from 54-66 hours (flow 0.23 to 0.40 m^3/s), PF from 68-72 hours (flow 1.41 to 2.12 m^3/s), and PPF from 74-96 hours (flow 1.64 to 0.34 m^3/s).

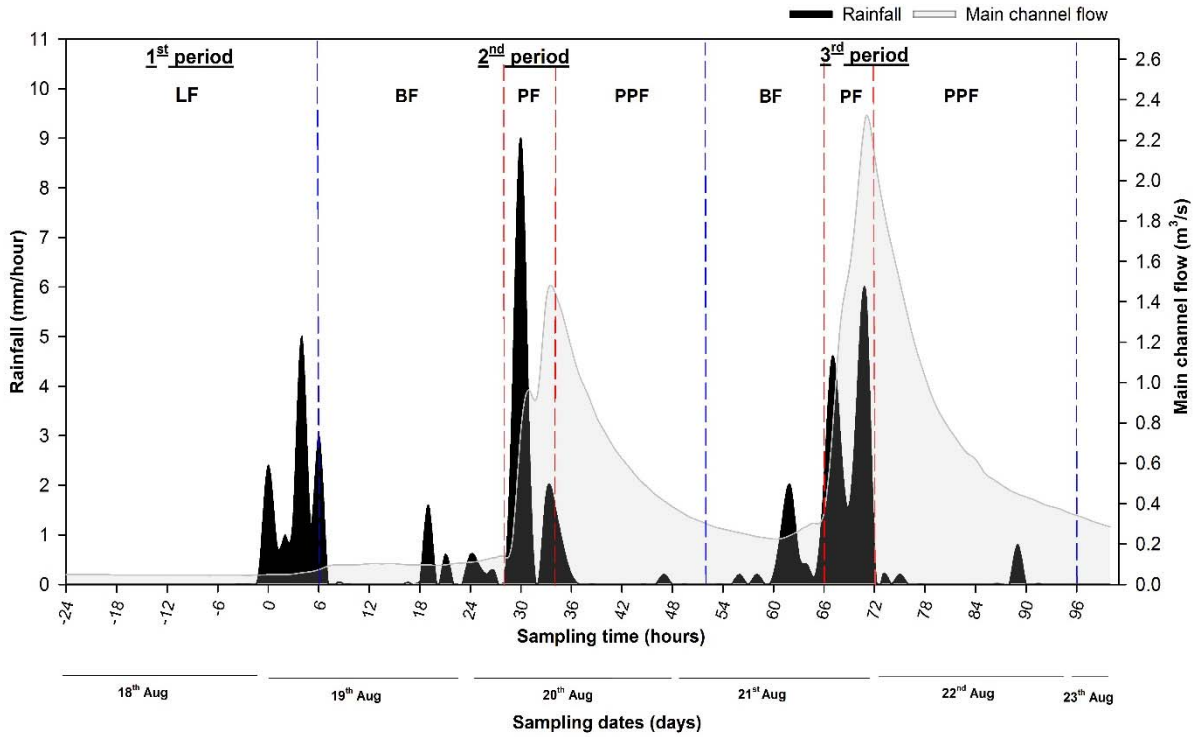

Figure S3. Hourly rainfall (mm) at Grimwith reservoir (station code: 62046; 54°04'16.4"N 1°54'47.7"W) and main channel flow at gauging station-F1960 (54°04'27.8"N 1°57'48.5"W) from 18 to 23 August.

Samples treatment and in situ measurements

Different treatments were applied based on the purpose of the analysis. For dissolved metals, subsamples were placed into a 15 ml tube (polypropylene) containing 300 µl of preservation solution (10% HNO_3, nitric acid-Sigma Aldrich 69% and Milli-Q water) to reach a pH ≤ 2. For the analysis of major ion, DIC and DOC filtered subsamples were placed individually into 15 ml tubes. All samples were kept in a cool box during sampling. In the laboratory all samples were refrigerated at 4°C.

Measurements of *in situ* water quality parameters (temperature and pH) were recorded by using pre-calibrated multiple sensor probes (Model HQ30d flexi 1032). Spot flow

measurements were recorded at all sites before setting the auto samplers and after 24 hours of water collection. Field blanks and replicates were processed as samples.

Data analysis

Geochemical modelling

The PHREEQC code (version 3) [2, 3] was used for identifying the mineral phases controlling dissolved metal concentrations. Equilibrium reactions and thermodynamic constants were retrieved from the built-in WATEQ4F database. [4-6] Mineral saturation indexes and metal free ions activities for hydroxide, carbonate and sulfate minerals were calculated at pCO_2 = 0.0012 atm, pH range of 6.5-8.5 and based on mean values across field sites and sampling dates: SO_4^{2-} (ET: 13090 μg/l, PT: 10970 μg/l, MC: 6280 μg/l), Cl^- (ET: 3600 μg/l, PT: 5960 μg/l, MC: 5080 μg/l) and temperature (ET: 16.9 °C, PT: 9.5 °C, MC: 14.0 °C).

Speciation modelling

The distribution of metal chemical species was estimated by applying the Windermere Humic Aqueous Model (WHAM/Model VII). Measurements of temperature and dissolved water chemistry were used as input data. Concentrations of dissolved organic carbon were converted to fulvic acid assuming DOM to be composed of 50% carbon and the active fraction considered to be 65% fulvic acid (FA= DOC x 1.3).[7] We considered the presence of oxides as being either active or inactive with respect to surface sorption as described in Valencia-Avellan *et al.* (2017b).[8] Activity of Al and Fe oxides was calculated from the dissolved metal data and the equations derived by Tipping[9] and Lofts and Tipping[10] respectively, with the lower of the two values being adopted, in order to exclude the likelihood of colloidal material being included in the dissolved fraction.

