Two DRBC Radiochemistry Monitoring Case Studies in the Delaware River Basin

New Jersey Water Monitoring Council
January 24, 2018

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WWW.DRBC.NET

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Delaware River Basin Commission

The Two Case Studies

* Monitoring Radiochemistry in the Upper Delaware Basin in Advance of Potential Natural Gas Development
  * John Yagecic
* Delaware Estuary Boat Run Radiochemistry Monitoring after High Outdoor Tritium Concentrations Detected
  * Elaine Panuccio

Background

* In May 2010 Commissioners postponed approval of shale gas development, called for new regulations.
* Perceived *narrow window of opportunity* to establish pre-drilling conditions.
* Marcellus shale underlies basin's Special Protection Waters area, requiring No Measurable Change to existing water quality.
* Aqueous wastes from hydraulic fracturing dramatically different than WWTP effluent or non-point runoff.

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DRBC Ambient Monitoring Framework for Natural Gas Development

* DRBC Monitoring Activities
  1. HOBO Conductivity Loggers
  2. Reanalysis of archived samples
  3. Biological Monitoring
  4. Toxicity Testing
  5. **Radiochemistry Monitoring**

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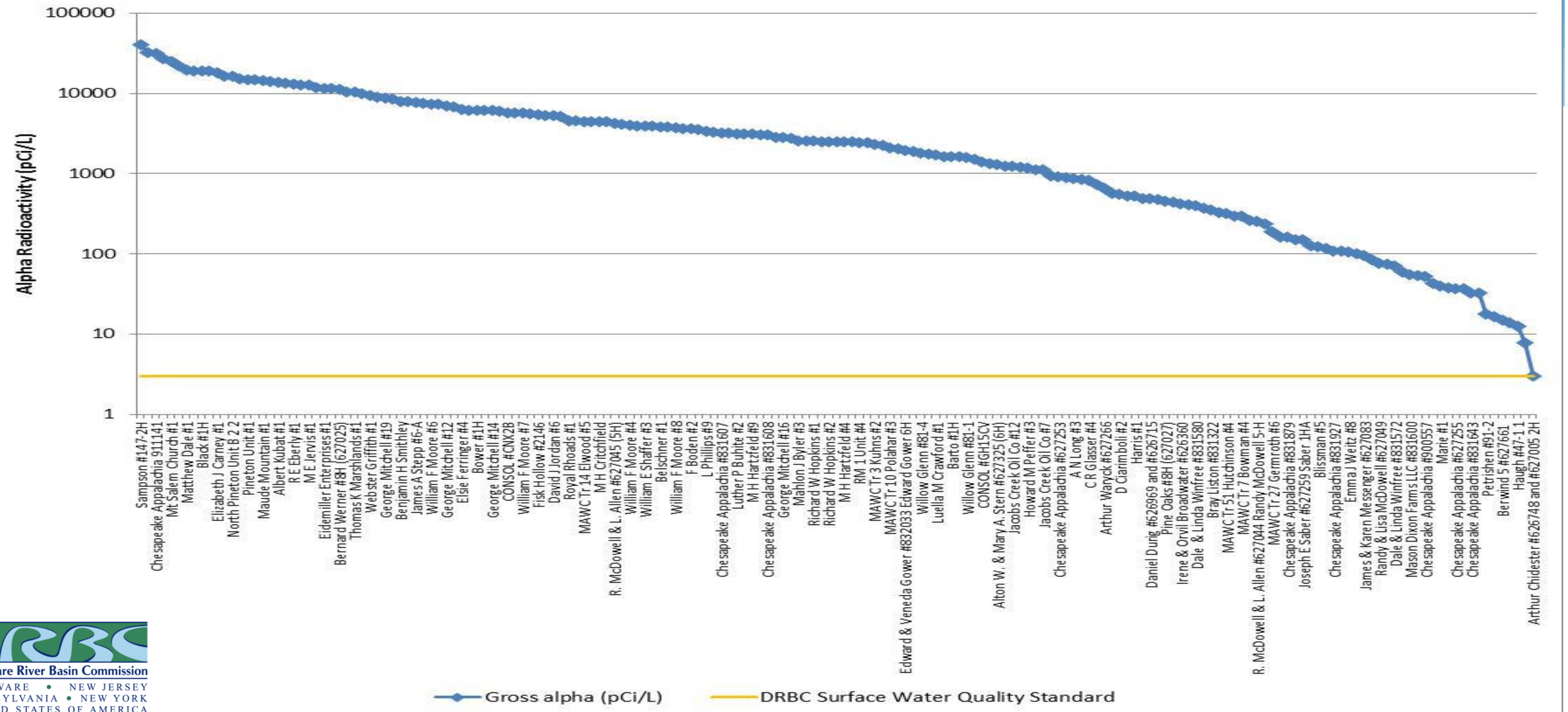
February 2011 NY Times Article & Data Set on Hydraulic Fracturing Aqueous Wastes



