Arsenic in the Delaware Inland Bays

Outline

- History of interest & concern
- Summary of findings
- Data & analyses supporting findings
- Recommendations

History

- Late 1990s/early 2000s:
  - *EPA working on new MCL*
  - *USGS NAWQA studies*
  - *Roxarsone (ROX) revelation*
- DNREC Response:
  - *Added routine surface water monitoring for arsenic in IBs*
  - *State-of-the-science arsenic speciation study in fish/shellfish*
  - *Coordinated with EPA EMAP/NCA on detailed sediment sampling*
  - *Engaged UD to study fate & transport of arsenic in DE soils*
  - *Adopted more stringent human health water quality criterion*
- Circa. 2008: Concerns voiced by the public over arsenic releases from fly ash at the IRPP
- Today: Roll-out of watershed-wide assessment

Summary of Findings

- Several natural & human sources of arsenic to IBs
- However, widespread arsenic problem does not exist in the Inland Bays. The data show that:
  - *Aquatic life criteria are not exceeded & few (~1%) samples exceed the applicable human health criterion*
  - *Sediments are not toxic to aquatic life*
  - *Consumption advisory for arsenic in fish & shellfish not needed*
  - *Atmospheric loading not high enough to cause problem*
- Arsenic from IRPP is localized. Programs in place to assess, control and mitigate as appropriate.
- Arsenic in poultry litter from ROX may contribute south of Indian River. Fortunately, iron in soil binds the arsenic & limits leaching to groundwater.
- Finally, lead-arsenate residue in Swan Creek soils may be important legacy source north of Indian River.

Sources of Arsenic to the IBs

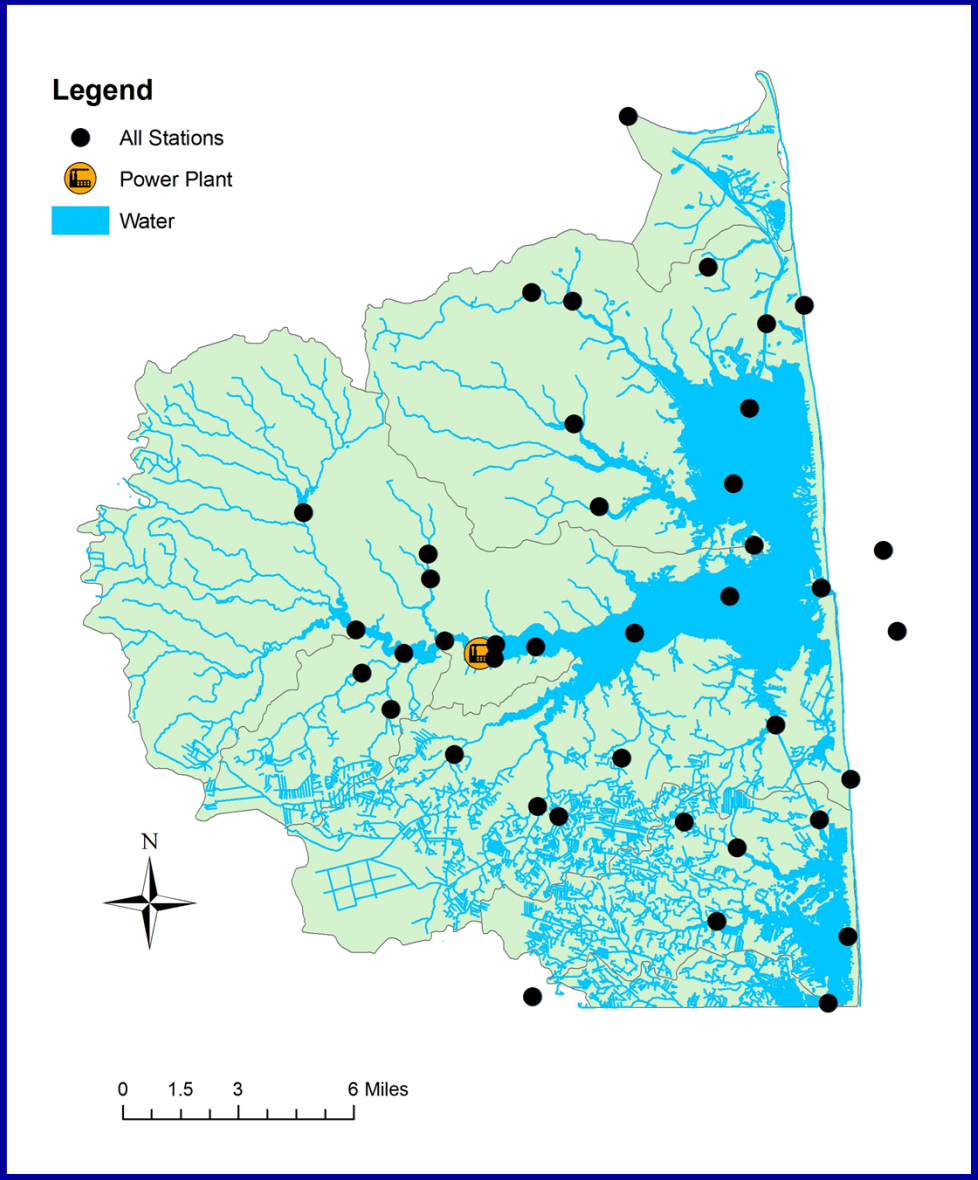
- Arsenic is a nonmetallic trace element that occurs naturally in water & soil due to weathering of rocks & minerals. Also in marine deposits known as 'greensands'.

- Anthropogenic sources in the IBs:
  - Coal, coal fly ash & leachate
  - Ag (*past use of lead-arsenate in orchards; current use of Roxarsone (ROX) feed additive in poultry*)
  - CCA-treated lumber in docks & boardwalks (voluntary phase out)
  - Atmospheric deposition (from local & distant sources)
  - Lesser amounts: anti-CA drugs, lead-acid batteries, semiconductors & LEDs
  - Historic: tanneries, green paint pigment, matches

Inland Bays Surface Water Data

- ✓ DNREC Ambient Monitoring Program
  - *Watershed-wide & long-term*
- ✓ IRPP Monitoring
  - *Local scale & synoptic*
- Other: UD Undergrad Research Project
  - *Watershed-wide & synoptic*
  - *Results included as supplemental info*

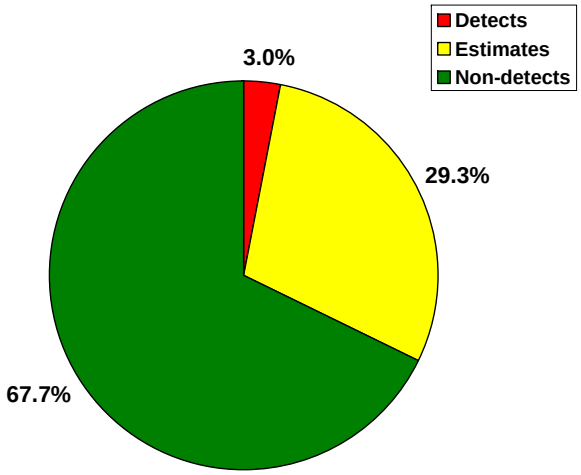
DNREC Ambient Monitoring - Arsenic



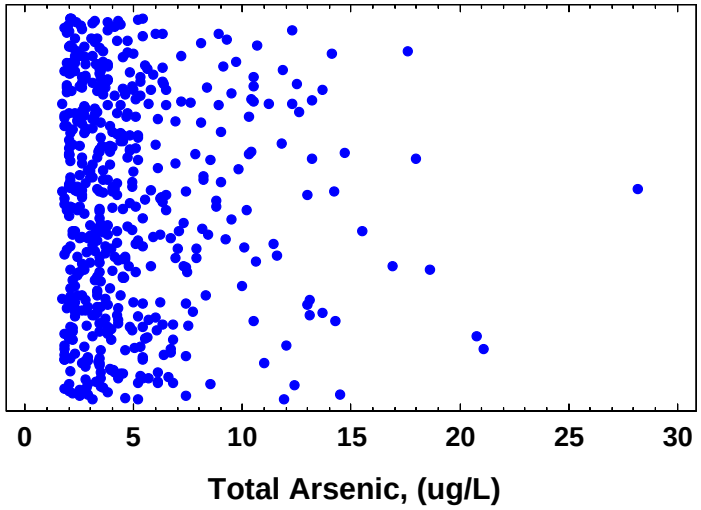
- 42 stations
- 1998 – 2008, variable frequency
- N = 1624 (total As)
  N = 1146 (diss. As)
- Method: EPA 200.7 Modified (ICP-AES)
- MDL = 1.7 – 3.2 ug/L

DNREC Ambient Monitoring - Arsenic

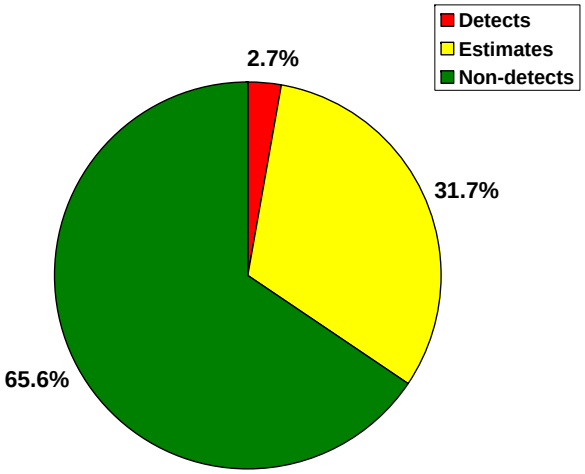
Detection Frequency Total Arsenic Inland Bays



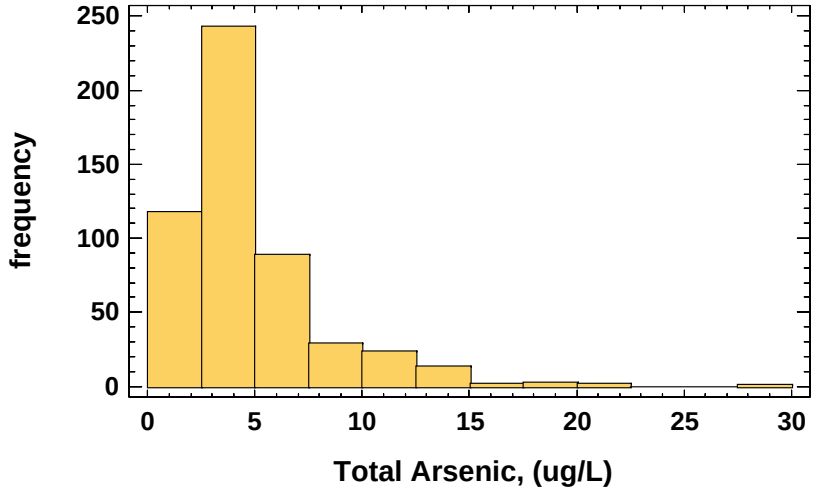
Scatterplot for Detected & Estimated Arsenic Concentrations



