Origin and fate of Vanadium in the Hazeltine Creek Catchment following the 2014 Mount Polley mine tailings spill, British Columbia, Canada

Supplementary Information

Karen A. Hudson-Edwards[1*], *Patrick Byrne*[2], *Graham Bird*[3], *Paul A. Brewer*[4], *Ian T. Burke*[5], *Heather E. Jamieson*[6], *Mark G. Macklin*[7], *Richard D. Williams*[8]

[1] Environment & Sustainability Institute and Camborne School of Mines, University of Exeter, Penryn Cornwall TR10 9FE, UK. *Corresponding author. Email k.hudson-edwards@exeter.ac.uk; Tel: +44-(0)1326-259-489.
[2] School of Natural Sciences and Psychology, Liverpool John Moores University, Liverpool, L3 3AF, UK. Email p.a.byrne@ljmu.ac.uk
[3] School of Natural Sciences, Bangor University, Bangor, Gwynedd, LL57 2UW, UK. g.bird@bangor.ac.uk
[4] Department of Geography and Earth Sciences, Aberystwyth University, Penglais, Aberystwyth, Ceredigion SY23 3DB, UK. pqb@aber.ac.uk
[5] School of Earth and Environment, University of Leeds, Leeds LS2 9JT, UK. i.t.burke@leeds.ac.uk
[6] Department of Geological Sciences and Geological Engineering, Queen's University, Kingston, Ontario K7L 3N6, Canada. jamieson@queensu.ca
[7] Lincoln Centre for Water and Planetary Health, School of Geography, College of Science, University of Lincoln, Brayford Pool, Lincoln, Lincolnshire LN6 7TS, UK. mmacklin@lincoln.ac.uk
[8] School of Geographical and Earth Sciences, University of Glasgow, Glasgow G12 8QQ, UK. Richard.Williams@glasgow.ac.uk

Submitted to: *Environmental Science & Technology*

Keywords: Vanadium; Mount Polley; tailings; magnetite; titanite; XANES

Supporting Information

Supplementary Information: Methodology

Field data collection

As described in Byrne et al.[1], a synoptic survey of water quality under low flow conditions was conducted in Hazeltine Creek on August 2nd 2015. High flow samples were collected at selected locations in 2016. The samples were collected when active creek reconstruction and remediation activities were being carried out. At each water sampling location, physico-chemical parameters (pH, specific conductivity and Eh) were measured using an AQUAREAD AP-5000 multi-parameter probe following appropriate calibration protocols. Alkalinity was estimated as bicarbonate by ion sum calculation. Three stream water samples were collected at each sample location for determination of major ion and trace element concentrations. Samples for total cation and trace metal analysis were preserved with concentrated HNO_3. Samples for filtered cation and trace metal analysis were filtered through a 0.45 µm cellulose nitrate filter before acidification, whereas those for anion analysis were filtered only. Physico-chemical measurements for pore water samples were made using the AQUAREAD probe and a flow-through cell. Treatment of pore water samples for ion and trace metal analyses followed the same procedure as above for stream samples.

