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ScienceDirect

Procedia Earth and Planetary Science 17 (2017) 610 – 613

Procedia
Earth and Planetary Science

15th Water-Rock Interaction International Symposium, WRI-15

Mobilization of mercury and arsenic from a carbonate-hosted ore deposit, central Idaho, U.S.A.

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Abstract

The Cinnabar and Fern mine sites in central Idaho are primary source areas for elevated mercury and arsenic entering the South Fork of the Salmon River, which provides critical spawning habitat for bull trout and Chinook salmon. Mercury mineralization is hosted by carbonate rocks, which generate waters dominated by Ca^{2+} and HCO_3^- at pH 7 to 9. A synoptic sampling was conducted on headwater tributaries to determine geologic background concentrations and quantify trace metal concentrations in stream water associated with historical mining. Geologic background concentrations in unfiltered Cinnabar Creek water were 8 - 14 ng Hg L^{-1} and 4.8 - 9.5 µg As L^{-1}. Immediately downstream from the mine site, concentrations increased to 257 ng Hg L^{-1} and 20.6 µg As L^{-1}. Groundwater inflow diluted these concentrations by approximately half before the confluence of Cinnabar Creek with Sugar Creek. As expected, mercury and arsenic concentrations increased downstream in Sugar Creek below the confluence with Cinnabar Creek. However, the final downstream reach on Sugar Creek showed an increase in unfiltered mercury, methylmercury, and iron concentrations relative to the upstream reach. This increase is associated with historical mining activity in a mineralized area of carbonate rock that intersects the reach.

Peer-review under responsibility of the organizing committee of WRI-15
Keywords: South Fork Salmon River, arsenic, mercury, mining impacts

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Peer-review under responsibility of the organizing committee of WRI-15
doi:10.1016/j.proeps.2016.12.163

1. Introduction

Historical mining initiated in the early 20th century has resulted in multiple poorly characterized sources for trace metals to the South Fork Salmon River (SFSR) in central Idaho (Fig. 1a,b). The East Fork South Fork Salmon River (EFSFSR), with a watershed area of 528 km^2, has had gold, silver, antimony, mercury, and tungsten mining activity in several districts including Stibnite and Cinnabar[1-3] (Fig. 1c).

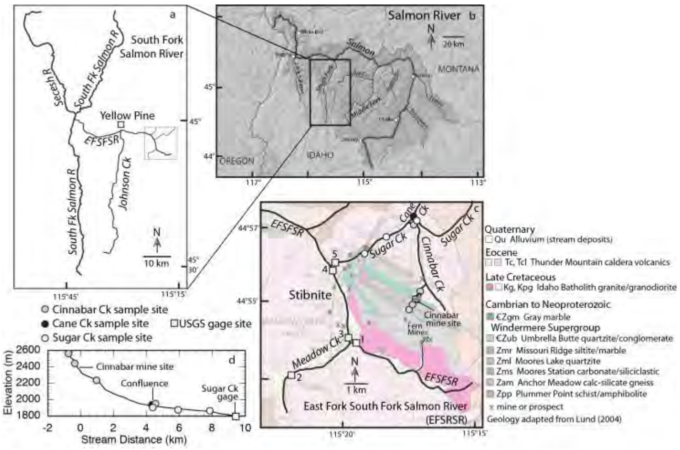

Fig. 1. (a) The South Fork Salmon River watershed; (b) Salmon River watershed in central Idaho; (c) East Fork South Fork Salmon River indicating a Cretaceous marble unit[4] that hosts the mercury ore deposit at the Cinnabar mine site; synoptic sample locations are indicated on Cinnabar, Cane, and Sugar Creeks as circles. USGS gage sites are shown as squares; (d) Stream elevation profile for Sugar/Cinnabar Creek showing sample locations as function of stream distance from Cinnabar mine site.

Mineralization at Cinnabar and Fern mine sites is in a silicified marble unit of a folded and fault-bounded sequence with metamorphosed sedimentary rocks in the Neoproterozoic Windermere Supergroup[4]. The EFSFSR provides critical habitat for spawning Chinook salmon, steelhead trout and bull trout, which are threatened, endangered, or sensitive species. The EFSRSR was proposed for inclusion on the U.S. Environmental Protection Agency (USEPA) National Priority List (NPL) in 2001 because of the trace metal contamination of sediments and water from the Stibnite mining area.

1.1. Mercury and arsenic source areas in upper East Fork South Fork Salmon River watershed

Load estimates calculated from monitoring data of 2012 to 2014 on the EFSFSR found 98 percent (20 kg Hg yr^{-1}) of the mean mercury load to the EFSFSR was from Sugar Creek[5], which includes the tributaries Cane Creek and Cinnabar Creek (gage site 5, Fig. 1c). The remaining mercury load was from the EFSFSR reach between Sugar Creek and Meadow Creek[5]. The EFSFSR reach above Sugar Creek (gage site 4, Fig. 1c), with an estimated mean load of 1600 kg As yr^{-1}, is below a pit lake. This reach contributed 52 percent of the mean arsenic load, while Sugar Creek with an estimated load of 271 kg As yr^{-1} contributed 14 percent of the mean load to the EFSFSR[5].