Toxicity modelling

Toxic effects of protons and metals were evaluated by using a parametrised version of WHAM called WHAM-F_{TOX}.[11] The metal toxicity function (F_{TOX}) is considered a product of each toxic cation-bound concentrations (v_i= mmol/g) and the toxicity coefficient of each metal (α_i) adopted from Stockdale *et al.* (2010).[11] The thresholds of F_{TOX} are defined as: Lower threshold (F_{TOX-LT} = 2.33) and Upper threshold (F_{TOX-UT} = 5.20). Calculations of F_{TOX} followed the same conditions applied in Valencia-Avellan *et al.* (2017b).[8] Thus, if F_{TOX} < 2.33, no toxicity occurs; while if F_{TOX} > 5.20, toxic response is present.

SI. Results

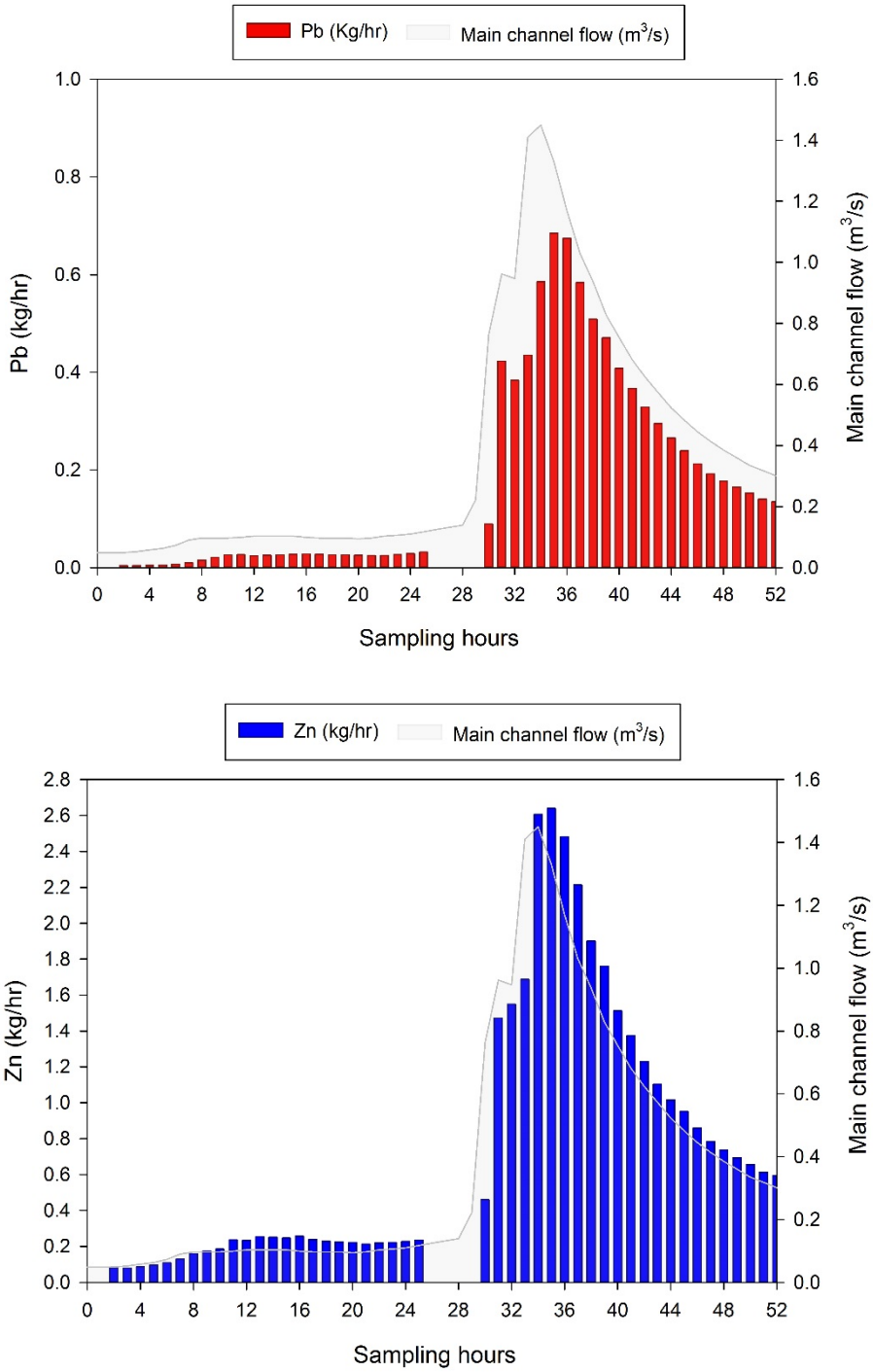

Figure S4. Mass of Pb and Zn (kg/hr) passing the main channel during episodic flow.

Different concentrations were measured for SO_4^{2-}, DIC and DOC possible due to overland flow or interflow have been identified. From LF to PPF, a 2300% increase in SO_4^{2-} concentrations occurred in ET, which are likely to be related to the degree of erosion and oxidation of mine wastes. In MC, a significant increase (6960%) was observed for DOC concentrations as result

of overland flow running through peat moorland areas[12] while DIC concentrations decreased (212%) due to interflow, attenuating rich-limestone groundwater[13] (Figure S5, Table S2).