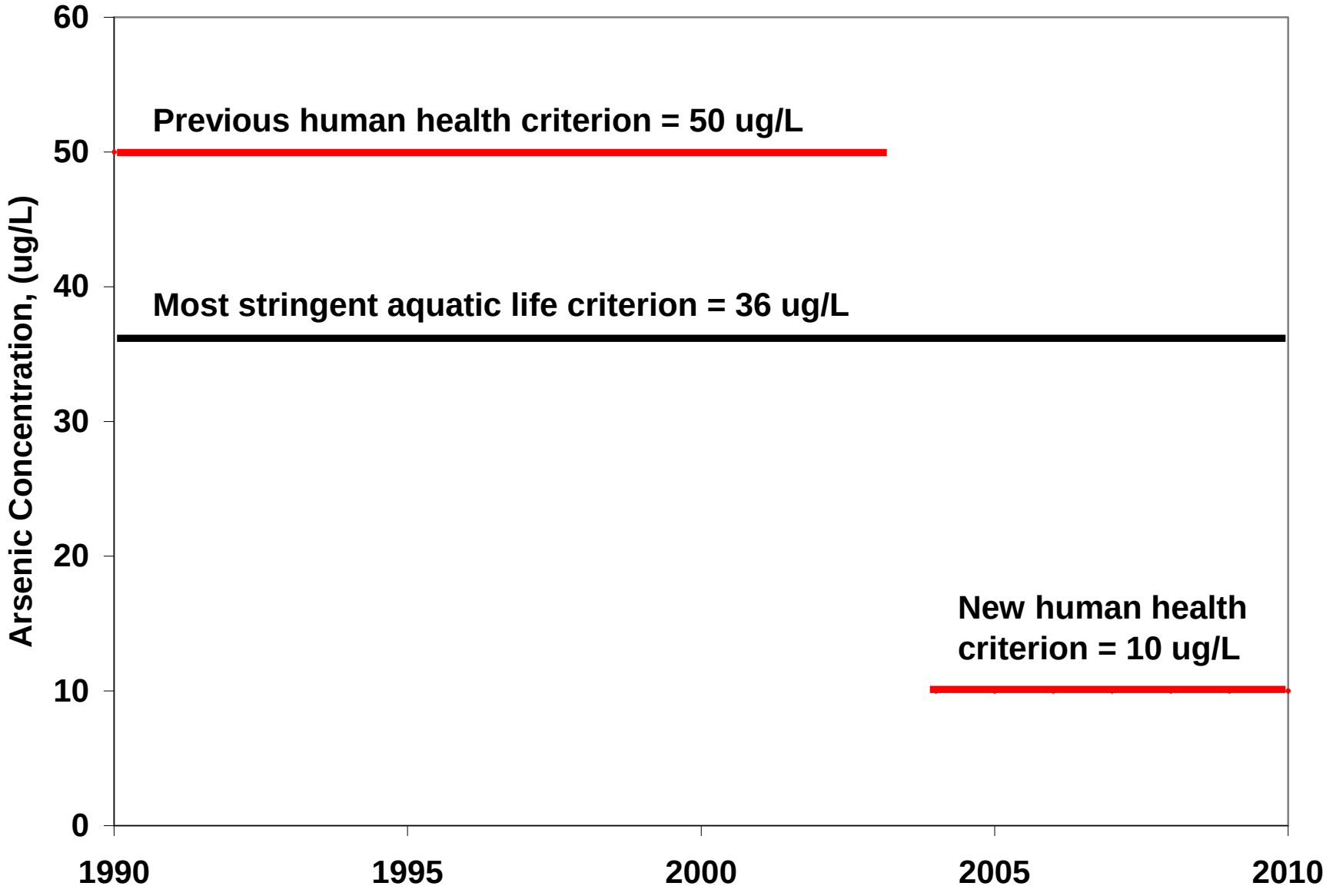
Detection Frequency Dissolved Arsenic Inland Bays



Histogram for Detected & Estimated Arsenic Concentrations



DE Surface Water Quality Criteria



EPA Human Health Criteria

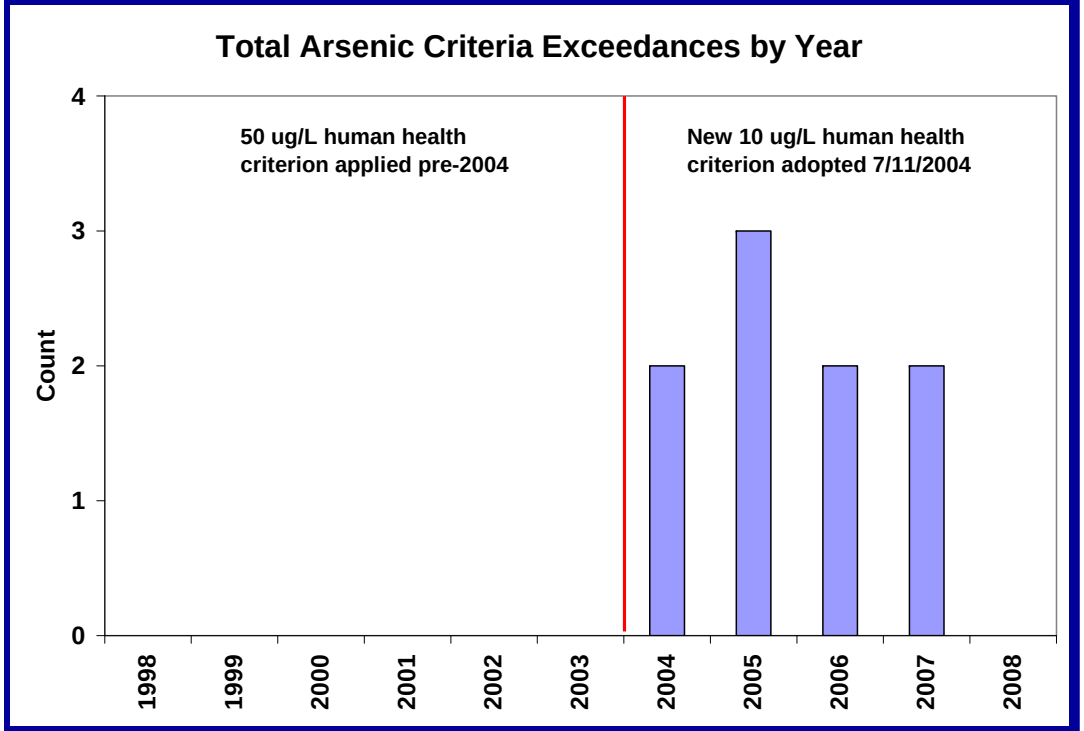
- EPA criteria at 10^{-6} cancer risk

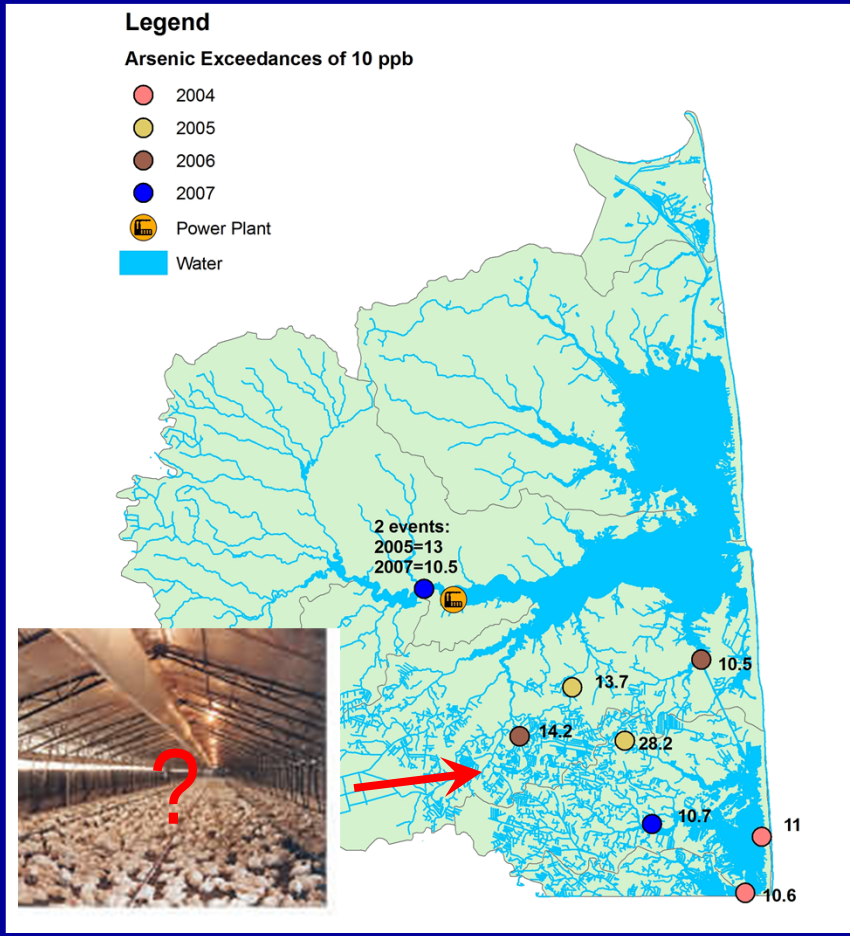
	Fish & Water Ingestion	Fish Ingestion Only
Arsenic (inorganic) (ug/L total)	0.018	0.14

- Flawed because:
  - *Bioconcentration Factor (BCF) used in criteria calc is not the ratio of inorganic As in fish to inorganic As in water, as it should be*
  - *Also, these criteria << natural background*

