Why radium in shales and how to process

- Returned water may contain radium because organic rich shales tend to be rich in uranium
- ~20% or water will be returned
- Waste water treatment facility like the one at Niagra Falls can treat return flow
- Whole issue can be avoided by fracking with gas

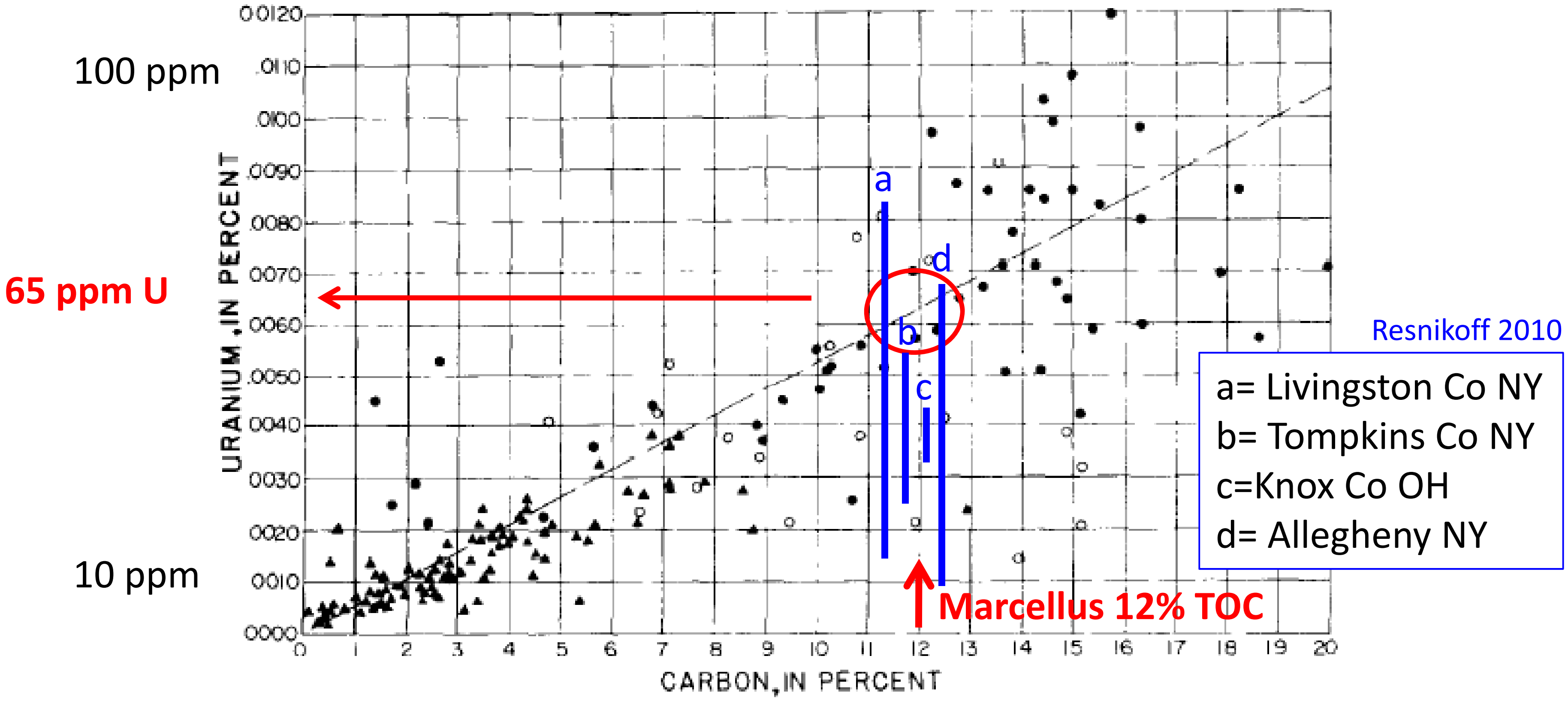
L. M. Cathles
Cornell University

Total Organic Carbon

Uranium increases with TOC richness of shale

Harper Pennsylv Geol 38(1) 2008 p5:
Radioactivity = organic richness = gas

- K, Th, U adsorbed on clays (Wignall and Meyers (1988)
- Th/U~4 (Faure, 1977)
- U can be authigenic (Wignall and Meyers (1988)



