



# EVALUATION OF VARIABILITY OF STORMWATER RADIONUCLIDE CONTAMINATION LEVELS IN A HOLDING BASIN

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October 28, 2015

## C-410 Building at the Paducah Gaseous Diffusion Plant

- › Original Feed Plant with Two East Expansions and One West Expansions
- › Infrastructure was removed in the 2011 – 2012 time frame under the American Recovery and Reinvestment Act Funding

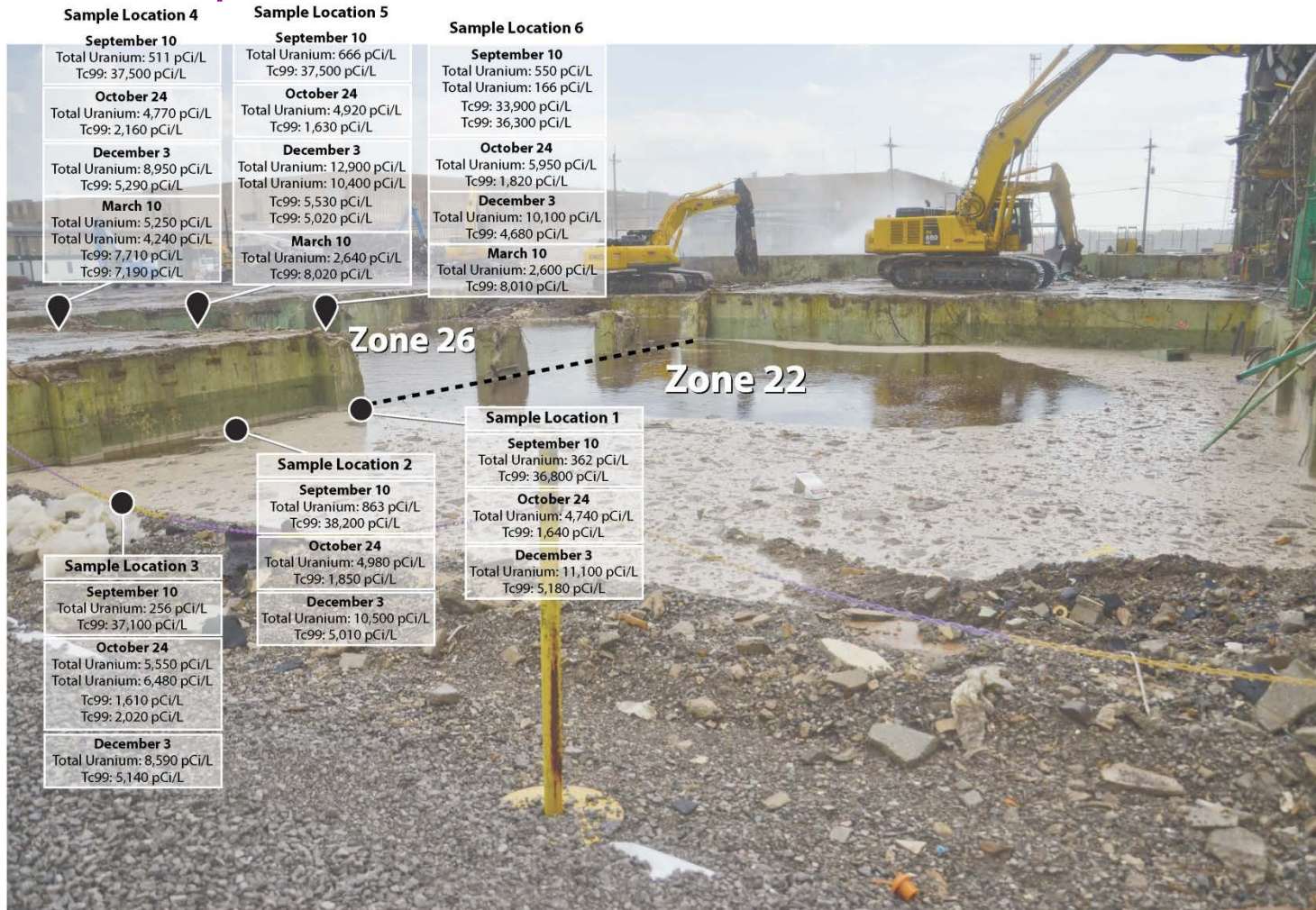


