From soils to streams: Characterizing Arsenic Sources and Movement into NJ Coastal Plain Streams

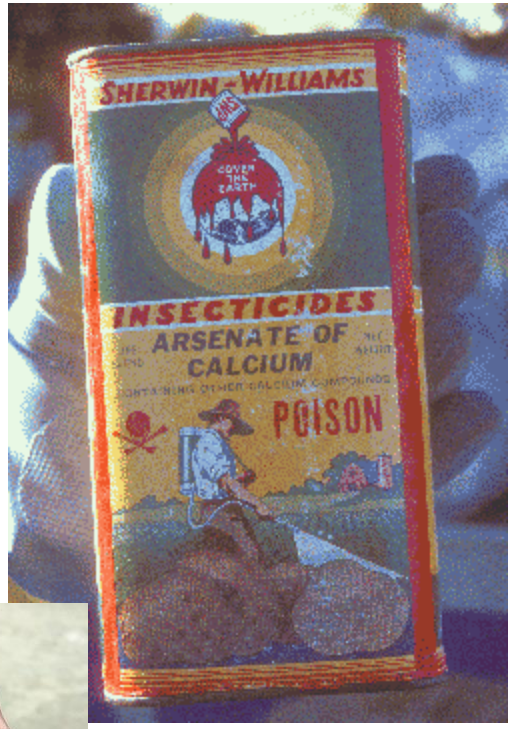
Pamela Reilly and Julia Barringer

U.S. Geological Survey

New Jersey Water Science Center

An elemental concern: Arsenic

- **Arsenic (As) is a metalloid**
  - Four oxidation states (-3, 0, +3, and +5)
- **Most prevalent forms in natural waters are Oxyanions**
  - Arsenite (H_3AsO_3 or As (III))
  - Arsenate (H_2asO_4 or As (V)
  - Health effects governed by form
- **Global health concern**
  - Carcinogen
  - Chronic exposure can damage multiple body systems



Hyperkeratosis

USGS science for a changing world

- Preliminary Information-Subject to Revision. Not for Citation or Distribution

Possible Arsenic Sources in Coastal Plain

"Natural" sources from arsenic-containing minerals

Historic pesticide, herbicide and fertilizer (?) use

USGS science for a changing world

- Preliminary Information-Subject to Revision. Not for Citation or Distribution

Study Objectives

- Preliminary Information-Subject to Revision. Not for Citation or Distribution

- Define sources (natural and anthropogenic)
- Define "Baseline" levels of arsenic in NJ streams
- Examine spatial distribution
- Examine factors affecting As speciation and mobility
- Examine anthropogenic influences on transport mechanisms

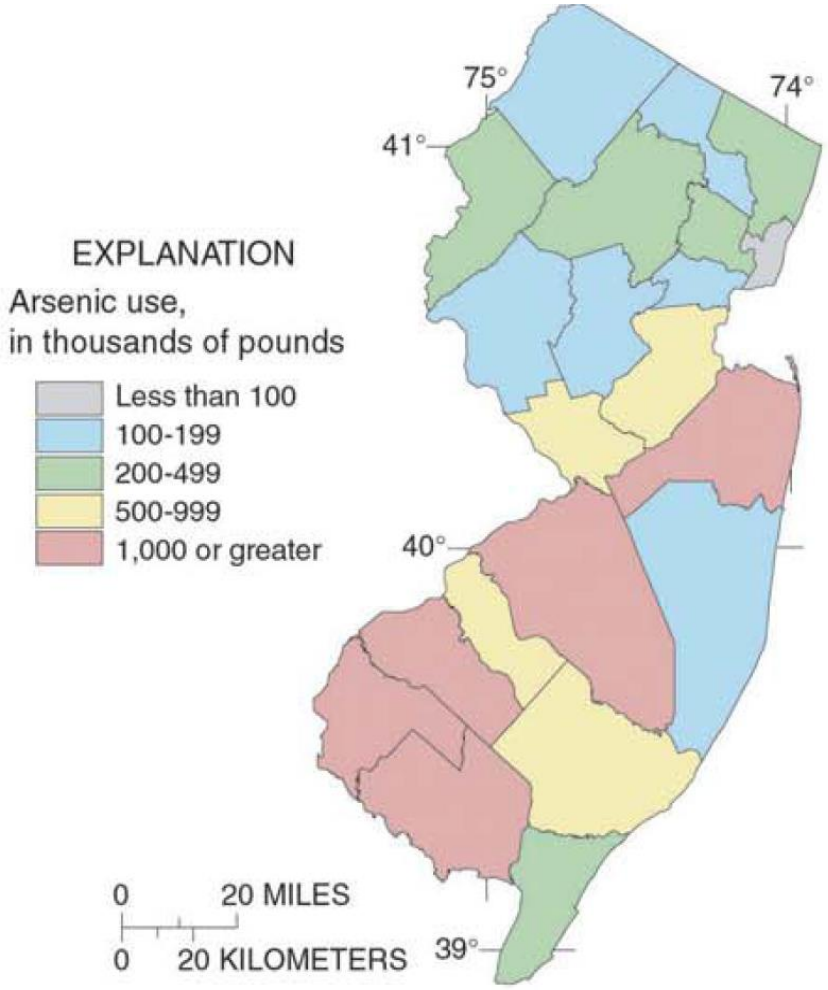


Figure 1. Estimated arsenic use in New Jersey, 1900-80. (Data from Murphy and Aucott, 1998)

Study Area

Five watersheds studied.

- Crosswicks (CRO), Raccoon (RAC), Oldmans (OLD) Creeks in the Inner Coastal Plain.
- Great Egg Harbor River (GEHR), Hammonton Creek (HAMM) in the Outer Coastal Plain.

- Preliminary Information-Subject to Revision. Not for Citation or Distribution

USGS science for a changing world

Study Approach

Examined relations among:

- Land use—past and present
- Geology of watershed
- Mineralogy of Sediments and Soils
- Stream-sediment chemistry and mineralogy
- Stream-water chemistry
- Chemistry of groundwater discharging to stream
- Stream and tributary hydrology
  - (flow regime, impoundments, hyporheic exchange)
- Microbiology (Rutgers University)