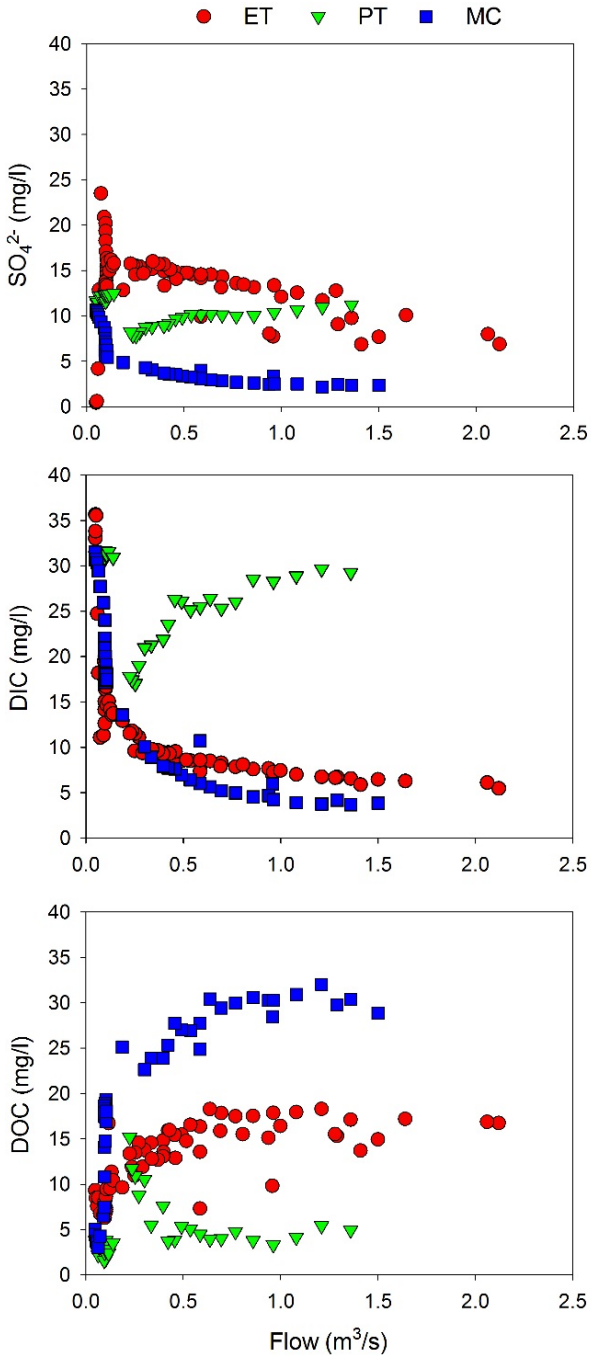

Figure S5. Effects of episodic flow in concentrations of SO_4^{2-}, DIC and DOC in the three sampling sites.

Ranges of SO_4^{2-} and DIC concentrations were higher in ET (0.4 to 23.5 mg/l SO_4^{2-}, 5.5 to 35.7 mg/l DIC) and PT (7.8 to 12.5 mg/l SO_4^{2-}, 17.0 to 31.7 mg/l DIC), while DOC concentrations showed the greatest variation in MC (3.0 to 32.0 mg/l) (Table S2).

Table S2. Water quality parameters and metal concentrations at different flow stages in ephemeral tributary (ET), perennial tributary (PT) and main channel (MC).