## C-410 Building Basement Structures

- › The remaining basement structures have been used as a basin over the last few years to store stormwater in two zones: 22 and 26



# Sampling and analysis of the stormwater began September 2014 and continued into 2015



A wall was built between the two zones in early 2015



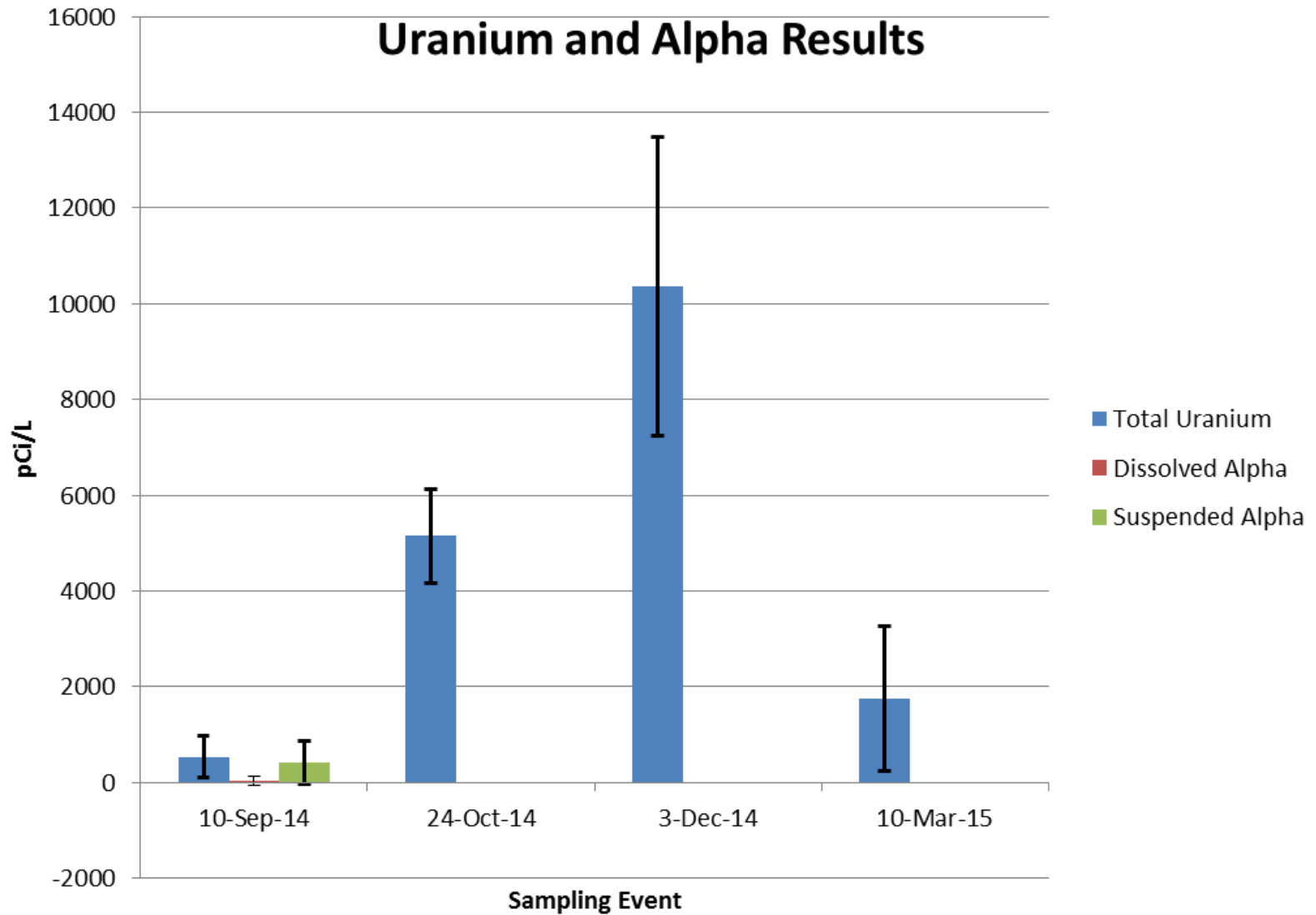
All water was pumped into Zone 26 and Zone 22 was filled with flowable fill