- EPA acknowledges the problem & supports DE's criterion of 10 ug/L

Arsenic Criteria Exceedances



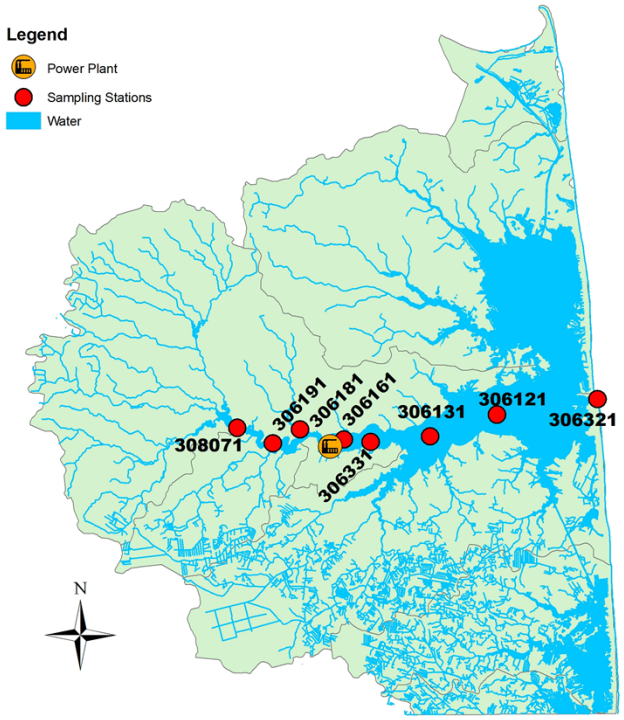


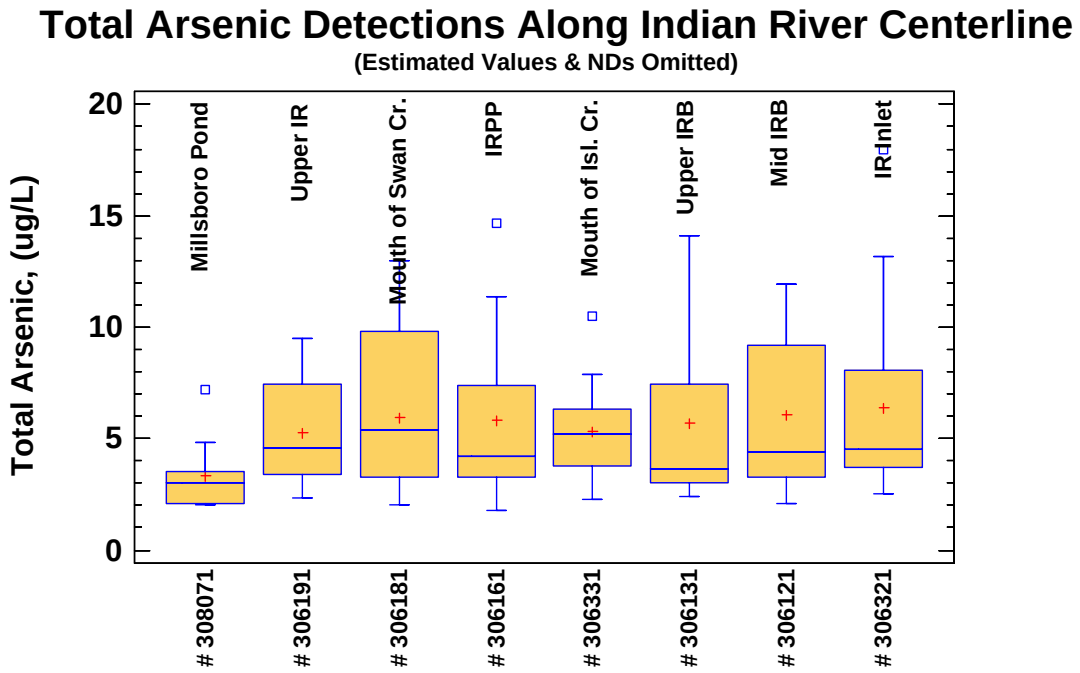
- 0 aquatic life criteria exceedances
- 9 exceedances of human health criteria starting 7/2004 (~1% of 800 samples)
  - *7 south of IR with max @ Beaverdam Ditch on 9/20/2005 (low flow). Results may reflect ROX usage + natural abundance.*
  - *2 in IR at mouth of Swan Creek, upstream of IRPP*

Why Above IRPP?

- Swan Cr drainage area once included 'Indian Swan Orchard'
- Lead-arsenate pesticide residue in soil likely
- Once eroded & delivered to upper IR, that arsenic + arsenic from other sources likely binds to Fe oxide from Wharton & Iron Br.
- Particles get trapped in depo zones and sediment-water exchange provides ongoing source of As to water column

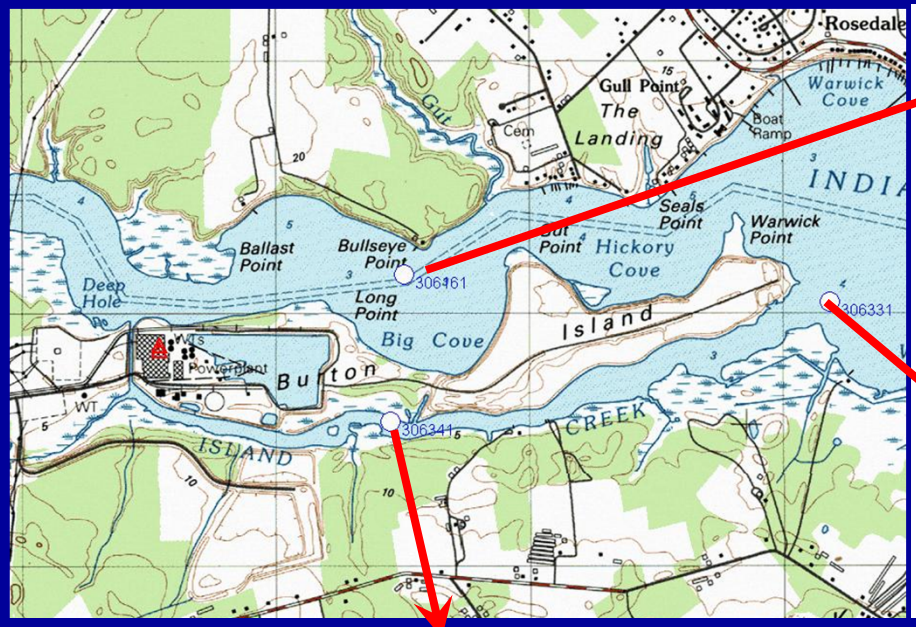
Tidal Indian River Profile - Detects

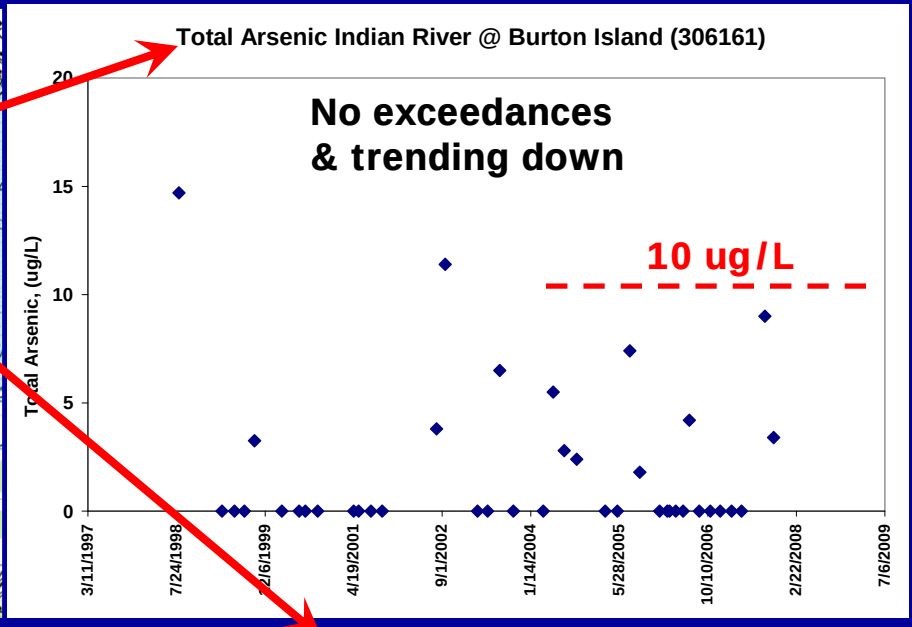


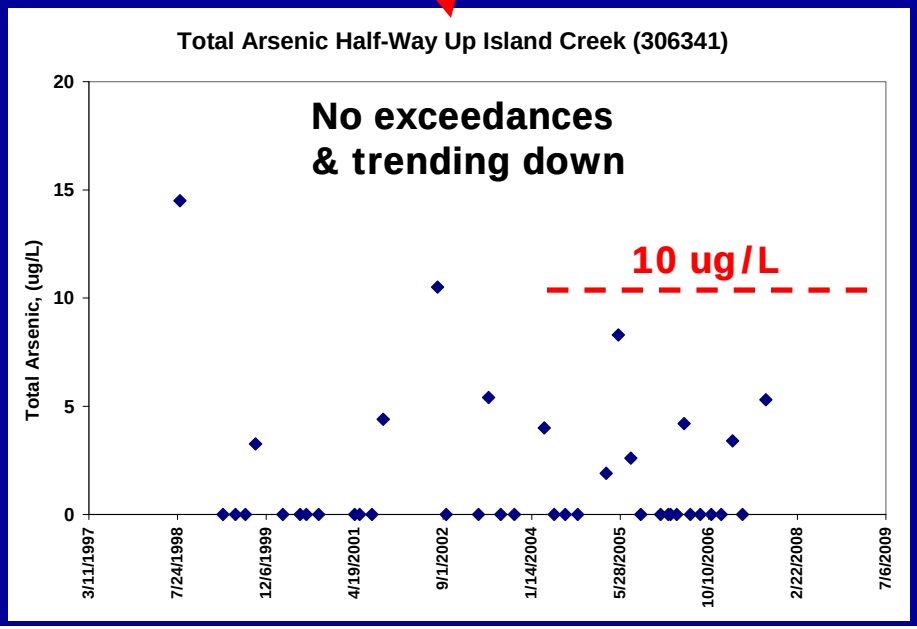


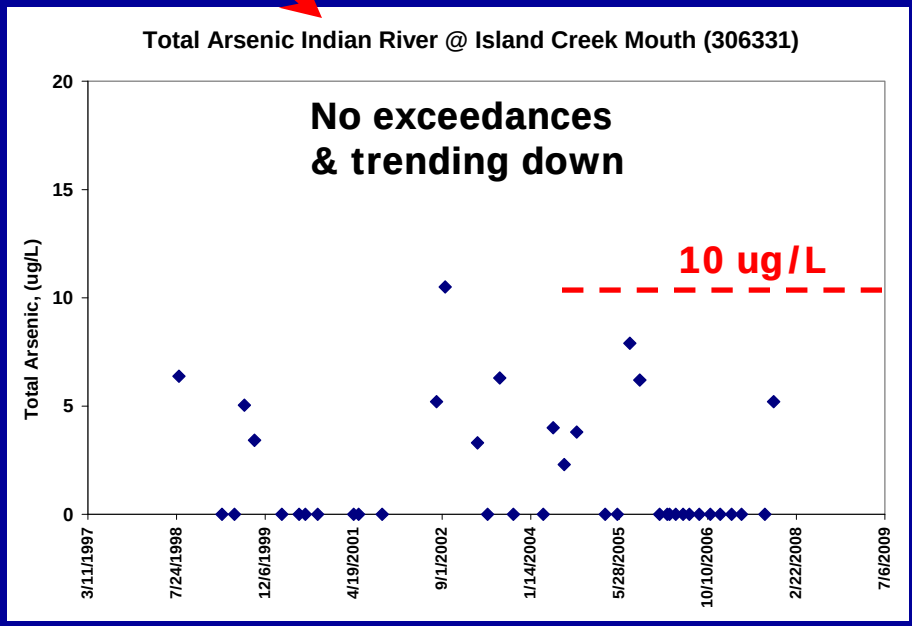
- Tidal stations not statistically different but subtle nominal increase upstream of IRPP apparent
- Also note slight increase towards IR Inlet

Time Series Tidal Stations near IRPP







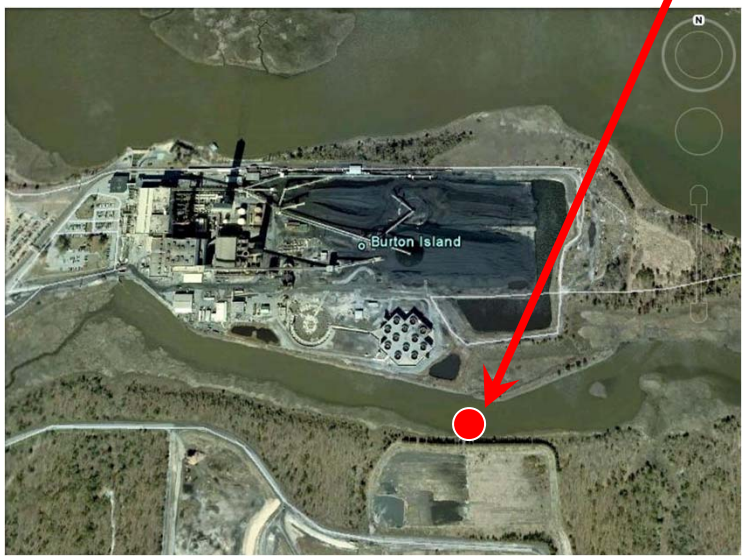


More IRPP Surface Water Data

IRPP Surface Water Data

- Surface water samples collected at SG-2 in Island Creek adjacent to Phase I waste facility.
  - *88 samples between 3/1982 – 2/2009*
  - *Steady increase to 1997/1998, then decrease*
- Burton Island FE report
  - *8 samples (4 from IR shoreline & 4 from Island Creek shoreline)*
  - *ND (1.6 ug/L) – 14.4 ug/L; max in Isl. Creek*

Total Arsenic at SG-2 in Island Creek



Exceedance frequency is high. However, sample location not representative & mass load not clear.

