



# POREWATER AND WHOLE SEDIMENT TIE APPROACHES FOR COMPLEX CHEMICAL MIXTURES



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## ABSTRACT

The Texas Commission on Environmental Quality is intensely monitoring Alligator Bayou in Jefferson Co., a river on the 1999 CWA 303(d) list, to develop total maximum daily loads (TMDL) for water column and sediment toxicity. This bayou presents challenges for toxicity identification evaluation (TIE) procedures and TMDL development because Alligator Bayou sediment is contaminated by complex chemical mixtures. We evaluated ambient water and sediment toxicity and chemistry, and performed porewater TIEs with *Ceriodaphnia dubia*, and whole-sediment TIEs with *Hyalella azteca* and *Chironomus tentans* during an 18 month study period. We used ion exchange resin and adsorbent media treatments parallel to and sequential with porewater TIE methods to selectively remove toxicity of organic and metal mixtures. The degree of contamination at one Alligator Bayou station was substantial, as porewaters had to be diluted to 6.25% with reconstituted laboratory water before various TIE treatments effectively reduced or removed toxicity. Because a number of metals and PAHs were consistently detected at concentrations above sediment screening levels, these TIE techniques could not precisely identify a specific cause of toxicity. Cumulative effects of such complex mixtures are likely causing in sediment toxicity. Therefore, when a causative pollutant cannot be identified and a TMDL developed, periodic monitoring of sediment toxicity should be conducted as an interim approach until methods are developed with which to address sediment toxicity.

## INTRODUCTION

Segment 0702A of Alligator Bayou is identified on the State of Texas 1999 and draft 2000 303(d) lists as partially supporting aquatic life uses due to ambient water and sediment toxicity. Alligator Bayou is a freshwater urban, industrial tributary to Taylor Bayou and is upstream of a salt water barrier. The bayou receives discharges from municipal and industrial facilities, with a smaller amount from agricultural runoff. Segment 0702A of the Neches-Trinity Coastal Basin is located in Jefferson County, Texas in and near the City of Port Arthur. The watershed for Alligator Bayou is approximately 40 square miles. (Figure 1).

Historic sediment toxicity data based on elutriate tests with *Ceriodaphnia dubia* and *Pimephales promelas*.

Three sampling stations: 10643, 14410, 14411.

Draft EPA TIE procedures available for porewaters; none for whole sediments.

### 1999 303 (d) Listing

Partial Support - Ambient toxicity in water occasionally exceeds the criterion established to assure optimum conditions for aquatic life.

Non Support - Toxicity in sediment sometimes exceeds the criterion established to assure optimum conditions for aquatic life.

### 2000 303 (d) Listing

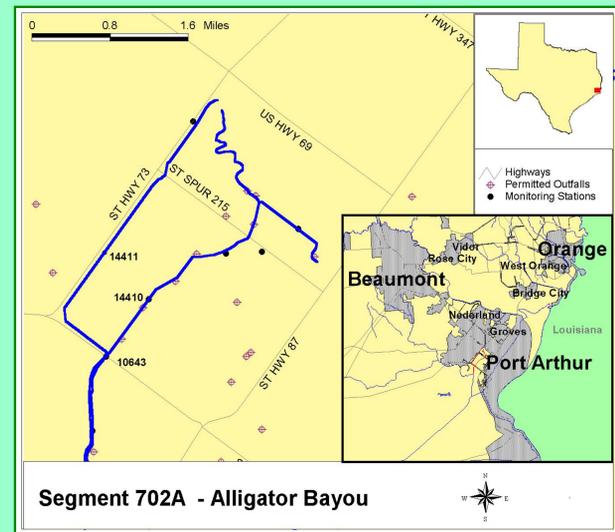
Partial Support - Significant effects in ambient water toxicity tests sometimes occur, indicating that conditions are not optimum for aquatic life.

Non Support - Significant effects in ambient sediment toxicity tests sometimes occur, indicating that conditions are not optimum for aquatic life.

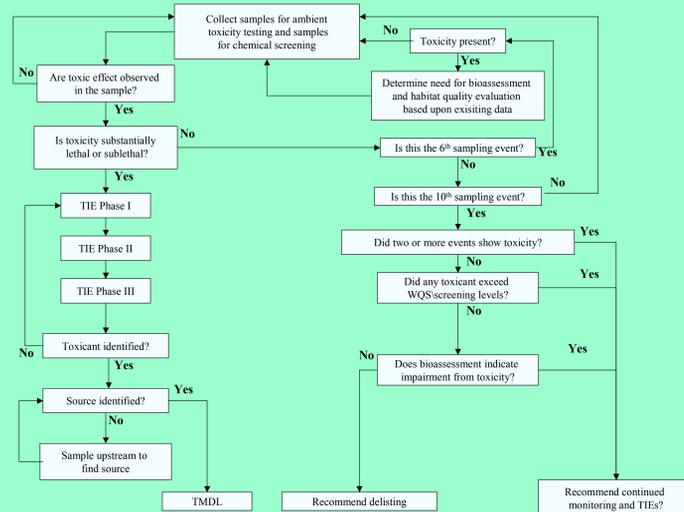
## ACKNOWLEDGEMENTS

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Figure 1. Segment 0702A – Alligator Bayou, Jefferson County, Texas.



## METHODS: Project Framework



## METHODS: Chemistry

• Temperature, pH, DO, and specific conductance were measured using a datasonde at the time of sample collection.

