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

Supplementary Information

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Supporting Information

Supplementary Information: Methodology

Field data collection
As described in Byrne et al., 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 HNO₃. 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 NaVO₃ 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 NaVO₃ 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 HVO₄²⁻ (> pH c. 8.1-8.3) to H₂VO₄⁻ (<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)\text{3am} | Al(OH)\text{3am} | -4.53 to -2.74 | -4.33 to -1.87 | -2.96 to -1.16 |
| Ca\text{2V}_2\text{O}_7 | Ca\text{2V}_2\text{O}_7 | -8.95 to -6.20 | -18.01 to -5.59 | -17.57 to -2.72 |
| Ca\text{3(VO}_4\text{)}_2 | Ca\text{3(VO}_4\text{)}_2 | -18.55 to -12.55 | -26.89 to -13.00 | -26.62 to -11.30 |
| Ca-vanadate | Ca\text{9.5VO}_3 | -9.58 to -8.38 | -19.23 to -7.93 | -18.31 to -3.93 |
| Fe-vanadate | Fe\text{0.5VO}_3 | -9.80 to -4.70 | -13.09 to -4.93 | -12.07 to -1.13 |
| Mg-vanadate | Mg\text{8.5VO}_3 | -15.81 to -14.64 | -25.45 to -13.83 | -24.60 to -9.98 |
| Mg\text{3V}_2\text{O}_7 | Mg\text{3V}_2\text{O}_7 | -18.74 to -16.26 | -28.01 to -15.27 | -27.76 to -12.42 |
| Mn-vanadate | Mn\text{1.0VO}_3 | -13.22 to -11.41 | -21.27 to -8.65 | -20.47 to -5.18 |
| Na\text{3VO}_4 | Na\text{3VO}_4 | -31.84 to -28.92 | -35.72 to -27.76 | -35.99 to -28.63 |
| Na\text{3V}_2\text{O}_7 | Na\text{3V}_2\text{O}_7 | -36.00 to -33.34 | -44.60 to -30.81 | -44.74 to -30.30 |
| Na-vanadate | Na\text{VO}_3 | -7.59 to -6.96 | -12.13 to -6.22 | -11.93 to -4.85 |
| V(\text{OH})\text{3} | V(\text{OH})\text{3} | -16.38 to -11.66 | -13.80 to -10.60 | -13.88 to -10.16 |
| V\text{2O}_5 | V\text{2O}_5 | -17.70 to -13.80 | -24.91 to -14.38 | -23.74 to -9.83 |
| V\text{2O}_3 | V\text{2O}_3 | -34.08 to -21.31 | -27.35 to -20.01 | -27.43 to -16.99 |
| V\text{3O}_7 | V\text{3O}_7 | -42.62 to -26.83 | -34.36 to -25.39 | -34.31 to -20.86 |
| V\text{2O}_1\text{3} | V\text{2O}_1\text{3} | -39.06 to -22.58 | -44.27 to -22.66 | -41.82 to -11.99 |
| V\text{Cl}_2 | V\text{Cl}_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(\text{OH})\text{2} | VO(\text{OH})\text{2} | -8.38 to -5.33 | -7.44 to -5.05 | -7.45 to -3.47 |
| VO\text{2Cl} | VO\text{2Cl} | -28.16 to -22.95 | -28.16 to -22.57 | -27.54 to -18.94 |
| VO\text{SO}_4 | VO\text{SO}_4 | -29.94 to -22.19 | -26.82 to -23.37 | -25.17 to -18.04 |
| Calcite | Ca\text{CO}_3 | -0.14 to 1.40 | 0.58 to 1.54 | 0.27 to 0.75 |
| Diaspore | Al\text{OOH} | -0.59 to 1.18 | -0.39 to 2.07 | 0.99 to 3.95 |
| Gibbsite | Al(\text{OH})\text{3} | 6.48 to 8.12 | -1.80 to 0.67 | -0.41 to 2.56 |
**Supplementary Table S2.** Distribution of $\text{V}^{3+}$ and $\text{V}^{5+}$ 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 | $\text{V}^{3+}$ | $\text{V}^{5+}$ | Stream waters | $\text{V}^{3+}$ | $\text{V}^{5+}$ | Inflow waters | $\text{V}^{3+}$ | $\text{V}^{5+}$ | Pore waters |
|--------|------------------|------------------|---------------|------------------|------------------|---------------|------------------|------------------|-------------|
| HC1    | 0                | 100              | S1 0          | 100              | 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$_2$VO$_4^{-}$ 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$_2$VO$_4^{-}$ | HVO$_4^{2-}$ | H$_2$VO$_4^{-}$ | HVO$_4^{2-}$ | H$_2$VO$_4^{-}$ |
|--------|---------------|----------------|---------------|----------------|---------------|----------------|
|        | 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.

| Mineral                  | POL5   | POL6   | POL7   | POL9   | POL12  | POL13  | POL14  |
|--------------------------|--------|--------|--------|--------|--------|--------|--------|
|                          | 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   | 0.19   | 0.00   | 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   | 0.00   | 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 E½ (±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 Joaquin 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.