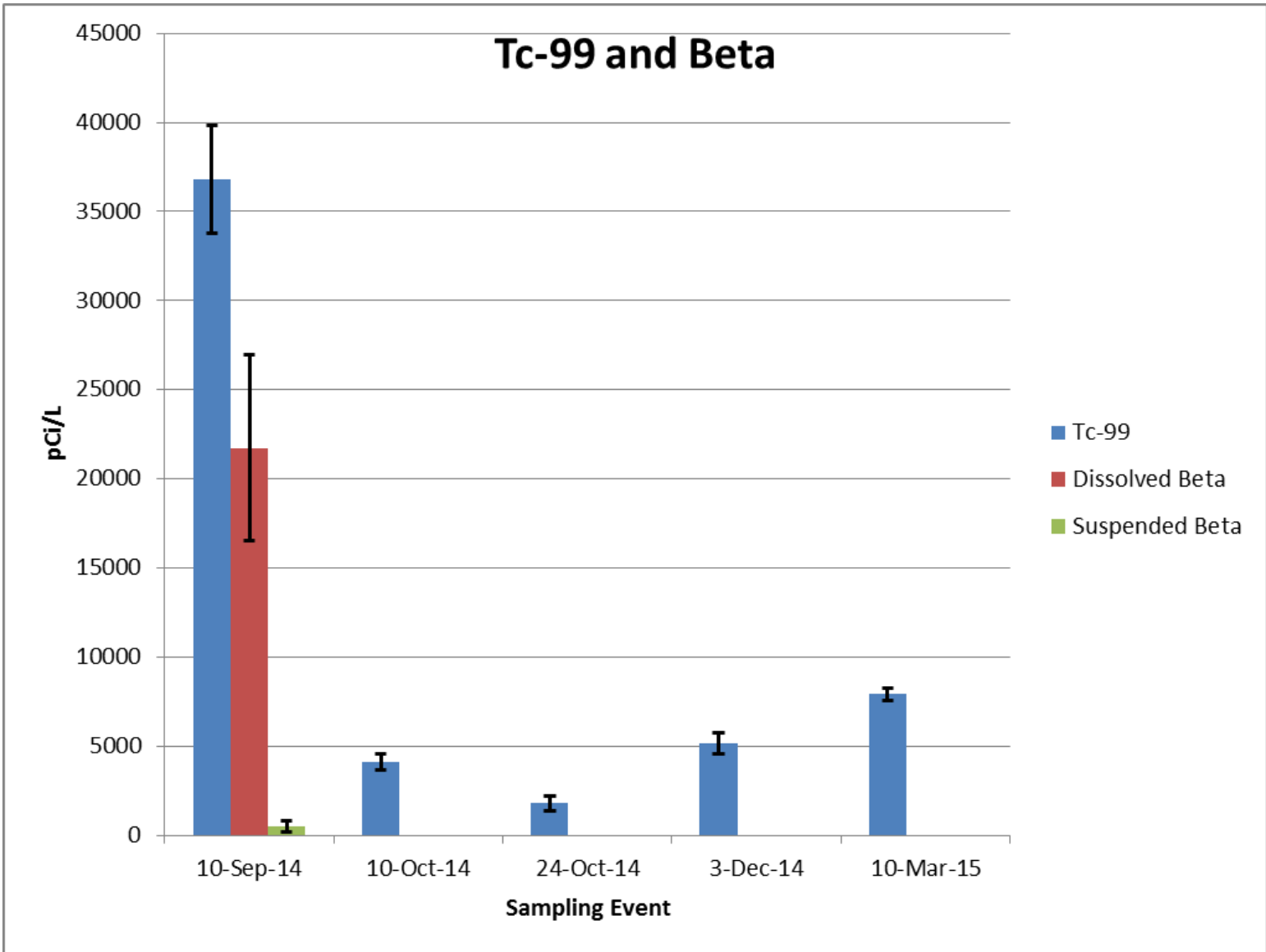
## Sampling Results for Total Uranium and Technetium-99