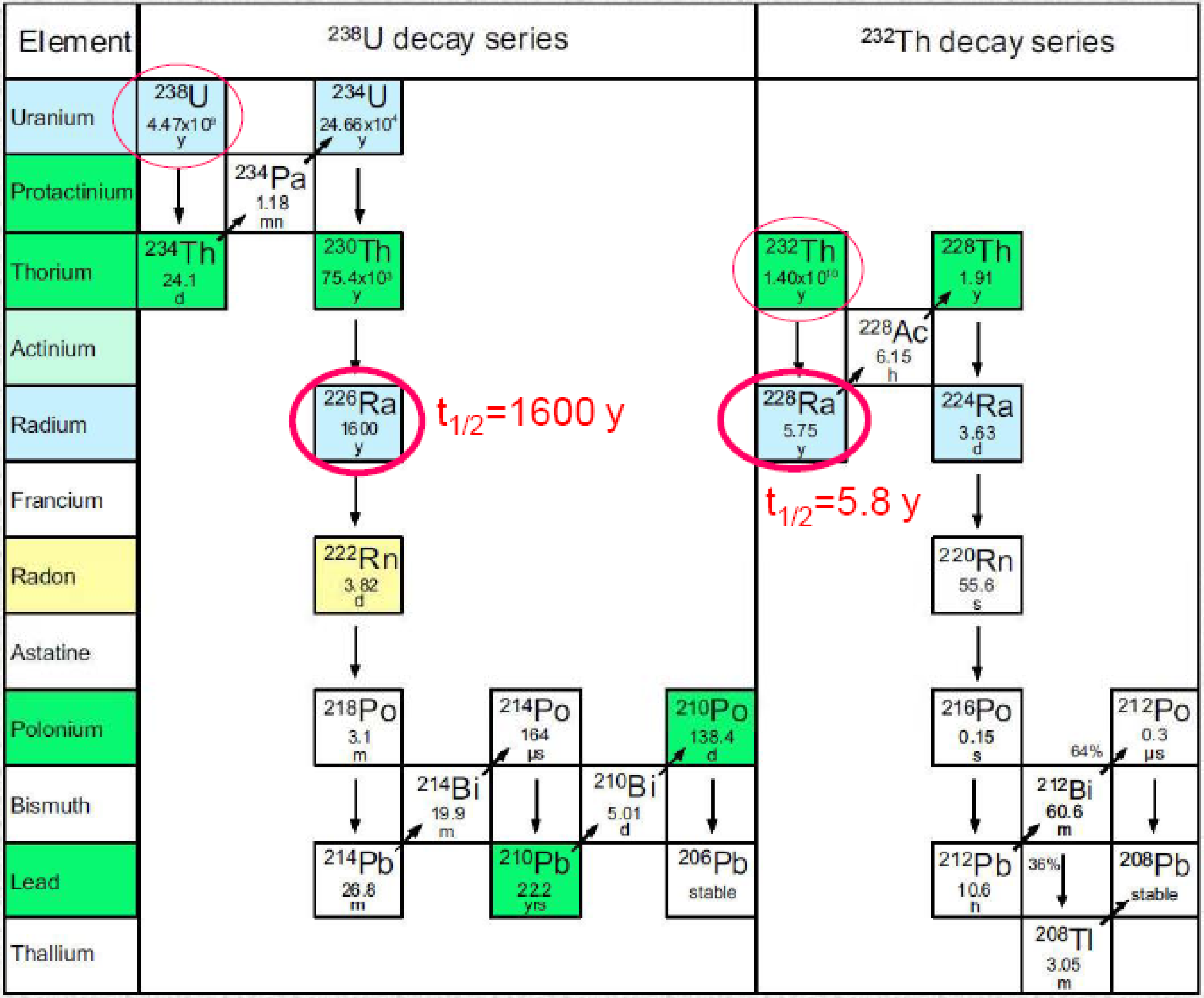
Resnikoff 2010

a= Livingston Co NY
b= Tompkins Co NY
c=Knox Co OH
d= Allegheny NY

Fig. 1. Organic carbon vs uranium in Appalachian Devonian shale samples. Solid circles and line of correlation represent data from SWANSON (1960); triangles show data from LEVENTHAL and GOLDHABER (1978), and LEVENTHAL (1979), open circles show data from this study.