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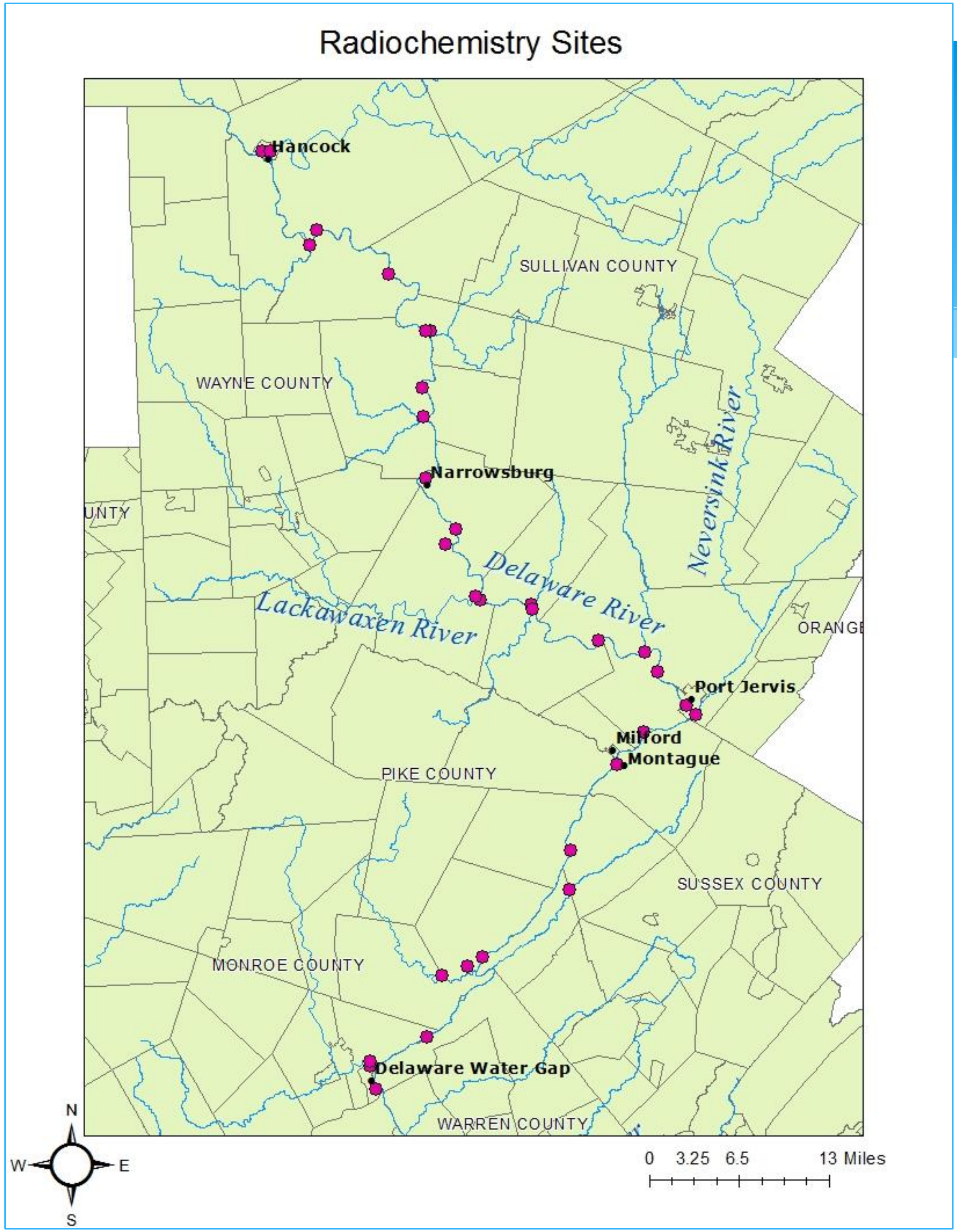
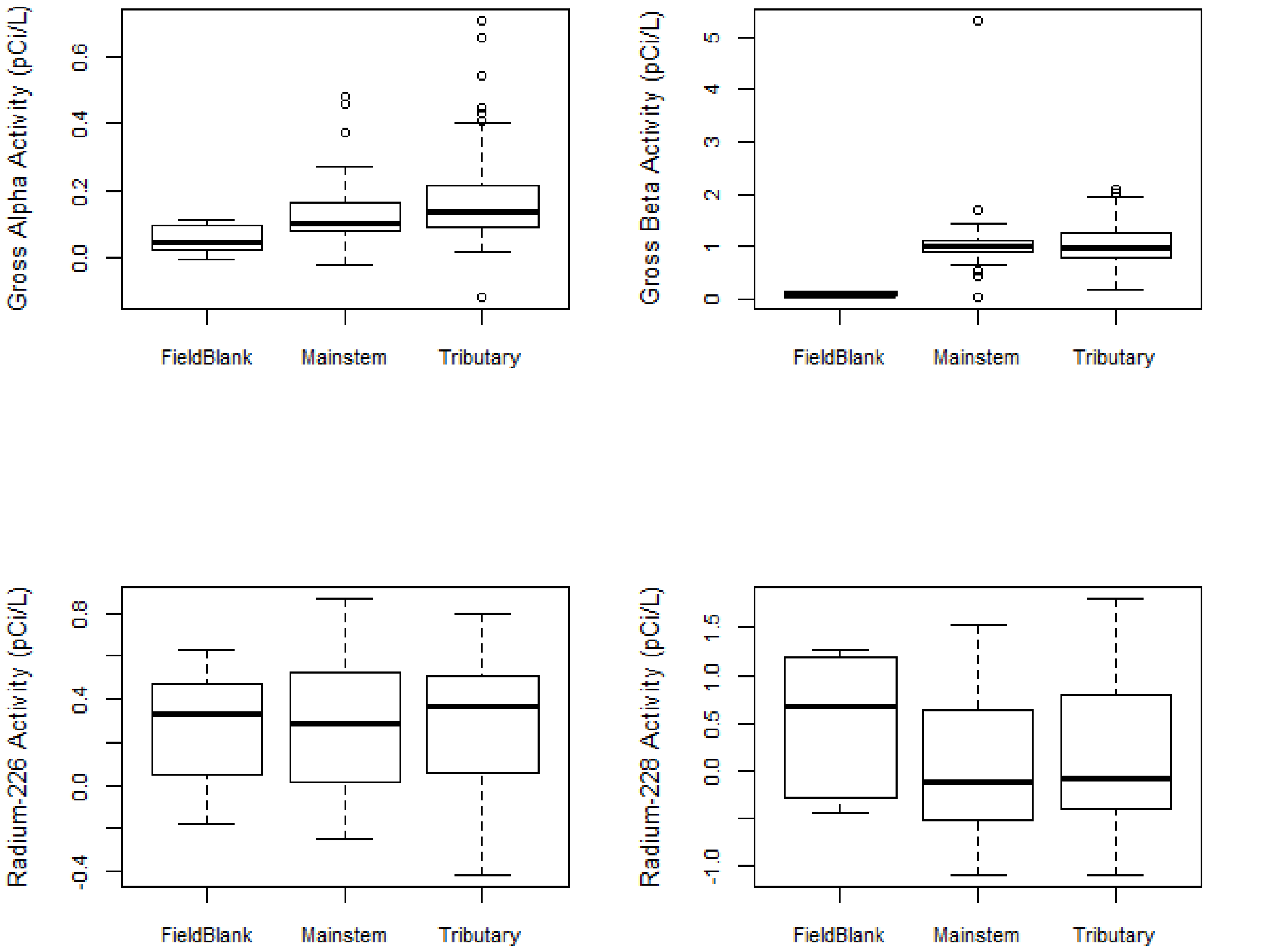


