TOXICITY IDENTIFICATION EVALUATION OF A LAKE SEDIMENT HISTORICALLY CONTAMINATED BY ARSENIC.

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ABSTRACT

Texas Commission on Environmental Quality (TCEQ) selected Bryan Municipal and Finfeather Lakes on the 1999 CWA 303(d) list for accelerated monitoring to support development of total maximum daily loads (TMDL). Because of historical arsenic contamination, we evaluated ambient sediment toxicity in these systems and performed toxicity identification evaluations (TIE) during an 18-month study period. Finfeather Lake in Brazos Co., is currently being evaluated for EPA's Superfund program. *Hyalella azteca* and *Chironomus tentans* were exposed to whole sediment both in an effort to ascertain ambient toxicity and to evaluate treatment with an arsenic specific adsorbent and a divalent metal specific cation exchange resins. Additionally, *Ceriodaphnia dubia* were exposed to porewater following traditional TIE and resin treatments. *C. tentans* survival and *H. azteca* survival or growth were consistently reduced in Finfeather sediments. *C. dubia* survival or reproduction was also significantly reduced in porewaters. Treatment of whole sediments with an arsenic specific resin resulted in improved *H. azteca* growth, however, improvements were not statistically significant. Porewater treated with EDTA or resins resulted in improved *C. dubia* reproduction. Results, coupled with a toxic units approach indicate copper, lead and zinc, not arsenic, to be metals of concern in porewater. Phase III TIE procedures subsequently confirmed only copper and zinc as problematic. Sediment and porewater TIE methodologies require further development in order to better substantiate sediment TMDLs. However, lack of quality criteria for porewater may complicate strategies addressing sediment TMDLs. Moreover, sediment TMDL development may be further complicated by the presence of legacy contaminants.

INTRODUCTION

- Finfeather Lake is a small municipal waterbody located in Bryan, TX, downstream of Bryan Municipal Lake.
- Finfeather Lake was placed on the CWA 303(d) list because of historical arsenic (surface and groundwater) contamination. It is now being considered under the EPA's Superfund program.
- Standards methods for sediment or porewater TIEs are lacking, however, draft guidance documents are available [1].
- Cation exchange and adsorbent resins have been used with some success in sediment TIE approaches [2-3].

Objectives

1) To assess the presence and cause(s) of whole sediment and porewater toxicity in Finfeather Lake
2) Develop approaches to sediment and porewater toxicity identification evaluations.
3) Confirm (Phase III TIE) cause(s) of toxicity in Finfeather Lake porewater.

MATERIALS and METHODS

Whole Sediment Toxicity Tests

- Whole sediment toxicity tests were performed with *Hyalella azteca* and *Chironomus tentans* following procedures recommended by the US EPA [4]. Three sites within Finfeather Lake were tested.
  - Survival and dry weight (60°C for 24 h) were determined for both organisms.
- Whole sediments were also amended with adsorbent and cation exchange resins (20% of the total volume).
- Control sediments were obtained from the University of North Texas Water Research Field Station ponds.

Porewater Toxicity Tests

- Porewater toxicity was assessed using the 7-day short-term chronic test with *Ceriodaphnia dubia* [5].
  - Porewater was obtained *via* centrifugation of whole sediment (7,500 rpm for 30 min at 4°C).
  - Three sites were assessed, however, only the one most consistently toxic was used in the majority of TIE procedures.
- Reconstituted hard or moderately hard water [6] served as control water for porewater tests.
- Traditional TIE procedures for chronic toxicity followed those recommended by the US EPA [7].
- Porewater samples were also treated with adsorbent or cation exchange resins. Resins were added to porewater as 20% (volume:volume ratio) and mixed (orbital shaker) for 20 to 24 h at 4°C.
- Phase III TIE procedures involved spiking SIR-300 resin-treated porewater with copper, lead or zinc based on measured concentrations of untreated porewater samples. SIR-300 was added as 50% of the total water volume.

Resins

- SIR-300 (Resin Tech Inc., Cherry Hill, NJ) is a cation exchange resin. SIR-300 chelates divalent metals.
- SIR-900 (Resin Tech Inc.) is a synthetic aluminum oxide adsorbent media specific for arsenic and lead.
- Ambersorb 563 (Supelco, Bellefonte, PA) is a carbonaceous adsorbent media designed for organics removal.

Toxic Units Calculation

- Chronic toxic units (TUc) were calculated by dividing measured metal concentrations in porewater by water quality criteria for protection of aquatic life against chronic effects.

Table 1. Finfeather Lake effective chronic TIE treatments.

Test Date	Test Type/Station	Organism	Effective Treatment(s)
07-2001	Porewater/11798	*C. dubia*	None[1]
08-2001	Porewater/11798	*C. dubia*	SIR-300, SIR-900
02-2002	Porewater/11798	*C. dubia*	SIR-300, SIR-900[2]
03-2002	Sediment/11798	*H. azteca*	SIR-900*
06-2002	Porewater/11798	*C. dubia*	EDTA, SIR-300[3]
06-2002	Porewater/11800	*C. dubia*	EDTA

[1]Only traditional TIE treatments assessed.
[2]EDTA not tested.
[3]SIR-900 not tested.
*Improved *H. azteca* growth but not statistically significant.

Table 2. Water Quality Criteria Used to Calculate Finfeather Lake, Station 11798, Porewater Chronic Toxic Units.