Leventhal JS (1981) … organic matter and … U..of Appalachian Devonian black shales, GCA 45 p883-889

Uranium and Thorium Decay Chains



Element

^{238}U decay series

^{232}Th decay series

Uranium

Protactinium

Thorium

Actinium

Radium

Francium

Radon

Astatine

Polonium

Bismuth

Lead

Thallium

^{238}U 4.47x10^{9} y

^{234}Pa 1.18 mn

^{234}U 24.66x10^{4} y

^{234}Th 24.1 d

^{230}Th 75.4x10^{3} y

^{226}Ra 1600 y

$t_{1/2}$=1600 y

^{222}Rn 3.82 d

^{218}Po 3.1 m

^{214}Pb 26.8 m

^{214}Bi 19.9 m

^{214}Po 164 µs

^{210}Pb 22.2 yrs

^{210}Bi 5.01 d

^{210}Po 138.4 d

^{206}Pb stable

^{232}Th 1.40x10^{10} y

^{228}Ra 5.75 y

$t_{1/2}$=5.8 y

^{228}Ac 6.15 h

^{228}Th 1.91 y

^{224}Ra 3.63 d

^{220}Rn 55.6 s

^{216}Po 0.15 s

^{212}Pb 10.6 h

^{212}Bi 60.6 m

64%

36%

^{212}Po 0.3 µs

^{208}Tl 3.05 m

^{208}Pb stable

Th/U Ratios:

