Matrix Complications in the Determination of Radium Isotopes in Hydraulic Fracturing Flowback Water from Marcellus Shale

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Marinea Mehrhoff
State Hygienic Laboratory (SHL)
at The University of Iowa

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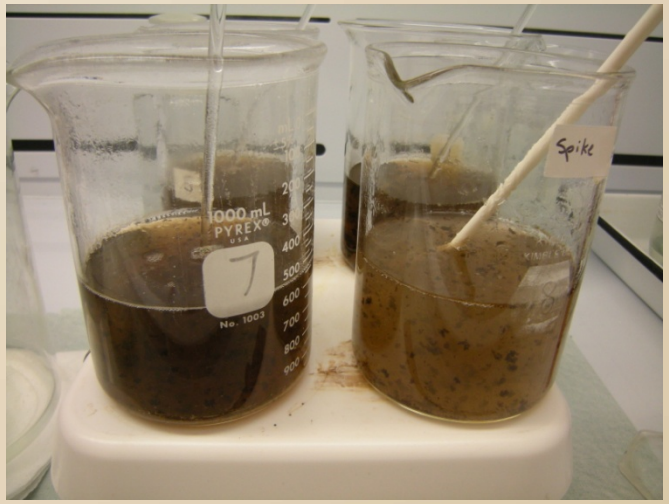
- The views and opinions expressed in this presentation are those of the authors and do not necessarily reflect the official policy or position of any agency.

- The mention of specific products are not an endorsement, but reference to products and the results used in this study.

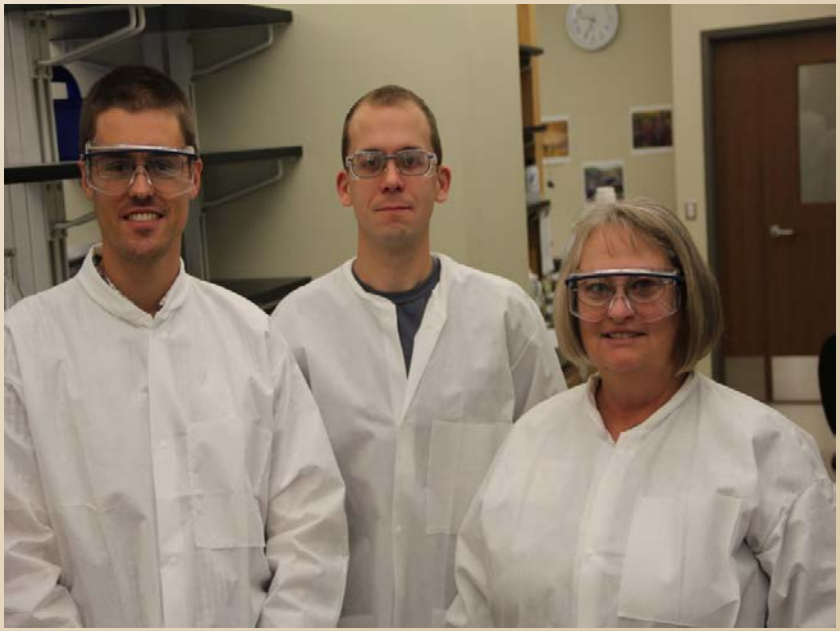
Topics

- Collaborative Effort
- Background Information
- Laboratory Testing
  - Sampling, sub-sampling
  - Method development issues
- Conclusions



Collaboration

- SHL worked with University of Iowa (UI) Assistant Professor Michael Schultz and graduate student, Andrew Nelson from the UI Radiology, Radiation Oncology and Chemistry departments.