Sites	Rainfall periods	Flow stages		pH	SO_4^{2-} mg/l	DIC mg/l	DOC mg/l	Ca mg/l	Pb µg/l	Zn µg/l	Fe µg/l	Al µg/l
ET	1st period (5mm/hour)	LF	Ave	7.2	6.1	27.4	8.5	41.47	55.1	2973.7	469.7	9.8
			Max	7.6	23.5	35.7	9.3	49.15	128.2	3578.3	2154.5	23.3
			Min	7.0	0.4	11.1	6.8	26.90	2.2	1728.5	138.7	1.8
		BF	Ave	7.5	15.6	16.4	8.4	30.97	150.4	3298.9	331.2	36.9
			Max	7.7	20.9	20.0	16.7	34.35	233.5	3823.0	500.5	54.4
			Min	7.2	12.7	11.3	6.3	26.45	106.5	2461.1	167.7	25.3
	2nd period (9mm/hour)	PF	Ave	7.6	9.2	8.0	12.0	16.32	335.3	2414.0	192.6	66.8
			Max	7.6	12.9	12.9	15.3	24.54	457.3	2883.9	234.9	106.2
			Min	7.6	7.7	6.4	7.3	13.32	206.7	1708.0	158.2	26.3
		PPF	Ave	7.4	13.9	8.3	16.6	19.02	467.7	3819.3	245.7	126.5
			Max	7.5	15.2	9.7	18.3	22.49	559.1	5016.8	309.0	160.7
			Min	7.2	9.8	6.5	13.8	15.26	323.6	3013.0	206.1	70.5
		BF	Ave	7.3	15.0	10.6	12.8	22.59	342.7	3807.5	263.7	66.1
			Max	7.4	15.8	11.8	14.6	24.85	394.8	4166.9	327.8	77.1
			Min	7.3	13.3	9.4	10.9	19.76	284.9	3332.4	221.9	54.8
	3rd period (5.8mm/hour)	PF	Ave	7.5	7.2	5.8	15.8	12.87	571.8	2538.1	190.3	131.1
			Max	7.5	8.0	6.1	16.9	13.64	649.2	2616.5	196.4	163.3
			Min	7.4	6.9	5.5	13.7	12.38	499.9	2437.2	187.1	98.3
		PPF	Ave	7.4	14.0	8.4	14.7	19.03	575.6	3884.9	264.9	125.4
			Max	7.4	16.0	9.7	17.2	21.57	690.3	4687.8	309.3	147.2
			Min	7.4	10.1	6.3	12.7	15.21	479.1	2914.5	189.7	99.4
PT	1st period (5mm/hour)	LF	Ave	7.4	11.8	30.9	3.1	47.62	50.3	988.4	75.4	42.6
			Max	7.4	12.2	31.1	3.8	47.87	63.6	1069.1	80.0	45.6
			Min	7.3	11.5	30.6	2.2	47.06	39.9	933.1	70.6	37.4
		BF	Ave	7.5	12.3	31.2	2.7	48.24	36.3	932.1	65.4	32.6
			Max	7.6	12.5	31.7	3.8	50.04	63.6	1069.1	80.0	57.3
			Min	7.4	11.6	30.8	1.6	46.80	31.2	868.2	58.9	27.4
	2nd period (9mm/hour)	PF	Ave	7.5	11.3	28.4	5.1	43.17	30.9	789.0	79.8	42.6
			Max	7.6	12.1	30.8	7.6	46.93	35.6	918.2	98.5	52.0
			Min	7.5	10.4	25.6	3.0	39.54	23.2	622.8	60.3	28.7
		PPF	Ave	7.4	9.5	24.0	6.3	36.95	87.6	659.4	110.6	91.6
			Max	7.5	11.2	29.7	15.1	43.77	211.7	771.7	178.6	159.2
			Min	7.3	7.8	17.0	3.3	28.38	33.2	567.2	71.0	41.6
MC	1st period (5mm/hour)	LF	Ave	8.1	10.2	30.1	4.0	42.98	27.6	467.4	164.3	39.7
			Max	8.1	10.7	31.5	5.0	44.75	38.5	495.5	253.6	51.2
			Min	7.8	9.4	27.7	3.0	39.75	23.3	449.5	129.3	34.1
		BF	Ave	8.0	6.4	19.2	16.2	31.68	71.1	622.8	940.3	104.0
			Max	8.1	8.7	26.0	19.3	60.36	79.8	693.6	1168.2	133.9
			Min	8.0	5.5	17.1	6.5	28.05	47.4	493.4	362.1	50.6
	2nd period (9mm/hour)	PF	Ave	7.4	3.3	7.2	27.9	14.13	124.9	512.0	1146.1	214.3
			Max	7.6	4.9	13.6	30.2	23.88	153.7	574.7	1326.1	250.7
			Min	7.3	2.3	3.8	24.8	9.03	110.6	447.2	1052.4	154.9
		PPF	Ave	7.3	3.2	6.4	27.7	12.77	127.8	507.1	1136.2	258.2
			Max	7.6	4.3	10.0	32.0	17.78	140.7	536.3	1314.3	293.6
			Min	7.2	2.2	3.7	22.6	9.13	116.4	489.3	933.1	230.2

Table S3. Pearson correlation coefficient showing relationships between flow water quality parameters and with metal concentrations at different flow stages in ephemeral tributary (ET), perennial tributary (PT) and main channel (MC). NC: no correlation as pH values were constant (standard deviation= 0), ND= no data available. Significance of *p-values* is denoted by asterisks.