Water quality analyses

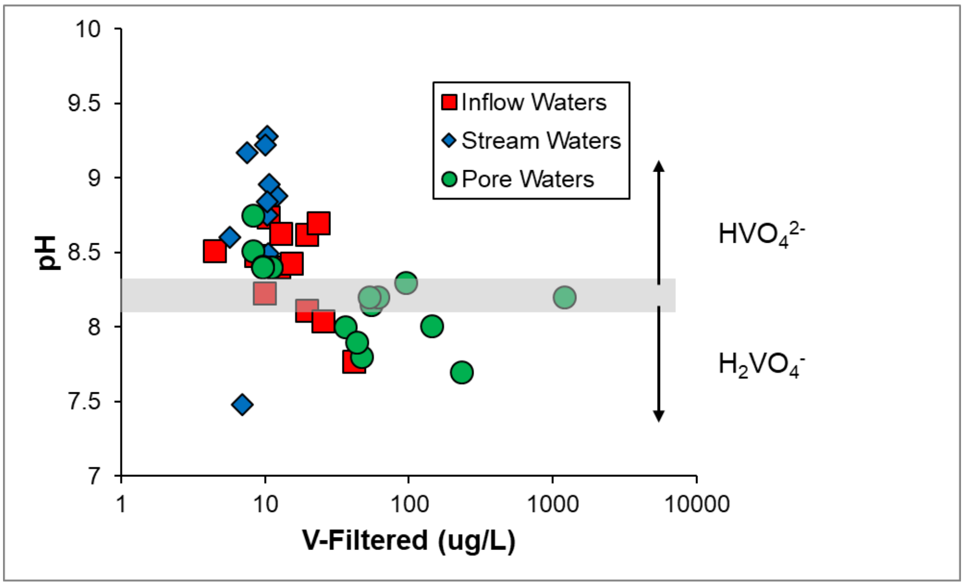
Analytical accuracy for the cation (ICP-OES – Thermo Scientific iCAP 6500 Duo) and trace metal (ICP-MS – Thermo X-series 2) analyses was assessed using the certified reference material SLRS-6 (National Research Council of Canada). Analytical accuracy for the anion (DIONEX ICS-2500) analyses was assessed using the certified reference material BATTLE-02 (National Water Research Institute, Environment Canada). Instrument and analytical precision for the ICP-OES, ICP-MS and Dionex IC, monitored using blind duplicates, was found to be ±5%.

Preparation of V(V)-FeOOH XANES standard

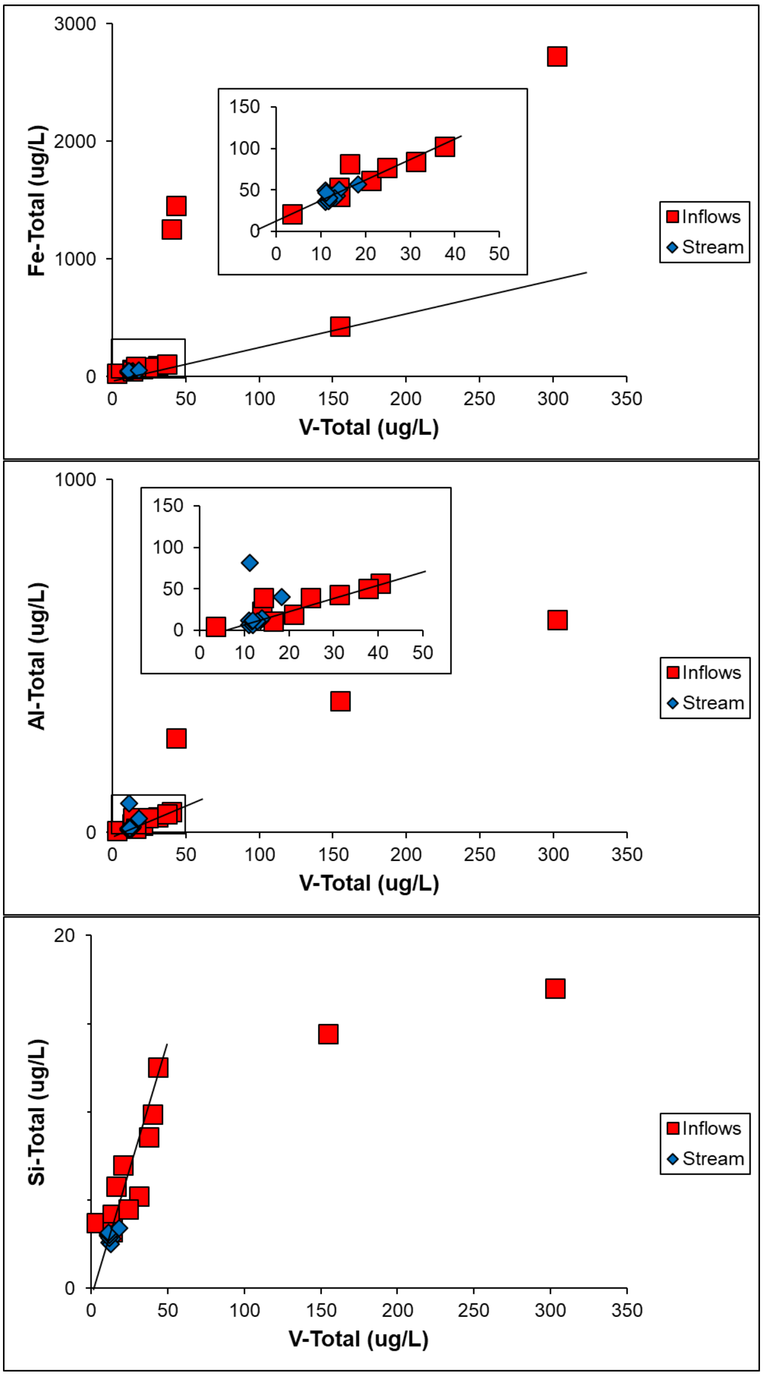
The V(V)-FeOOH standard was prepared by adding 20 mL 100 ppm $NaVO_3$ dropwise over 20 min to 0.2 g goethite suspended in 2 L Milli-Q DIW to achieve a sorbed V concentration of ~1 wt %. Solution pH was maintained at pH 8 by adding 0.1 M HCl or 0.1 M NaOH as required. Once all $NaVO_3$ had been added the suspension was left overnight prior to vacuum filtering at 0.2 µm. The residue was dried in an oven at 40 °C for 24 h.