Total Arsenic, (ug/L)

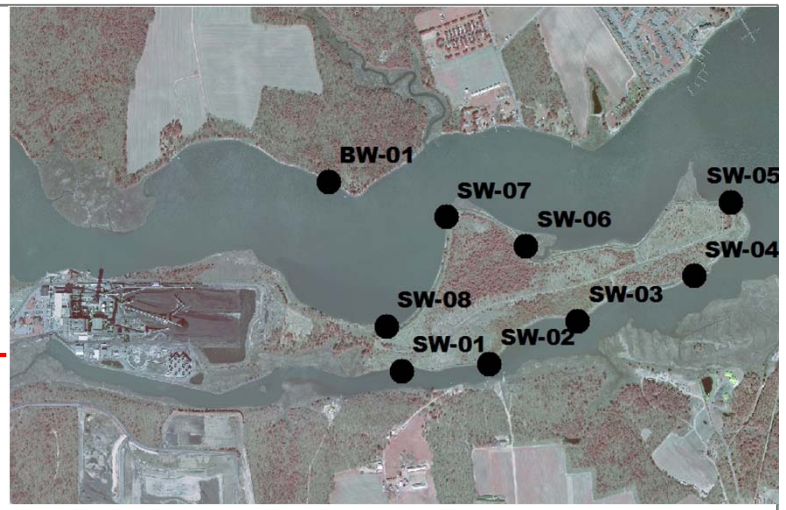
200
180
160
140
120
100
80
60
40
20
0

50 ug/L

10 ug/L

1982
1995
2009

Total Arsenic in Surface Water - Burton Island FE



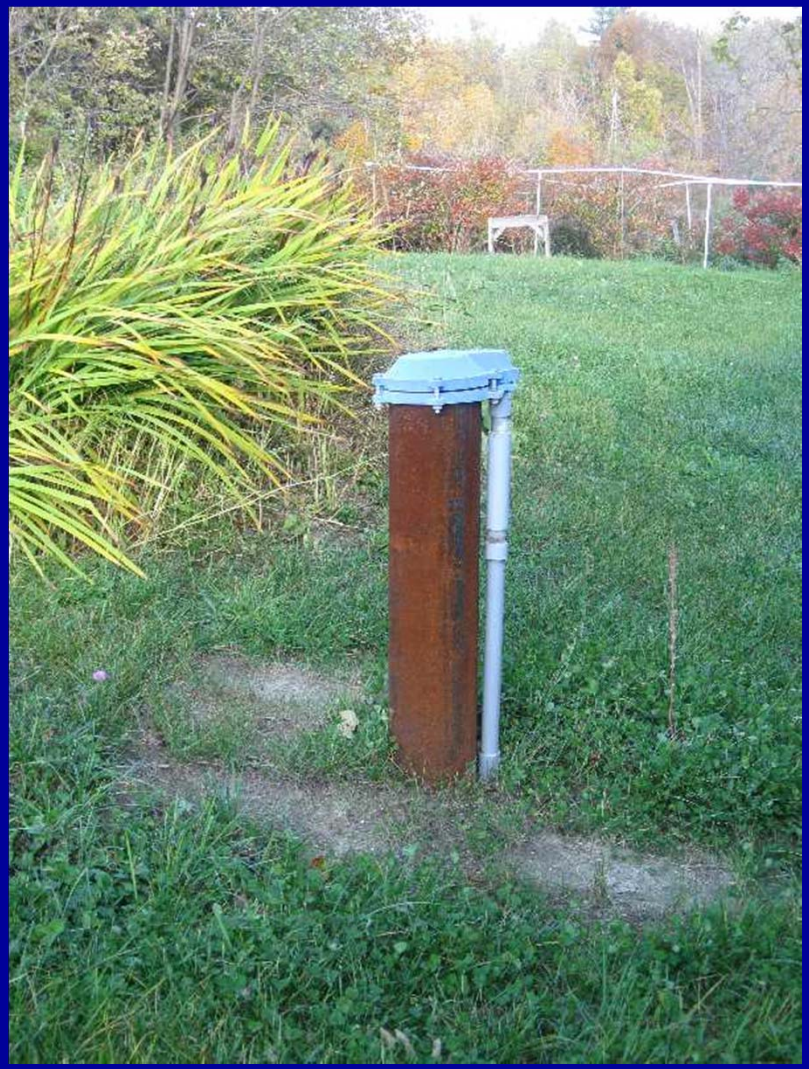
Total Arsenic, (ug/L)

16
12
8
4
0

WQC = 10 ug/L

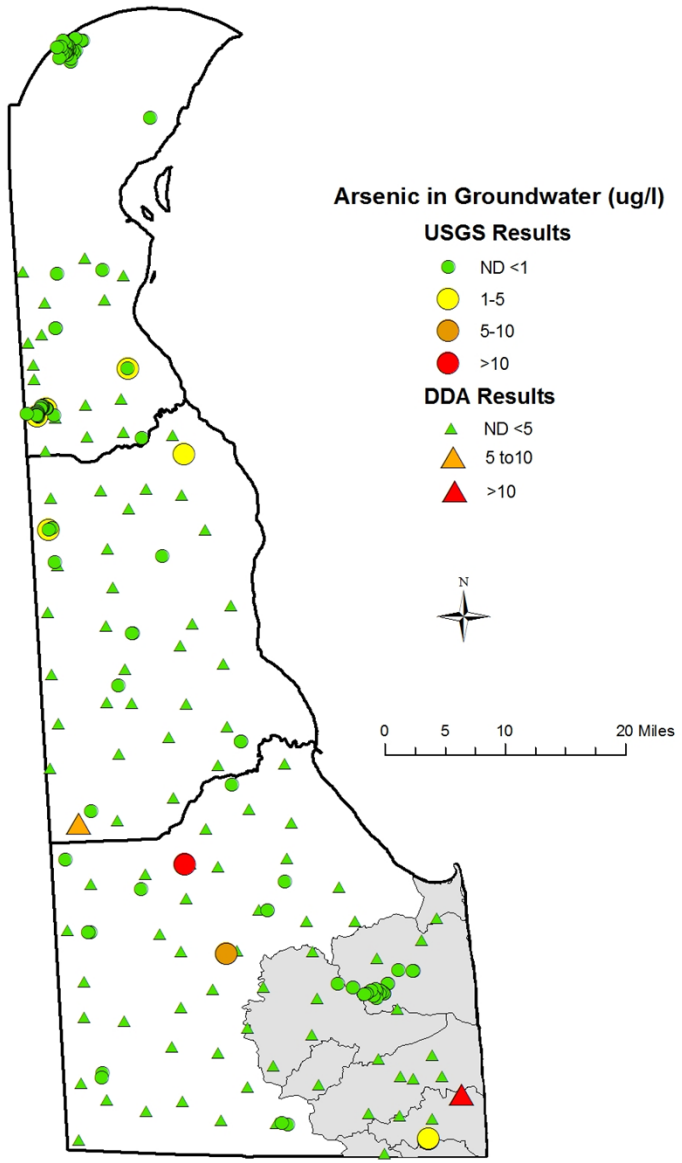
BW-01
SW-01
SW-02
SW-03
SW-04
SW-05
SW-06
SW-07
SW-08

Arsenic in Groundwater Data



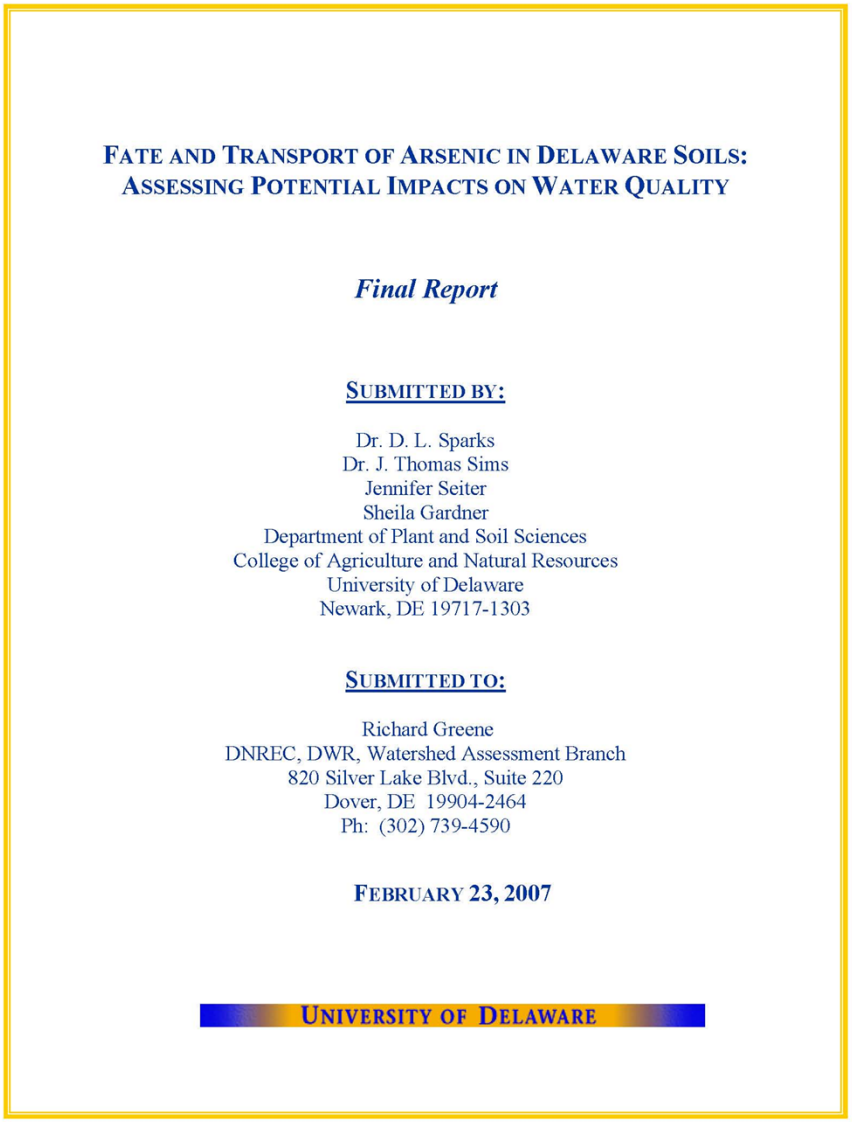
- ✓ USGS (Focazio et al. 1999)
  - *120 samples*
  - *1987 - 1991*
- ✓ DDA (Blair 2003)
  - *164 samples from shallow aquifer*
  - *2001 - 2003*
- IRPP Monitoring
  - *To be covered by G. DeCowsky*