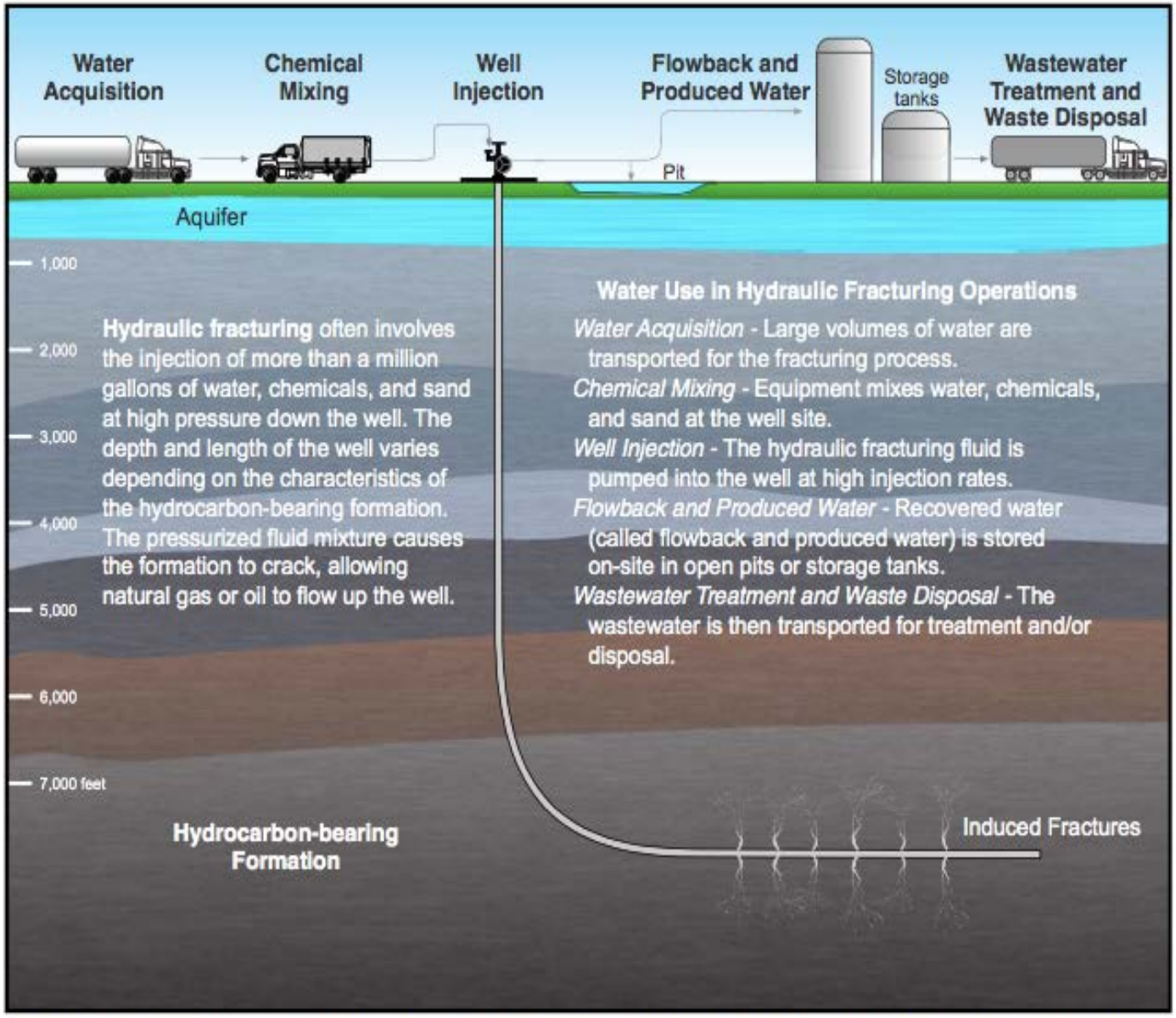


FIGURE 6a. ILLUSTRATION OF A HORIZONTAL WELL SHOWING THE WATER LIFECYCLE IN HYDRAULIC FRACTURING

Image

Radium Activity in Marcellus Flowback Water

- USGS and PA DEP
  - Flowback >600 Bq/L (or >16,000 pCi/L)
- Waste trucks set off radiation alarms
- Contamination downstream of Treatment plants
  - Warner *et al.* (2013)

Picture taken by Andrew Nelson from a fracking site in W. Virginia.

Naturally Occurring Radioactive Material (NORM) Fate and Transport Model

Waste Discharge

Ra-228 Ra-226

Current

Stream

Ra-228 Ra-226

Surface water Streambed ecosystem

Streambed worms, plants, mussels, clams

1600 y	Ra-226	Rn-222	Pb-210	Po-210	
6 y	Ra-228	Ac-228	Th-228	Ra-224	Rn-220

Sediments

Would you expect Po-210 to be relatively soluble or to remain in the sediments?