	Hardness (mg/L as $CaCO_3$)				
Metal	60 mg/L[1]	80 mg/L[2]	120 mg/L[3]	128 mg/L[4]	Source
Aluminum	NL	NL	NL	NL	-----
Arsenic	190	190	190	190	1
Barium	1000	1000	1000	1000	2
Cadmium	0.7	0.9	1.2	1.25	1
Chromium	100	100	100	100	2
Copper	7.9	10.6	14.3	15.17	1
Iron	1000	1000	1000	1000	2
Lead	1.3	2.02	3.2	3.45	1
Mercury	1.3	1.3	1.3	1.3	2
Nickel	102	136	183	194	1
Selenium	5.0	5.0	5.0	5.0	2
Silver	1.7	3.01	5.5	6.20	2
Zinc	67.8	90.1	122	129	1

[1]Reconstituted moderately hard water after treatment with SIR 300 and calcium and magnesium reintroduced.
[2]Reconstituted moderately hardwater.
[3]Porewater following treatment with SIR-300 and Ca and Mg reintroduced.
[4]Porewater.
Source 1 = TCEQ; Source 2 = EPA

Table 3: Summary of metal concentrations (µg/L) during Phase III TIE procedures.

	Untreated Porewater[1]		Measured after SIR-300 treatment		Measured Post-spiking	
Metal	Prelim.	Phase III	Total	Dissolved	Total	Dissolved
Cu	280	256	220	59	411	172
Pb	23.3	26.4	9.09	ND	31.6	5.03
Zn	296	317	149	19.7	350	42.7

[1] Total

Table 4: Results on *C. dubia* survival and reproduction following Phase III TIE of Finfeather porewater.

Treatment	% Survival	Mean # Neonates	1 SD
RMHW	100	27.4	2.07
RMHW+SIR	100	21.0	3.0
Pw	80	2.0	0.82
Pw+SIR	100	16.0	2.12
Pw+EDTA (3mg/L)	100	15.2	1.92
Pw+EDTA (8mg/L)	100	16.0	3.39
Treated Pw+Cu	100	4.2	1.3
Treated Pw+Pb	100	14.0	2.35
Treated Pw+Zn	0	0	—

RMHW=reconstituted moderately hard water.
SIR=SIR-300 cation exchange resin
Pw=untreated porewater.

RESULTS

Whole Sediment

- Mean (n=5) measured concentrations of As, Cu, Pb and Zn in Finfeather sediments were 104 (SD=71), 194 (SD=219), 34 (SD=20) and 517 (SD=447) mg/Kg dry weight, respectively. All measurements except two for Pb were above acceptable sediment quality screening indices.
- *H. azteca* survival was significantly affected in 50% of samples tested. Growth was significantly reduced, where survival was not affected, in all but one sample.
- Similarly, survival of *C. tentans* was also significantly reduced in 50% of samples tested. Growth was significantly lower in all but two samples where survival was not affected.
- *H. azteca* growth improved in SIR-900-treated sediments (Table 1), although improvements were not significant. Survival was 60 and 68% in control and SIR-900-treated sediments, respectively.

Porewater

- Mean (n=4) measured concentrations of As, Cu, Pb and Zn in Finfeather porewater were 174 (SD=48), 347 (SD=254), 24 (SD=8) and 350 (SD=52) µg/L, respectively.
- *C. dubia* survival was significantly affected in 1 out of 9 porewater tests from Station 11798, whereas reproduction was significantly lower in 7 out of 9 tests.
- Station 11798 was chosen for most TIE manipulations due to higher ambient metal concentrations in sediment.
- Porewater treated with EDTA or resins resulted in significantly improved *C. dubia* survival or reproduction (Table 1), however, mean neonate production still often fell short of controls.
- SIR-900 significantly reduced arsenic concentrations (from 266 to 11.4 ug/L), however, this did not coincide with significant improvement in *C. dubia* reproduction in 50% porewater. SIR-300 treatment generally reduced metal concentrations and improved reproduction except in 100% porewater.
- In one study, where porewater resulted in 80% mortality, SIR-300 treatment improved survival to 100% with mean neonate production of 8.6 neonates. Control survival was 100%, and mean neonate production was 25.8. TUc in porewater were highest for copper (16.5), lead (7.01) and zinc (2.91). TUc for arsenic were 1.12. Water quality criteria used are listed in Table 2.
- Arsenic was discounted as the metal of concern in porewater due to lower toxic units, and others [8] have shown that As concentrations as high as 1.46 mg/L do not affect *C. dubia* reproduction.
- Measured metal concentrations during Phase III TIE procedures are summarized in Table 3.
- Results of *C. dubia* survival and reproduction following Phase III treatments is summarized in Table 4.

DISCUSSION and CONCLUSIONS

- Finfeather Lake sediments were toxic to *C. tentans* and *H. azteca*.
  - Use of cation exchange and adsorbent resins resulted in improved growth of *H. azteca*.
- Finfeather Lake sediment porewaters were chronically (sometimes acutely) toxic to *C. dubia*.
  - EDTA and resin treatments improved reproduction.
- SIR-300 showed greater promise for reducing porewater toxicity to *C. dubia*, however, calcium and magnesium had to be reintroduced to waters treated with SIR-300.
- Arsenic was determined not to be the sole metal of concern in Finfeather Lake porewater. Lead was also discounted as problematic following Phase III TIE procedures. Although 100% mortality was observed in treated, zinc-spiked porewater, chronic toxic units suggest copper as being more important.
- It is worth noting that calculated toxic units in porewater studies were based on water quality criteria. There is currently no accepted link between surface water quality criteria and porewater quality. Sediment quality criteria (or screening indices) may also not be appropriate for use in assessing porewater quality.
- Sediment and porewater TIE procedures require further development in order to better substantiate sediment TMDLs. Moreover, development of sediment TMDLs may be further complicated by issues of legacy contamination.

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