Arsenic in DE Groundwater



- USGS Data (circles):
  - *92% of samples < 1 ug/L*
  - *1 detection > 10 ug/L (14 ug/L @ Rt. 36 between Greenwood & Ellendale); well not used for drinking.*
- DDA Data (triangles):
  - *97% of samples < 5 ug/L*
  - *2 detections > 10 ug/L (1 domestic well in Harrington at 12 ug/L and 1 monitoring well in Ocean View at 33 ug/L.*
  - *2010 Ocean View resample at 15.8 ug/L*

UD Study of Arsenic in DE Soils



FATE AND TRANSPORT OF ARSENIC IN DELAWARE SOILS:
ASSESSING POTENTIAL IMPACTS ON WATER QUALITY

Final Report

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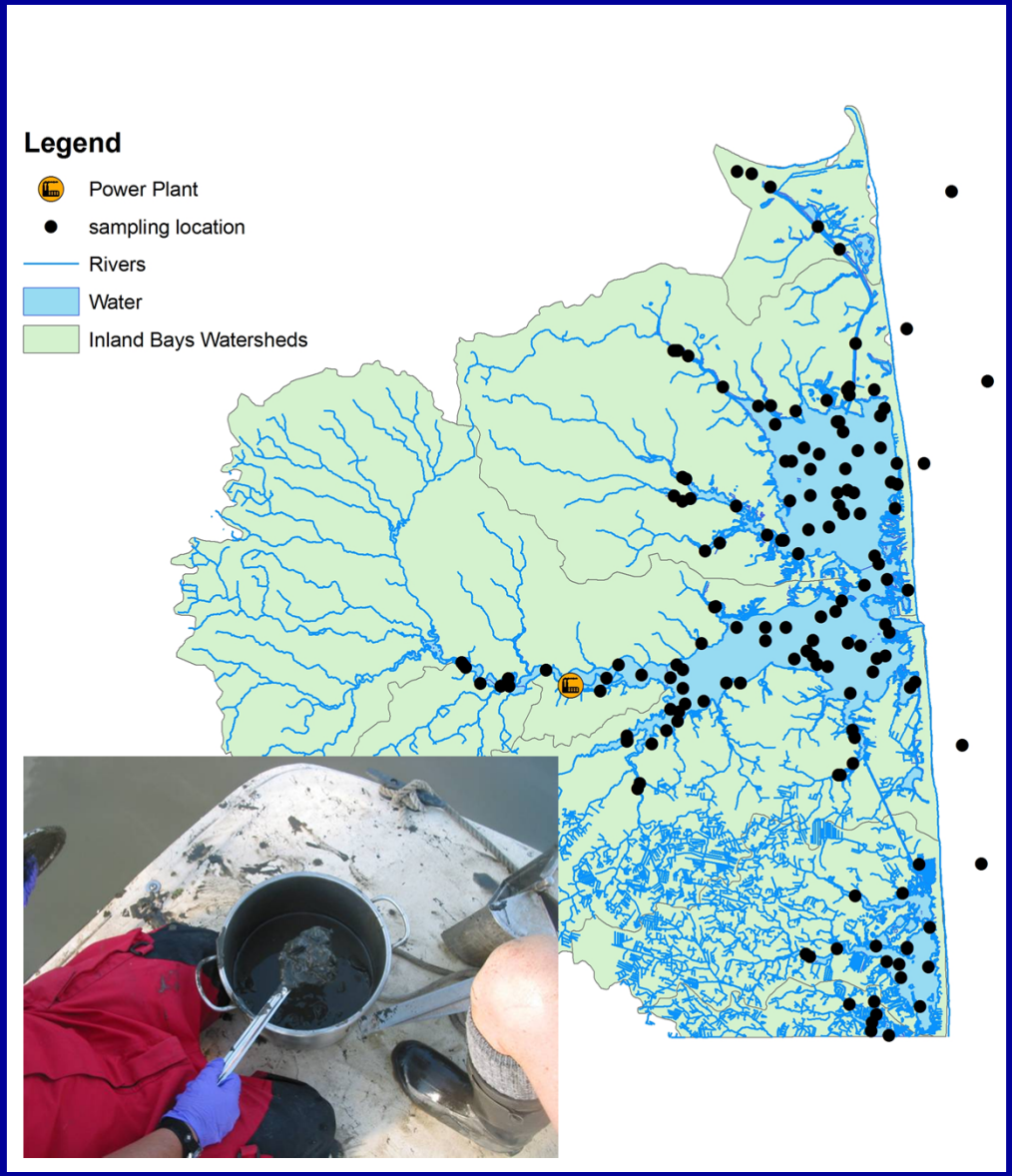
FEBRUARY 23, 2007

UNIVERSITY OF DELAWARE

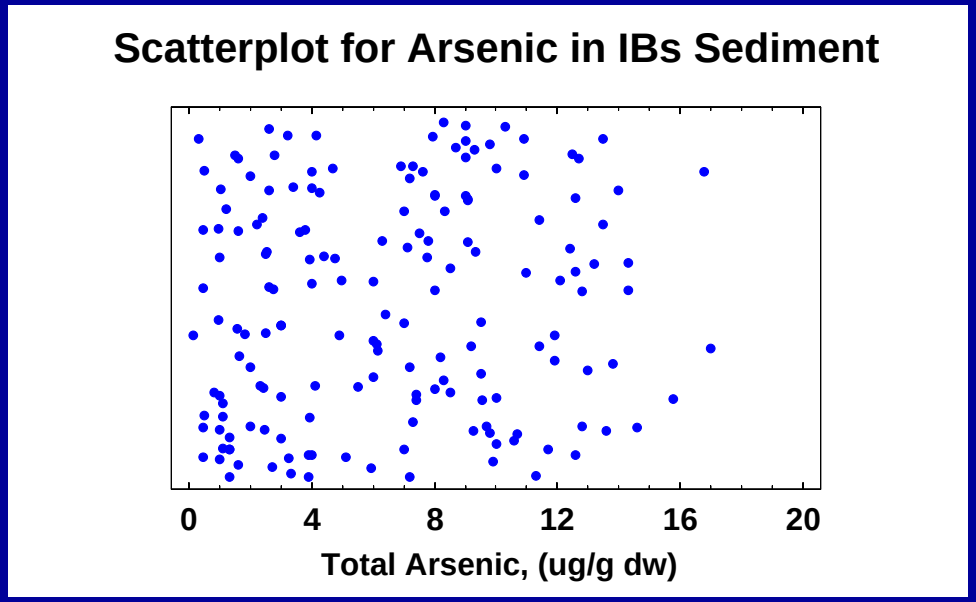
- Risk of leaching to groundwater or running off low overall
- Farms where broiler litter applied did not have high As conc. in soils; however few farms sampled.
- Speciation showed As in ROX within litter is rapidly converted to soluble arsenate during storage. Soluble As then sorbs to soil, although P inhibits As sorption.
- Gradual build-up of As in soil possible over long term if current practice continues. Use of ROX not a sustainable practice.
- Recommendations: Seek alternative to ROX and use manure storage sheds to prevent leaching & runoff. Alum.

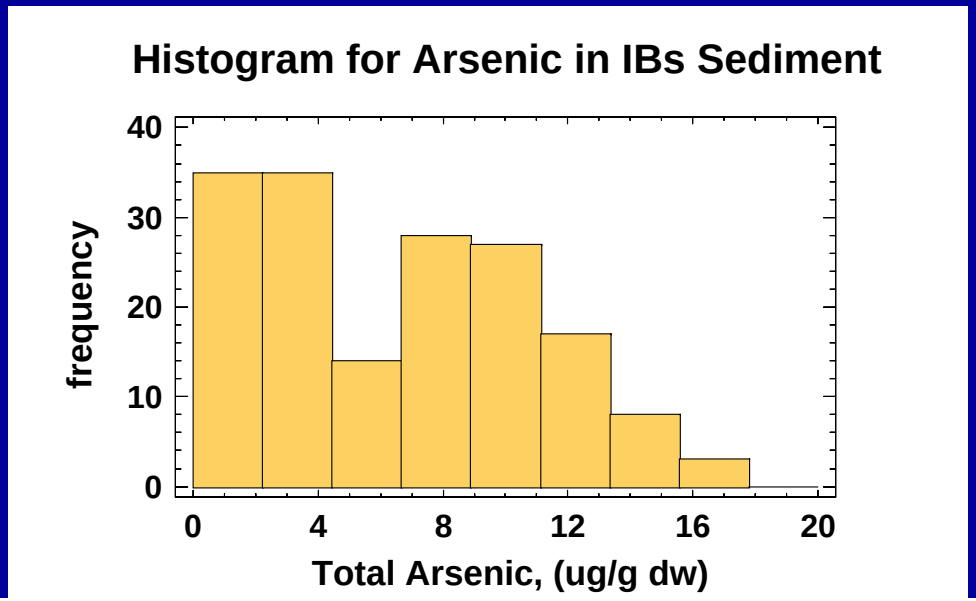
Inland Bays Sediment Data



- Arsenic sorbs to sediments & so are important to test
- N = 167 surface sediment samples collected as part of EPA EMAP/NCA between 1990 – 2006.
- Matching sediment toxicity tests for 142 samples
- Other dataset: Burton Island FE (Shaw 2008)