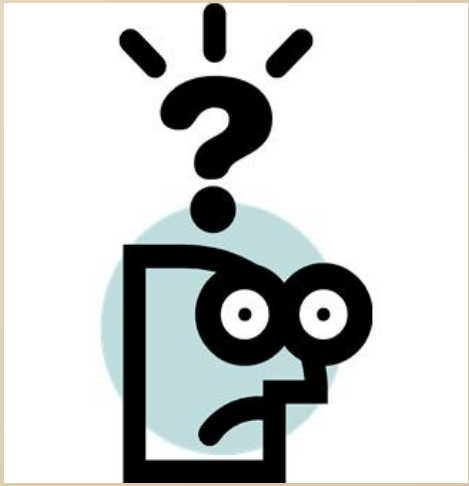
How long would it take for Po-210 to grow into equilibrium with Pb-210 in the sediments?

And Thus Our Study Begins…

On May 7, 2013 SHL received a 55 gallon drum of fracking flow back water (FBW) from the Marcella shale region of northern Pennsylvania.

FBW sample issues

- Lack of control regarding the sampling container.
- Sample was not preserved, thus platting is of concern and how to preserve in this container?
- What is the solids content?
- Volatile compounds hazard?
- How to sub-sample?



Now what do we do?

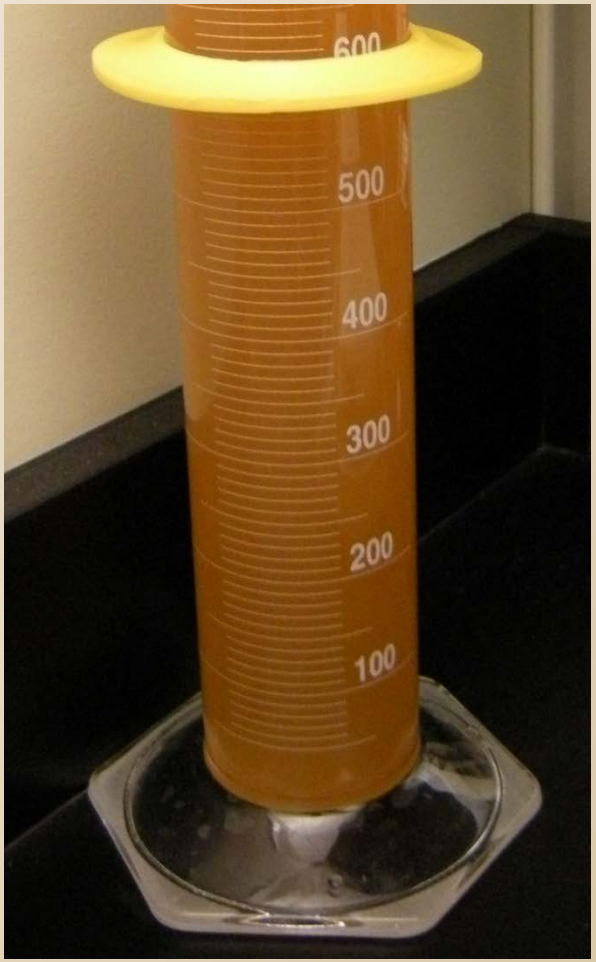
Inorganic Analyses

(major analytes of concern)

Analyte	Concentration mg/L
Chloride	147,000
Strontium	36,000
Sodium	29,000
Calcium	13,000
Barium Ba:Ra ≈ 10^9	9,000
Magnesium	850
Manganese	3
Iron	43
Total solids	278,000
Suspended solids	780

Matrix problems

- Some groups use/propose
  - EPA 903.0 and 904.0
- Methods not validated
- Complicated Matrix:
  - Divalent cations
  - Suspended solids
- Unclear that precipitation or pre-concentration techniques will work



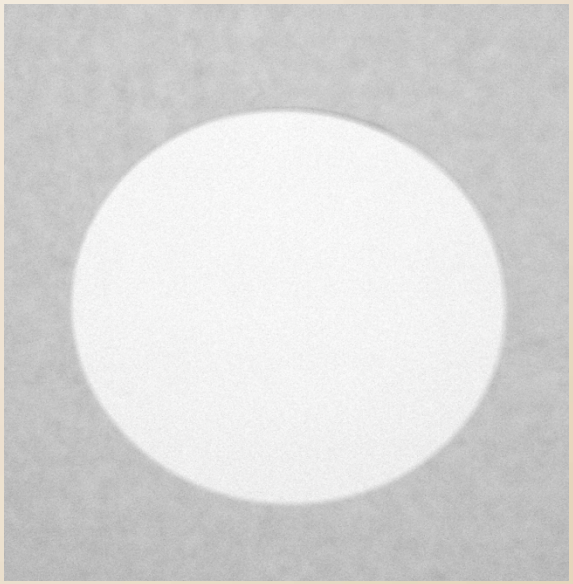
Hypothesis

- High levels of barium in flowback water confound precipitation or pre-concentration techniques
  - Test:
    - EPA 903.0 ($BaSO_4$ co-precipitation)
    - MnO_2 pre-concentration
    - Empore™ Rad radium disks
    - RAD7 portable radon emanation
    - High purity germanium gamma spectroscopy (HPGe)

