Toxicity of Metal-Mine Drainage Before and After Biochemical Reactor Treatment: National Tunnel in the Clear Creek Watershed, Colorado, USA

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Abstract

Many miles of streams in the US (and worldwide) are contaminated by metals originating from both active and abandoned mine-sites. Streams affected by mine drainage are often toxic to aquatic life. Thus, it is desirable to remediate these sites through treatment of the source(s). Passive-treatment biochemical reactor (BCR) systems have been shown to be effective at removing metals contamination from these systems. An issue that is of recent interest is whether the toxicity of these waters is reduced and/or eliminated by the BCR treatment. BCRs generally facilitate sequestration of metals as sulfides within the reactor, but sorption of metals onto mineral or organic surfaces may occur also. In most cases, the concentration of metals in BCR effluent is greatly reduced compared to the influent. This study evaluated the reduction in acute toxicity to *Ceriodaphnia dubia* and *Pimephales promelas* through BCR treatment of drainage from the National Tunnel, a primary point source of metals to the North Fork of Clear Creek, Colorado. The BCRs being evaluated for efficiency of metals removal at the site contain four different substrates: ethanol, hay/wood, corn stover/wood, and chitin [crab shells] and are being operated in duplicate. BCR effluent was less toxic than the influent, except from the BCR containing chitin, which also was the only effluent to have substantial concentrations of un-ionized ammonia (0.25 mg/l and 0.41 mg/l for the replicates). Toxicological response varied between the substrate types, with the BCRs having ethanol and one of the replicates having cornstover/wood providing the least toxic effluent. There also was a substantial difference in effluent toxicity observed between the replicates having the hay/wood and the cornstover/wood substrates. A correlation analysis suggests toxicity may be related to NH_3, S (presumably as sulfide), Al, Cd, Ni, alkalinity, and/or conductivity. Because this study indicated toxicity from the BCR effluents, studies are underway to evaluate further these types of effluents at several other abandoned mine-sites having different substrate types, as well as testing to evaluate which of the water chemistry parameters is causing any observed toxicity.

Introduction

Passive treatment systems are useful for removing metals from mine-drainage and have the attributes of being self-sustaining, require only minimal monitoring, and capitalize on natural processes.

Anaerobic biochemical reactors (BCRs) are designed to enhance microbial production of sulfide for subsequent precipitation of metals in the drainage as metal sulfides. Metals may also be removed from the dissolved phase through adsorption onto minerals and/or organic material present.

The desired and expected outcome of BCR treatment is to reduce the toxicity of the mine-drainage prior to its discharge into an adjacent stream.

Questions Asked:

Are the effluents from the different pilot BCRs toxic?

Is the toxicity reduced, relative to the influent?

If effluents are toxic, is a toxicant identifiable?

Experimental

- Water samples from National Tunnel Adit (NT influent) and BCR effluents collected August 2007
  - BCR organic substrate sources
    - Ethanol (E) *(operation began June 2006)*
    - Hay/Wood mix (HW) *(operation began June 2006)*
    - Corn Stover/Wood mix (CSW) *(operation began June 2006)*
    - Chitin (C) *(operation began May 2007)*
- 48-hour WET (whole effluent toxicity) tests
  - Organisms
    - *Ceriodaphnia dubia*
    - *Pimephales promelas*
  - Moderately hard reconstituted water as diluent and for controls
  - LC_{50} endpoint
  - Chemistry parameters: dissolved oxygen (DO), ammonia, pH, alkalinity, and conductivity
- Dissolved metals (filtered at 0.45-µm) analyzed via ICP-AES

55-Gallon Drum Reactors

Results/Discussion

Chemical Parameters

Sample ID	pH	Alkalinity (ppm as $CaCO_3$)	Conductivity (uS/cm)	Total ammonia (ppm)	DO (ppm O_2)
E Rep1	6.88	1000	2770	0.53	10
E Rep 2	7.58	800	2441	0.11	8.8
HW Rep 1	6.69	750	1441	0.04	9.6
HW Rep 2	6.58	840	1370	0.03	4.3
CSW Rep 1	6.76	650	1330	0.12	4.2
CSW Rep 2	6.82	1000	1610	1.93	9.9
C Rep 1	6.79	2000	5730	74	5.2
C Rep 2	6.78	1750	6520	120	3.6
NT influent	4.33	not measured (pH < 4.7)	1560	0.03	11.8

Correlation Coefficients (r)