- > Four sampling events in 2014 and one in 2015 showed significant changes in uranium and technetium-99 concentrations which led to concerns about possible leakage of contamination out of the holding basins.
- > Some water loss could not be accounted for by evaporation.
- > However, sampling of the groundwater around the basins did not show changes in contaminants consistent with their loss from the holding basins.

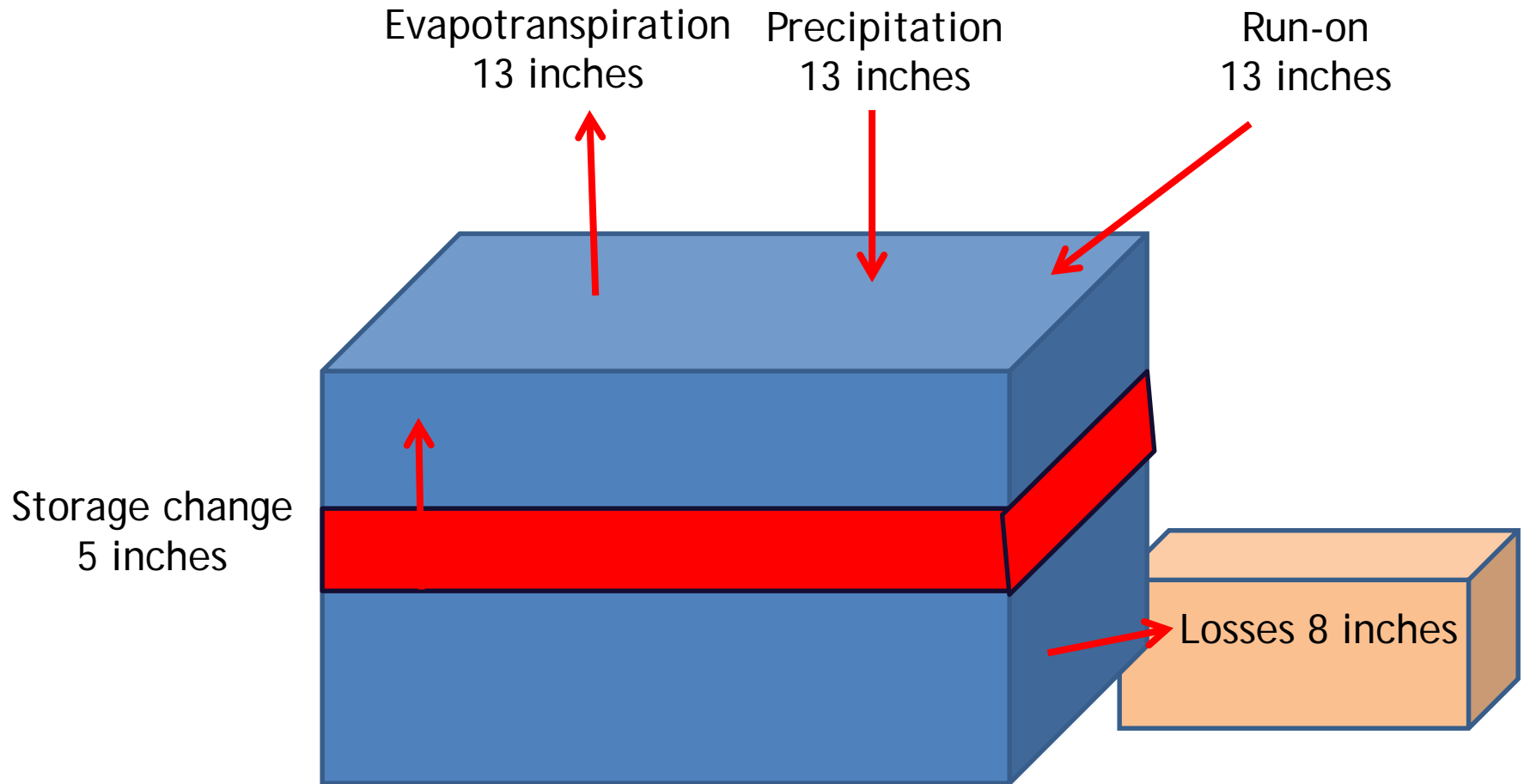
# Uranium and Alpha Results







# Water Balance of Zone 22 (Jan-March 2015)



$$\text{Storage change} = \text{precipitation} + \text{run-on} - \text{evapotranspiration} - (\text{losses})$$

## Are there Data Quality Issues? - Data Validation Results

- > Only some of the data had previously received Level 3 validation.
- > Level 4 validation was performed on all data.
- > The only issues discovered was that in summing uranium isotopes together for a total uranium alpha result, the isotopic uncertainties were summed in quadrature. However, since all uranium isotopes use the same isotopic tracer for quantification and since there was significant uncertainty in the isotopic tracer due to low recoveries, the results are not independent and this was not appropriate.
- > Total uranium uncertainties were recalculated using a straight sum of isotopic uncertainties.

## What are the uncertainties in sampling and analysis?

- > Analytical uncertainties were compared to sample variability.
- > The standard deviation of the sample results from the same Zone for each sampling event significantly exceeded the reported analytical uncertainties.
- > Error bars in the plots of the data shown earlier represent the  $2\sigma$  distribution of the sampling results for each sampling event.
- > However, neither analytical uncertainty or sampling variability account for variability of results over time.