USGS science for a changing world

- Preliminary Information-Subject to Revision. Not for Citation or Distribution

Inner Coastal Plain – Land Use

- Preliminary Information-Subject to Revision. Not for Citation or Distribution

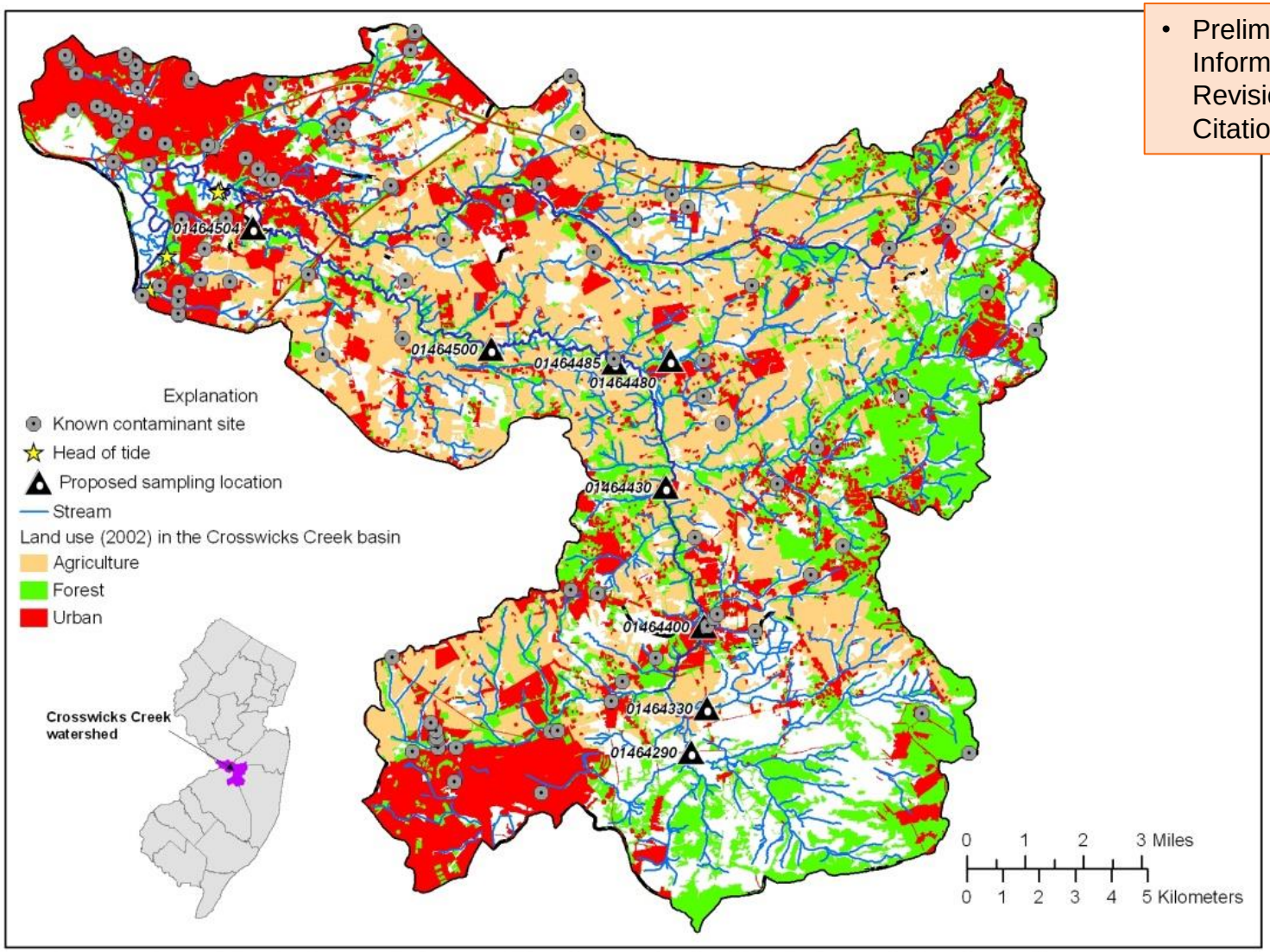
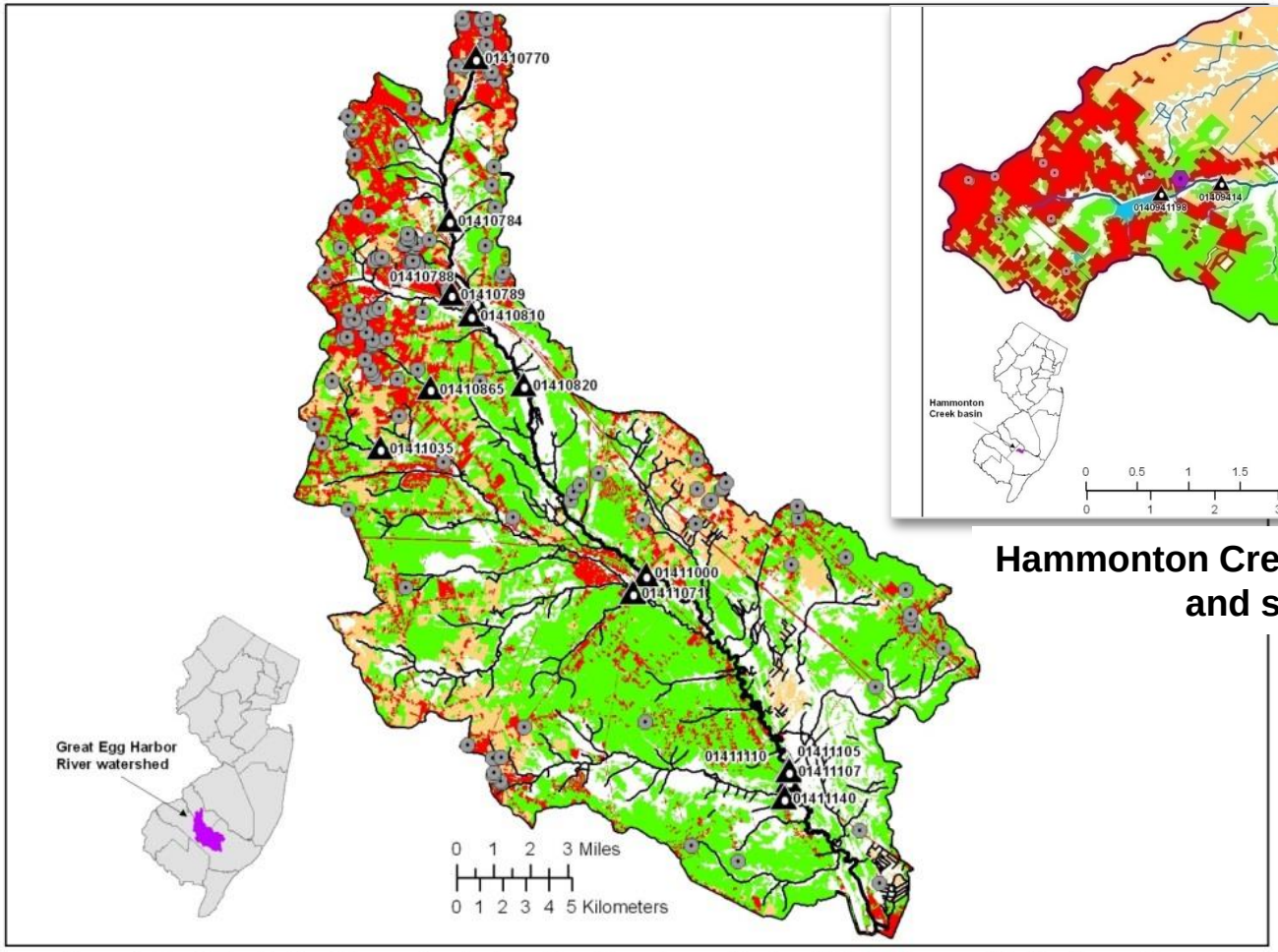


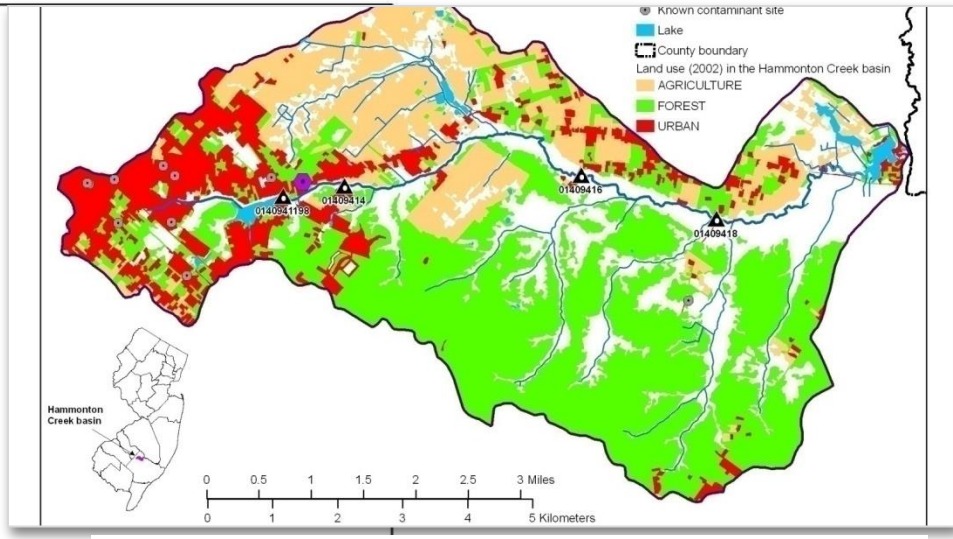
Figure 1. Crosswicks Creek watersheds central New Jersey, showing 2002 land use, the locations of known contaminant sites, and proposed sampling sites

Outer Coastal Plain

Sediments (deltaic and near-shore deposits) are quartz-rich and arsenic-poor.



Great Egg Harbor River watershed, 2002 land use and sampling locations



Hammonton Creek watershed, 2002 land use and sampling locations

- Preliminary Information-Subject to Revision. Not for Citation or Distribution

USGS science for a changing world

Arsenic in Aquifer Sediments

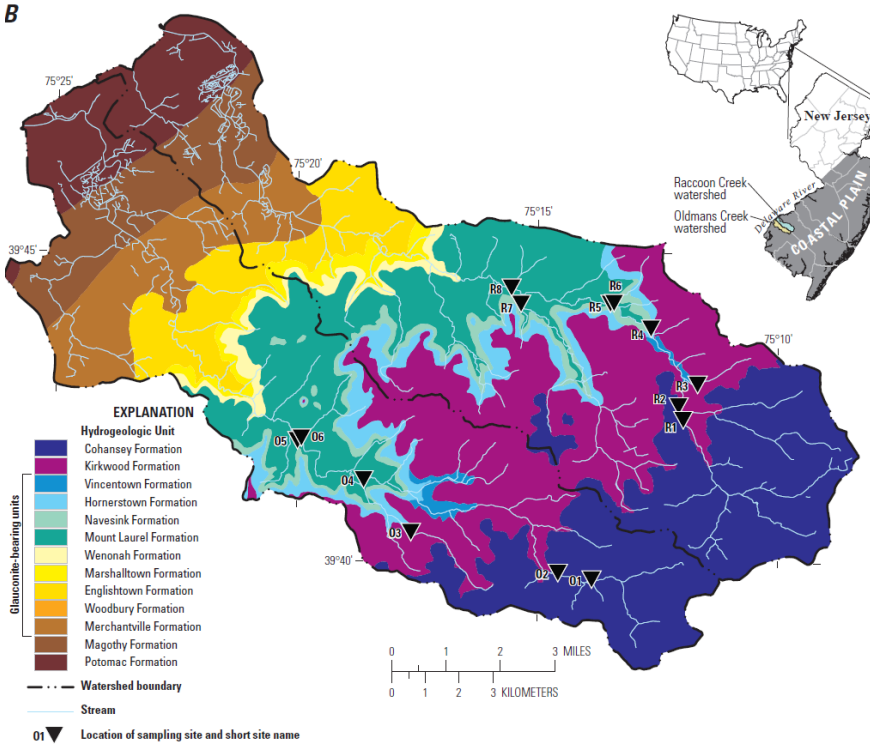
	Inner Coastal Plain	Outer Coastal Plain
Medium	***As (mg/kg)***	***As (mg/kg)***
Aquifer sediments	7-136; median 24 (Dooley, 2001)	<1.0-7.7; median 3.4 n = 11

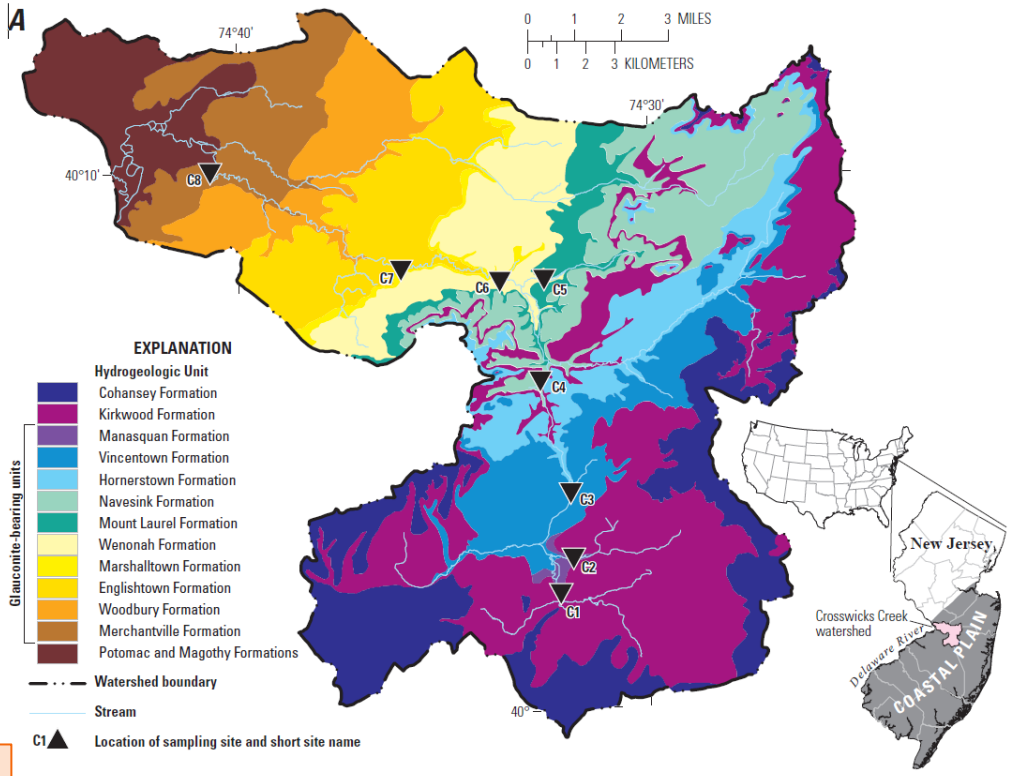
USGS science for a changing world

- Preliminary Information-Subject to Revision. Not for Citation or Distribution

Inner Coastal Plain – Sediments

- Some ICP formations contain glauconite
- As content of glauconite mineral separates and soils
  - 7-136 mg/kg (Dooley 2001)