• Extensive chemical screening (metals, organics, inorganics) was performed on water, sediment, and porewater samples.

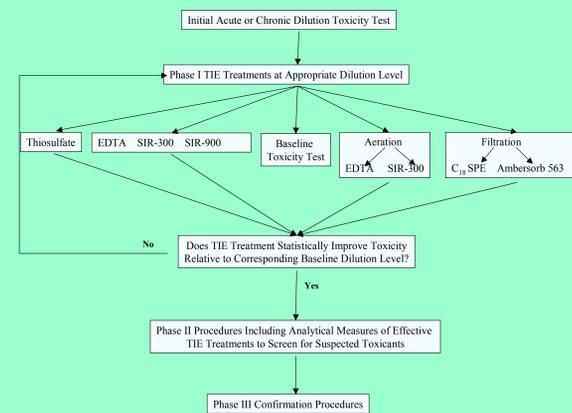
## METHODS: Toxicity Tests

• *C. dubia* and *P. promelas* were used for all porewater toxicity tests.

• *Hyalella azteca* and *Chironomus tentans* were used as test organisms for whole sediment toxicity tests.

• After the first sampling event in April 2001, a TIE was initiated due to significant toxicity at Stations 10643 and 14410. The TIE was performed on five different occasions on pore water and one occasion on whole sediment from samples collected at Station 10643. A TIE was performed on sediment pore water from samples collected at Station 14410.

## METHODS: Porewater TIE Framework



## TIE Resins/Sorbents

SIR-300 (Resin Tech Inc.) used as a parallel TIE treatment to EDTA.

- SIR-300 a cation exchange resin, styrene and divinylbenzene copolymer with iminodiacetic functional group in the sodium form; chelates divalent metal cations.
- Reported SIR-300 affinity for metals: Hg<sup>2+</sup>>Cu<sup>2+</sup>>V<sup>2+</sup>>Pb<sup>2+</sup>>Ni<sup>2+</sup>>Zn<sup>2+</sup>>Co<sup>2+</sup>>Cd<sup>2+</sup>>Fe<sup>2+</sup>>Be<sup>2+</sup>=Mn<sup>2+</sup>>Mg<sup>2+</sup>=Ca<sup>2+</sup>>Sr<sup>2+</sup>>Ba<sup>2+</sup>>Na<sup>2+</sup>.
- We found Mg<sup>2+</sup>, Ca<sup>2+</sup> to be taken out by SIR-300.

Ambersorb 563 (Supelco) is a carbonaceous adsorbent media designed for organics removal.

- Used as a parallel TIE treatment to C18 SPE. Advantage: C18 SPE may also remove metals.
- Looks promising for porewater; PAH removal equivalent to C18 SPE, no metal removal.
- Not effective on Alligator Bayou whole sediment. No *C. tentans* survival even when diluted to 90% with reference sediment.

## RESULTS: Ambient Toxicity

Whole sediment acutely toxic to *H. azteca*, *C. tentans*.

Porewaters acutely toxic to *C. dubia*, *P. promelas* at 12.5% dilution.

## RESULTS: Ambient Chemistry

AVS-SEM < 1. TOC = 54500 mg/kg. Silt = 55%; Clay = 42%; Sand = 3%.

As, Cd, Cr, Cu, Pb, Ni, Zn, Hg higher than lowest sediment screening values in *Equilibrium and Non-Equilibrium Partitioning-Based Sediment Quality Screening Indices* tables.

13 PAHs (2400-58800 µg/Kg – dry), Chlordane, 4,4'-DDE higher than sediment screening values.

Table 1. Summary of Sediment Toxicity Identification Evaluation Procedures.

Test Date	Test Type	Station	Organism	Effective Treatment
24–26 August 2001	Porewater	10643	<i>C. dubia</i>	Aeration + EDTA, C18
14-16 December 2001	Porewater	10643	<i>C. dubia</i>	S300, EDTA, Aeration + EDTA
22 May – 01 June 2002	Sediment	10643	<i>H. azteca</i>	None
12-14 July 2002	Porewater	14410	<i>C. dubia</i>	C18 @48h; Filt, S300,
08-10 August 2002	Porewater	10643	<i>C. dubia</i>	C18, A563 @48h; Filt, S300 @24hr

## Results: Porewater TIE

TIE identified significant acute toxicity reduction at 25% porewater dilution using EDTA, SIR-300 and Aeration + EDTA, but not by Aeration treatments.

Toxicity reduction with these treatments suggests that metals are causative acute toxicants to *C. dubia*.

Chemical analysis on baseline porewater, Aeration, SIR-300 and Aeration + SIR-300 samples indicates that SIR-300 reduced or removed Al, Cr, Fe, Pb, Ni, & Zn.

Alligator Bayou contains a complex mixture of numerous PAHs, metals.

## CONCLUSIONS

Pore water and whole sediment exhibited toxicity.

Sediment toxicity is attributable to a combination of metals and organic compounds.

Current TIE methods are not able to identify the exact cause of toxicity.

The degree of contamination on Alligator Bayou at Station 14410 is substantial as demonstrated by the significant sample dilution (6.25%) needed to show toxicity improvement using various treatments.

**Recommendation** - Periodic monitoring of the sediment toxicity while avenues are explored within the agency for addressing sediment toxicity when a single pollutant cannot be identified as the cause and a TMDL developed.

## REFERENCES

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