Supplementary Information: Results

Supplementary Figure S1. V-filtered (µg/L) versus pH for Hazeltine Creek stream, inflow and pore waters. Grey bar shows the boundaries for the transition from HVO_4^{2-} (> pH c. 8.1-8.3) to $H_2VO_4^-$ (<pH c. 8.1-8.3)[2,3].

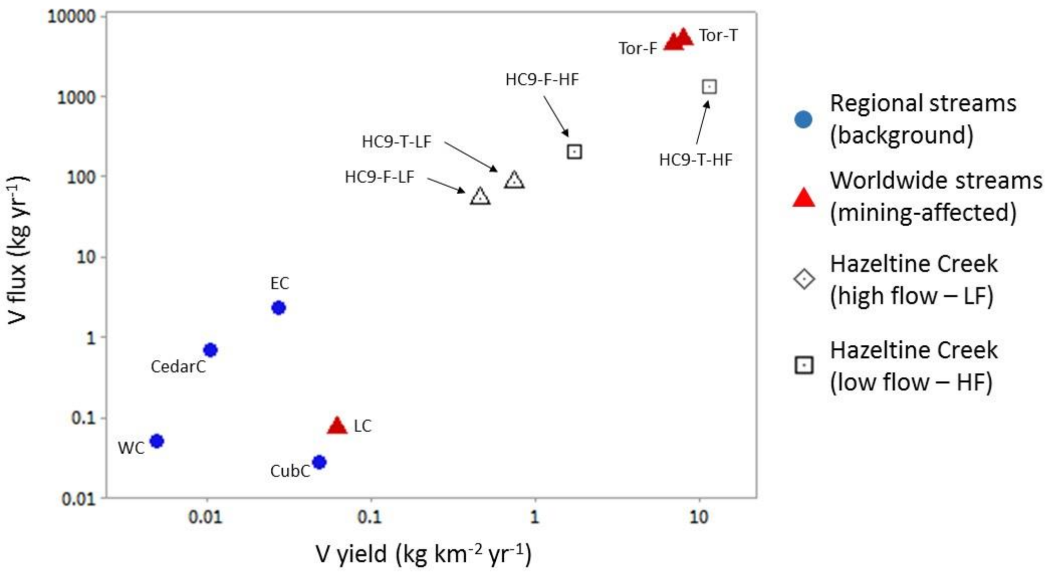


Supplementary Figure S2. V-total (µg/L) versus Fe-total (µg/L), Al-total (µg/L) and Si-total (µg/L) for Hazeltine Creek stream and inflow waters.



Supplementary Figure S3. Photograph taken in August 2015 near site of sample S-1 (Figure 1), showing orange-yellow Fe oxyhydroxides forming in water seeping from beneath deposited tailings. This is an example of a low-flow seep which were present in 2015 though not volumetrically significant in the Hazeltine Creek catchment.