Radiochemistry Monitoring

* Funding from William Penn Foundation
* 32 sites, mainstem & tributaries
* Hancock, NY to Delaware Water Gap
* 5 events, January 2014 & May 2015
* 163 samples (including blanks & replicates)
* Gross alpha & gross beta
  * NJDHSS ECLS-R-GA & GB
* Radium -226 + Radium-228
  * NJDHSS ECLS-RA-RA226/228
* Analysis & technical support by NJDOH lab

Mainstem, tribs, & blanks



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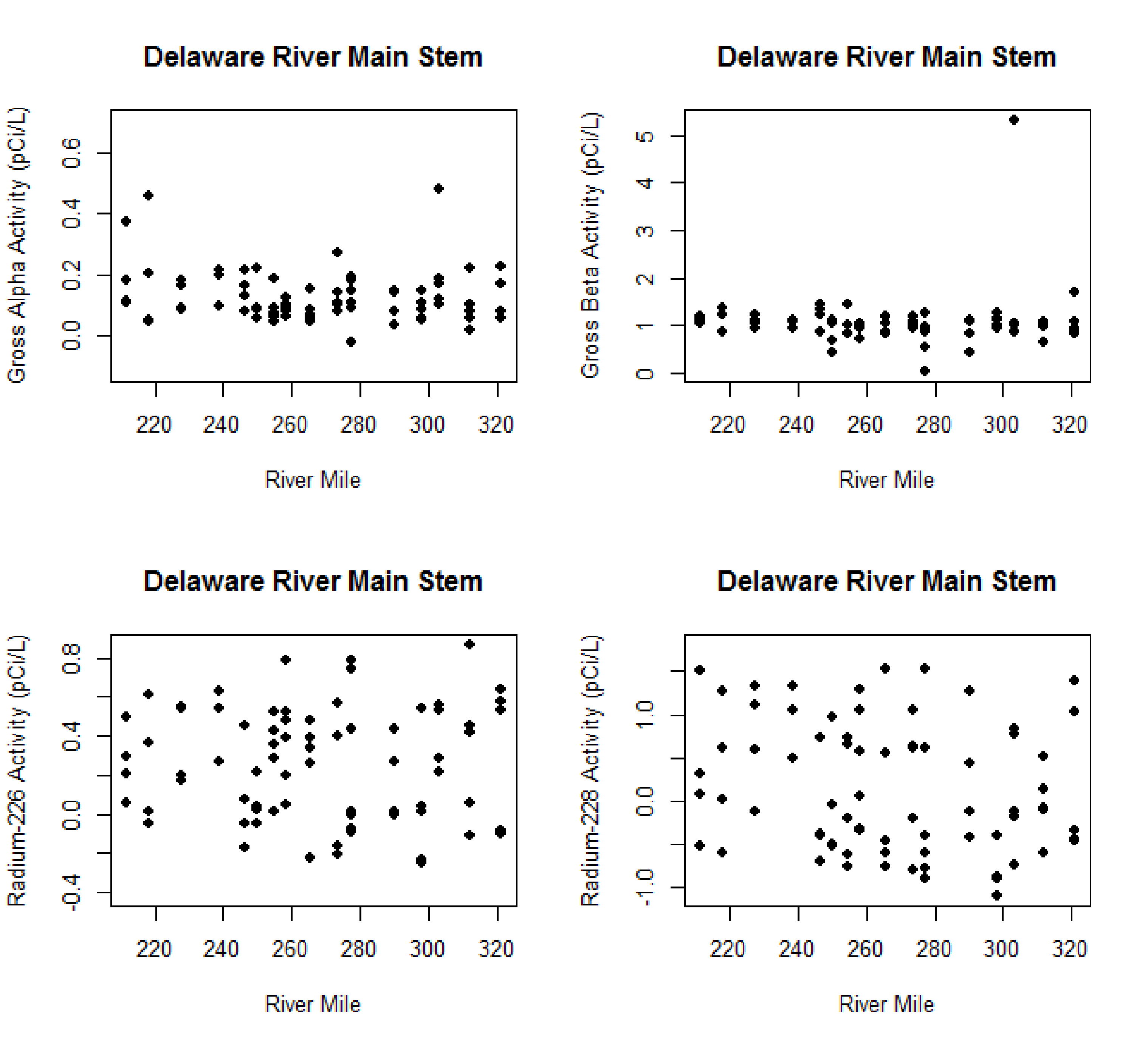
Activity by River Mile