USGS science for a changing world

- Preliminary Information-Subject to Revision. Not for Citation or Distribution

Aquifer Sediment Core

Outer Coastal Plain

- Preliminary Information-Subject to Revision. Not for Citation or Distribution

Site name/ depth (m)	Description	As (mg/kg)	Pb (mg/kg)	Org. C (%)
Academy/15.5-15.7	fine quartz sand, ilmenite	1.20	2.06	0.07
Academy/29.0-29.1	quartz sand, clay, ilmenite	5.40	10.4	0.28
Denise/9.0-9.1	fine sand, gray clay	3.80	2.27	0.09
Denise/25.6-25.7	brown/black clay	3.40	10.0	1.97
Denise/33.0-33.1	black clay	7.70	17.1	2.85
Oak/15.6-15.7	medium sand, silt, mica	5.90	2.24	0.14
Oak/22.4-25.6	sand, clay, lignite	4.90	19.7	2.06
Oak/39.8	coarse quartz sand	0.50	5.64	0.19
Oak/39.9-40.1	black sand, lignite	1.30	2.74	0.33
Church/26.9-27.0	gray clay, mica	3.40	13.3	0.16
Church/27.1-27.2	sand, ilmenite	0.50	9.83	0.08

USGS science for a changing world

Arsenic in Coastal Plain Soils

	Inner Coastal Plain	Outer Coastal Plain
Medium	***As (mg/kg)***	***As (mg/kg)***
Soils	13-131; median 29.5 (from Dooley 2001)	<1-13.3; median 3.9 n = 12

USGS science for a changing world

- Preliminary Information-Subject to Revision. Not for Citation or Distribution

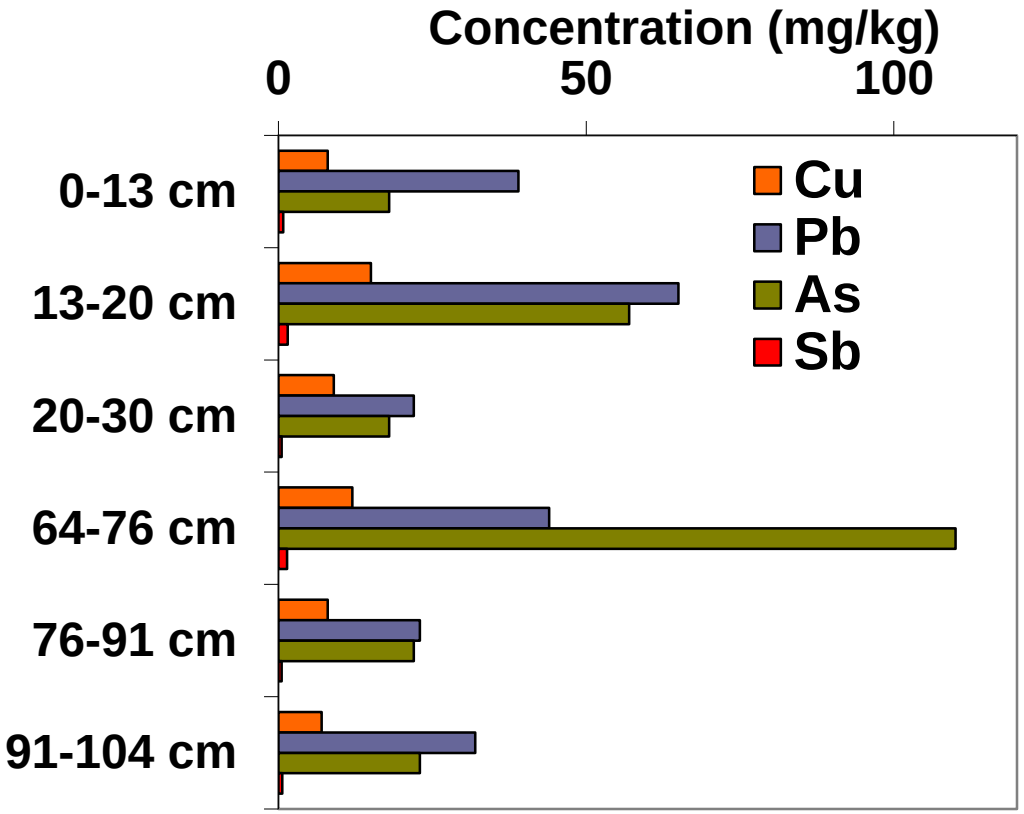
Inner Coastal Plain - Soils

- Pesticide residues may amplify As of geologic origin

Raccoon Creek

- Coastal Plain
  - 16→3 mg/kg As with depth

- Glauconitic soils:
  - 12-45 mg/kg As in bankside soils



Depth profile of a bankside soil core within Glauconite-bearing soils of an old orchard area, Crosswicks Creek, NJ

USGS science for a changing world

- Preliminary Information-Subject to Revision. Not for Citation or Distribution

Streambank Soil Core

Outer Coastal Plain

Squankum Branch - site number and location	Sample number	Depth interval (m)	Arsenic (mg/kg)	Copper (mg/kg)	Lead (mg/kg)
01410862					
Left bank	MA1	0-3	4.4	29.8	115
Left bank	MA2	0.3-1.0	<1	2.3	3.83
Right bank	MC1	0-0.3	12.4	70.1	337
Right bank	MC2	0.3-1.0	6.2	58.2	229
01410863					
Left bank	DA1	0.4-0.7	12.7	158	245
Left bank	DA2	0.7-1.0	3.3	36.2	65.6
Right bank	DC1	0-0.3	13.3	65.9	386
Right bank	DC2	0.3-0.8	9.5	101	404

As contents >10mg/kg may indicate pesticide residues amplifying geogenic inputs in Outer Coastal Plain

- Preliminary Information-Subject to Revision. Not for Citation or Distribution

USGS science for a changing world

Arsenic in Streambed Sediments

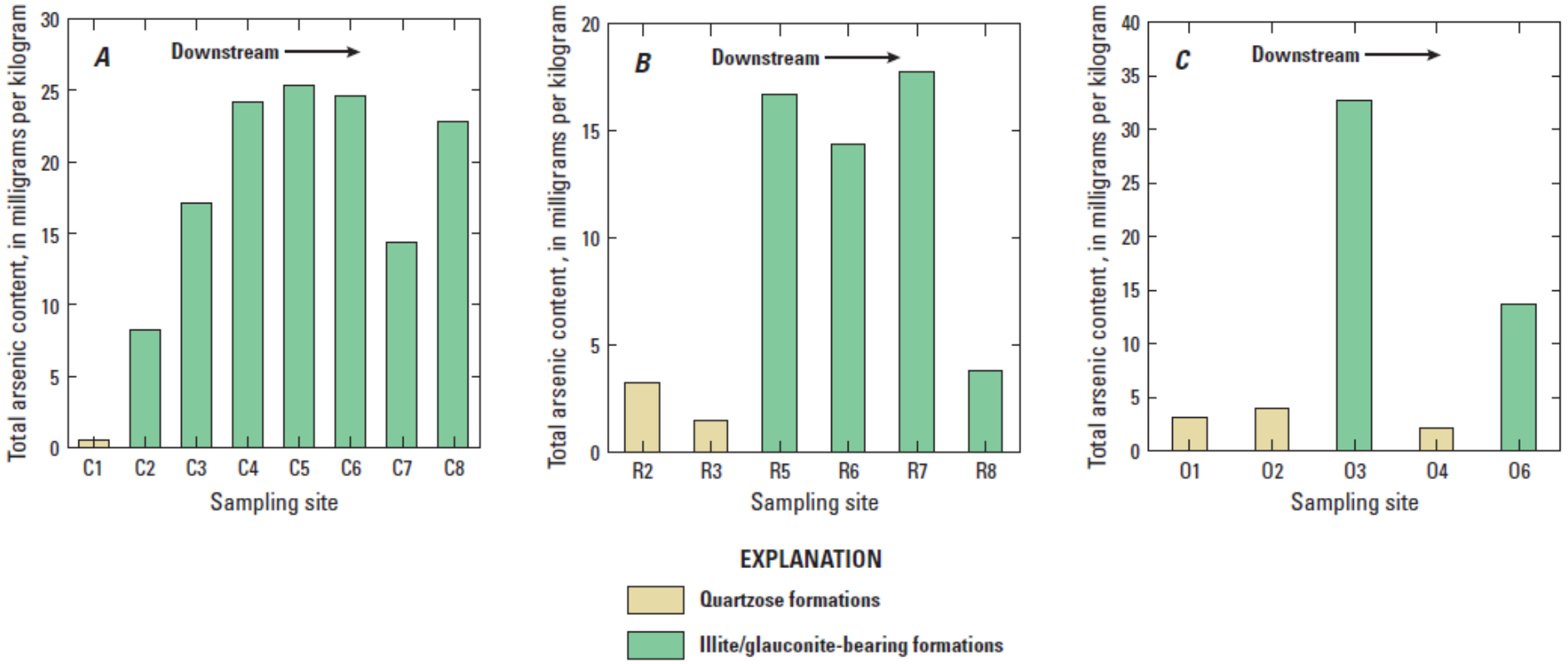
	Inner Coastal Plain	Outer Coastal Plain
Medium	***As (mg/kg)***	***As (mg/kg)***
Streambed sediments	<1-34.7; median 14.1 n = 25	<1-2.4; median <1 n = 16

- Preliminary Information-Subject to Revision. Not for Citation or Distribution

USGS science for a changing world

Streambed Sediments

Inner Coastal Plain



Contents of total arsenic in streambed sediments at A) Crosswicks Creek, B) Raccoon Creek, and C) Oldmans Creek. Downstream direction from left to right.