	C. dubia NOAEL	*P. promelas NOAEL*
Al	-0.05	**-0.47**
B	-0.09	0.02
Ba	0.29	**0.88**
Ca	-0.17	0.10
Cd	0.02	-0.36
Fe	0.01	**0.45**
K	-0.21	0.10
Mg	-0.32	-0.24
Mn	0.16	0.32
Na	-0.32	-0.24
Ni	**-0.43**	**-0.52**
P	-0.27	-0.38
S	**-0.45**	**-0.48**
Zn	-0.38	-0.28
Sr	-0.33	-0.32
pH	0.34	0.40
Alkalinity	-0.37	-0.34
Conductivity	**-0.43**	-0.30
Ammonia	**-0.49**	**-0.49**
DO	**0.75**	**0.81**
Ionic Strength (M)	-0.23	0.01

Results/Discussion (Continued)

Metal Concentrations

	Al (ug/l)	Ba (mg/l)	Cd (ug/l)	Cu (ug/l)	Fe (mg/l)	Mn (mg/l)	Ni (ug/l)	S (mg/l)	Zn (ug/l)	Ionic Strength (mM)
E Rep 1	0.5	3.40	4.40	nd	3.82	18.68	nd	6.05	9.30	49
E Rep 2	0.5	1.82	2.50	nd	0.01	9.15	nd	93.49	7.20	40
HW Rep 1	53.0	0.06	7.00	nd	5.03	12.66	8.70	7.12	8.40	19
HW Rep 2	61.0	0.07	5.50	nd	0.01	13.96	8.20	30.80	3.40	17
CSW Rep 1	72.0	0.07	6.40	nd	0.06	15.85	9.20	29.63	4.70	17
CSW Rep 2	75.0	0.09	6.80	nd	0.11	15.23	6.30	15.60	4.50	17
C Rep 1	98.0	0.05	4.70	5.60	0.68	19.10	8.30	117.55	50.50	21
C Rep 2	0.5	0.25	6.00	nd	0.06	5.47	21.70	121.96	12.50	99
NT influent	130.0	nd	12.80	97.50	44.78	21.69	272.40	303.50	8509.00	34

nd = none detected

Toxicity Results

Sample ID	*Ceriodaphnia dubia*			*Pimephales promelas*		
	LC_{50} (%)	Limits (%)	NOAEL (%)	LC_{50} (%)	Limits (%)	NOAEL (%)
E Rep1	70.7	n/a	50	>100	n/a	100
E Rep 2	>100	n/a	50	68.9	39.5-120	50
HW Rep 1	35.8	32.8-39.1	25	35.4	39-43	25
HW Rep 2	9.5	8.6-10.4	6.25	7.7	6.7-8.8	5
CSW Rep 1	32.2	28.9-35.8	25	17.7	15-21	12.5
CSW Rep 2	>100	n/a	100	83.5	69-101	50
C Rep 1	11.4	9.6-13.5	6.25	6.2	5.4-7.0	5
C Rep 2	8.8	n/a	6.25	3.4	2.6-4.3	1.25
NT influent	8.7	6.8-11.1	2.5	20	n/a	10

% refers to the percentage of sample water

Answers to Questions Asked:

Are the effluents from the different pilot BCRs toxic?
Yes and No. The Ethanol Rep 2 and Corn Stover/Wood Mix Rep 2 samples, were not toxic, but others showed some degree of toxicity.

Is the toxicity reduced, relative to the influent?
Yes and No. Not in the Chitin BCRs or in Rep 2 for the Hay/Wood substrate.

If effluents are toxic, is a toxicant identifiable?
Ammonia and sulfur (not speciated) were highest in the Chitin BCRs. It is possible that sulfide and/or ammonia are the toxic agent (s).

- Initial DO concentrations were strongly positively correlated (higher NOAEL with higher DO), but cannot be considered as the toxicant in the WET tests (DO is increased due to dilution water and method requirements); however, this could be an issue in the field.
- Other potential toxicants include conductivity, dissolved Al, and dissolved Ni, based on moderate negative correlations (lower NOAEL with higher concentration).
- Interestingly, correlation suggests a protective effect from Ba and Fe, with higher NOAELs being associated with higher concentrations.

Current Research

- Ecotoxicological testing of larger field pilot reactors (subsurface) at 4 sites
- Measurements of sulfide, ammonia, DO, total organic carbon, and metals
- Toxicity Investigation Evaluation (TIE) assessments for BCR effluent samples that show toxicity

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