		ET					PT					MC				
		Pb	**Zn**	**Fe**	**Ca**	**Al**	**Pb**	**Zn**	**Fe**	**Ca**	**Al**	**Pb**	**Zn**	**Fe**	**Ca**	**Al**
LF	pH	0.9 **	-0.9 **	0.3	-0.9 **	1.0 **	-0.8	0.4	-0.01	-0.6	-0.4	0.2	0.2	0.3	-0.4	0.2
	flow	0.9 **	-0.8 *	0.1	-1.0 ***	0.9 **	-0.8	0.04	-0.4	-0.8	-0.6	0.9 **	0.9 *	1.0 **	-1.0 ***	0.9 *
	SO_4^{2-}	0.8 *	-0.8 *	-0.1	-1.0 ***	0.9 ***	-0.3	0.2	-0.04	-0.7	-0.2	-0.9 **	-0.9 *	-1.0 **	1.0 ***	-0.9 *
	DIC	-0.9 **	0.9 *	-0.1	1.0 ***	-1.0 ***	0.9 *	0.4	0.7	0.6	0.8	-1.0 **	-0.9 *	-1.0 ***	1.0 **	-0.9 *
	DOC	-0.8 *	0.5	-0.4	0.8 *	-0.8 *	0.6	-0.5	-0.2	0.2	-0.1	-0.1	-0.2	-0.1	0.3	-0.3
BF	pH	-0.1	0.3	0.4	0.5 *	0.03	-0.2	-0.03	-0.2	-0.2	-0.1	-0.6 **	-0.6 **	-0.6 **	0.1	-0.8 ***
	flow	0.8 ***	-0.2	-0.03	-0.5 *	0.7 ***	-0.4	-0.1	-0.3	-0.4	-0.2	0.6 *	0.3	0.5	-0.3	0.6 **
	SO_4^{2-}	-0.3	-0.5 *	-0.9 ***	-0.7 ***	-0.3	0.04	0.2	0.1	-0.2	0.1	-0.8 ***	-0.7 ***	-0.8 ***	0.1	-0.9 ***
	DIC	-0.2	0.7 ***	0.8 ***	1.0 ***	-0.1	0.1	-0.1	0.01	-0.2	0.2	-0.8 ***	-0.7 ***	-0.8 ***	0.2	-1.0 ***
	DOC	0.6 **	-0.4	-0.01	-0.3	0.5 *	0.04	-0.02	0.03	-0.2	-0.2	0.8 ***	0.8 ***	0.8 ***	-0.2	0.9 ***
PF	pH	NC	NC	NC	NC	NC	-0.3	0.1	-0.4	0.4	-0.6	0.4	0.4	0.9 *	0.8	-0.8 *
	flow	1.0 ***	0.3	-0.3	-0.8 *	0.9 *	0.01	-0.5	0.8	-0.7	0.9 *	0.1	-0.6	-0.4	-0.9 **	0.9 **
	SO_4^{2-}	-0.8	0.01	0.6	0.9 **	-0.6	0.3	0.9 *	-1.0 **	1.0 **	-0.9 *	-0.02	0.6	0.7	1.0 ***	-1.0 ***
	DIC	-0.7	0.2	0.7	1.0 ***	-0.5	0.4	0.9 *	-1.0 ***	0.9 **	-0.9 **	0.1	0.7	0.7	1.0 ***	-1.0 ***
	DOC	0.8	0.8 *	0.4	-0.3	1.0 **	-0.4	-0.9 *	0.9 **	-1.0 **	0.9 *	-0.3	-0.7	-0.8	-0.9 **	0.9 *
PPF	pH	0.7 **	0.1	0.04	-0.6 *	0.6 **	-0.7 ***	-0.4	-0.7 ***	0.8 ***	-0.8 ***	-0.9 ***	0.2	-1.0 ***	1.0 ***	-0.9 ***
	flow	0.6 *	-0.5 *	-0.6 *	-1.0 ***	0.7 **	-0.8 ***	0.03	-0.8 ***	0.9 ***	-0.9 ***	0.9 ***	0.3	0.7 **	-0.9 ***	0.8 ***
	SO_4^{2-}	-0.5	0.6 *	0.6 *	0.9 ***	-0.6 *	-0.9 ***	-0.3	-0.9 ***	1.0 ***	-0.9 ***	-1.0 ***	-0.1	-0.9 ***	1.0 ***	-0.9 ***
	DIC	-0.7 **	0.4	0.5	1.0 ***	-0.8 ***	-0.9 ***	-0.3	-1.0 ***	1.0 ***	-1.0 ***	-1.0 ***	-0.02	-0.9 ***	1.0 ***	-0.9 ***
	DOC	0.7 **	-0.3	-0.5	-0.8 ***	0.7 **	0.9 ***	0.5 *	0.9 ***	-0.8 ***	0.8 ***	0.9 ***	-0.01	0.9 ***	-1.0 ***	0.8 ***

** significant at p < 0.05; ** significant at p < 0.01; *** significant at p < 0.001. No asterisk = no significant.*

Table S3 (continued). Pearson correlation coefficient showing relationships between flow water quality parameters and with metal concentrations at different flow stages in ephemeral tributaries (ET), perennial tributaries (PT) and main channel (MC). NC: no correlation as pH values were constant (standard deviation= 0), ND= no data available. Significance of *p-values* is denoted by asterisks.

		ET					PT					MC				
		Pb	**Zn**	**Fe**	**Ca**	**Al**	**Pb**	**Zn**	**Fe**	**Ca**	**Al**	**Pb**	**Zn**	**Fe**	**Ca**	**Al**
BF	pH	0.8 *	-0.7 *	-0.3	-0.7	-0.6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	flow	0.7	-0.5	-0.4	-0.7	0.4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	SO_4^{2-}	-0.7	0.8 *	0.6	0.9 **	-0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	DIC	-0.7	0.9 **	0.7	1.0 ***	-0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	DOC	-0.1	0.4	0.4	0.3	0.6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PF	pH	-0.6	-1.0	0.04	-1.0	-0.6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	flow	0.8	-0.3	-1.0 *	0.3	0.8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	SO_4^{2-}	0.9	0.7	-0.5	1.0	0.9	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	DIC	0.4	1.0 *	0.2	0.9	0.4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	DOC	0.9	-0.2	-1.0	0.4	0.9	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PPF	pH	-0.6	-0.4	0.2	0.4	-0.6 *	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	flow	0.8 ***	-0.7 **	-0.9 ***	-1.0 ***	0.7 **	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	SO_4^{2-}	-0.9 ***	0.6	0.9 ***	1.0 ***	-0.8 **	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	DIC	-0.9 ***	0.6 *	0.9 ***	1.0 ***	-0.8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	DOC	0.8 ***	-0.4	-0.7 *	-0.8 **	0.7 **	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

** significant at $p < 0.05$; ** significant at $p < 0.01$; *** significant at $p < 0.001$. No asterisk = no significant.*