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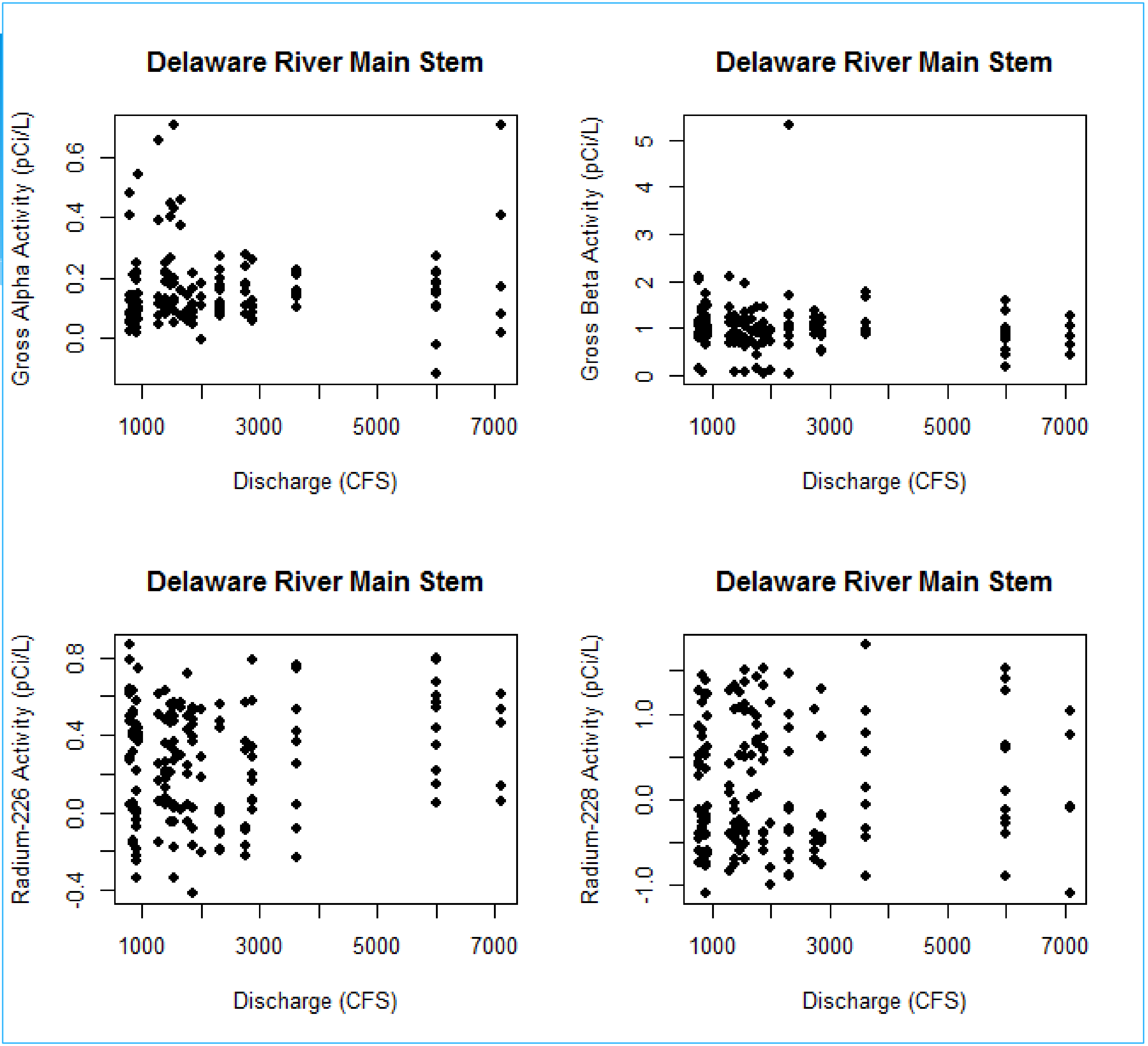
Activity by Discharge



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Bottom Line

* Established good documentation of pre-natural gas radiochemistry activities
* All results below the DRBC standards for gross alpha & gross beta at all locations
* Funded by the William Penn Foundation
* Report & data at:
  * http://www.nj.gov/drbc/library/documents/BaselineRadiochemReport_October2015.pdf

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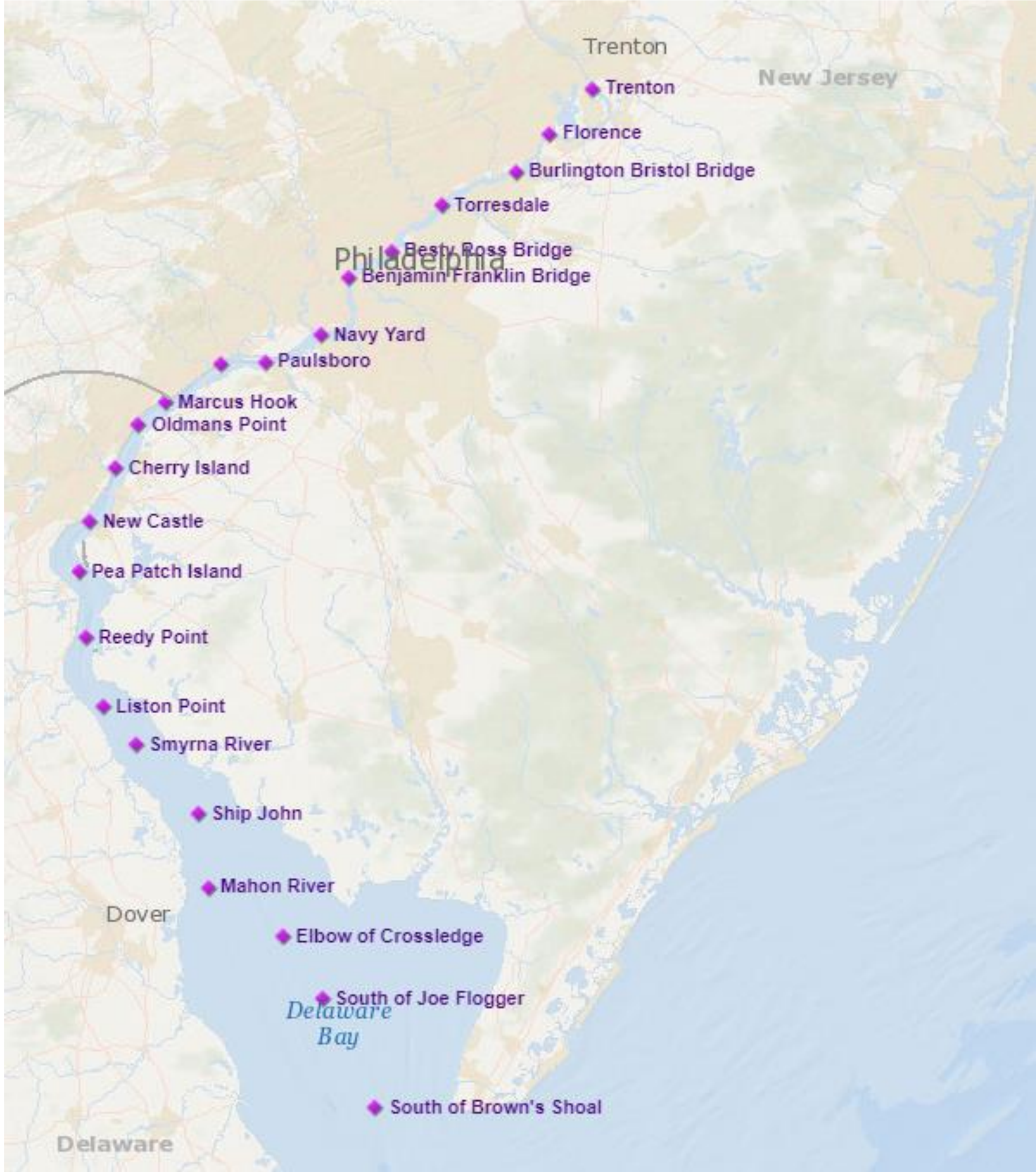
Delaware Estuary Boat Run Radiochemistry

