

Seasonal mineralogical transformations influence heavy metals release from mine-impacted Coeur d'Alene River (ID) wetlands

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The Coeur d'Alene (CDA) mining district in the Idaho panhandle is a major region of historical and contemporary mining of Ag, Au, Cd, Cu, Pb and Zn. Over the last century, 70 million tons of mine tailings were discharged directly into the CDA River [1]. These discarded tailings proceeded downstream into a series of wetlands and lateral lakes along the CDA River floodplain, and consequently the sediments in the river and lateral areas contain elevated trace metal concentrations. Here, we examine the geochemical processes that control the distribution and release of arsenic, lead and cadmium within the CDA River and associated wetlands.

Chemical extractions, diffraction and X-ray absorption spectroscopy, were used to characterize sediment mineralogy and the mechanism of trace element retention. Heavy metals are often associated with iron (hydr)oxides, as expected due to the strong retention of these metals on iron (hydr)oxides. However, adsorption on such phases alone is not able to describe trace element concentrations; trace metal retention is dynamic and responds to changing environmental conditions [2, 3]. These fluctuations in trace metal retention involve redox processes and are likely driven by microbiological processes. Arsenic speciation fluctuates between As(III) vs. As(V), and also may be associated with sulfide minerals when sediments and soils are flooded. These seasonal fluctuations in trace element speciation may significantly alter pore water concentrations, and must be considered when evaluating the fate of these contaminants. Furthermore, the transitory and mixed phase associations of arsenic and other elements leads to conditions in which either oxidation and reduction may release trace elements into solution.

References

- [1] Funk, W., et al., 1975. An integrated study on the impact of metallic trace element pollution in the Coeur d'Alene-Spokane Rivers and Lake drainage system. Office of Water Research and Technology Project Completion Report, Title II, WSU-UI: Pullman, WA. p. 332.
[2] La Force, M.J. et al. ES&T, 2000. 34: 3937-3943.
[3] Bostick, B.C., et al. ES&T, 2001. 35, 3823-3829.

The mineralogical facies developed within an Apatite II PRB for Pb, Cd and Zn acid mine drainage

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Apatite II™, in a subsurface permeable reactive barrier, treated acid mine drainage containing elevated levels of Zn, Pb, Cd, SO₄ and NO₃. The special properties of Apatite II™ make it ideal for this application allowing it to immobilize 20% of its weight in metals. The PRB, operating since January 2001, is reducing Cd and Pb to below detection, Zn to near background (100 ppb), and SO₄ and NO₃ to below detection. Geochemical facies, evidenced by sphalerite, pyromorphite and chlorapatite, combined with variable redox conditions, dissolved oxygen, and biological activity, have developed, as predicted by MINTEQA2 and confirmed by solids analyses. The PRB, filled with 100 tons of Apatite II™, has removed 10,000 lbs of Zn, Pb, and Cd, and should last for at least twelve more years.

Dissolved Metal Concentrations Entering and Exiting PRB

Date	Entering Barrier (ug/L;ppb)				Exiting Barrier (ug/L;ppb)			
	pH	Cd	Pb	Zn	pH	Cd	Pb	Zn
03/23/01	4.5	333	1,230	44,700	6.0	<2	<5	27
10/27/01	5.0	437	1,110	71,300	6.5	<2	<5	74
01/10/02	5.0	779	1,210	116,000	6.5	<2	<5	66
10/19/02	4.5	414	1,030	68,350	6.5	<2	<5	69
03/14/03	4.5	650	1,190	48,700	6.6	<1	<1	55
10/03/03	4.6	587	1,330	86,800	7.0	<2	<5	<5
03/30/04	5.2	404	497	64,500	6.9	<2	<5	95
06/09/04	4.9	436	658	68,000	6.9	<2	<5	34



Apatite II™ collected from the PRB after 3 years showing sphalerite on surface