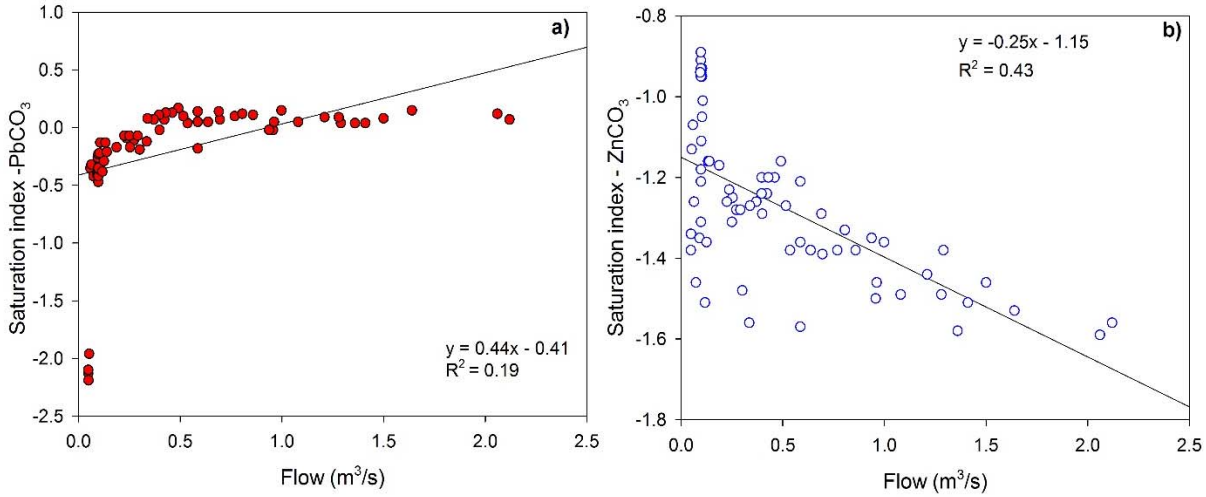

Figure S6. Relationships between saturation indexes for cerussite ($PbCO_3$) and smithsonite ($ZnCO_3$) with episodic flow in ephemeral tributary (ET). Indexes were computed with PHREEQC model. Note Y axis have different scales.

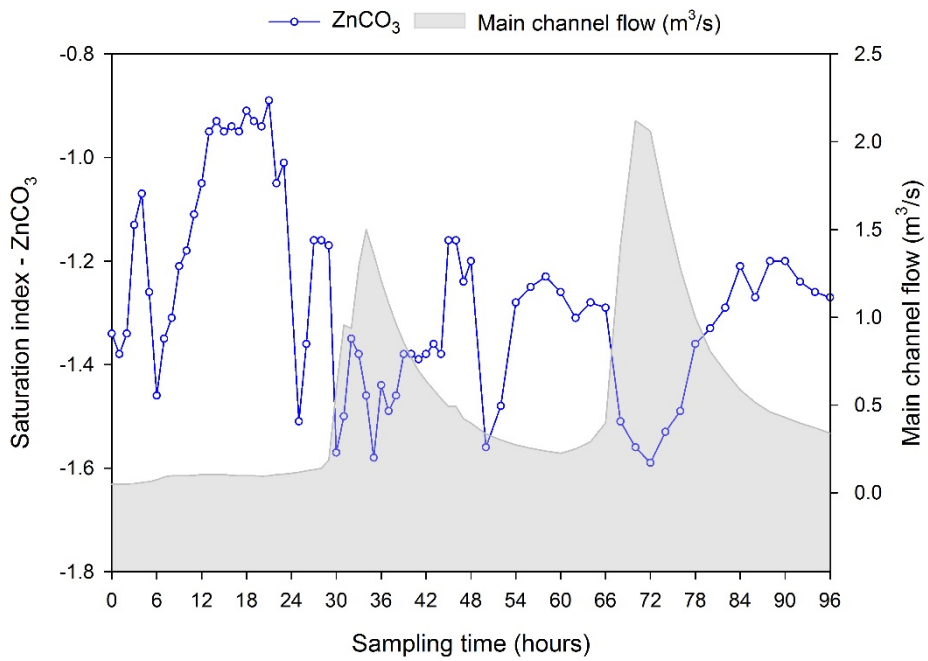

Figure S7. Effect of peak flow on the smithsonite ($ZnCO_3$) saturation index in ephemeral tributary (ET).