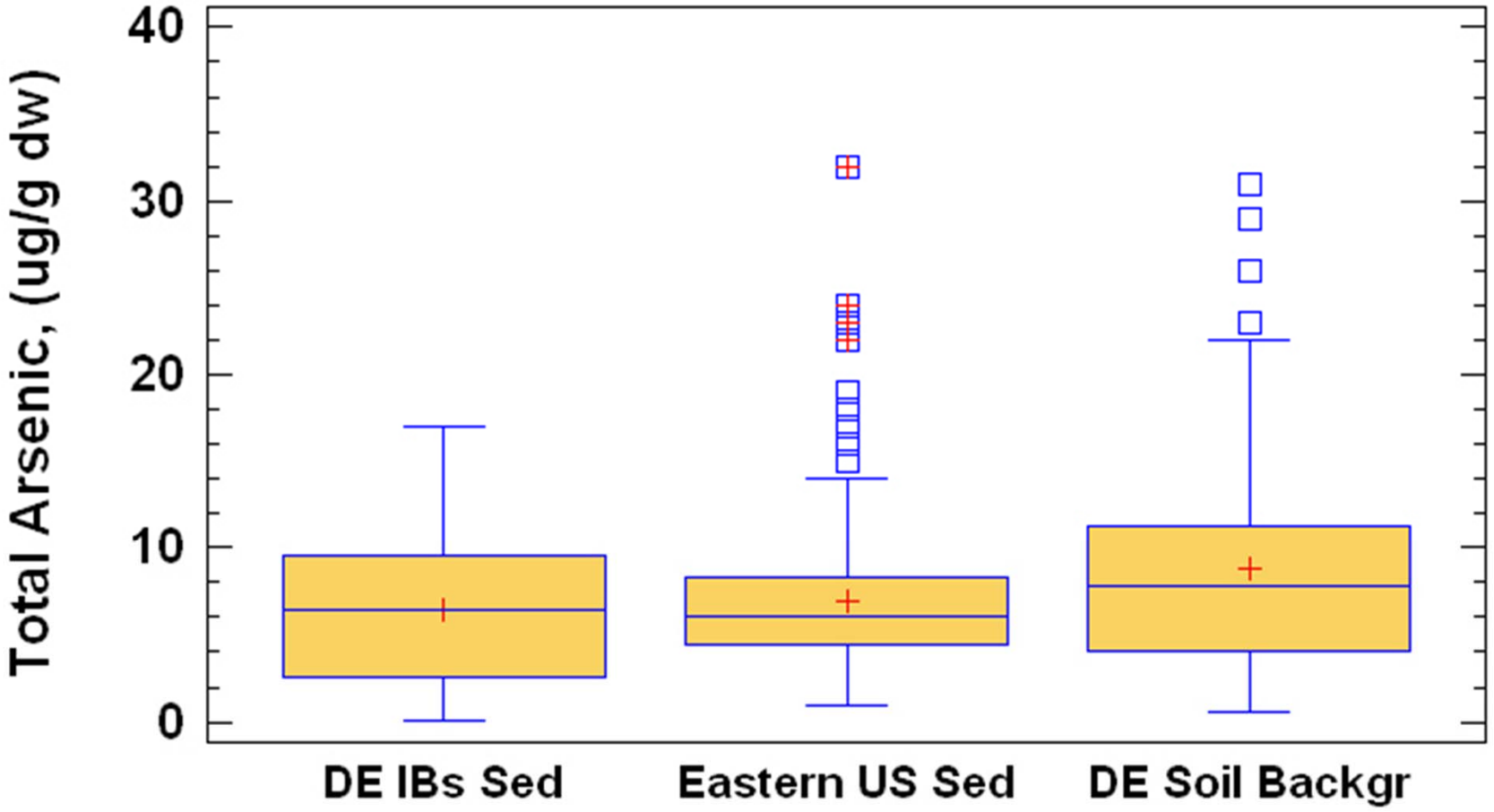
EPA EMAP / NCA Sediment Data



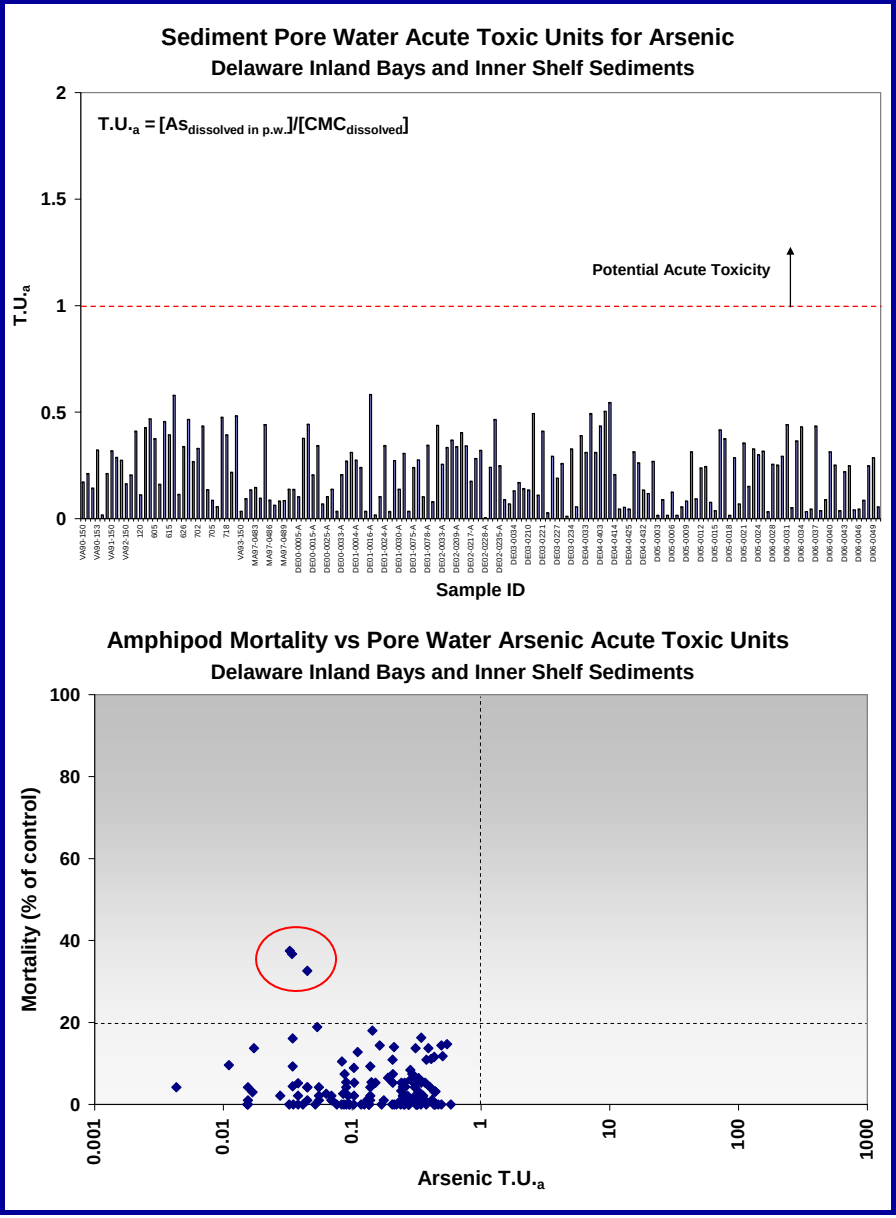


- Range: 0.125 – 17 ug/g dw; 6.5 ave.
- Not different from Eastern US seds nor DE background soils
- Toxicity to benthic organisms unlikely

Comparison of Arsenic in Sediments and Soils

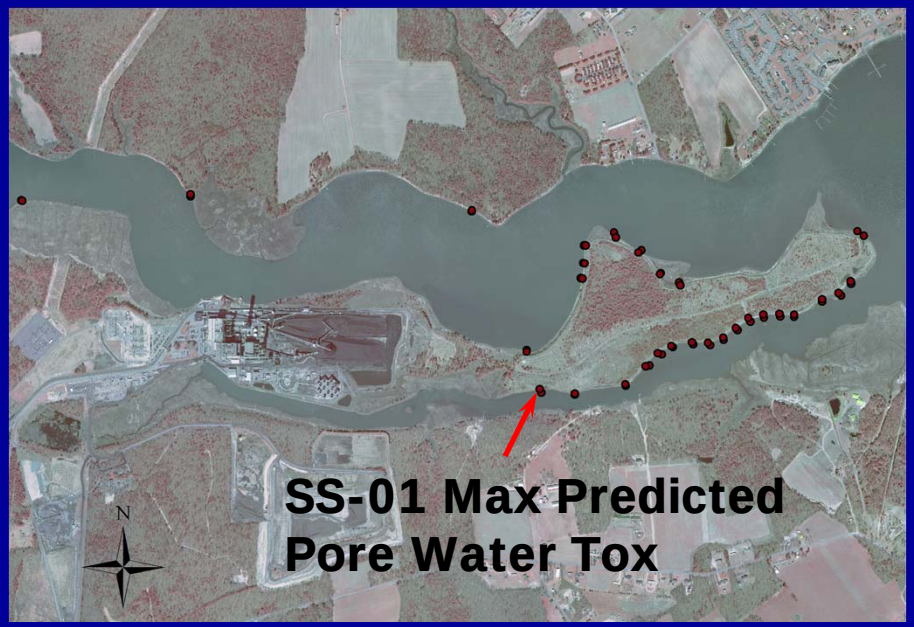


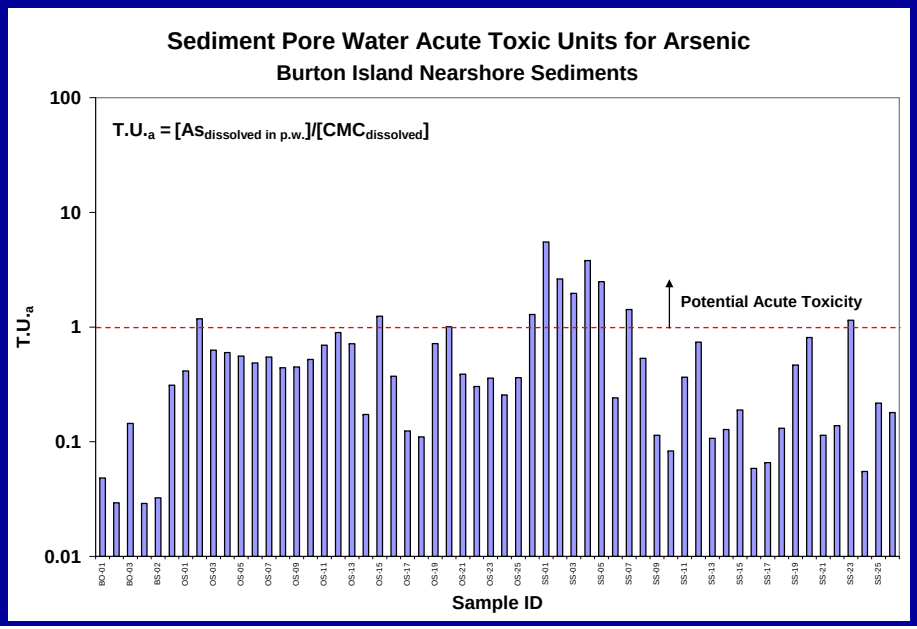
Predicted vs Observed Acute Tox EMAP / NCA Sediments



- Pore water arsenic conc. predicted using EqP & then compared to marine acute criterion
- Predicted values much less than criterion
- Predictions consistent with observations
- Acute tox observed in 3 samples likely due to other contaminants (e.g. ammonia, H_2S)