Sandstone: ~4

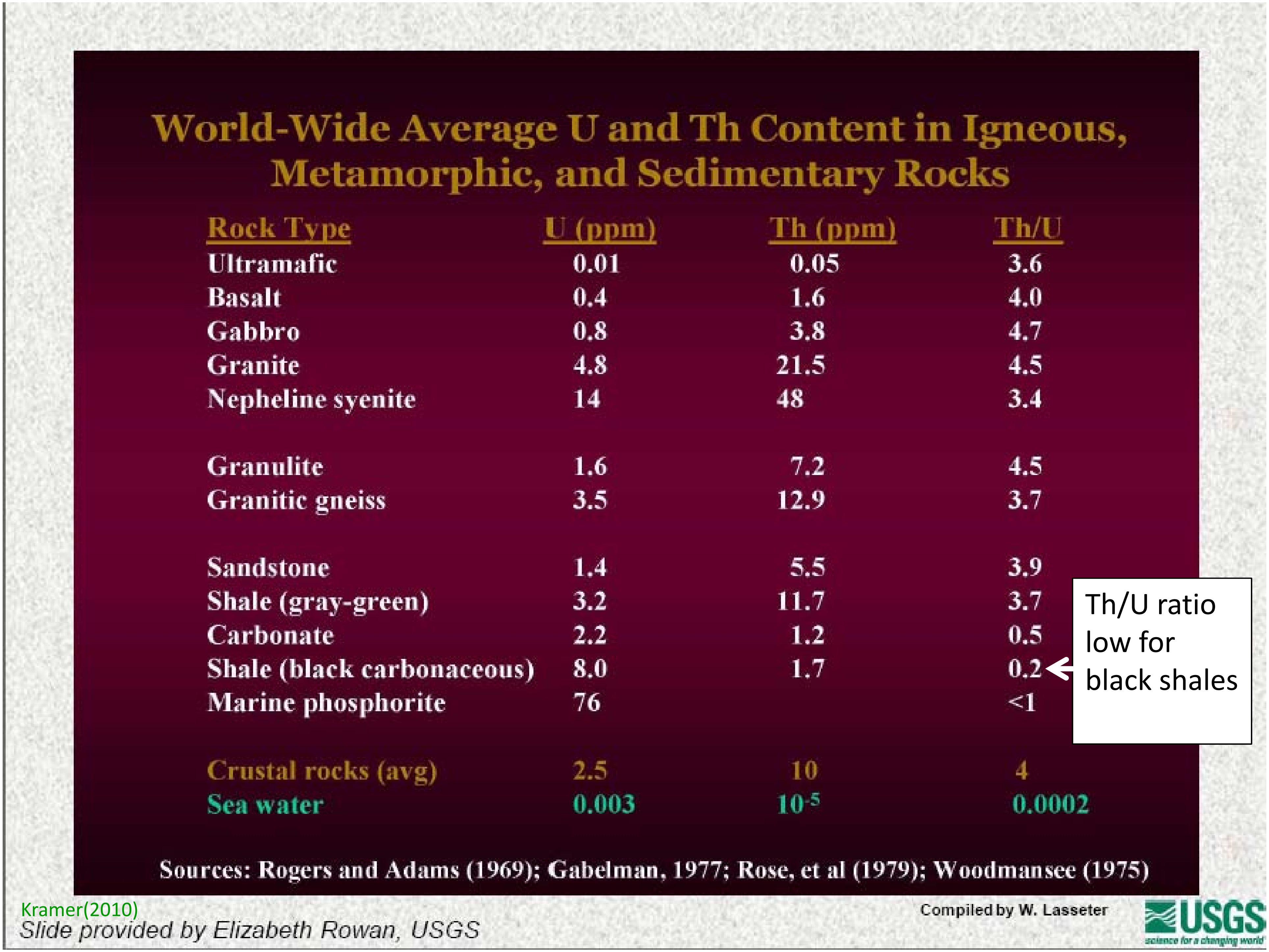
Black Shale: ~0.2

Kramer(2010)

Slide provided by Elizabeth Rowan, USGS

Modified from Schmidt and Kirk, 2010

USGS science for a changing world



World-Wide Average U and Th Content in Igneous, Metamorphic, and Sedimentary Rocks

Rock Type	U (ppm)	Th (ppm)	Th/U
Ultramafic	0.01	0.05	3.6
Basalt	0.4	1.6	4.0
Gabbro	0.8	3.8	4.7
Granite	4.8	21.5	4.5
Nepheline syenite	14	48	3.4
Granulite	1.6	7.2	4.5
Granitic gneiss	3.5	12.9	3.7
Sandstone	1.4	5.5	3.9
Shale (gray-green)	3.2	11.7	3.7
Carbonate	2.2	1.2	0.5
Shale (black carbonaceous)	8.0	1.7	0.2
Marine phosphorite	76		<1
Crustal rocks (avg)	2.5	10	4
Sea water	0.003	10^{-5}	0.0002

Th/U ratio low for black shales

Sources: Rogers and Adams (1969); Gabelman, 1977; Rose, et al (1979); Woodmansee (1975)

Compiled by W. Lasseter

Kramer(2010)

Slide provided by Elizabeth Rowan, USGS

^{226}Ra can be calculated

$$\frac{{}^{226Ra}m}{{}^{238U}m} = \frac{{}^{226Ra}\tau_{1/2}}{{}^{238U}\tau_{1/2}} = \frac{1600\,y}{4.47\times10^{9}\,y} = 3.58\times10^{-7}$$