- Preliminary Information-Subject to Revision. Not for Citation or Distribution

USGS science for a changing world

Mineralogy of Streambed Sediments

Inner Coastal Plain

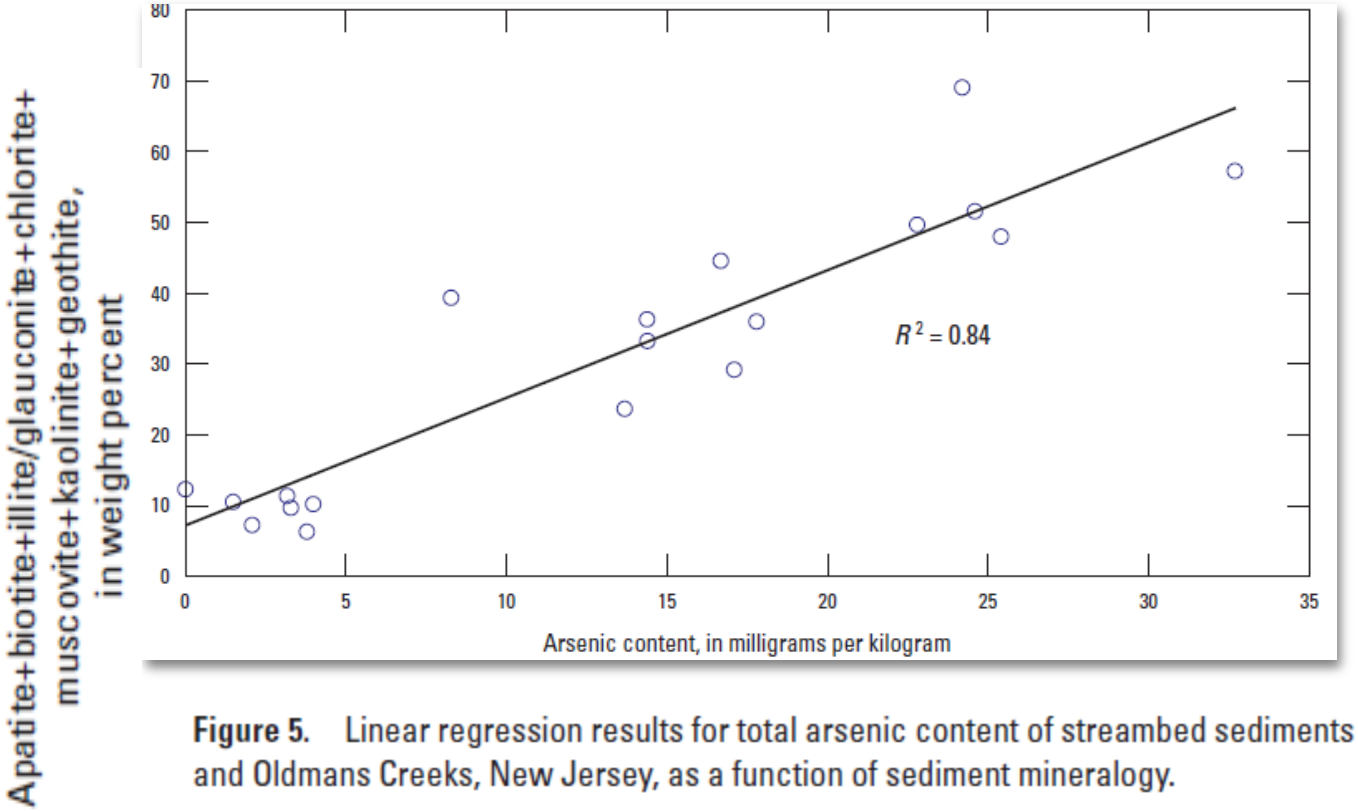


Figure 5. Linear regression results for total arsenic content of streambed sediments from Crosswicks, Raccoon, and Oldmans Creeks, New Jersey, as a function of sediment mineralogy.

The total As content of the sediments was strongly related to apatite, phyllosilicates, aluminum and iron.

- Preliminary Information-Subject to Revision. Not for Citation or Distribution

USGS science for a changing world

Streambed Sediments

Outer Coastal Plain

Total As content of streambed sediments generally < 2mg/kg or ND

As Content in HAMM sediments highest downstream of lake and STP

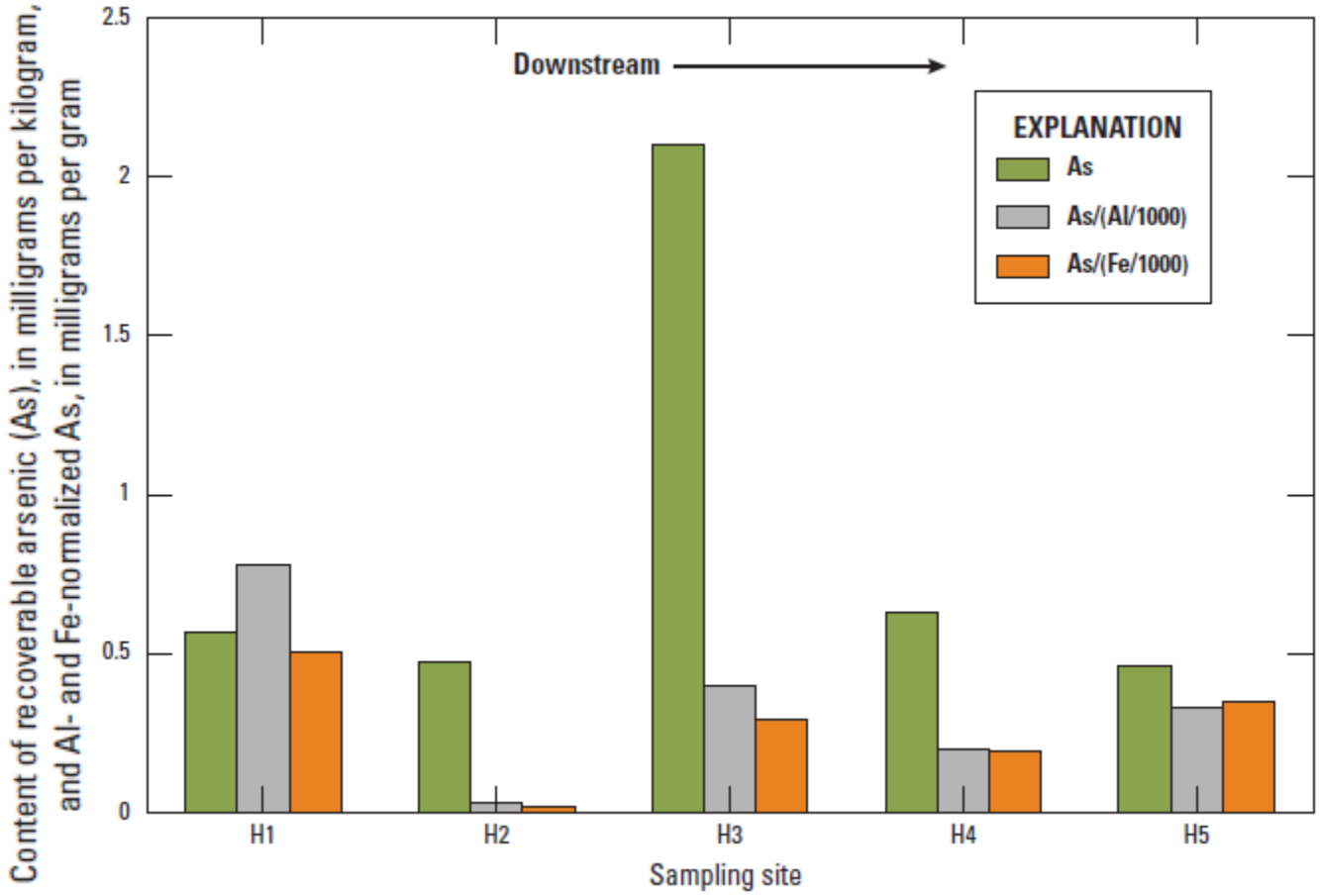


Figure 7. Streambed-sediment contents of recoverable arsenic (As) and As normalized to iron (Fe) and aluminum (Al) at five sampling sites on Hammonton Creek (HAMM), Outer Coastal Plain, New Jersey, 2007.

USGS science for a changing world

Water Quality Sampling

- Stream water sampled at high and low flows.
- Groundwater sampled using PVC piezometers installed ~0.5-1 m below streambed in gaining reaches
- Ultraclean sampling techniques used.
- All equipment acid-washed, rinsed with de-ionized-water.
- Analysis for major ions, nutrients, trace elements, organic carbon.

