Evaluation and remediation of an abandoned mercury mine site in South-western, Alaska.

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Background
Alaska has a well-characterized mercury (Hg) mineralisation belt that was mined for mercury for most of the 20th century (Gray et al., 1998), of which the most productive mine was Red Devil in the Kuskokwim region of southwest Alaska (Figure 1), which operated from 1937 until 1971, after which it was abandoned. Over 1,224 tonnes of Hg were produced at the site during its operational life. Despite successive remediation efforts, the Red Devil mine site remains contaminated by waste tailings from mining and ore processing.

Arsenic minerals, especially pyrite (FeS2) and arsenopyrite (FeAsS), are commonly associated with epithermal and mesothermal ore deposits, to the extent that As is a useful pathfinder element for geochemical prospecting. Mining increases the availability of As through the exposure and oxidation of mine tailings, which can continue to enter water draining abandoned mine sites for decades after mine closure and are further compounded by drainage from the mine workings. Hg is present at Red Devil as the mineral cinnabar, which is found in quartz veins within a Cretaceous greywacke sequence, in association with stibnite (Sb2S3). Hg was extracted from cinnabar at the mine site using a simple retort/furnace to reach the ore and condense Hg vapour sublimated from the ore; at least three generations of retorts operated at Red Devil. Other metals were not recovered from the ore, so waste calcines from the furnace have elevated levels of Hg, As and Sb, with the potential to pollute local water systems.

Sampling
Inorganic arsenic species were separated in the field using anion-exchange chromatography prepared using 10 mL 0.8 x 4 cm PolyPrep® columns purchased from Bio-Rad Laboratories (Hercules, USA), and filled with AG 1-X8 resin (50 - 100 mesh, chloride form). AG 1-X8 is a strong cation exchange resin, composed of sulphonic acid functional groups attached to a styrene divinylbenzene co-polymer lattice. The resin was converted in bulk to the acetate form by washing 50 g with 150 mL of 1M NaOH solution (J. T. Baker), rinsing with Nanopure water and repeating two times until the pH of the rinse was neutral. This was followed by washing with approximately 150 mL of 1M acetic acid (BDH Aristar Ultra) and rinsing with Nanopure water until neutral.

In the field, a 50 mL aliquot was filtered (0.45 μm), acidified with concentrated nitric acid and slowly passed through a fresh column and collected. Arsenic (As) species are absorbed by the column matrix, while neutral As(V) species pass through, allowing the identification of both species present in the sample to be determined by comparison with total dissolved metal analysis. This approach avoids the considerable difficulties of preserving arsenic species and allows routine analysis methods to be used to determine the total As in each fraction.

Results
Red Devil creek shows no visible signs of pollution, with the exception of a same ‘yellow boy’ mineralisation associated with a spring on the north bank. Total As in Red Devil creek increased from 1 μg L-1 at the source of the creek to 102 μg L-1 at the yellow boy spring then dropped sharply to around 60 μg L-1 at its confluence with the Kuskokwim River. Total As in excess of 2 μg L-1 was measured from a spring in the vicinity of the mercury retort.

As speciation is shown in Figure 3. Arsenic (As(V)) is the dominant inorganic species, with arsenite (As(III)) accounting for less than 25% of the total. The total exception to this pattern is downstream of the spring, where As(III) increases to over 50% of the total. The concentration of As, Sb and Hg along the length of the creek is shown in Figure 3B. There is a steady increase in total Sb along the length of the Red Devil creek, with a maximum Sb concentration of 129 μg L-1 at the creek mouth.

Remediation
Remediation options are complicated by the remoteness of the site and absence of any road access, which escalates the costs of removing material from the site. Engineered barriers, to limit to extent of the tailings, coupled with permeable reactive barriers to remove As and Sb may be a viable option for this site.

Arsenic Speciation
In addition to ICP-MS and IC to determine major and trace elements present in Red Devil creek, atomic fluorescence spectrometry (AFS) was used to determine total As and As(III) in field-separated aliquots using a Millennium Excalibur spectrometer (Instrument Systems Ltd., Ovington, Kent, UK). AFS is an EPA approved analytical method that is particularly sensitive for the determination of As, Hg, Se, Bi, Sb, Pb and Cd (Cal, 2000). AFS is based on the absorption of a vapour phase (pyrolysis) and the detection of specific wavelengths and the detection of specific wavelengths (fluorescence) at wavelengths that are characteristic of the elements under investigation. Detection limits of 0.010 μg L-1 can be readily achieved for total inorganic As.

Inorganic As speciation is a useful indicator of arsenic mobility and toxicity. To determine the species present at the site, water samples were collected from Red Devil creek, which insets the site and is currently ending the mine tailing piles. Inorganic arsenic species were separated in the field using anion-exchange chromatography prepared using 10 mL 0.8 x 4 cm PolyPrep® columns purchased from Bio-Rad Laboratories (Hercules, USA), and filled with AG 1-X8 resin (50 - 100 mesh, chloride form). AG 1-X8 is a strong cation exchange resin, composed of sulphonic acid functional groups attached to a styrene divinylbenzene co-polymer lattice. The resin was converted in bulk to the acetate form by washing 50 g with 150 mL of 1M NaOH solution (J. T. Baker), rinsing with Nanopure water and repeating two times until the pH of the rinse was neutral. This was followed by washing with approximately 150 mL of 1M acetic acid (BDH Aristar Ultra) and rinsing with Nanopure water until neutral.

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Conclusions
The pattern of arsenic speciation at the Red Devil site can be interpreted as resulting from interaction of two distinct groundwater plumes with Red Devil creek, as shown in Figure 3. Likely contaminant pathways include:

1. Groundwater seeping into the creek from mine workings on the north side of the creek that are characterised by a As(III) / As(V) ratio of 1 : 1, reflecting low oxygen and low pH conditions, and approximately six times more As than Sb.
2. A contaminated plume of groundwater originating from the retort area moving down gradient towards the Kuskokwim River that is characterised by dominant As(III) speciation and a ratio of As : Sb of 1 : 3. Red calcines from the furnace visibly oxidised and enriched in Sb.
3. Erosion of remnant cinnabar from the tailings piles by Red Devil creek. Although largely insoluble, inorganic Hg can be bio-mobilised by bacteria in the Kuskokwim River and bio-accumulate as methyl mercury in some fish species to toxic levels.

References