for 60 ppm U get 2.15×10^{-5} ppm ^{226}Ra

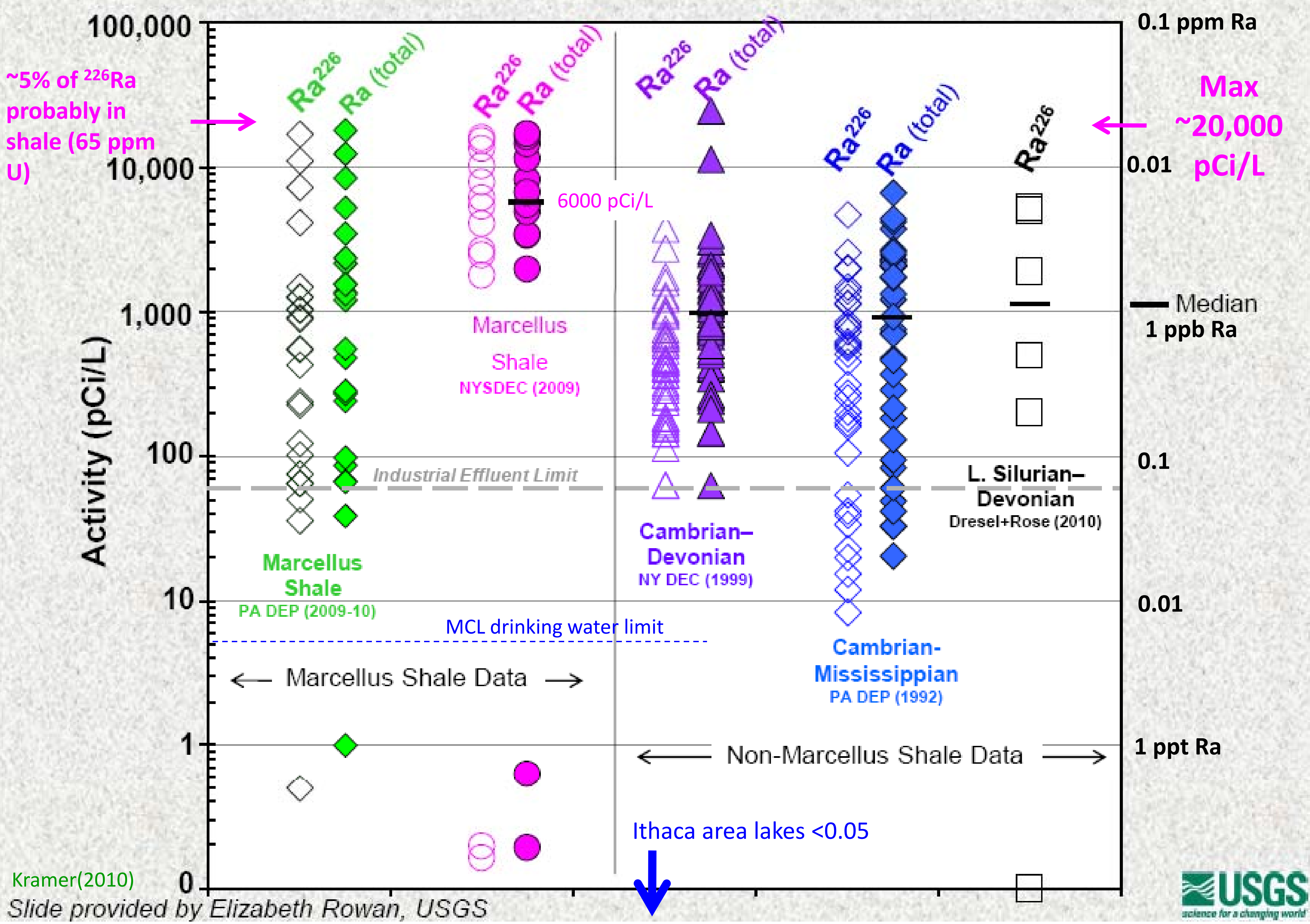
10^{-6} ppm $^{226}Ra = 1 pCi/g_{rock}$

Thus 60 ppm U = 21.5 pCi/g_{rock}

At 2g_{rock}/cm^3, 10% porosity, 60 ppm U could put 420,000 pCi/L into pore water