Arsenic in Coastal Plain waters

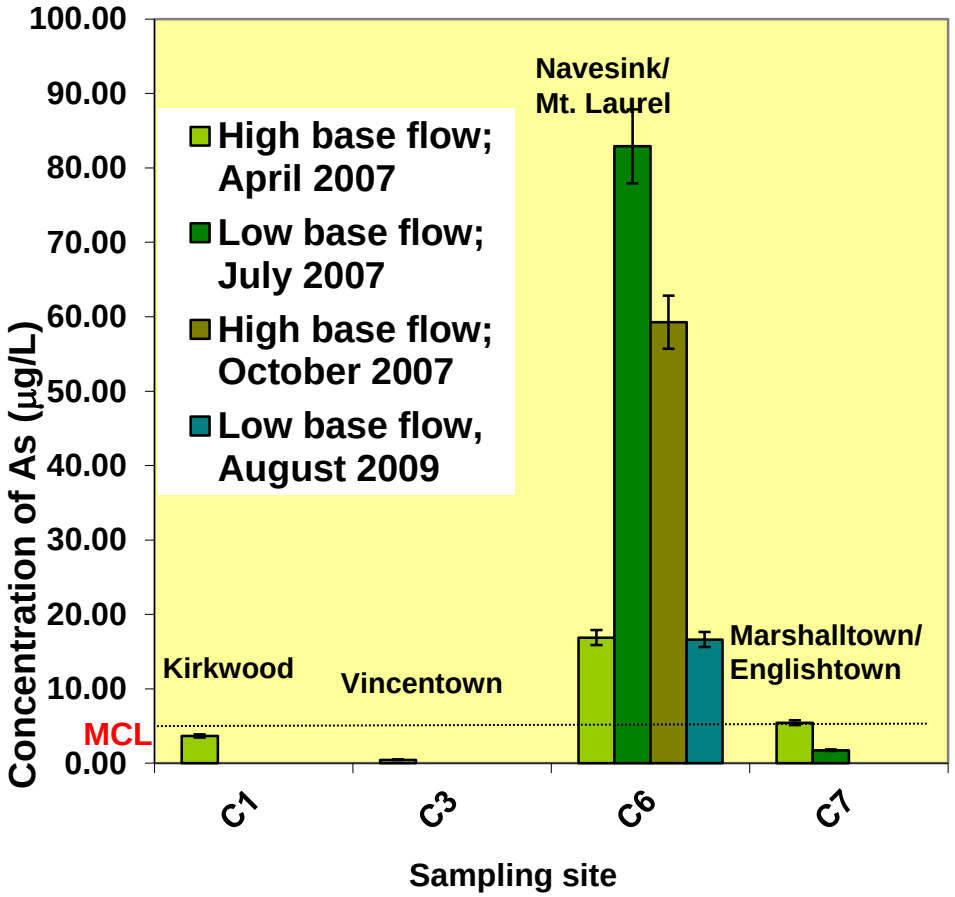
USGS science for a changing world	**Inner Coastal Plain**	**Outer Coastal Plain**
Medium	***As (μg/L)***	***As (μg/L)***
Groundwater	<0.12-**89.2** median 6.31 n =16	<0.12-**6.92** median 0.10 n = 21
Streamwater	0.18-1.27 median 0.59 n = 48	0.21-1.09 median 0.46 n =31

Arsenic in filtered water, sampled over various flow regimes.

- Preliminary Information-Subject to Revision. Not for Citation or Distribution

Shallow Groundwater

Inner Coastal Plain



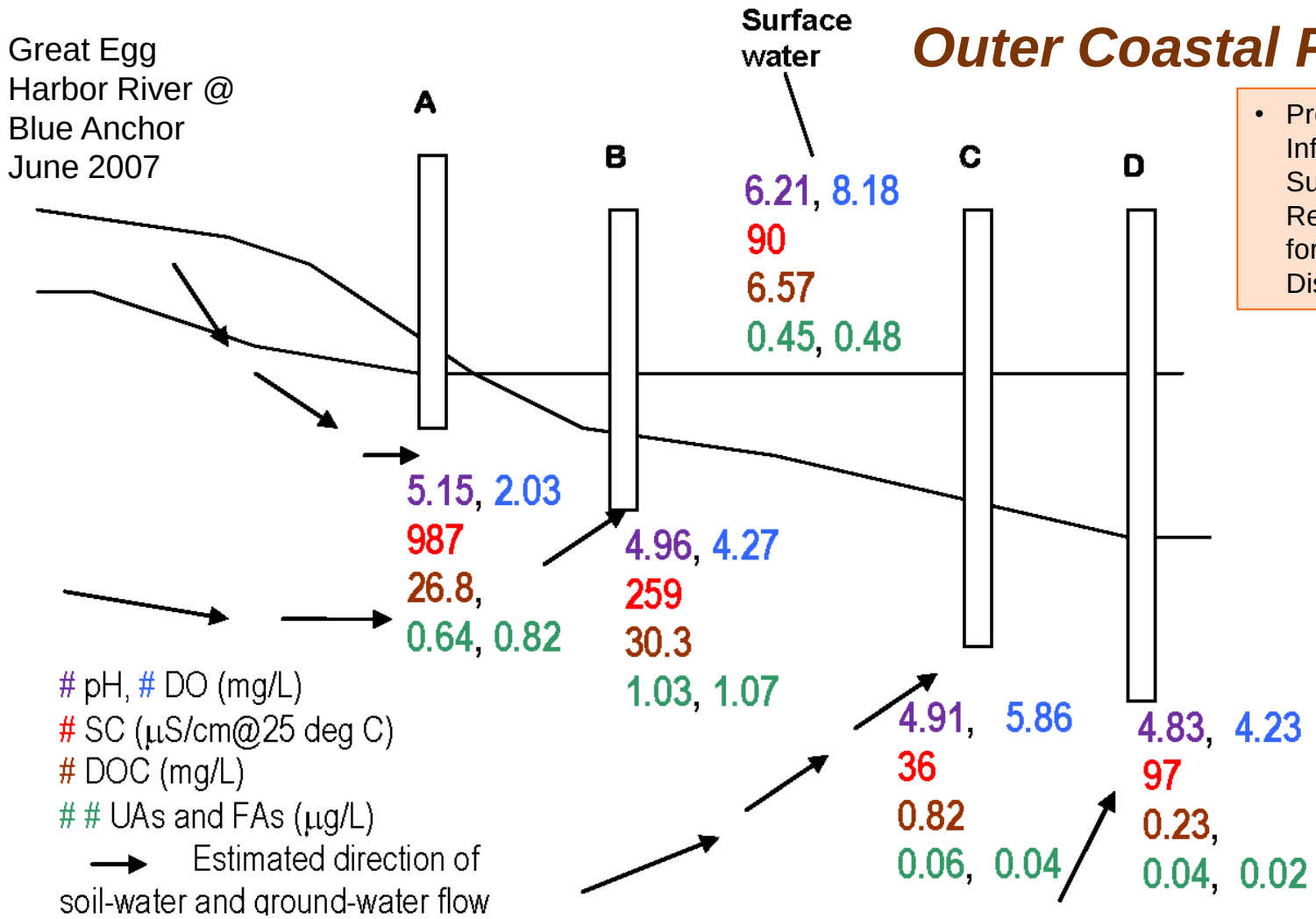
Concentrations of unfiltered As (Asf) in ground water discharging to Crosswicks Creek, 2007 and 09. Geologic formations indicated.

- Shallow groundwater varied seasonally and with hydrologic conditions (2007 was a dry year, and 2009 a wet year).
- As species were about 50% each As(III) and As(V)
- Elevated As in groundwater seen in urban areas underlain by As bearing sediments in ICP
- As concentration of 49ug/L correlated with Iron at a GW seep

USGS science for a changing world

Shallow GW Transect

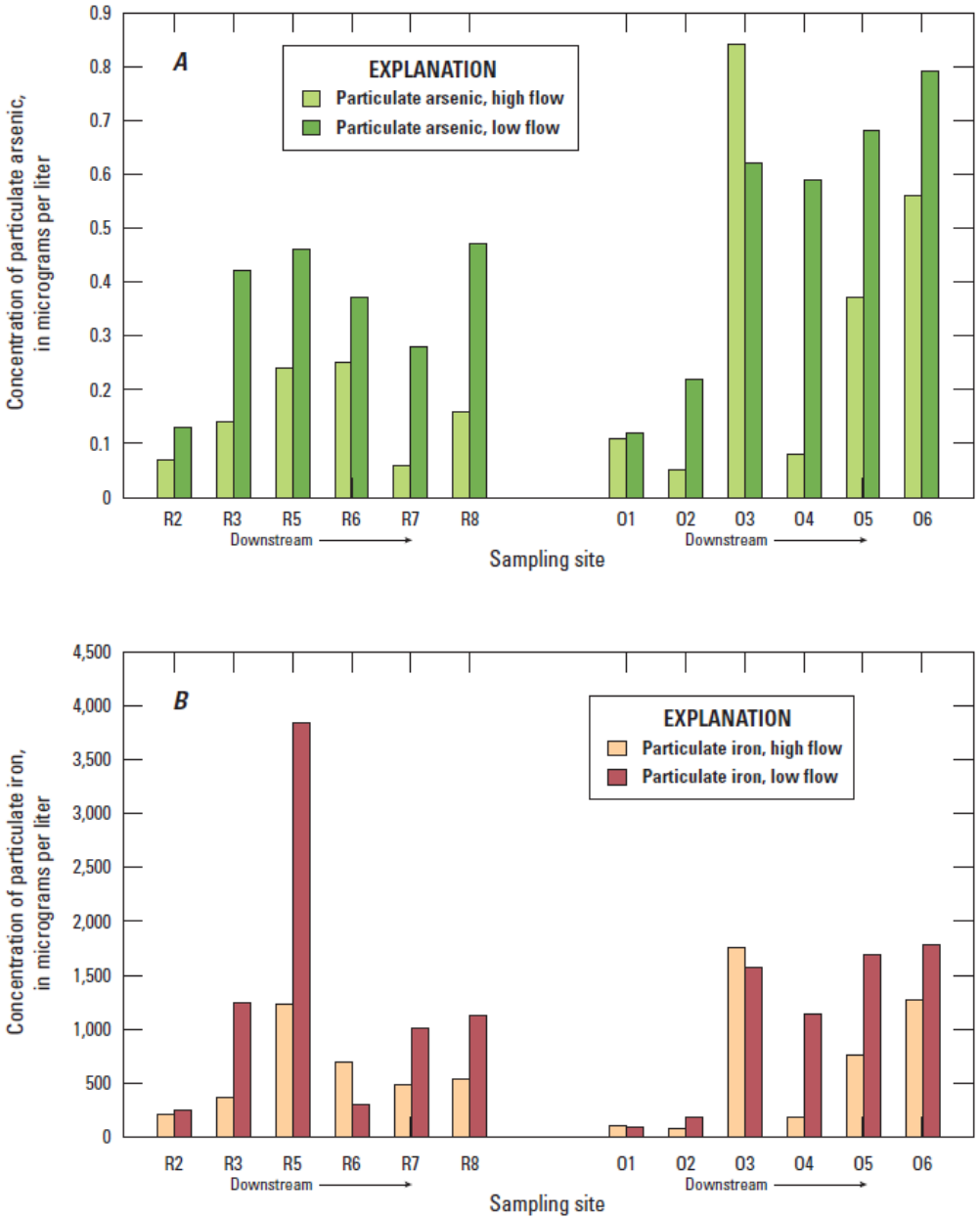
Great Egg Harbor River



USGS science for a changing world

Surface water - ICP

- Dissolved As similar over various flow regimes
- At high-flow at CRO most As in particulate form
- Strong association between Particulate As and Fe
- High particulate As at low flow indicative of in-stream processes



Concentrations of *A*, particulate arsenic and *B*, particulate iron under different flow regimes from Raccoon Creek and Oldmans Creek, 2007.