Background

* Discovery of radioactive tritium detected in snow and ice outside of PSE&G Nuclear's Hope Creek Generating Station with concentrations estimated at 10 million pCi/L (picocuries per liter) in March 2015;
  * Has since been addressed and area is now contained;
* Second-highest concentration reported tritium leak nationwide. The highest reported tritium leak occurred at the nearby PSE&G Salem plant at 15 million pCi/L in 2002;
* Federal drinking water limit for tritium is 20,000 pCi/L.

Delaware Estuary Boat Run Monitoring



- One of the longest-running monitoring programs in the world, initiated in 1967;
- Samples are collected at 22 stations to manage water quality and to ensure that water quality criteria are being met;
- Radiochemistry analyses conducted by New Jersey Department of Health Environmental and Chemical Laboratory;
- As a follow-up to the elevated tritium concentrations at the PSE&G Hope Creek/Salem nuclear plant, NJDEP had requested radiochemistry analyses.

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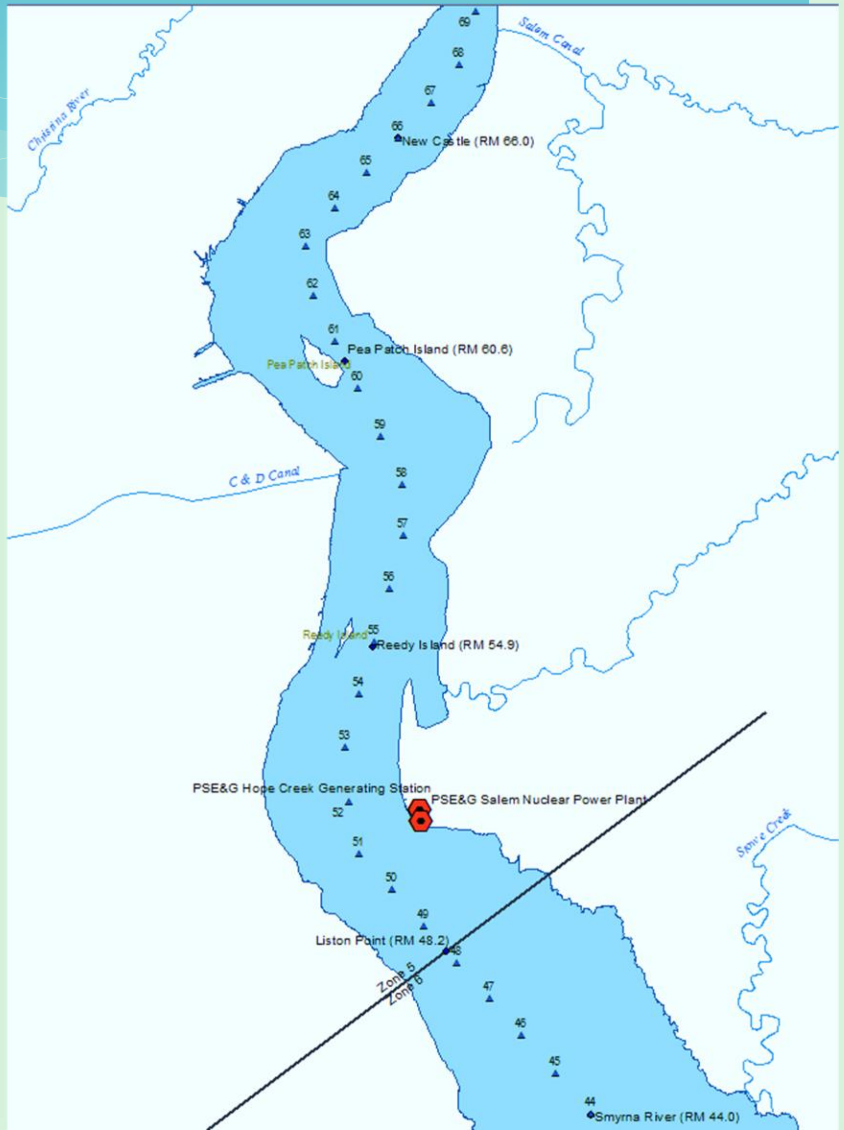
Delaware Estuary Boat Run Radiochemistry Monitoring 2016

* At the request of NJDEP, DRBC added tritium as a parameter at 5 stations between River Mile 66 and 44 following the reports of elevated outdoor tritium concentrations near the PSE&G Hope Creek and Salem Generating Stations;
* In addition to the tritium analyses at the 5 locations near the plant, NJDEP also requested that DRBC monitor gross alpha and gross beta emitters to the Boat Run program in 2016 as DRBC has criteria for these radiochemistry parameters.