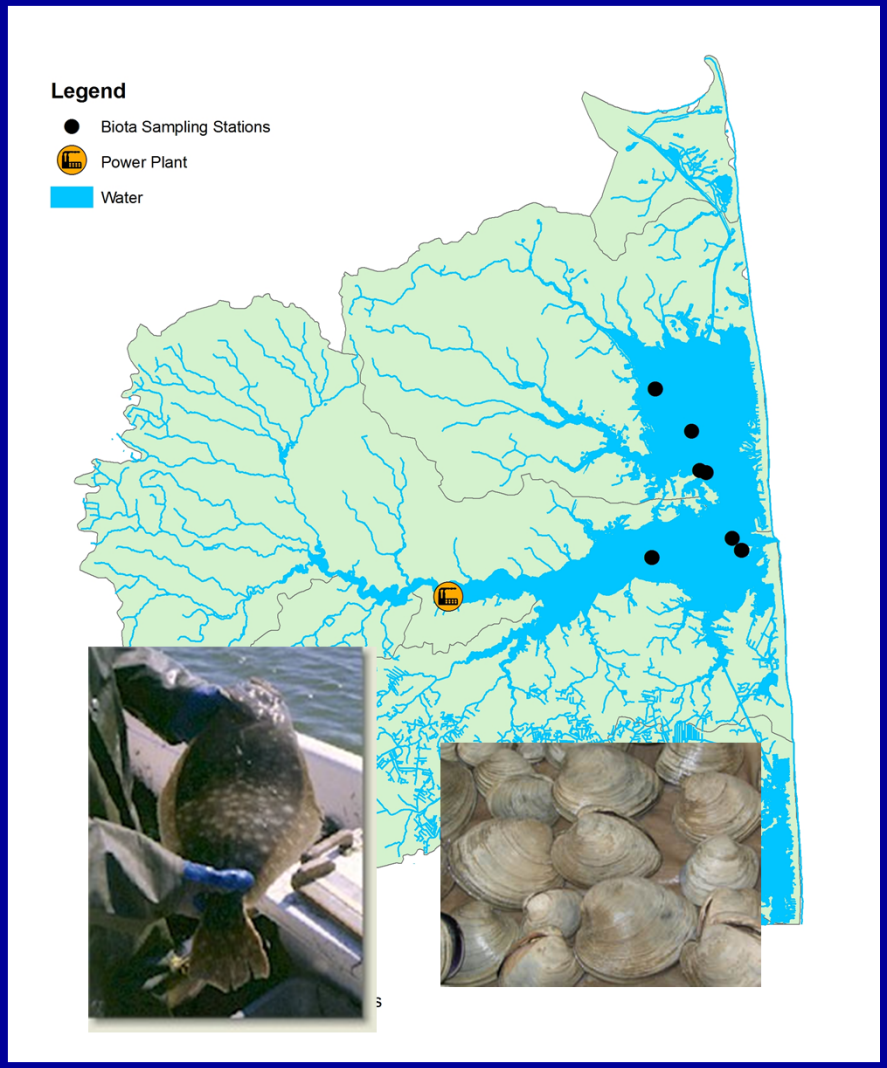
Burton Island Sediments





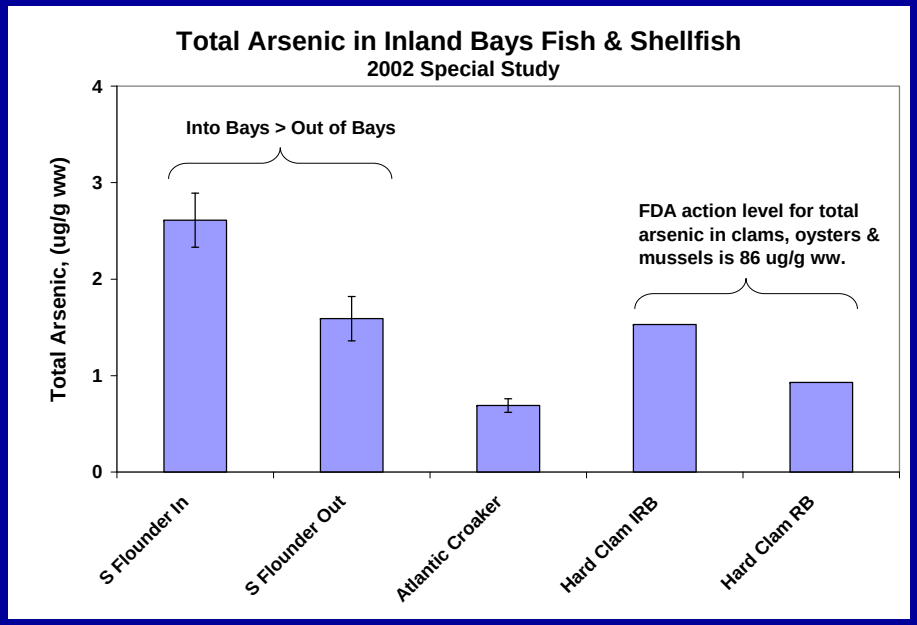
- Surface sediment samples collected May 2007 along the shoreline and slightly offshore as part of the Burton Island FE
- Again pore water arsenic conc. predicted using EqP & compared to acute aquatic life criteria
- Localized exceedances predicted along south shore of Burton Island at SS-01 through SS-05

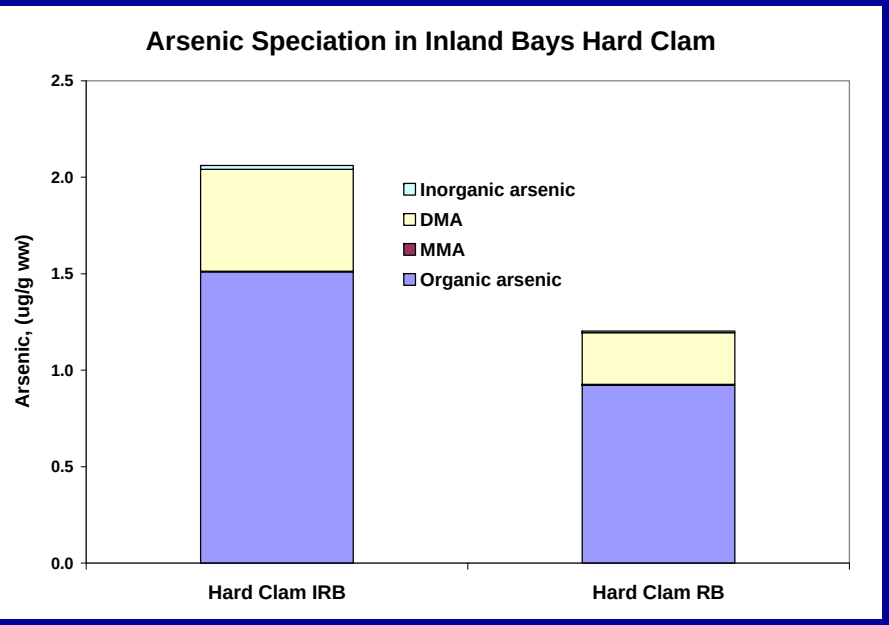
Fish/Shellfish Tissue Data

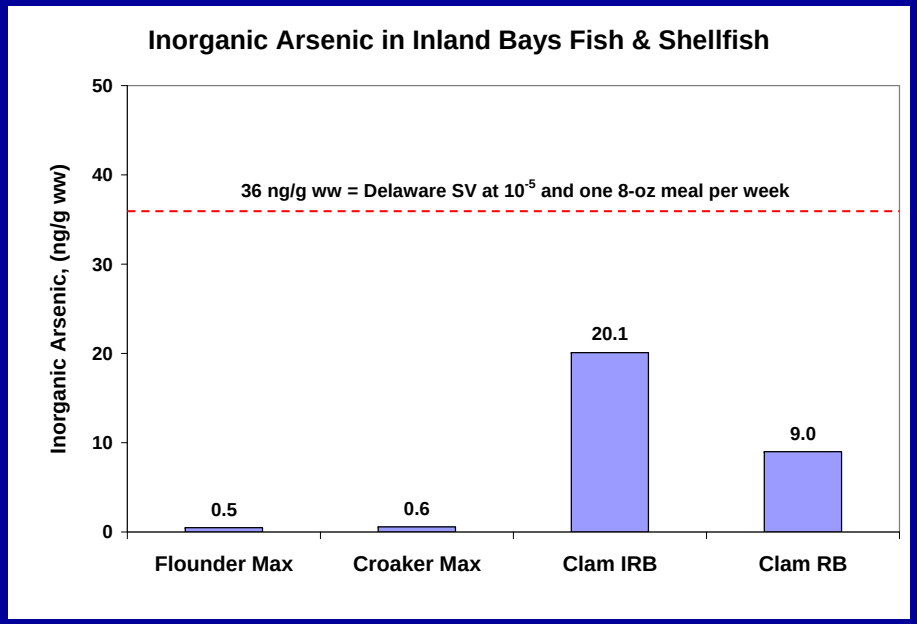


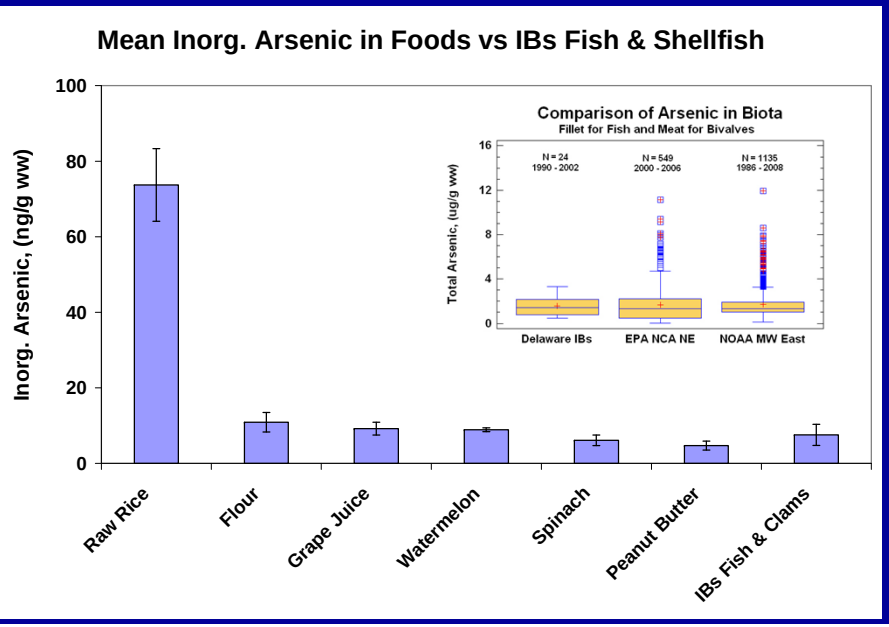
- DNREC data
  - *Total arsenic hard clam, flounder & croaker fillets (1990, 1991, 1992, & 1999)*
  - *Arsenic speciation study done on these same species (2002)*
  - *Data published in Greene & Crecelius (IEAM 2006)*
- EPA EMAP/NCA
  - *Not much fish data for IBs*
  - *No speciation data*