- Preliminary Information-Subject to Revision. Not for Citation or Distribution

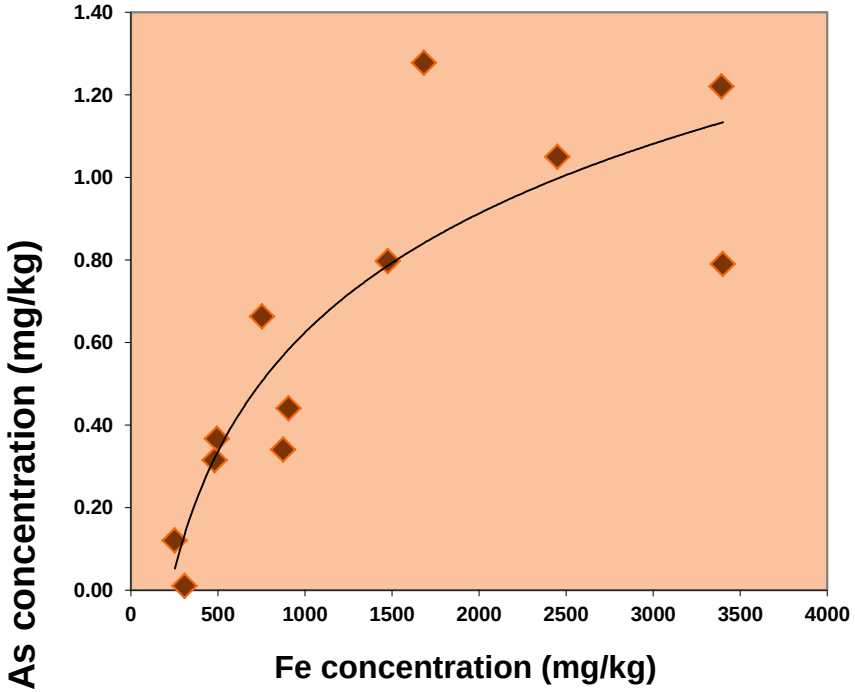
Surface water

Outer Coastal Plain

- **As concentrations:**
  - Generally 0.4-0.65 ug/L
  - Increased in areas of urban/residential land use (0.76-1.0 ug/L) with higher concentrations of particulate As
  - Varied seasonally at Hammonton Lake

Where is the Arsenic in streams?

- Elevated As(III) GW released to surface water at a gaining reach.
- As(III) oxidized and sorbs or precipitates with iron and then sorbs onto sediments in stream
- At high flow arsenic load in SW higher due to sorption on sediments

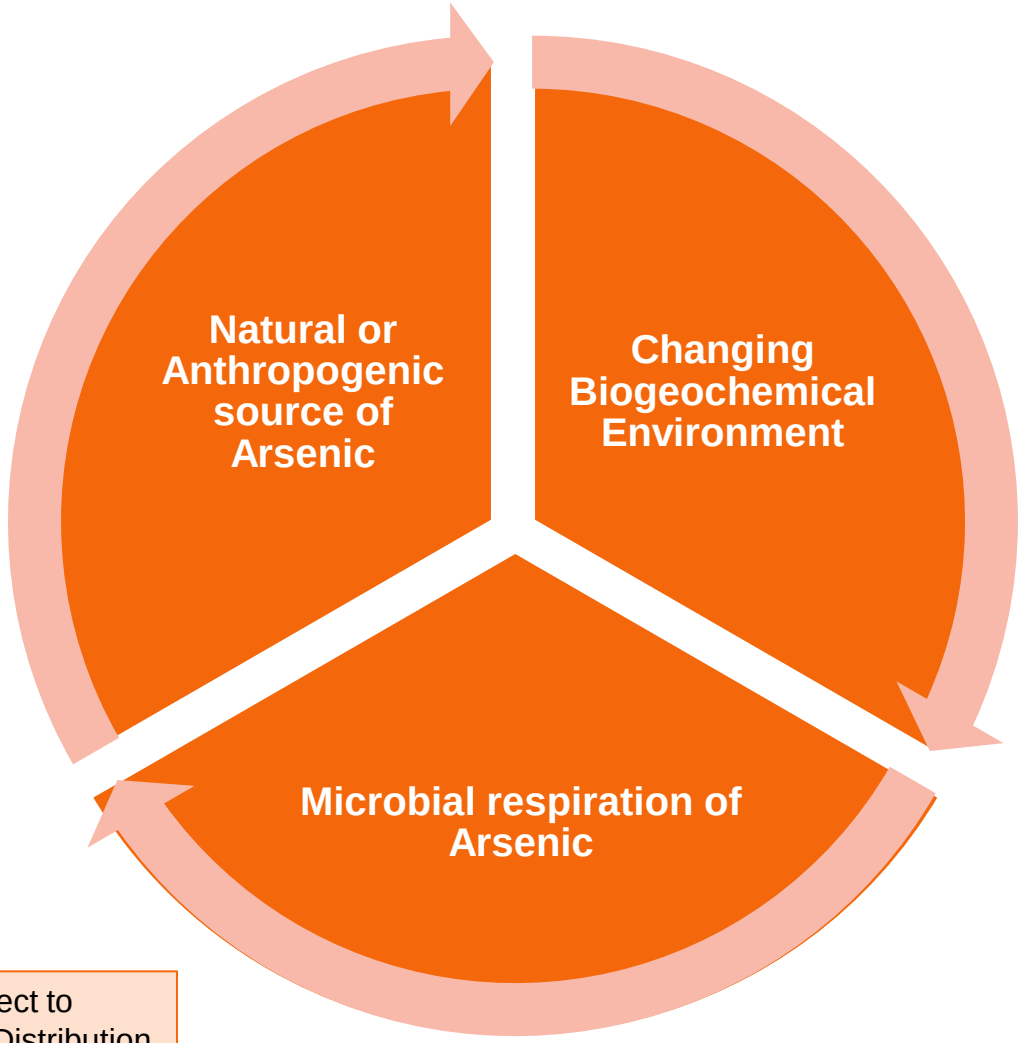


Relation of recoverable concentrations of As to Fe, bed sediments from the GEHR and its tributaries, October-December 2006

- Preliminary Information-Subject to Revision. Not for Citation or Distribution

USGS science for a changing world

Biogeochemical conditions influence arsenic mobility



- Preliminary Information-Subject to Revision. Not for Citation or Distribution

USGS science for a changing world

Microbial Ecology of GW and Streambed Sediments

- **Characterization of microbial communities by sequence analysis**
  - **Presence of arsenic respiratory reductase gene (*arrA*).**
- **Microbial Community indicate potential for arsenic release:**
  - **Geobacter species and Alkaliphilus oremlandii**

Such bacteria have been shown to reduce As (also Fe) contained in minerals, and to mobilize As.