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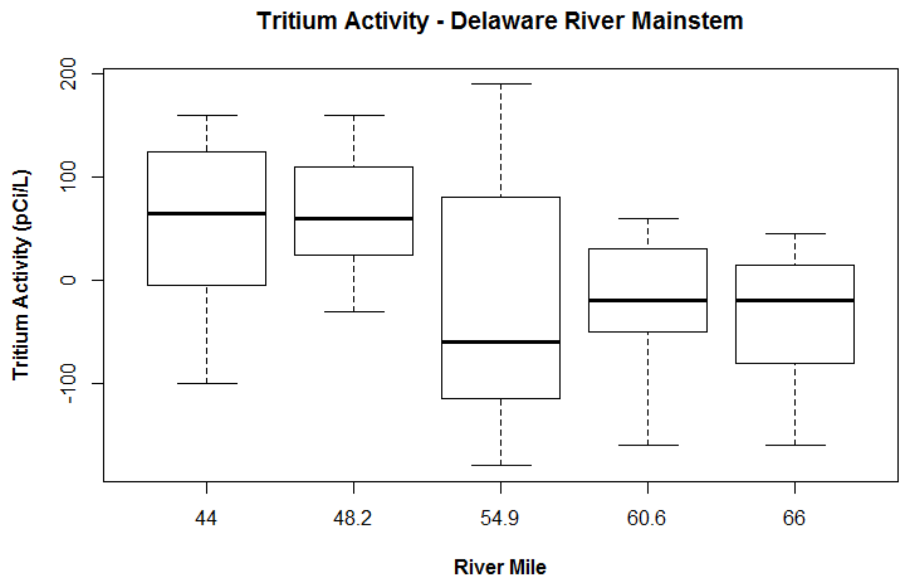
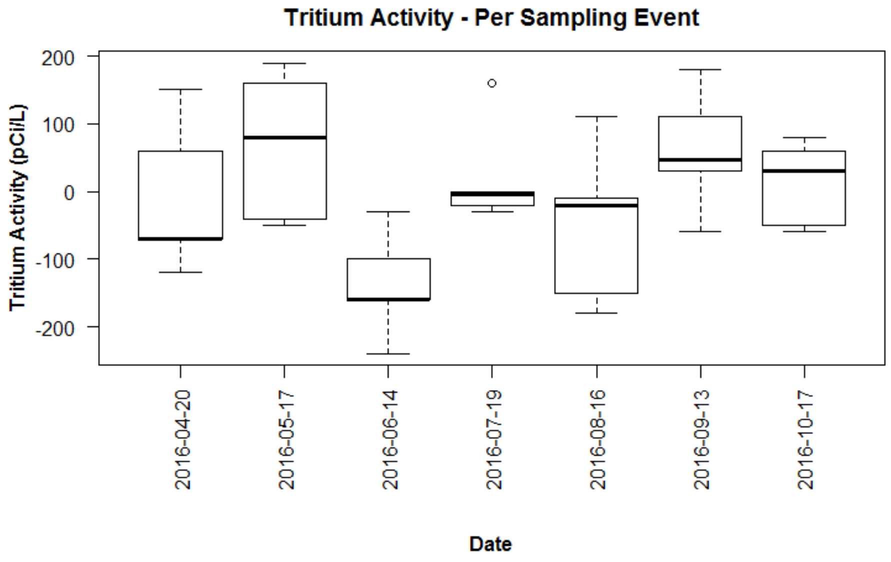
Tritium Results 2016

Previous EPA Maximum Contaminant Level of 20,000 pCi/L for tritium later superseded in the subsequent radionuclides rules. Exceedances of the previous MCL occurred (estimated 10 million pCi/L) at PSE&G Hope Creek Generating Station in 2015.

- In 2016, surface water sample results indicate no exceedances for tritium;
- Boxplots shown are by River Mile (by site) and by Date





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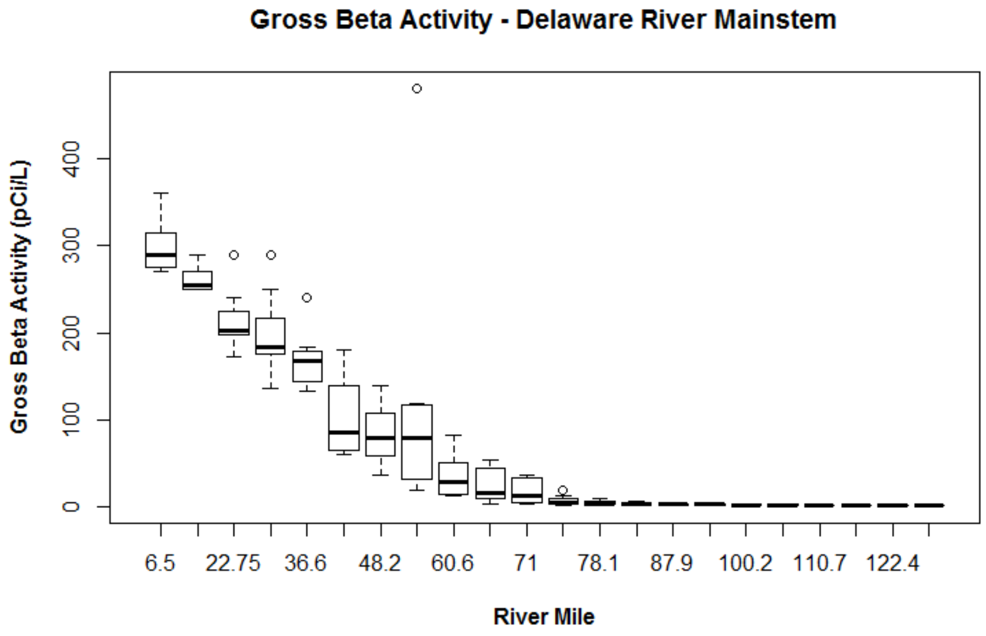
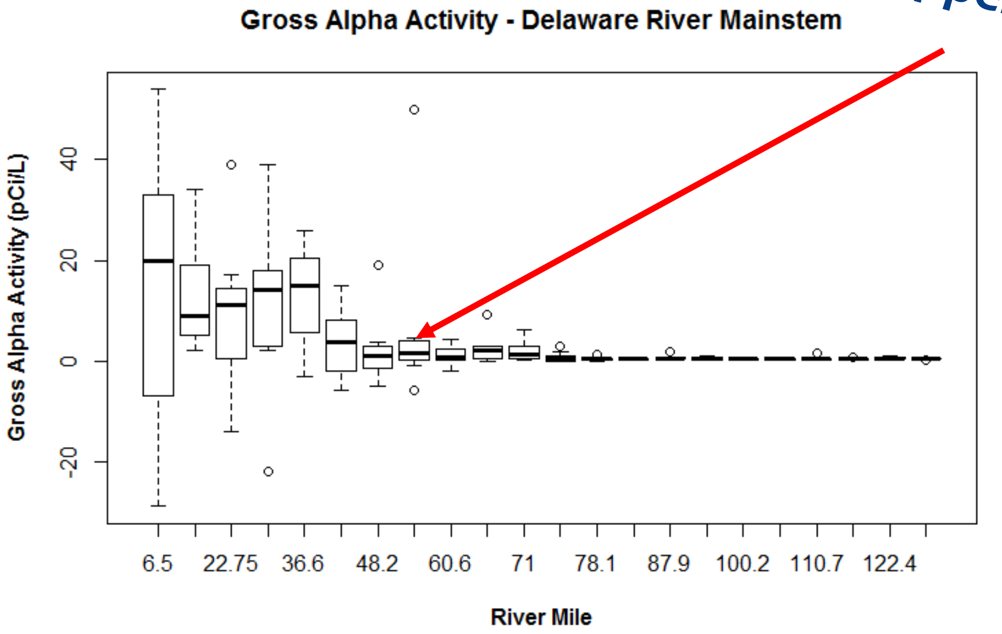
Alpha Emitters and Beta Emitters Results 2016