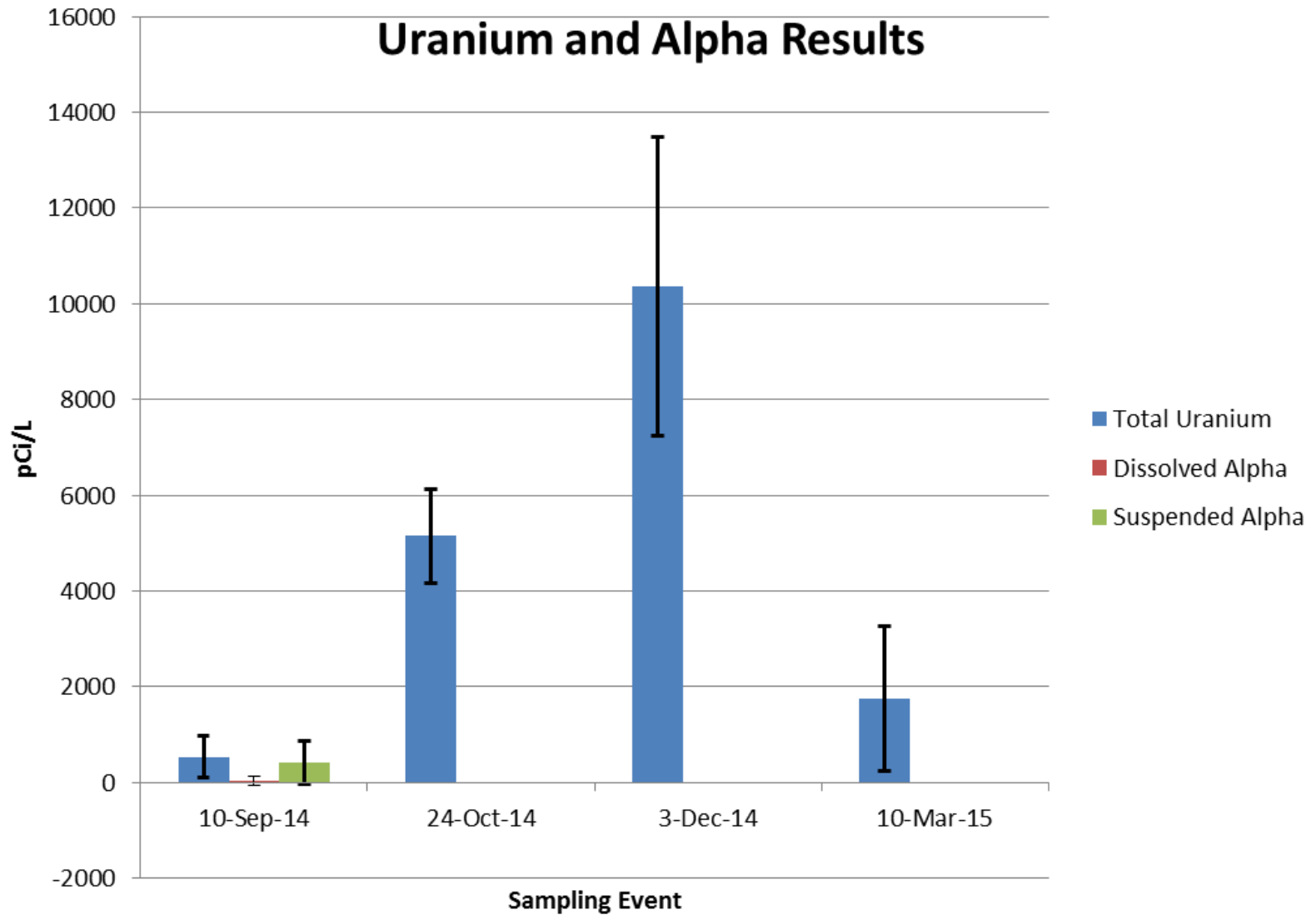
## Clues to Possible other Explanations of the Variability

- > Experience with holding ponds at ORGDP in the past showed significant change in concentrations in discharge effluents due to temperature inversions stirring up the sludge layer on the bottom.
- > Suspended gross alpha/beta results from the first sampling showed most of the uranium is in the suspended fraction (insoluble) whereas the Tc-99 at that time was mostly in the dissolved fraction (soluble).
  - > Accounts for the variability between samples taken at the same sampling event being greater for uranium than for technetium

## What are the possible explanations for the Total U variability?

- > December sampling provided samples of both the water and the sludge.
  - > Uranium concentration in the sludge is about 100 times the concentration in the water. If the volume of sludge is only 1% that of the volume of the water, there would be as much uranium in the sludge as in the water.
  - > The amount of sludge that is suspended as particulates in the water samples varies by location and depends on how much stirring up of the sludge has occurred.
  - > The sludge can be stirred up by thermal heating from the sun and from cooling of the surface water due to significant drops in air temperature causing a temperature inversion.
  - > This likely accounts for the large changes in uranium concentrations from sampling event to sampling event.

## Uranium and Alpha Results



## What are the possible explanations for the Tc-99 variability?

- > Solubility of Tc-99 depends on its oxidation state (+VII vs +IV) which in turn depends on the oxidation environment, such as the presence or absence of oxygen.

Redox Potential versus pH shows that near neutral solutions the equilibrium between +IV and +VII will depend on the redox potential supplied by dissolved oxygen.