Actually see up to 5% of this loading, or 20,000 pCi/L in return fluids

Radium Activity Ranges in Produced Water, NY and PA



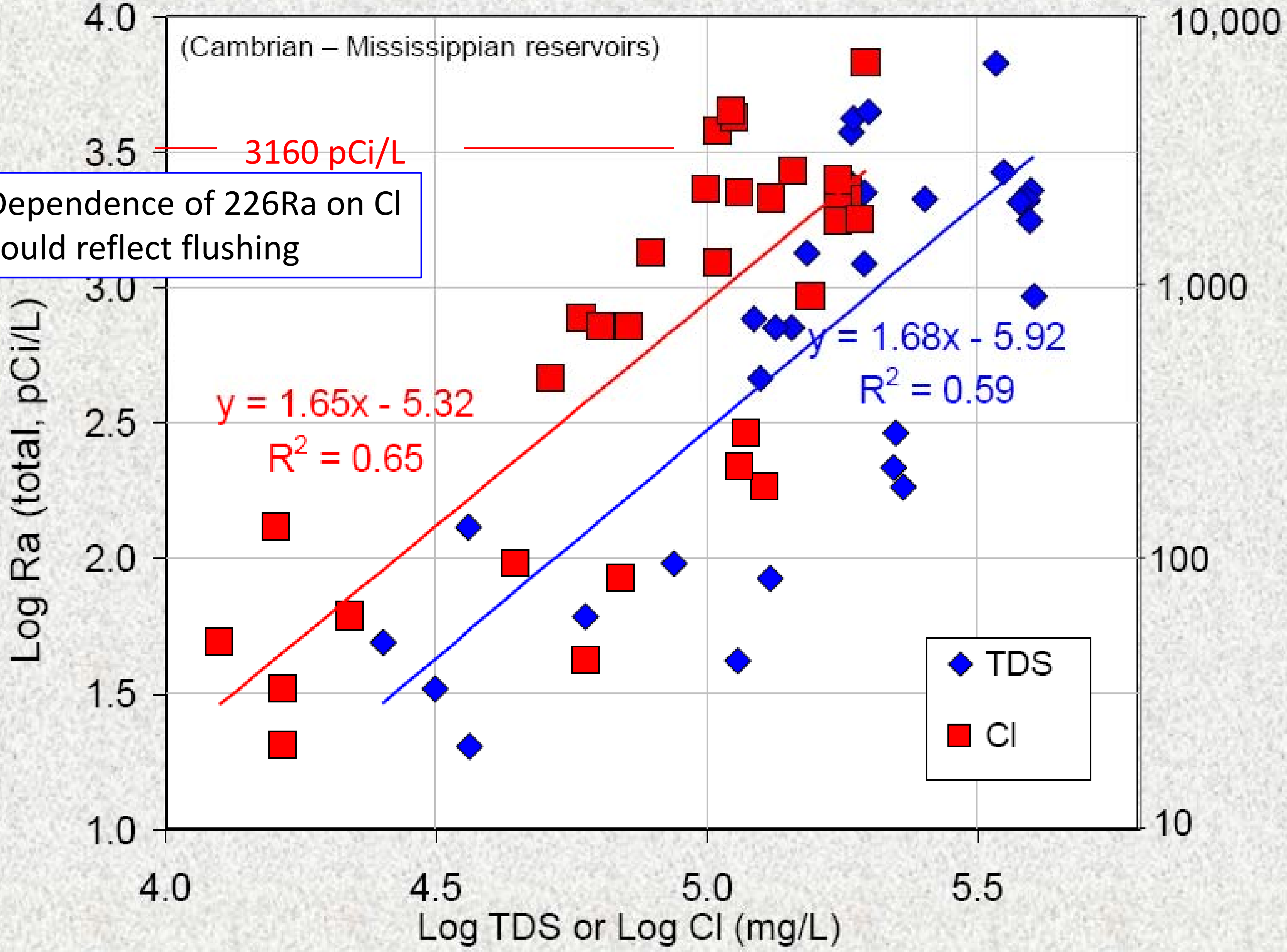
~5% of ^{226}Ra probably in shale (65 ppm U)

Max ~20,000 pCi/L

Kramer(2010)

Slide provided by Elizabeth Rowan, USGS

Ra vs. Cl and TDS, Oil and Gas Well Brines, PA



Dependence of 226Ra on Cl could reflect flushing

Source: PA DEP NORM Survey1992

Kramer(2010)

Slide provided by Elizabeth Rowan, USGS

Radio decay adds ^{4}He to Marcellus gas

$$^{238}_{92}U \rightarrow ^{206}_{82}Pb + 8\,^{2}_{4}He + 6\beta^{-},\ \tau = 6.48\,\mathrm{Ga}$$

$$^{232}_{90}Th \rightarrow ^{208}_{82}Pb + 6\,^{2}_{4}He + 4\beta^{-},\ \tau = 20\,\mathrm{Ga}$$

$$\frac{m_{He}}{m_U} = 6R_{Th/U}\left(\frac{t}{\tau_{Th}}\right) + 8\left(\frac{t}{\tau_U}\right)$$