Supplementary Figure S4. V flux and yield for Hazeltine Creek (HC-9 in 2016[1]), regional streams (background) and worldwide streams (mining-affected). Note the logarithmic axes. Hazeltine Creek: HF=high flow; LF=low flow; T=total load; F=filtered load. Regional streams: WC = Winkley Creek; CubC = Cub Creek; CedarC = Cedar Creek; EC = Edney Creek; LC = Lion Creek (USA)[6]; Tor = Torna Creek (Hungary)[7].



Supplementary Table S1. Mineral saturation indexes based on Hazeltine Creek stream and pore water compositions given in Byrne et al.[1] (Table S1). Results based on PHREEQC modelling[4]. Major phases calculated using data from the minteq.dat.v4 database.

Phase	Species	Hazeltine Creek	Inflows	Pore waters
$Al(OH)_3am$	$Al(OH)_3am$	-4.53 to -2.74	-4.33 to -1.87	-2.96 to -1.16
$Ca_2V_2O_7$	$Ca_2V_2O_7$	-8.95 to -6.20	-18.01 to -5.59	-17.57 to -2.72
$Ca_3(VO_4)_2$	$Ca_3(VO_4)_2$	-18.55 to -12.55	-26.89 to -13.00	-26.62 to -11.30
Ca-vanadate	$Ca_{0.5}VO_3$	-9.58 to -8.38	-19.23 to -7.93	-18.31 to -3.93
Fe-vanadate	$Fe_{0.5}VO_3$	-9.80 to -4.70	-13.09 to -4.93	-12.07 to -1.13
Mg-vanadate	$Mg_{0.5}VO_3$	-15.81 to -14.64	-25.45 to -13.83	-24.60 to -9.98
$Mg_2V_2O_7$	$Mg_2V_2O_7$	-18.74 to -16.26	-28.01 to -15.27	-27.76 to -12.42
Mn-vanadate	$Mn_{0.5}VO_3$	-13.22 to -11.41	-21.27 to -8.65	-20.47 to -5.18
Na_3VO_4	Na_3VO_4	-31.84 to -28.92	-35.72 to -27.76	-35.99 to -28.63
$Na_4V_2O_7$	$Na_4V_2O_7$	-36.00 to -33.34	-44.60 to -30.81	-44.74 to -30.30
Na-vanadate	$NaVO_3$	-7.59 to -6.96	-12.13 to -6.22	-11.93 to -4.85
$V(OH)_3$	$V(OH)_3$	-16.38 to -11.66	-13.80 to -10.60	-13.88 to -10.16
V_2O_5	V_2O_5	-17.70 to -13.80	-24.91 to -14.38	-23.74 to -9.83
V_3O_5	V_3O_5	-34.08 to -21.31	-27.35 to -20.01	-27.43 to -16.99
V_4O_7	V_4O_7	-42.62 to -26.83	-34.36 to -25.39	-34.31 to -20.86
V_6O_{13}	V_6O_{13}	-39.06 to -22.58	-44.27 to -22.66	-41.82 to -11.99
VCl_2	VCl_2	-69.32 to -57.42	-62.86 to -51.99	-62.23 to -52.48
VMetal	VMetal	-87.97 to -76.34	-82.69 to -69.81	-83.02 to -69.30
VO	VO	-35.34 to -28.16	-31.87 to -25.46	-32.03 to -25.65
$VO(OH)_2$	$VO(OH)_2$	-8.38 to -5.33	-7.44 to -5.05	-7.45 to -3.47
VO_2Cl	VO_2Cl	-28.16 to -22.95	-28.16 to -22.57	-27.54 to -18.94
$VOSO_4$	$VOSO_4$	-29.94 to -22.19	-26.82 to -23.37	-25.17 to -18.04
Calcite	$CaCO_3$	-0.14 to 1.40	0.58 to 1.54	0.27 to 0.75
Diaspore	AlOOH	-0.59 to 1.18	-0.39 to 2.07	0.99 to 3.95
Gibbsite	$Al(OH)_3$	6.48 to 8.12	-1.80 to 0.67	-0.41 to 2.56

Supplementary Table S2. Distribution of V^{3+} and V^{5+} dissolved species (in %) for the Hazeltine Creek stream, inflow and pore waters, as obtained from PHREEQC equilibrium calculations. Calculations were not carried out for PW-1_0 or PW-1_20 because no Cl^- or SO_4^{2-} data were available for these samples.