USGS science for a changing world

Microbial As release

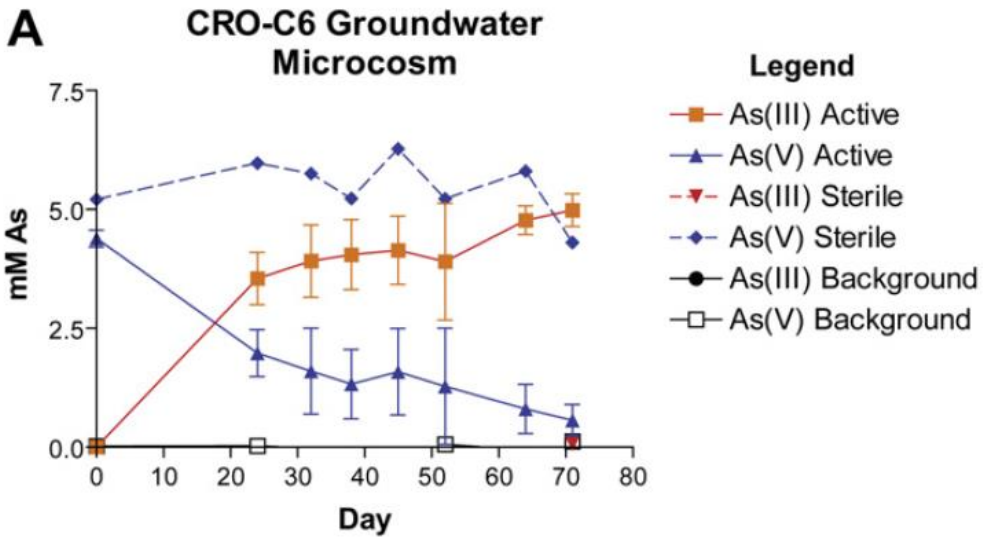
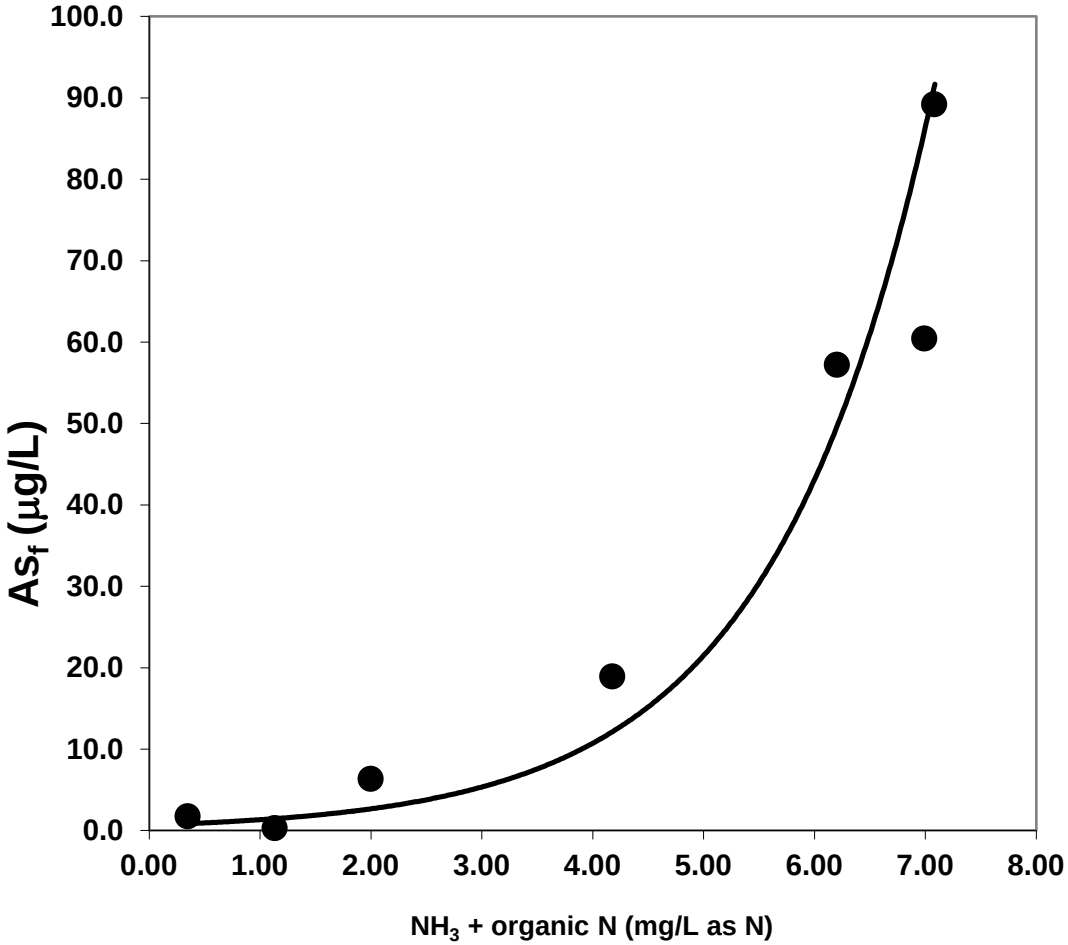


Figure 6. Results of microcosm studies inoculated with groundwater from C6

- **Geogenic As release by direct reduction of As(V) to mobile As(III) by arsenic-respiring microbes.**
- **Reductive dissolution of iron hydroxides by microbes may release arsenate**

Anthropogenic influences on As release to groundwater



Relation of As_f to NH_3 + organic N in shallow groundwater discharging to Crosswicks Creek from illite/glauconite-bearing aquifers

Higher As concentrations seen with:

- Elevated Cl-
- Elevated Boron
- Elevated DOC
- Redox Indicators
  - Low Dissolved Oxygen
  - Low NO^{-3}
  - Elevated NH^{3+}
  - Elevated Iron

- Preliminary Information-Subject to Revision. Not for Citation or Distribution

USGS science for a changing world

Changing geochemical conditions may mobilize As

Inner Coastal Plain

Crosswicks Creek (C6)c

- As(f) <1-89 ug/L
- High DOC (13-14 mg/L)
- NH4+ (3.2-7.0 mg/L as N)
- Chloride (20 mg/L)

Raccoon Creek

- As(f) 4-12 ug/L
- Increased DOC
- Increased Cl-
- Increased Phosphorus

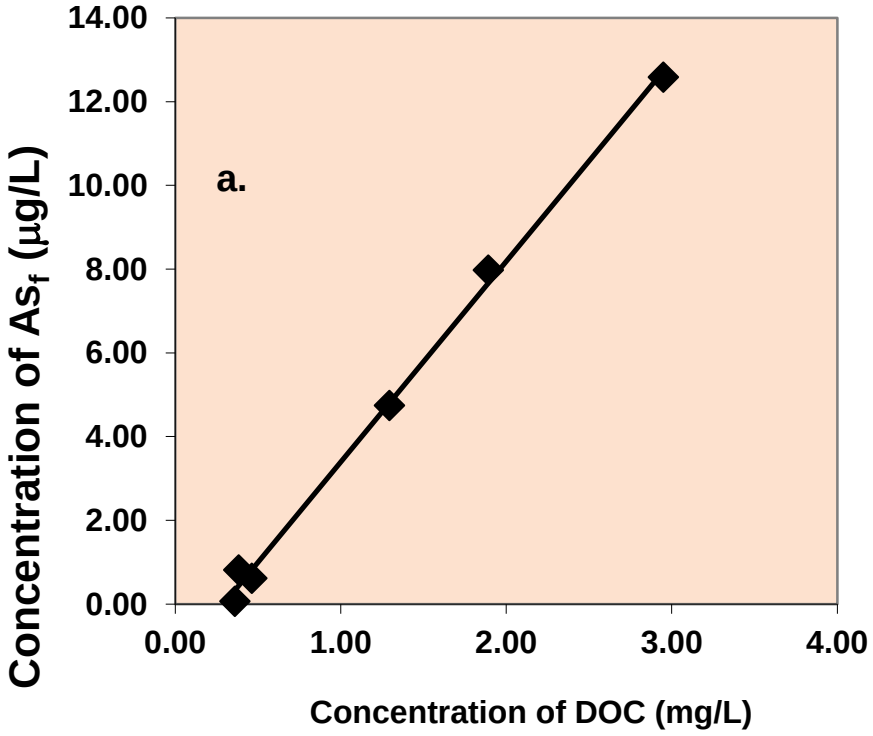
Outer Coastal Plain

Great Egg Harbor River

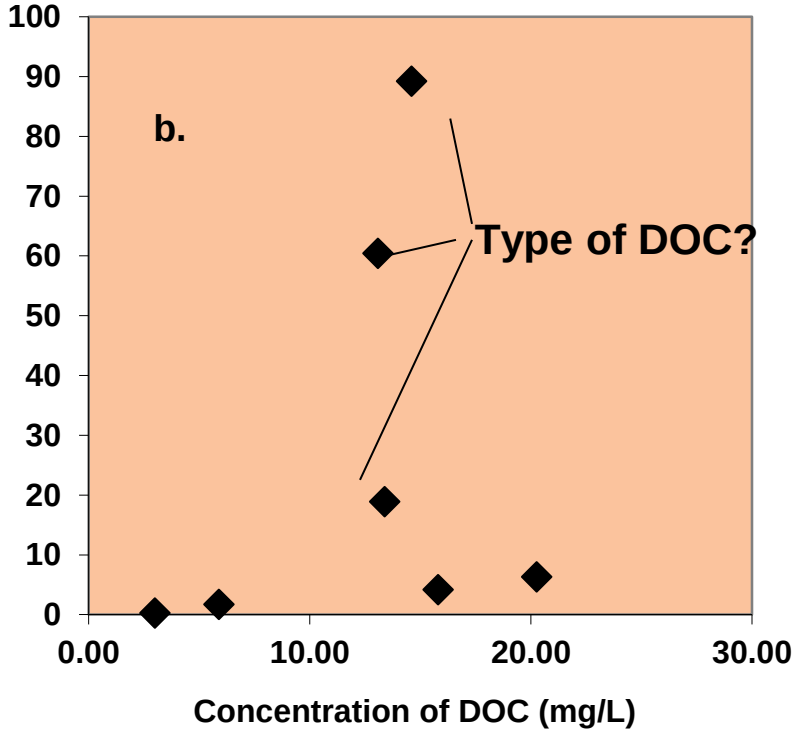
- GA– urban land use
  - As (f) ~7.0 ug/L
  - Chloride (79.9 mg/L)
  - Increase NH4+
  - Iron 29,600 ug/L
  - Increased DOC
- GC – Mixed land use
  - more oxidizing conditions
  - Increased As(u) ~ 7.0 ug/L
  - Increased DOC
  - Sulfate

USGS science for a changing world

The role of organic matter on As release



Relation of concentrations of filtered arsenic (As_f) to DOC, groundwater discharging to RAC, 2007



Relation of concentrations of As_f to DOC, groundwater discharging to CRO, 2007

- Preliminary Information-Subject to Revision. Not for Citation or Distribution

USGS science for a changing world

Wrap up

- Preliminary Information-Subject to Revision. Not for Citation or Distribution

- Most of the arsenic in the Inner Coastal Plain streams is of geologic origin; differentiating additional pesticide inputs to these streams is challenging.