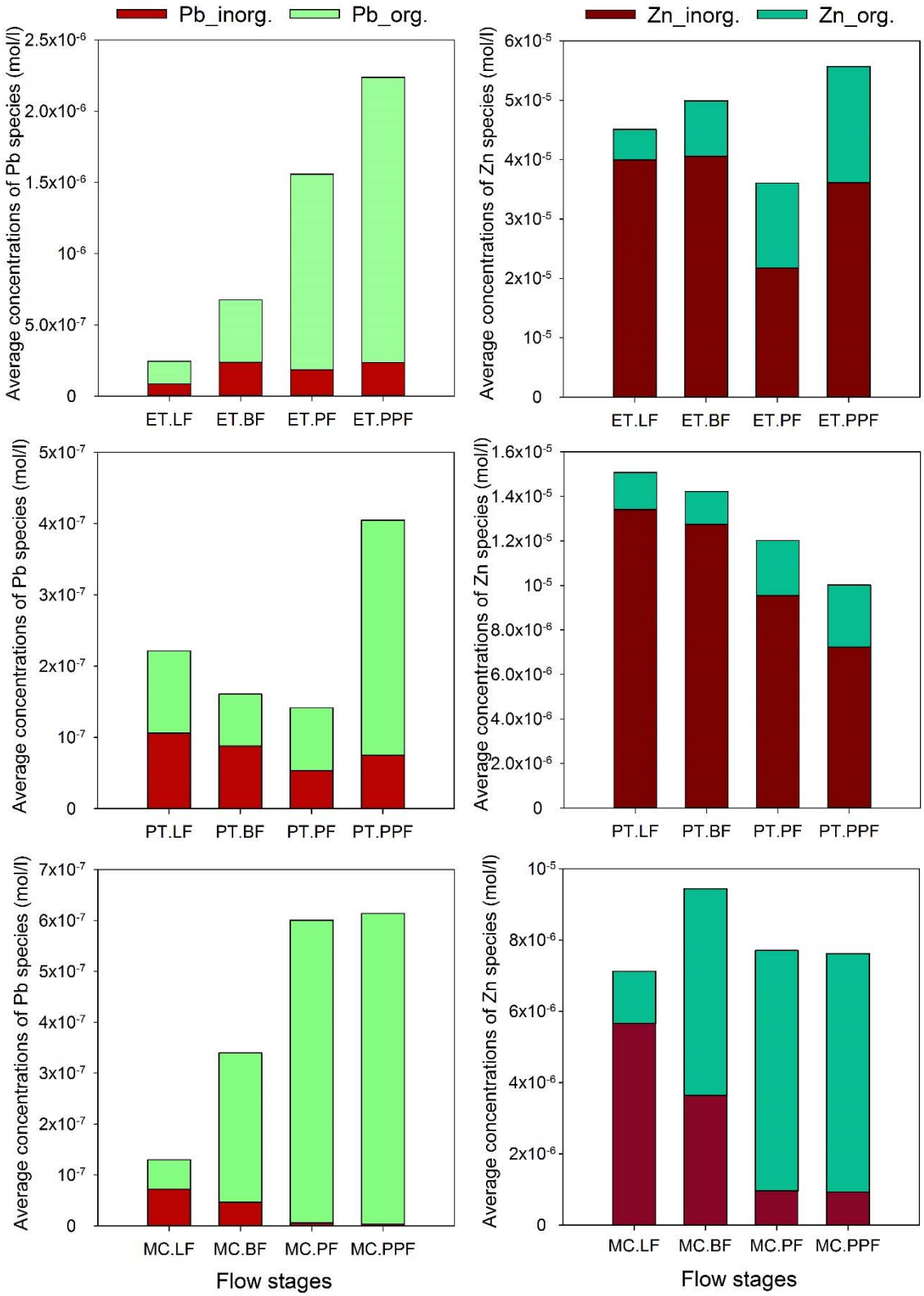

Figure S8. Inorganic and organic metal concentrations in absence of active oxide precipitates calculated by WHAM/Model VII at different flow stages in all sampling sites. Left hand side panels show average concentrations of Pb species. Right hand side panels show average concentrations of Zn species.

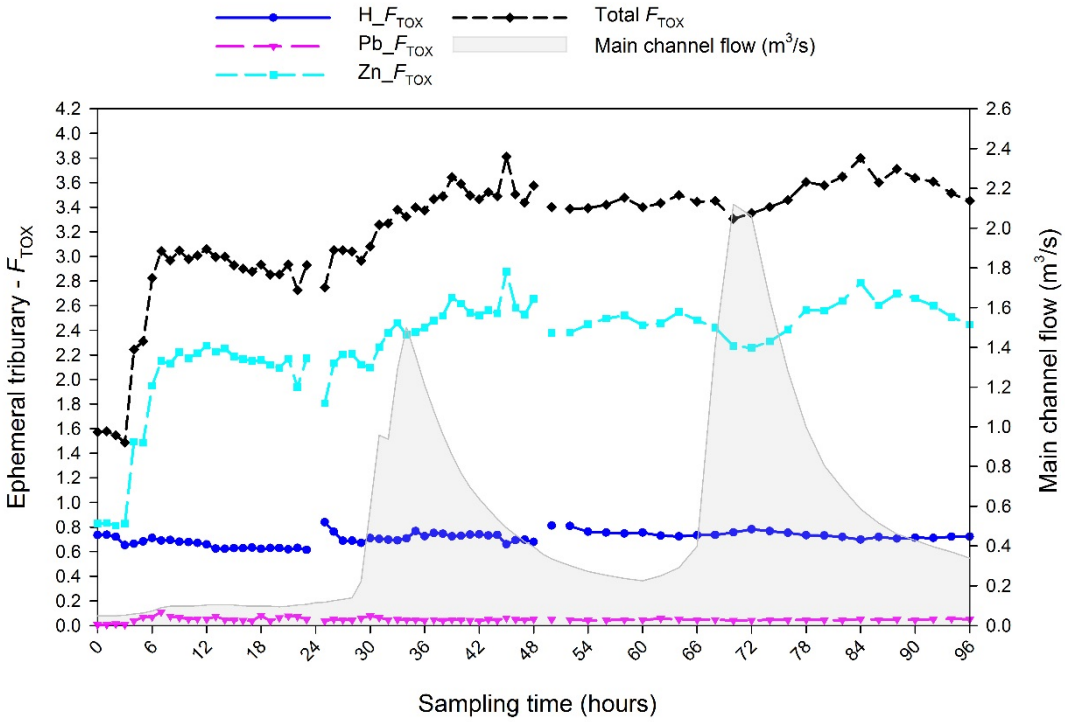

Figure S9. Variations in F_{TOX} in ephemeral tributary at different flow stages.