EPA 903.0 ($BaSO_4$ co-precipitation)

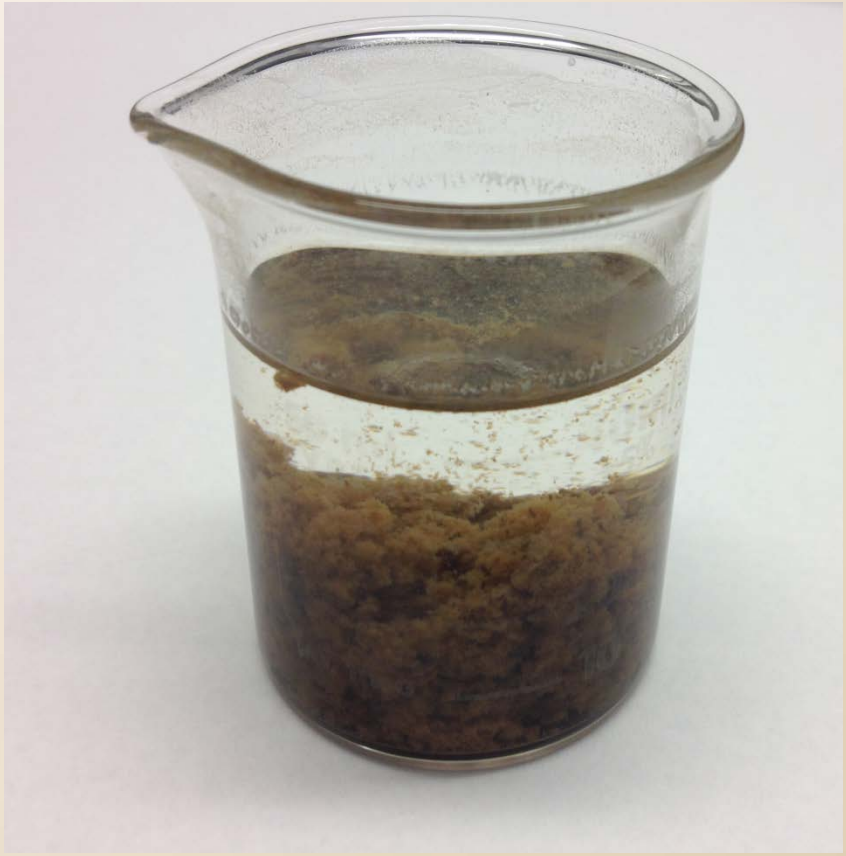
Less than 1% recovery

Empore™ RAD Disks



10% Recovery

MnO_2 pre-concentration

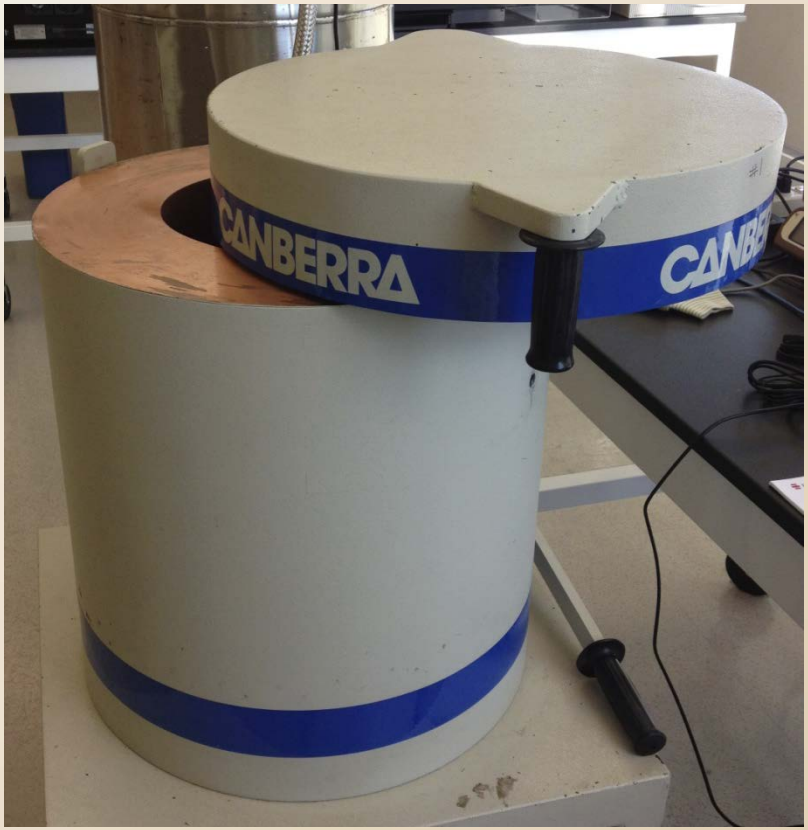


Less than 1% recovery in ppt.