Table 1. Water and sediment arsenic and mercury, East Fork South Fork Salmon River gage sites, June 2016.

		Filtered (<0.45μm)					Unfiltered		Sediment	
USGS gaging station	pH	DOC mg L^{-1}	As(T) μg L^{-1}	As(III) μg L^{-1}	Hg ng L^{-1}	MeHg ng L^{-1}	THg ng L^{-1}	TMeHg ng L^{-1}	As μg g^{-1}	Hg μg g^{-1}
EFSFSR above Meadow Ck (1)	6.78	1.3	9.0	0.6	6.37	<0.04	8.18	0.06	5.20	1.14
Meadow Ck (2)	7.51	1.6	1.1	<0.5	5.26	<0.04	7.27	0.04	8.48	0.04
EFSFSR below Meadow Ck (3)	6.95	1.7	23.6	2.8	3.44	0.06	5.33	0.07	42.8	2.42
EFSFSR above Sugar Ck (4)	7.85	1.5	64.1	13.2	3.00	0.05	4.24	0.06	7176	1.31
Sugar Ck (5)	7.49	1.1	10.0	<0.5	9.38	0.38	29.1	0.08	51.8	26.4

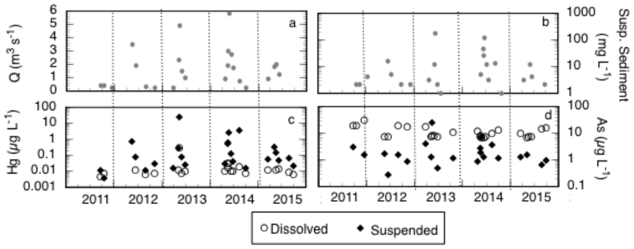

Fig. 2. Water quality monitoring data from USGS Gage 13311450, Sugar Creek near Stibnite, Idaho, showing (a) stream discharge; (b) suspended sediments; (c) concentration for filtered mercury, shown as an open symbol, and suspended mercury, shown as a closed symbol; and (d) concentration for filtered arsenic, shown as an open symbol, and suspended arsenic, shown as a closed symbol.

2. Synoptic sampling: Stibnite area stream gages

Water collected under low-flow conditions from gaged streams in June 2015 (Table 1) had circumneutral pH and very low dissolved organic carbon (DOC) concentrations (>2 mg C L^{-1}). Streambed sediment arsenic was within geologic background concentrations (>10 μg kg^{-1}) for Meadow Creek (1) and the upper EFSFSR reach (2), but was elevated in the other three reaches, notably in the EFSFSR reach above Sugar Creek (4), with over 7000 μg As g^{-1}. The reduced species As(III) is 10 to 20 percent of the total dissolved arsenic (24 – 64 μg As L^{-1}) in the EFSFSR below Meadow Creek and above Sugar Creek, suggesting the input of reduced groundwater along these stream reaches.

Streambed sediment mercury concentrations were elevated in all reaches except for Meadow Creek. The source area for mercury concentrations in Sugar Creek sediment (26.4 μg Hg g^{-1}) and unfiltered stream water (29.1 ng L^{-1}) is the Cinnabar mine site at the headwaters of Cinnabar Creek. The Fern mercury mine in the upper EFSFSR watershed is a likely source for somewhat elevated mercury concentrations in sediment (1.14 μg Hg g^{-1}) and streamwater (8.18 ng Hg L^{-1}) at the EFSFSR gage above Meadow Creek. Groundwater input is also a potential source of elevated streamwater mercury, including at Meadow Creek (7.27 ng Hg L^{-1}). The low DOC concentrations may limit the formation of methylmercury, which was 1.6 to 2.0 percent of the total mercury in stream water for Sugar Creek, and the EFSFSR below Meadow Creek and above Sugar Creek.

3. Arsenic and mercury source areas for Sugar Creek

3.1. Seasonal fluxes

Water quality data accessed from http://nwis.waterdata.usgs.gov for Sugar Creek (USGS 13314500) are shown in Fig. 2. Suspended mercury and arsenic were calculated as the difference between dissolved (<0.45μm) and unfiltered concentrations (Fig. 2b,c). Dissolved mercury concentrations are <0.004 to 0.3 μg Hg L^{-1} with peak concentrations coinciding with peak discharge. Suspended sediment mercury concentrations also crest at peak discharge, with 0.004 to 26 μg Hg L^{-1}. There is a secondary peak concentration from August 2014 of 4.1 μg Hg L^{-1} that corresponds to a major storm event on August 13 and 14, which also generated a pulse of sediment. Peak dissolved arsenic concentrations (7 to 31 μg Hg L^{-1}) were at baseflow (Fig. 2d), reflecting a primary groundwater input to the stream. Suspended arsenic concentrations (0.3 to 27 μg As L^{-1}) increased with discharge, indicating that arsenic sorbed to particulate organic matter and clay particles can be as much as half of the Sugar Creek arsenic load during snowmelt.