DRBC Stream Quality Objectives for Radioactivity in Zones 2-6:

- ***Beta emitters not to exceed 1,000 pCi/L***
- ***Alpha emitters not to exceed 3 pCi/L (EPA MCL of 15 pCi/L)***



What is happening here?



Delaware Estuary Boat Run Radiochemistry Alpha Emitters Exceedances

Why are there exceedances of Gross Alpha activity closer to the mouth of the bay?

- The results prompted a discussion between staff of NJDEP's Bureau of Nuclear Engineering (Karen Tuccillo and Jay Vouglitois) and DRBC (John Yagecic and Elaine Panuccio);
- Similar results seen in NJDEP studies. The exceedances may not be a cause for concern given the concentrations in the relatively high-salinity areas opposed to the up-river sites (stay tuned…)

Possible Explanation…

- A USGS Study, *Examining Freshwater-Saltwater Interface Processes with Four Radium Isotopes*, identifies the possible cause of the Gross Alpha exceedances;
  - "In freshwater, radium (an Alpha Emitter) is chemically bound onto particle surfaces. As these particles become exposed to higher salinity waters during estuarine mixing, radium will undergo a phase transformation and will eventually reside exclusively in the dissolved phase in the open ocean."

USGS
science for a changing world

Examining Freshwater-Saltwater Interface Processes with Four Radium Isotopes

Tracking the cycling of nutrient-laden ground water in upper Florida Bay with a suite of radium isotopes yields information on the rate and quantity of water exchange

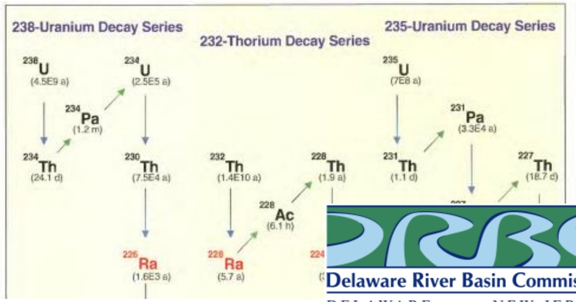
Introduction

The complex exchange of fluvial, subsurface, and marine material within an estuary directly affects global biogeochemical cycles. Environmental scientists have few tools to accurately quantify such processes directly and must therefore rely on various tracer techniques. Satellite imagery, for example, provides an invaluable means for tracking some freshened river plumes into the open ocean, often for many hundreds of kilometers. However, the mixing of fresh water into seawater cannot always be tracked remotely and generally cannot yield information on the movement and rate of water mixing. Fortunately, natural and artificially produced radioactive tracers can be used to determine recent chronologies of such processes as: recently deposited sediments, water mass mixing, and exchange processes across the sediment-water interface.

In order for a chemical constituent to be implemented successfully as an environmental tracer, its source and sink functions, as well as all processes that regulate them, must be known and quantifiable. For example, methane (CH_4) and radon-222 (^{222}Rn) are two natural tracers that have been utilized successfully in coastal ground-water studies because their respective concentrations in ground water are usually much higher than in surrounding seawater. There are some known caveats in using these two tracers success-

Radium Isotopes as Tracers

There are four radium isotopes (fig. 1) in the uranium-238, thorium-232, and uranium-235 decay series; and their wide range in half-lives ($t_{1/2}$) corresponds well with the duration of many coastal processes. These four radium isotopes are ^{223}Ra ($t_{1/2}$ = 11.4 d), ^{224}Ra ($t_{1/2}$ = 3.7 d), ^{228}Ra ($t_{1/2}$ = 5.7 yr), and ^{226}Ra ($t_{1/2}$ = 1600 yr). Their wide range in half-lives corresponds well with the duration of many coastal processes. A suite of highly particle-reactive thorium isotopes decays to form the four radium isotopes. In fresh water, radium is chemically bound onto particle surfaces. As these particles become exposed to higher salinity water during estuarine mixing, radium will undergo a phase transformation and will eventually reside exclusively in the dissolved phase in the open ocean. In contrast, thorium will continue to remain bound to particles, regardless of salinity. Consequently, estuarine sediments provide a continuous source for radium isotopes to coastal waters, and the production rate is defined directly by their individual isotopic decay constants (fig. 2). The combined source functions for radium in an estuary thus include a) riverine particulates and dissolved, b) oceanic dissolved, c) estuarine sediments, and d) ground water. The relative significance of each of these sources is usually a function of the site-specific hydrogeology and where the samples are taken relative to the salinity gradient (extent of freshwater-saltwater mixing).