RAD7 portable radon emanation

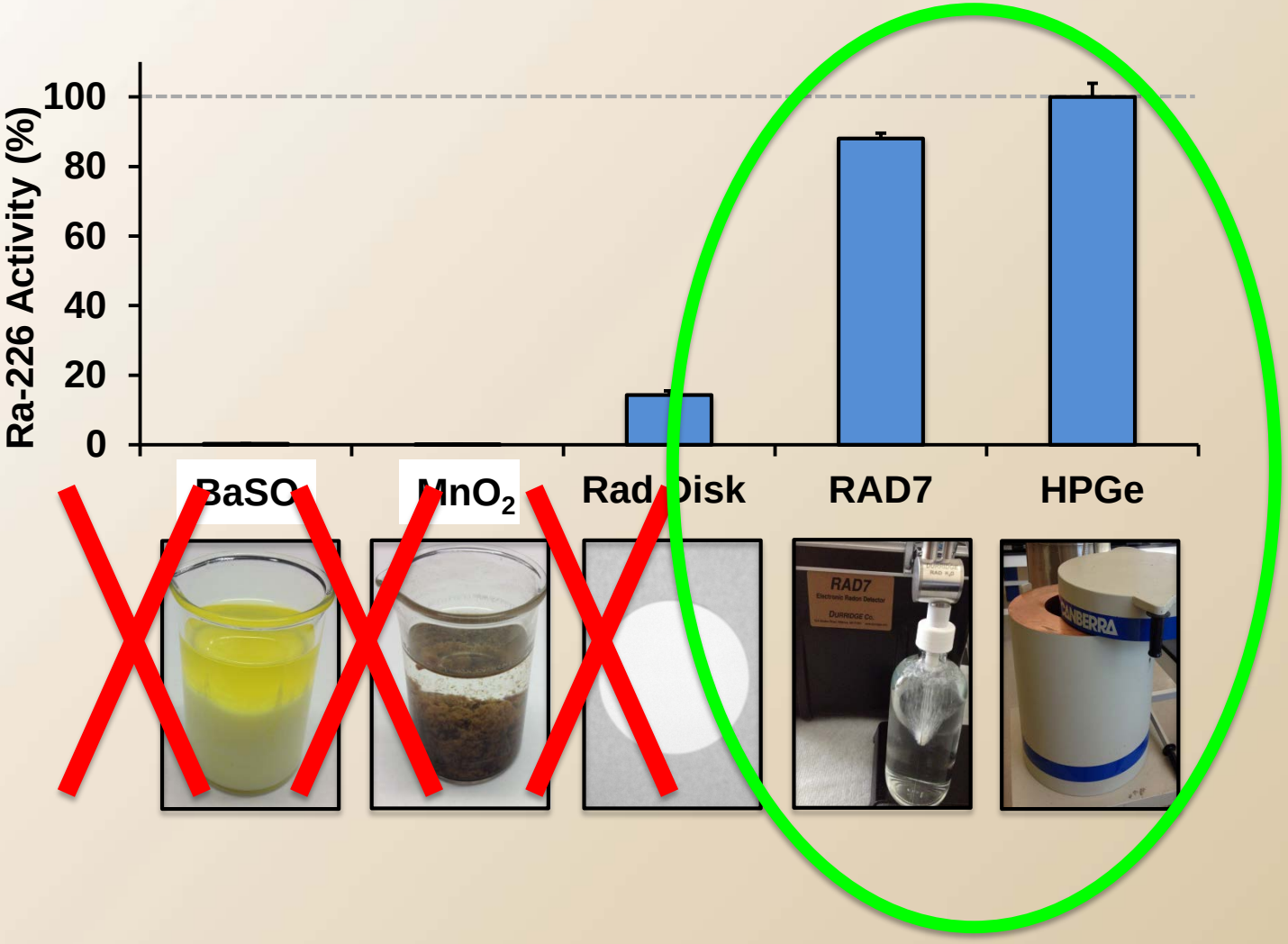
90% Recovery

HPGe Gamma Spectroscopy



100% recovery Non-Destructive, Easy, Reliable

Conclusion


Ra-226 Activity (%)
100
80
60
40
20
0
BaSO
MnO2
Rad Disk
RAD7
HPGe
RAD7