Sample	**V^{3-}**	**V^{5+}**		**V^{3-}**	**V^{5+}**		**V^{3-}**	**V^{5+}**
Stream waters			*Inflow waters*			*Pore waters*		
HC1	0	100	S1	0	100	PW-1_10	51	49
HC2	0	100	S2	100	0	PW-2_0	1	99
HC3	0	100	S3	0	100	PW-2_10	0	100
HC4	0	100	S4	0	100	PW-2_20	75	25
HC5	0	100	S5	6	94	PW-3_0	2	98
HC6	0	100	S6	77	23	PW-3_10	24	76
HC7	0	100	S7	0	100	PW-3_20	91	9
HC8	1	99	S8	100	0			
HC9	65	35	S9	11	89			
HC10	0	100	S10	7	93			
			S11	11	89			
			S12	1	99			

Supplementary Table S3. Distribution of HVO_4^{2-} and $H_2VO_4^-$ dissolved species (in %) for the Hazeltine Creek stream, inflow and pore waters, as obtained from PHREEQC equilibrium calculations. Calculations were not carried out for PW-1_0 or PW-1_20 because no Cl^- or SO_4^{2-} data were available for these samples.

Sample	**HVO_4^{2-}**	**$H_2VO_4^-$**		**HVO_4^{2-}**	**$H_2VO_4^-$**		**HVO_4^{2-}**	**$H_2VO_4^-$**
Stream waters			*Inflow waters*			*Pore waters*		
HC2	75	25	S2	23	77	PW-1_10	30	70
HC3	64	36	S3	51	49	PW-2_0	46	54
HC4	83	17	S4	61	39	PW-2_10	34	66
HC5	86	14	S5	55	45	PW-2_20	21	79
HC6	84	16	S6	31	69	PW-3_0	45	55
HC7	69	31	S7	63	37	PW-3_10	34	66
HC8	50	50	S8	49	51	PW-3_20	29	71
HC9	9	91	S9	36	64			
HC10	57	43	S10	49	51			
			S11	36	64			
			S12	60	40			

Supplementary Table S4. Tailings and Fe oxyhydroxide sample descriptions and V concentrations. Samples POL-5 and POL-6 were donated by Mount Polley Mining Corporation, and further details are given in SNC-Lavalin Inc[5]. The remaining samples were collected by the authors in August 2015.

Sample	Sample Date	Sample Description	V (mg/kg)
POL-5	15/09/2014	Tailings (ST 09-02-01-140915)	170
POL-6	12/09/2014	Tailings (WT 17-08-02-140912)	231
POL-7	12/07/2016	Tailings (magnetite sand) deposit c. 1.5 m thick	205
POL-9	12/07/2016	Tailings (magnetite sand) deposit c. 1 m thick	85
POL-12	12/07/2016	Magnetite sand scraped from seep draining tailings	51
POL-13	12/07/2016	Ochre deposit scraped from seep draining re-profiled stream bank	185
POL-14	12/07/2016	Tailings (magnetite sand) deposit between rock armour on stream bank	124

Supplementary Table S5. Automated mineralogical analysis of Hazeltine Creek tailings, sediment and ochre samples. Minerals with area % abundances < 0.03% for all samples are not included.