DNREC Arsenic in IBs Biota Data

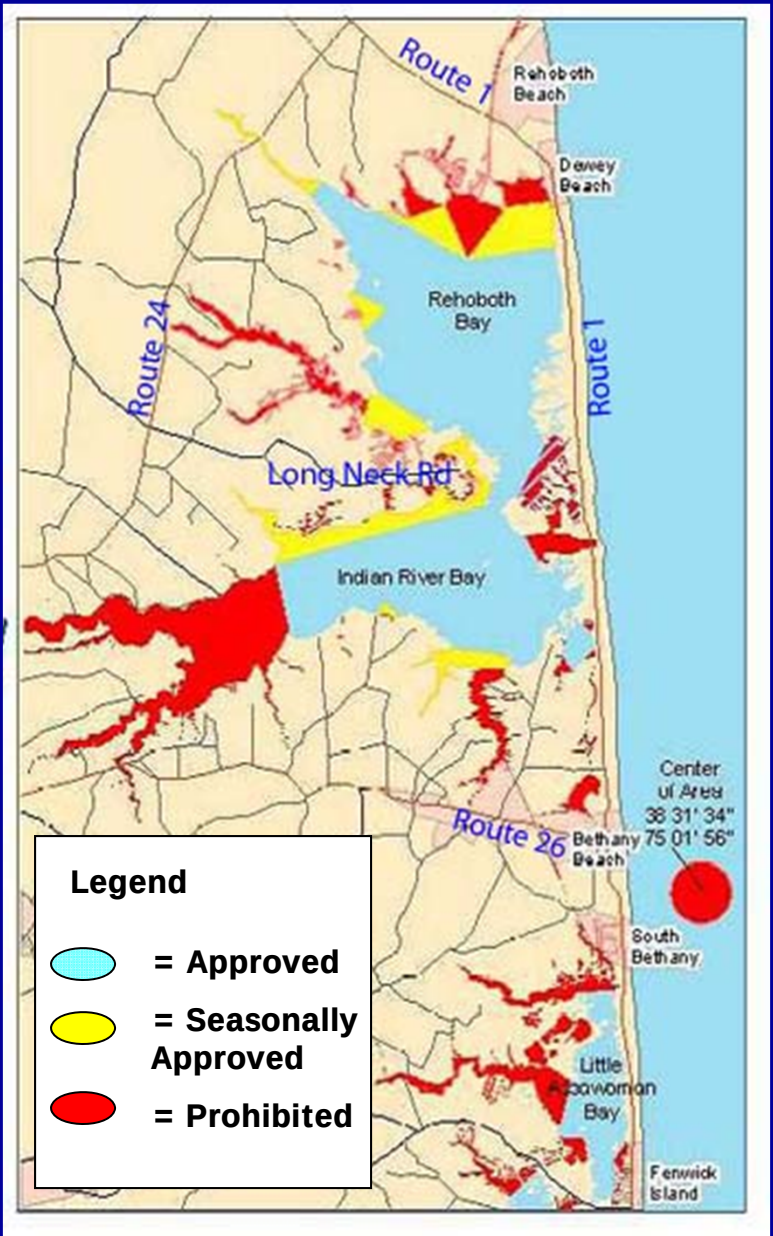








Key Findings from Special Study



- For fish & shellfish, it's critical to measure inorganic arsenic.
- Inorganic arsenic only detected in a few samples & at low levels (0.7% to 1.7% of total), per other studies.
- No specific advisory for arsenic warranted. General advice of 1meal/wk applies.
- New testing of clams in upper IR not justified since area already closed by DNREC. No exposure = No risk.

Air Data

- Scudlark & Church (UD CMS) measured bulk As dep at Cape Henlopen State Park 1985 to early 1990s
- LTA = 0.29 ug m^{-2} d^{-1}
- Loading translates to a conc of 0.088 ug/L in the IBs using a simple 1-box model (Greene 2010)

Summary of Findings

- Several natural & human sources of arsenic to IBs
- However, widespread arsenic problem does not exist in the Inland Bays. The data show that:
  - *Aquatic life criteria are not exceeded & few (~1%) samples exceed the applicable human health criterion*
  - *Sediments are not toxic to aquatic life*
  - *Consumption advisory for arsenic in fish & shellfish not needed*
  - *Atmospheric loading not high enough to cause problem*
- Arsenic from IRPP is localized. Programs in place to assess, control and mitigate as appropriate.
- Arsenic in poultry litter from ROX may contribute south of Indian River. Fortunately, iron in soil binds the arsenic & limits leaching to groundwater.
- Finally, lead-arsenate residue in Swan Creek soils may be important legacy source north of Indian River.

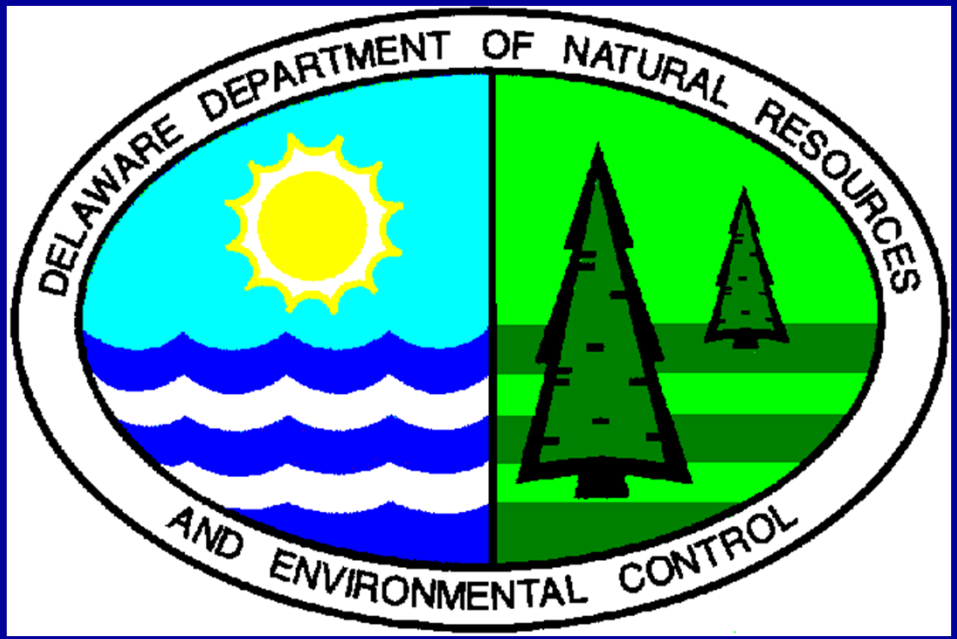
Recommendations

- Restore ambient monitoring for arsenic in Inland Bays surface water to track changes
- Estimate groundwater to surface water flux of arsenic from IRPP fly ash piles
- Collect representative samples at SG-2 in Island Creek
- Verify extent of current ROX usage by poultry industry. Promote use of manure sheds & alum to prevent leaching & runoff. Multiple benefits.
- Follow-up on possible legacy lead-arsenate residues in Swan Creek soils (small research project?)

Acknowledgements

- Dave Wolanski: mapping support
- Frank Gavas: IRPP landfill data
- Greg Decowsky & Step Scholl: Burton Island FE data
- Ben Pressley: ELS methods
- Andy Howard: aerial photo of IRPP
- Laura Mensch: DDA arsenic in groundwater data
- UD/DGS/USGS: colleague review
- Chris Bason & Dr. Bill Ullman: IBs STAC invitation

Questions?


DELAWARE DEPARTMENT OF NATURAL RESOURCES
AND ENVIRONMENTAL CONTROL

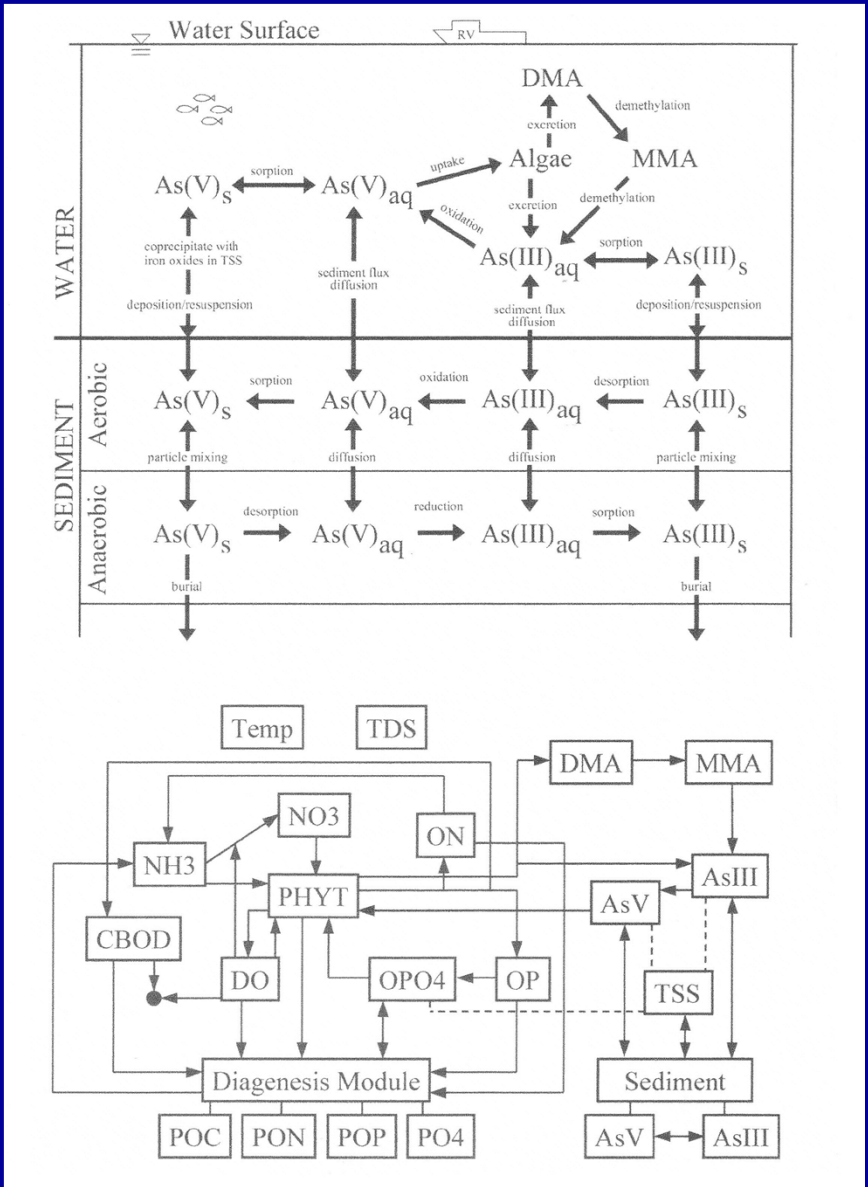
Bonus Material

- Chemical Profile
- Biogeochemical cycling of arsenic
- Coal & coal fly ash
- UD Undergrad Research Project

Chemical Profile – 

- *Natural background:* 0.15 - 2.1 ug/L (freshwater); 0.8 - 8 ug/L (ocean); 0.58 - 31 ug/g (DE soils)
- *Forms:* Arsenate (+V); arsenite (+III); arsine (-III), MMA, DMA, & organoarsenicals. As(V) dominant in surface water & fly ash; mostly organic forms in biota.
- *Toxicity:* Inorganic As toxic to humans & aquatic life. As(+III) more toxic than As(+V). Organic As in fish non-toxic & excreted following ingestion.
- *Mobility:* Affected by pH, redox & sorbents (e.g. Fe oxides & DOC). As(+III) more mobile than As(+V). Biogeochemistry determines arsenic form & fate.

Arsenic Biogeochemical Cycling



- Fate, transfer, & transformation is complex (Nice, Lung, & Riedel, ES&T 2008).
- Arsenic cycling is coupled to the eutrophication cycle.
- Arsenate “looks” like phosphate to algae & forams. Uptake & settling produce ‘greensand’ deposits.

Arsenic in Coal & Fly Ash

- Arsenic in bituminous coal = 9.0 ± 0.9 ppm (world ave)
- On an ash basis: 50 ± 5 ppm
- Potential release pathways to surface water: wind, runoff, leaching
- Mass loading from IRPP to IBs not fully quantified

UD Undergrad Research Project

- Done by Jenn Jennings under the direction of Dr. Thomas Church, CMS
- 36 surface water samples collected 1999/2000 (30 non-tidal & 6 tidal)
- Low-level, speciation method used to measure As(+V), As(+III), MMA & DMA, in addition to total arsenic
- Total (unfiltered) and dissolved (filtered) results reported.
- Some analytical problems with speciation data but totals appear OK.

UD Undergrad Research Project