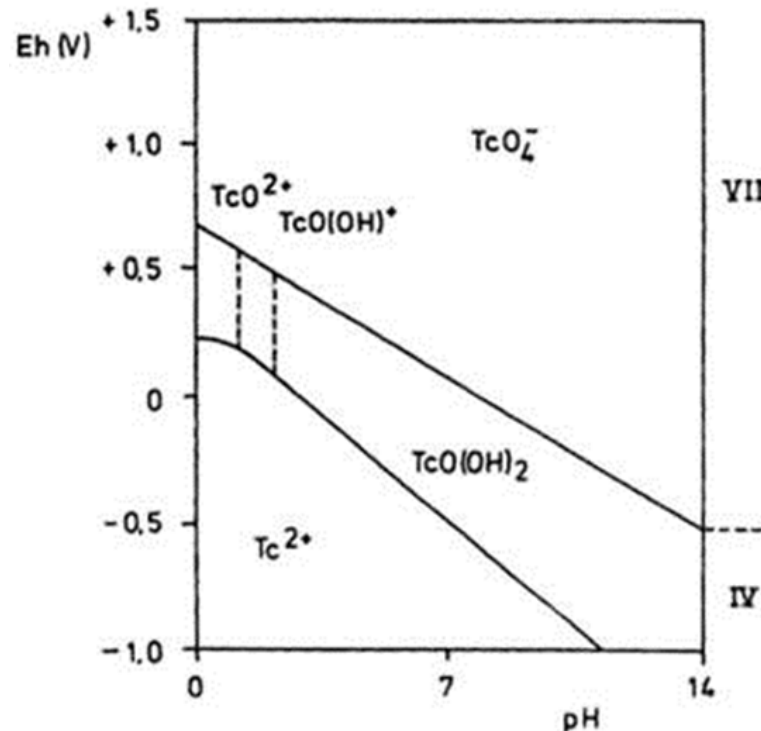


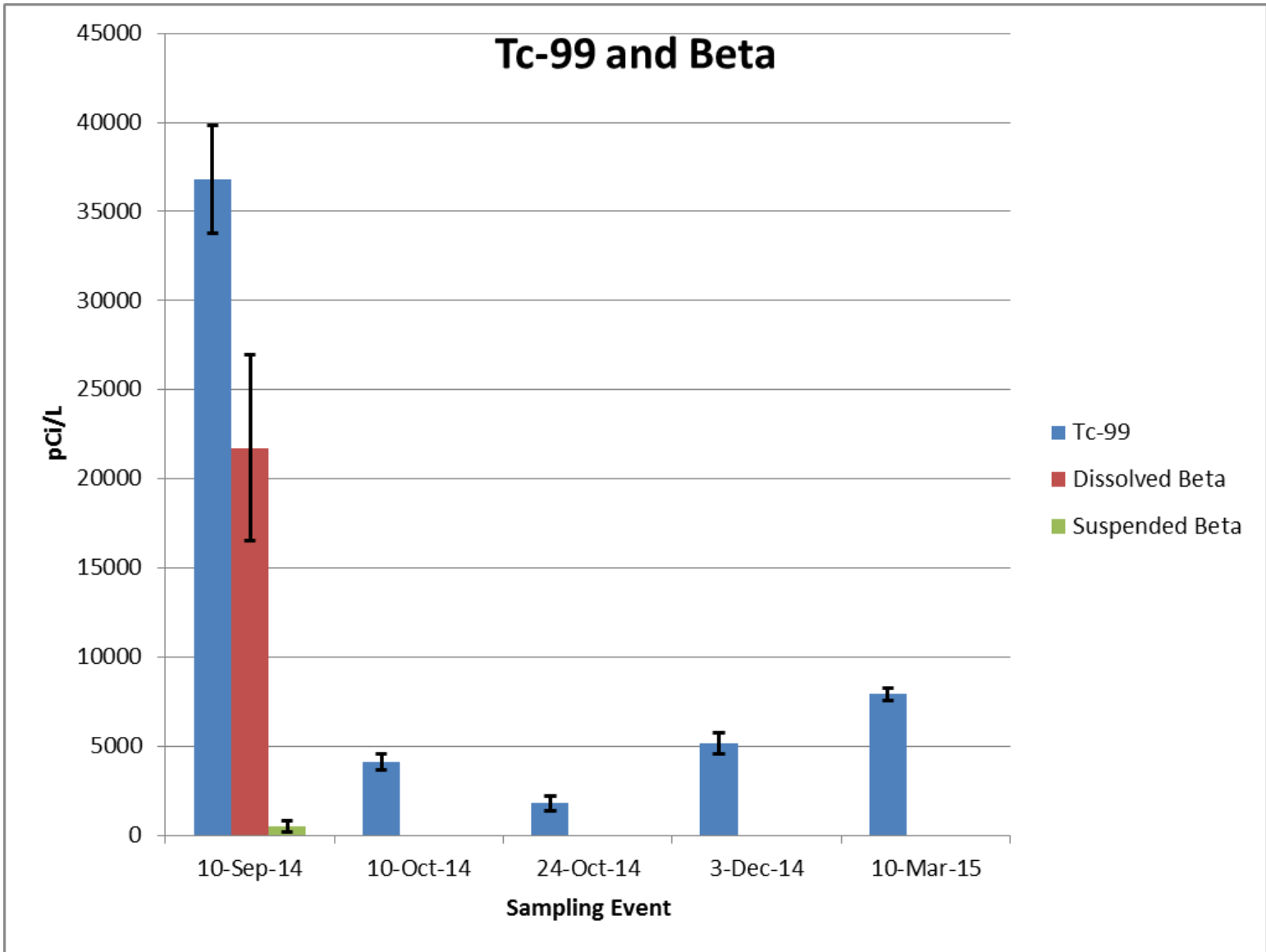
FIG. 1.  $E_h$ -pH diagram of Tc [1].

If dissolved oxygen levels are high, the technetium will more likely be in the +VII state and be soluble. But if the oxygen levels are lower the technetium will more likely be in the +IV state and be insoluble.



## What are the possible explanations for the Tc-99 variability?

- > Solubility of Tc-99 depends on its oxidation state (+VII vs +IV) which in turn depends on the oxidation environment, such as the presence or absence of oxygen.
  - > Dissolved oxygen levels at the surface may increase while at depth they may not because of thermal stratification.
  - > Levels of algae and microorganisms impact oxygen levels of dissolved oxygen during their life cycles.
    - > Cooler temperatures and less sunlight can cause algae die-off in the fall and resulting lower dissolved oxygen levels.
- > The sludge is likely serving as a reservoir for technetium in the winter months that will likely become soluble in the summer months as temperatures and oxygen levels in the held stormwater rise. However, temperature inversions can still affect the amount of particulate in the sample in winter.



## Is contamination likely escaping the holding basins?

- > Basement floors and walls are likely not impermeable to water due to hydraulic pressure.
- > However, it is not likely that the mostly insoluble uranium would permeate through the wall significantly.
- > It is likely that even soluble technetium in the +VII state would not permeate as fast as the water due to adsorption onto and reduction to the +IV state by the concrete medium.

## Conclusions and Recommendations

- > The uranium and technetium are likely being mostly retained and it is not likely that loss from the basin is responsible for the large fluctuations in water concentrations that have been seen in the held stormwater.
- > The varying solubility of the Tc-99 due to varying oxygen levels and the stirring of the sludge by temperature inversions were considered the likely causes of the variability of the data.
- > Further sampling in the summer was recommended to validate the theory.
- > Measurement of oxygen levels as well as temperature and pH levels in the holding basin water over the next several months was also recommended.

# Point of Contact

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