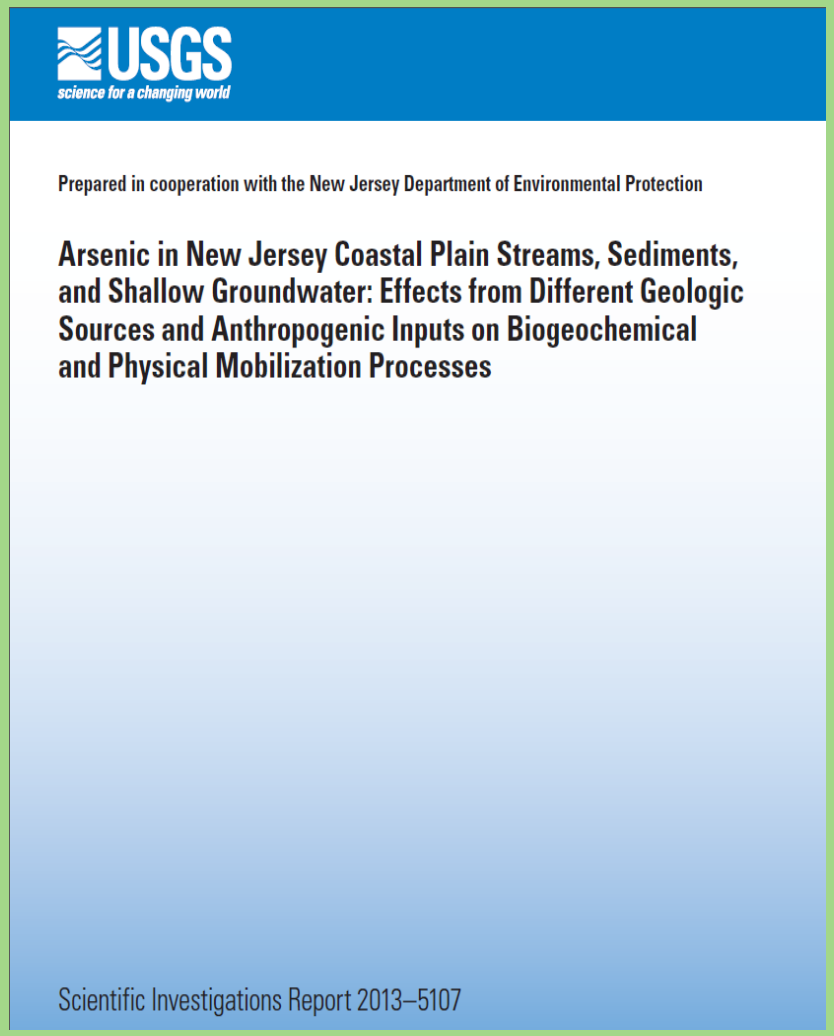
- Arsenic concentrations in Outer Coastal Plain streams are generally <1 ug/L, but still exceed the SWQS of 0.017 ug/L.

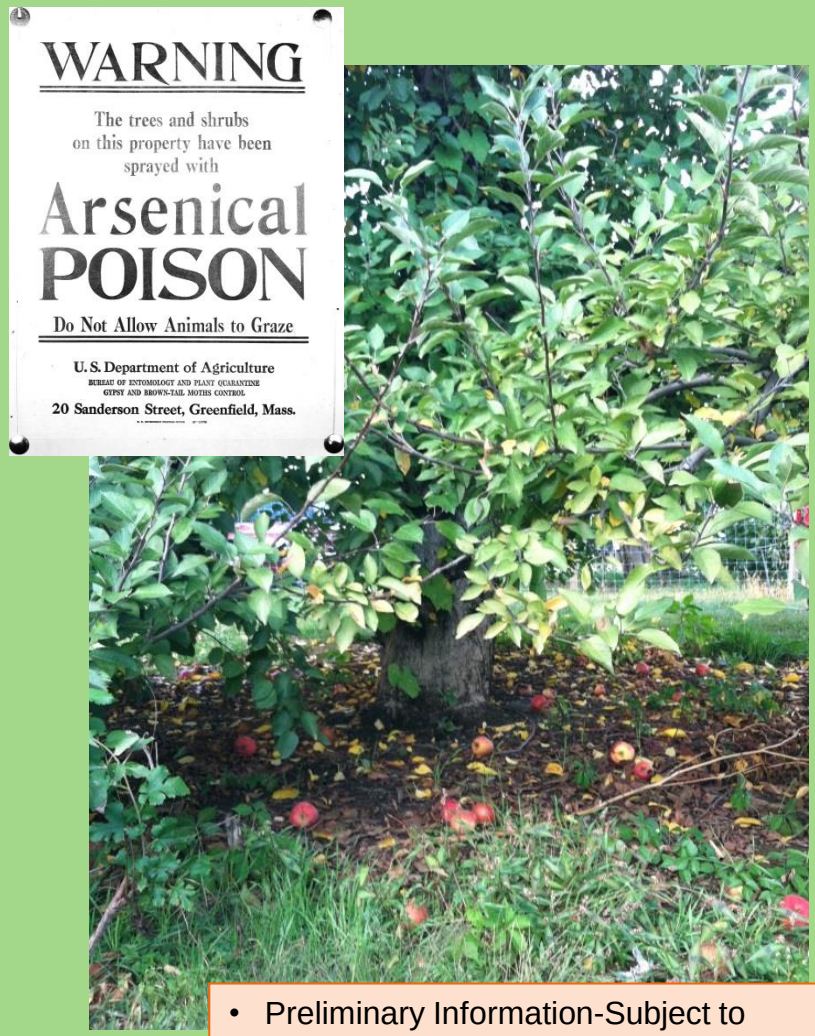
- The net arsenic contribution to a stream from discharging ground water is controlled by the complex geochemical and biological processes within, sediments, streambed and overlying waters.

- Anthropogenic inputs (DOC, Nutrients, etc..) may create geochemical changes within shallow groundwater that appear to enhance release of sediment bound As.

- Changes in land use may increase pH and lead to As desorption.

Report and references online at: http://pubs.usgs.gov/sir/2013/5107/

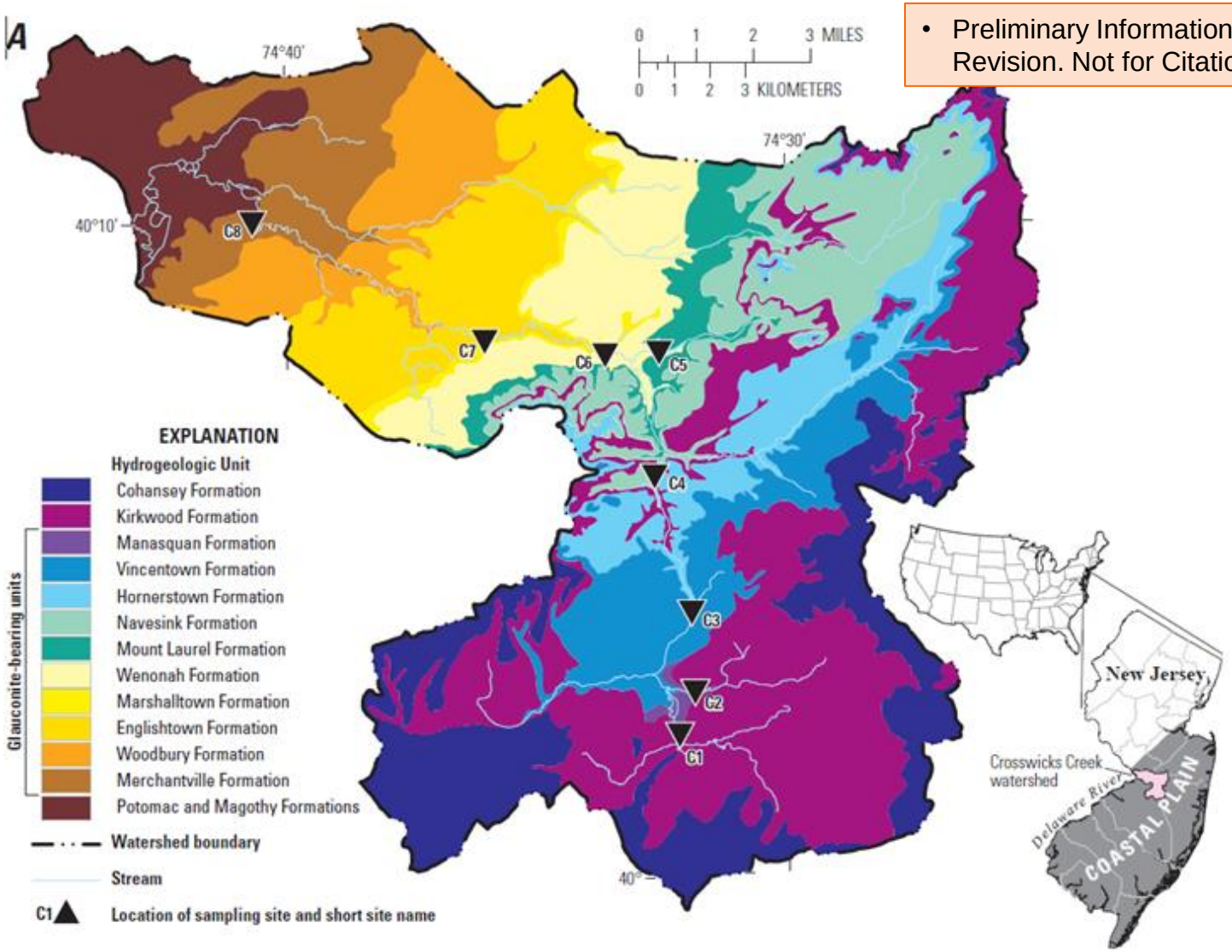




- Preliminary Information-Subject to Revision. Not for Citation or Distribution

Crosswicks Creek

- Preliminary Information-Subject to Revision. Not for Citation or Distribution



USGS science for a changing world

Arsenic in soils and sediments

USGS science for a changing world	Inner Coastal Plain	Outer Coastal Plain
Medium	***As (mg/kg)***	***As (mg/kg)***
Soils	13-131; median 29.5 (from Dooley 2001)	<1-13.3; median 3.9 n = 12
Stream-bed sediments	<1-34.7; median 14.1 n = 25	<1-2.4; median <1 n = 16
Aquifer sediments	7-136; median 24 (from Dooley 2001)	<1.0-7.7; median 3.4 n = 11

Arsenic content of soils, streambed sediments, and aquifer sediments, Inner and Outer Coastal Plain.

- Preliminary Information-Subject to Revision. Not for Citation or Distribution