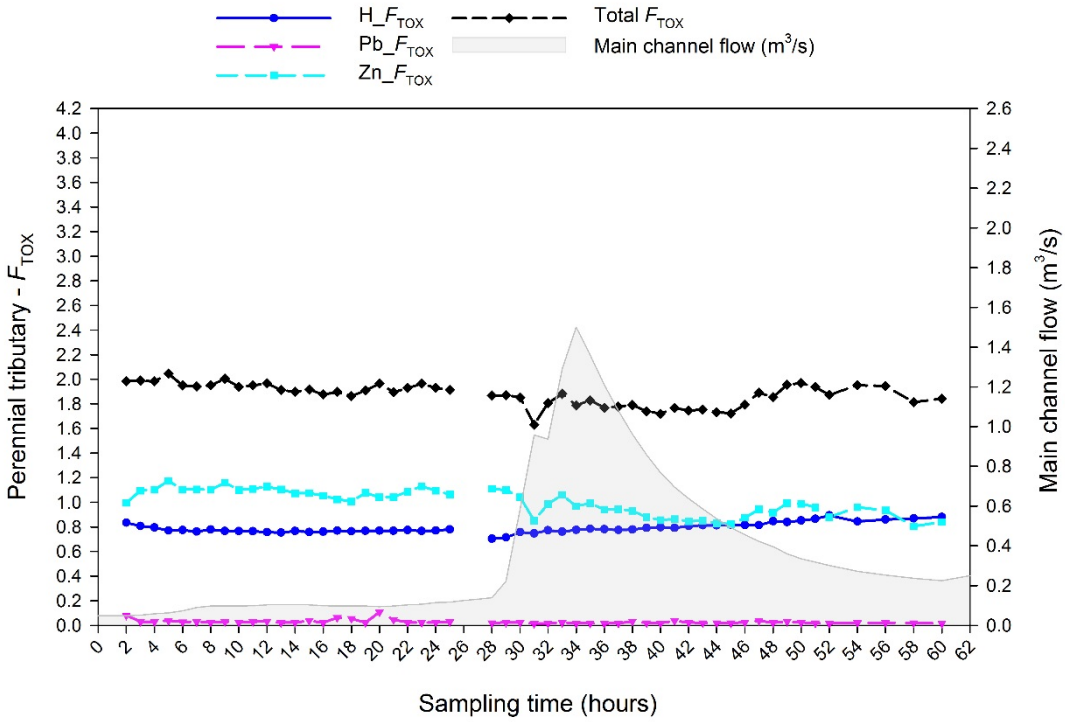

Figure S10. Variations in F_{TOX} in perennial tributary at different flow stages.

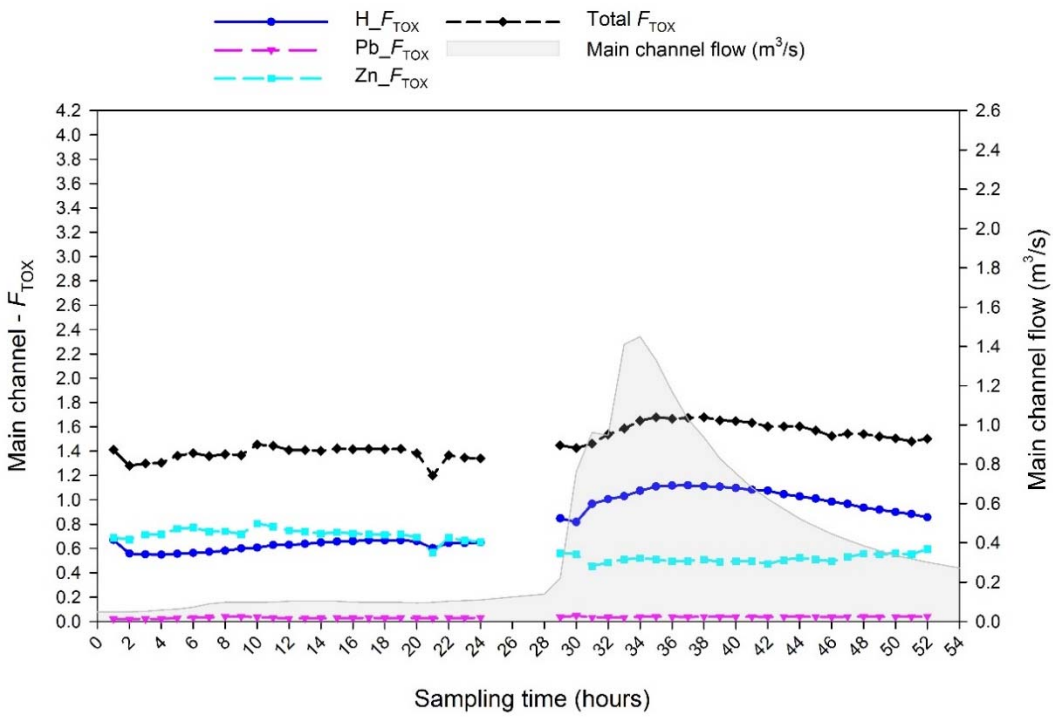

Figure S11. Variations in F_{TOX} in main channel at different flow stages.

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