	POL5	POL6	POL7	POL9	POL12	POL13	POL14
Mineral	Area%	Area%	Area%	Area%	Area%	Area%	Area%
Fe Oxides	3.05	2.38	2.40	1.16	0.58	4.70	1.62
Cu-bearing Fe oxide	2.32	1.91	0.63	0.51	0.67	4.32	0.64
Titanite	0.67	0.46	1.69	0.73	0.46	1.44	1.28
Epidote	4.67	4.83	4.92	3.52	0.81	3.70	3.97
Hornblende/Augite	5.07	4.72	4.14	3.88	7.21	10.70	4.63
Enstatite	0.00	0.00	0.00	0.00	0.19	0.00	0.00
Chlorite	1.39	1.33	1.47	1.77	0.84	2.04	1.16
Orthoclase	38.13	39.07	39.50	41.14	7.01	20.31	28.11
Albite	32.26	32.71	32.98	34.68	16.24	20.18	22.28
Plagioclase	2.27	2.35	1.60	2.46	3.05	2.43	1.73
Quartz	1.56	1.30	1.85	2.37	50.36	20.23	27.18
Apatite	0.37	0.38	0.34	0.26	0.12	0.16	0.26
Muscovite	3.21	3.38	3.65	3.77	10.11	3.76	2.97
Ilmenite	0.05	0.04	0.03	0.02	0.15	0.05	0.02
Ti-Fe-Ca-Si phase	0.01	0.00	0.04	0.02	0.00	0.04	0.03
Ilmenorutile	0.06	0.06	0.06	0.02	0.10	0.13	0.04
Rutile	0.01	0.01	0.01	0.00	0.03	0.01	0.01
Fe Ti Silicate	0.01	0.01	0.01	0.00	0.01	0.06	0.00
Ti-Muscovite	0.30	0.34	0.40	0.27	0.41	0.38	0.26
Vermiculite	1.55	1.61	1.92	1.02	0.14	1.65	1.34
Calcite	1.67	1.83	1.94	2.04	0.48	1.55	1.57
Ankerite	0.10	0.07	0.05	0.03	0.09	0.57	0.04
Dolomite	0.00	0.00	0.00	0.00	0.00	0.01	0.05
Chalcopyrite	1.05	1.09	0.12	0.12	0.00	0.03	0.04
Pyrite	0.10	0.08	0.08	0.04	0.00	0.02	0.04

Supplementary Table S6. V K-edge XANES data measured for minerals present in Mount Polly samples.

Sample	**Pre-edge Peak Energy (±0.3 eV)**	**Normalised pre-edge peak height (±0.10)**	**Main adsorption edge $E_{1/2}$ (±0.3 eV)**
Magnetite	5468.8	0.13	5478.3
Titanite	5469.4	0.16	5478.6
Iron oxide	5469.8	0.43	5479.7

References

(1) Byrne, P.; Hudson-Edwards, K. A.; Bird, G.; Macklin, M. G.; Brewer, P. A.; Williams, R D.; Jamieson, H. E. Water quality impacts and river system recovery following the 2014 Mount Polley mine tailings dam spill, British Columbia, Canada. *Appl. Geochem*. **2018** *91*, 64-74.

(2) Wright, M. T.; Stollenwerk, K. G.; Belitz, B. K. Assessing the solubility controls on vanadium in groundwater, northeastern San Joaqin Valley, CA. *Appl. Geochem*. **2014** *48*, 41-52.

(3) Huang, J. –H.; Huang, F.; Evans, L.; Glasauer, S. Vanadium: Global (bio)geochemistry. *Chem. Geol.* 417 **2015** *417*, 8-89.

(4) Parkhurst, D. L.; Appelo, C. A. J. Description of input and examples for PHREEQC version 3: a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. US Geological Survey Techniques and Methods, book 6, chap. A43, 497 p.; 2013.

(5) SNC-Lavalin Inc Mount Polley Mining Corporation post-event environmental impact assessment report, Appendix A: Hydrotechnical and geomorphological assessment, 621717; 2015.

(6) Byrne, P.; Runkel, R. L.; Walton-Day, K. Synoptic sampling and principal components analysis to identify sources of water and metals to an acid mine drainage stream. *Environ. Sci. Pollut. Res.* **2017** *24*, 17220-17240.

(7) Mayes, W. M.; Jarvis, A. P.; Burke, I. T.; Walton, M.; Feigl, V.; Klebercz, O.; Gruiz, K. Dispersal and attenuation of trace contaminants downstream of the Ajka bauxite residue (red mud) depository failure, Hungary. *Environ. Sci. Technol*. **2011** *45*, 5147-5155.