3.2. Synoptic sampling

The Cinnabar Creek watershed is in moderately steep terrain, with a peak elevation of 2714 m. In July 2015, Sugar Creek and its tributaries Cane and Cinnabar Creeks, were sampled at near-baseflow conditions for total and dissolved trace metals including mercury, methylmercury and iron (Fig. 1c,d). Four reaches were sampled for

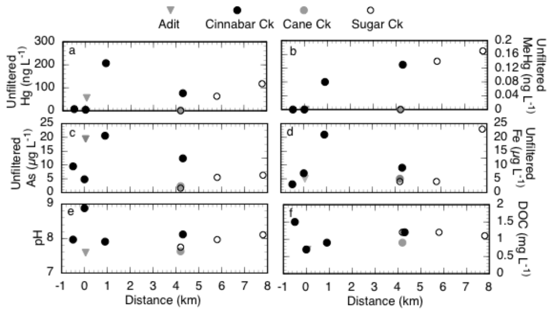

Fig. 3. Synoptic sampling results from Cinnabar and Sugar Creeks; unfiltered concentrations of (a) mercury, (b) methylmercury (c) arsenic; and (d) iron; (e) field pH; (f) dissolved organic carbon. The x-axis for all panels is the stream distance relative to the top of the Cinnabar mine site. Upper reaches are at a 0 or negative distance. The confluences between Cane, Sugar and Cinnabar are at ~4.3 km from the top of the mine site.

Cinnabar Creek: a low-order tributary at 2600 m elevation; the west fork of just above mining activity; Cinnabar Creek at the base of tailings; and above the confluence with Sugar Creek. The first two sampling sites were selected as background sites to better constrain contributions of trace metals from mining. Cane and Sugar Creeks were sampled above Cinnabar Creek to determine background concentrations of mercury and arsenic in from a different geologic setting within the same watershed. Sugar Creek was sampled below Cinnabar Creek at 5.8 and 7.8 km. Background samples from Cinnabar Creek had 7 and 3 ng Hg L^{-1} and <0.04 ng MeHg L^{-1} (Fig 3a,b). The mine adit sample had 86 ng Hg L^{-1} with <0.04 ng MeHg L^{-1}. Total mercury and methylmercury increased (257 ng Hg L^{-1} and 0.08 ng MeHg L^{-1}) at the Cinnabar reach. Mercury decreased over the next 3.2 km to 112 ng Hg L^{-1} while methylmercury increased to 0.13 ng MeHg L^{-1} above the confluence with Sugar Creek. Both Cane Creek above the confluence with Sugar Creek and Sugar Creek above the confluence with Cinnabar Creek resulted in mercury concentrations of 4.6 and 3.6 ng Hg L^{-1}, respectively, with methylmercury below detection limits for both samples. The mercury species concentrations in the Sugar Creek reach increase downstream from the confluence with Cinnabar Creek. Arsenic and iron (Fig 3c,d) had similar concentrations in unfiltered water, with background concentrations in Cinnabar Creek <10 μg L^{-1}. The Cinnabar reach below the mine site increased to 19 μg As L^{-1} and 21μg Fe L^{-1}, with 12 μg As L^{-1} and 9 μg Fe L^{-1} above the confluence with Sugar Creek. Background concentrations for arsenic and iron in Cane and Sugar Creeks were <5 μg L^{-1}, with total arsenic increasing to 6.3 μg As L^{-1} below the confluence with Cinnabar Creek. Unfiltered iron increased from 4 μg Fe L^{-1} to 23 μg Fe L^{-1} in the 7.8 km reach. The increase in mercury species and iron in the 7.8 km reach of Sugar Creek may be due to a shift in bedrock geology and input from small prospects upstream. While the primary source area for mercury in Sugar Creek is the Cinnabar mine site, there are additional groundwater inputs from geologic sources along gaining reaches.

Our synoptic data indicate a low geologic background concentration for mercury and arsenic, with mining activity increasing trace metal concentrations, particularly in suspended sediment. Monitoring data demonstrated that the greatest concentrations of trace metals in suspended sediment occur during spring snowmelt.

Acknowledgements

The authors wish to thank Danny Rutherford, Cyrus Berry, John DeWild, Sara Breitmeyer, and Kenna Butler for their analytical support. This work was funded through the U.S. Geological Survey Mineral Resources Program.

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