CANBERRA

Full Details: http://pubs/acs.org/loi/estlcu

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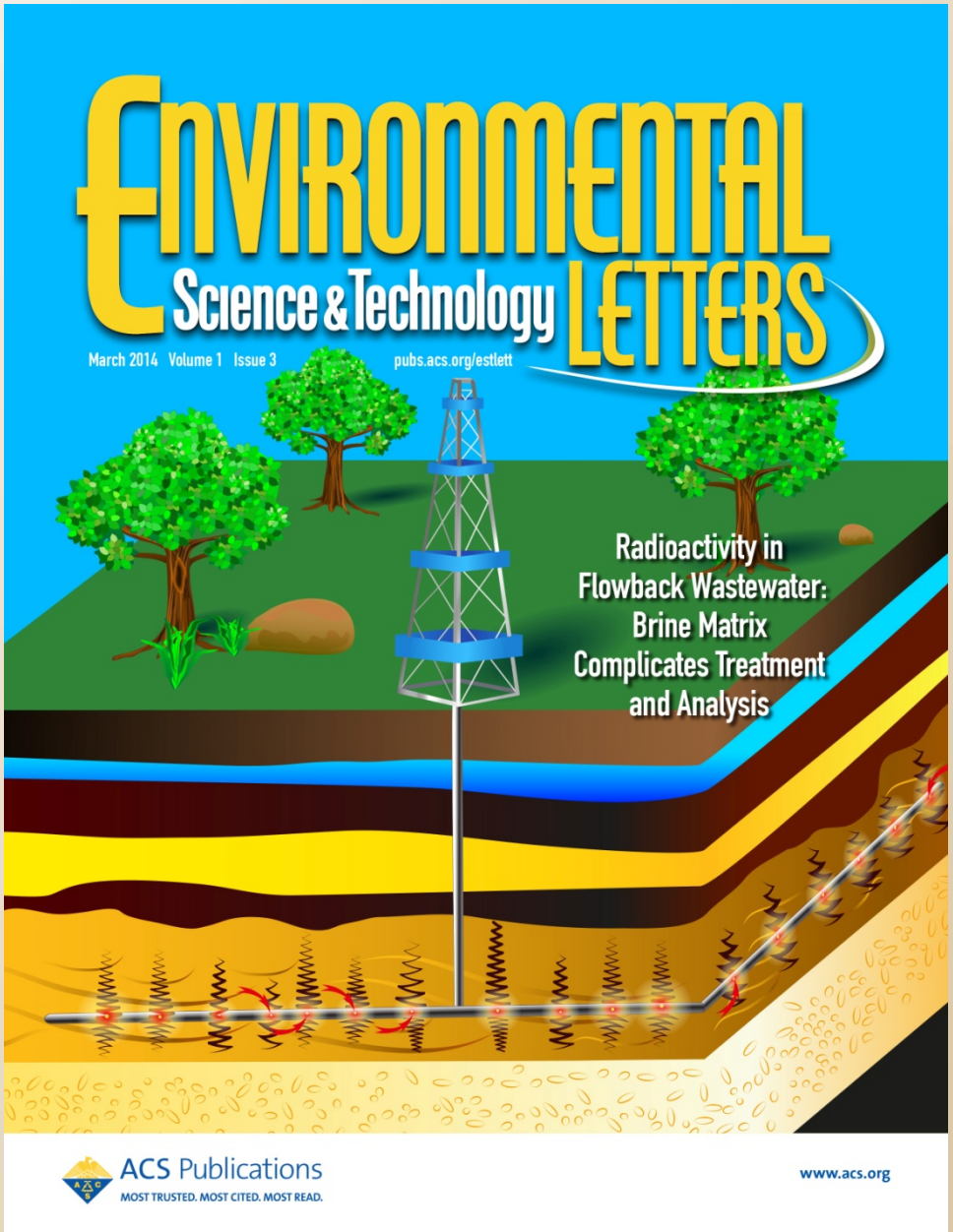
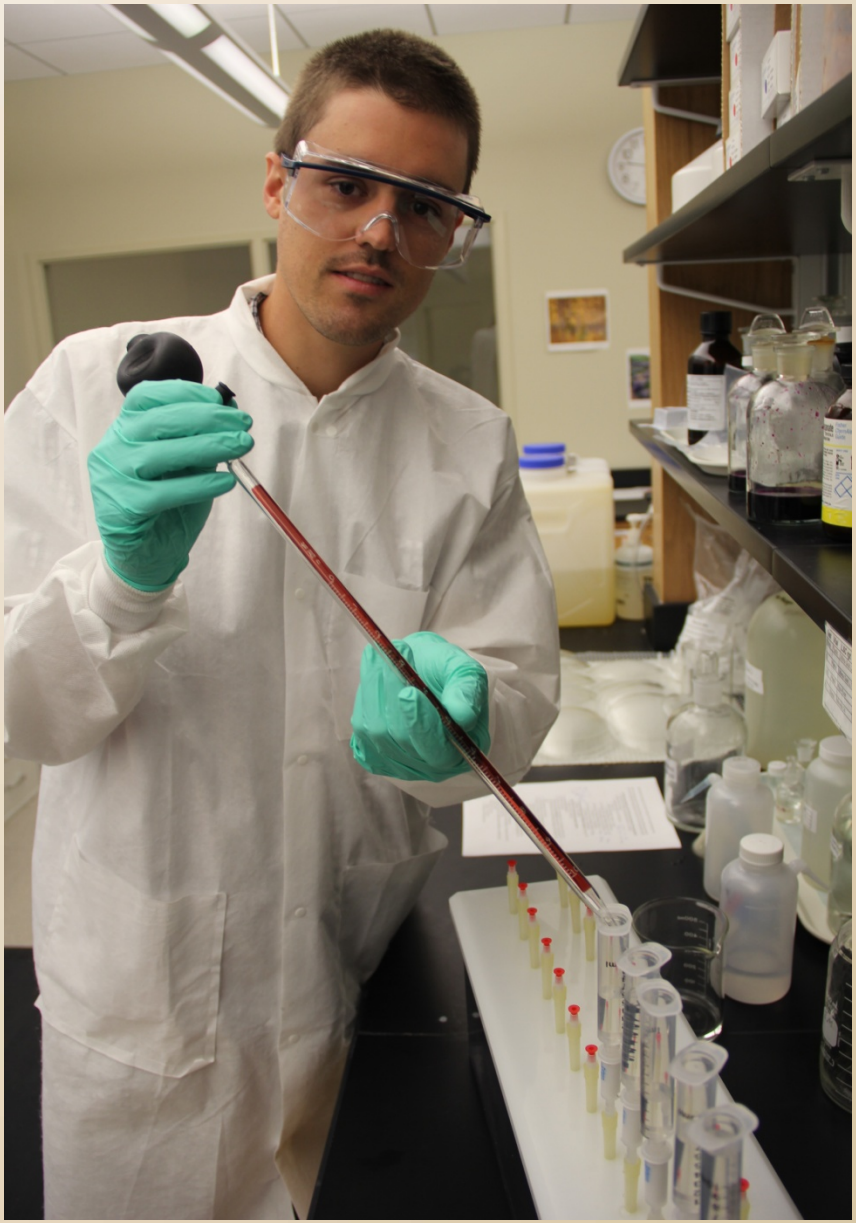


Acknowledgement

Collaboration

- Dr. Schultz
- Andrew Nelson
  - providing some of the slides
  - Publication
- Dustin May
  - SHL analyst



Questions?
Thank you

Marinea Mehrhoff B.S. M.T. A.S.C.P.

Radiochemistry Section Supervisor

Telephone: 319-335-4500

Email: marinea-mehrhoff@uiowa.edu