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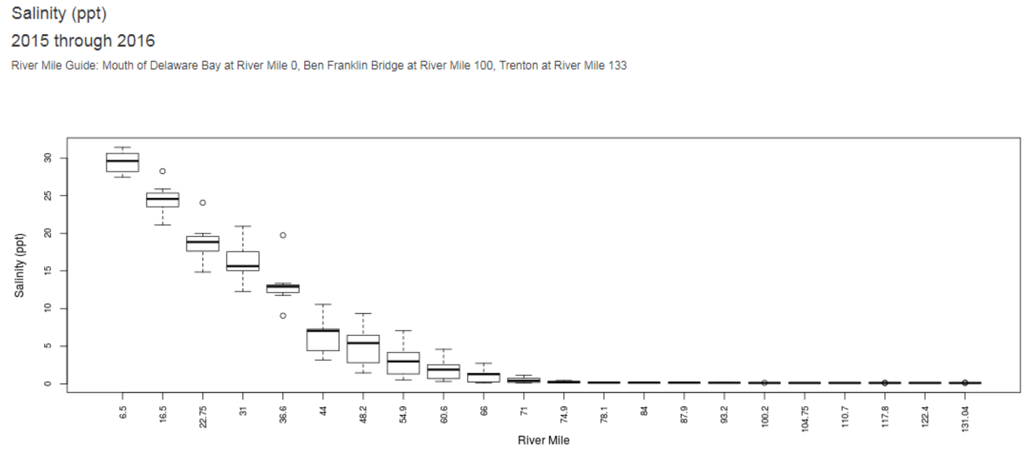
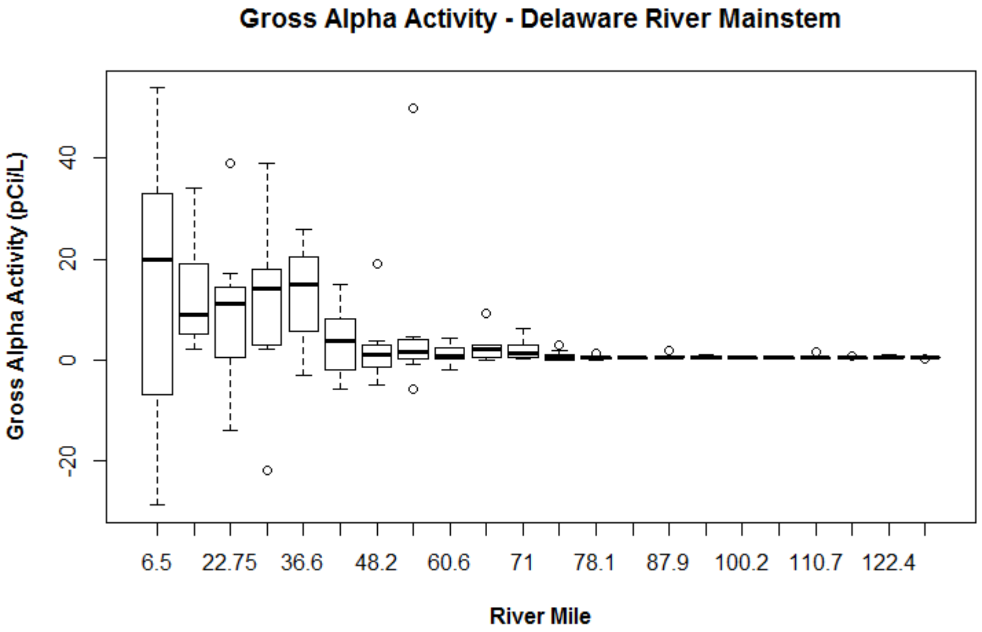
Possible Explanation (continued)…

* Going towards the ocean from the Delaware River, the DRBC-designated River Miles decrease, thus River Mile 6.5 (South of Brown Shoal site) is the closest site to the ocean boundary;
    * Upon discussion with NJDEP staff, it was concluded that the higher concentrations detected closer to the open ocean may possibly indicate that radium, an Alpha Emitter, is in the dissolved phase.





….Or are there issues with the method used?

* EPA Method 900.0
  * "In this method for gross alpha and gross beta measurement, the radioactivity of the sample is not separated from the solids of the sample…"
  * TDS is a limiting factor for gross alpha activity;
    * Alpha particles adsorb to solids easily in comparison to beta particles, in which the solids are not as much a limiting factor;
    * The Delaware Bay sites have high concentrations of TDS

Bottom Line

* DRBC monitored for tritium at 5 locations in 2016 near PSE&G's Hope Creek and Salem Nuclear Plants in response to the discovery in early 2015 of tritium at levels 500 times higher than the federal water quality standards;
    * **The results indicate that no exceedances occurred in surface water samples surrounding the nuclear plant and results are well below EPA's Maximum Contaminant Level across all 5 stations.**
* In addition to tritium, NJDEP requested DRBC to monitor for gross alpha emitters and gross beta emitters as DRBC has criteria for these parameters;
    * Results for gross beta emitters across all 22 stations indicate no exceedances of water quality criteria, whereas exceedances of gross alpha emitters criteria were reported in the higher-salinity areas closer to the ocean;
        * Results indicate that DRBC may need to take into consideration the effects of salinity on gross alpha activity and update the regulations to better represent this phenomenon;
        * Lastly, field filtration may be necessary in the future when assessing gross alpha activity in high TDS samples to better represent the activity of the water itself.

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