Powerful cross-checks are potentially available

ppm U indicated by ^{4}He in Marcellus gas

			% gas-saturated						
RTh/U	ppm U	Time[Ma]	porosity		grain density [kg/m3]		rock density[kg/m3]		
0.2	60	350	10		2750		2475		
			mol wt CH4		Tsufr	grad T [K/km]	grad P bar/km		depth [km]
T1/e U [Ga]	T1/e Th [Ga]		16		20	20	100		3
6.5	20								
	mHe/mU		0.451769		moles of He generated per mole of U				
	mU/m3		0.62395		moles uranium per m3 of rock				
	mHe/m3		0.281881		moles He per m3 rock				
	kg He /m3		0.001128		kg He per m3 rock				
	pore space		0.1		m3 pore space per m3 rock				
	T source [C]		80		temperature in the source shale				
	P source [bars]		301		Pressure in the source shale				
	density CH4 kg/m3		178.4716		gas law density of methane in the source shale				
	kg CH4/m3		17.84716		kg CH4 pre m3 of source rock				
	ppm He in CH4		63.17671		ppm 4He in CH4 pore space gas				

200 ppm U = 210 ppm 4He, etc.

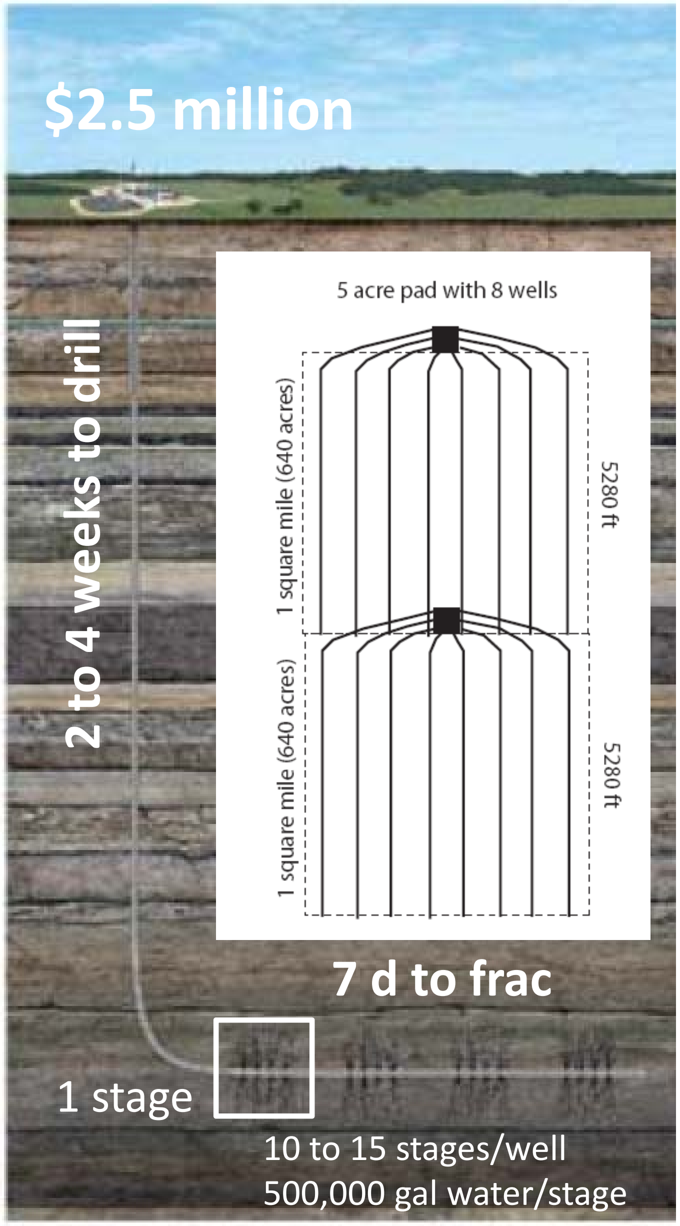
For Tompkins Co will need to process ~1 cfs return flow

Hydrofracking

- 1 horizontal well can tap 80 acres
- 8 wells per ~5 acre pad
- 5x10^6 gal/well; **40x10^6 gal/pad**
- water return ~20% =**8x10^6 gal/pad**
- 1 pad per square mile

Tompkins County (pop 100,153)

- 421 mi^2 could be drilled
- if 50% developed over 10 years with 1 pad/mi^2
  - 21 pads/yr
  - 210 wells /yr
  - 2,500 jobs (10 p/well) ~4% TC workforce
  - 10^9 gallons of water /yr = 5 cfs
  - **1 cfs return water/yr**

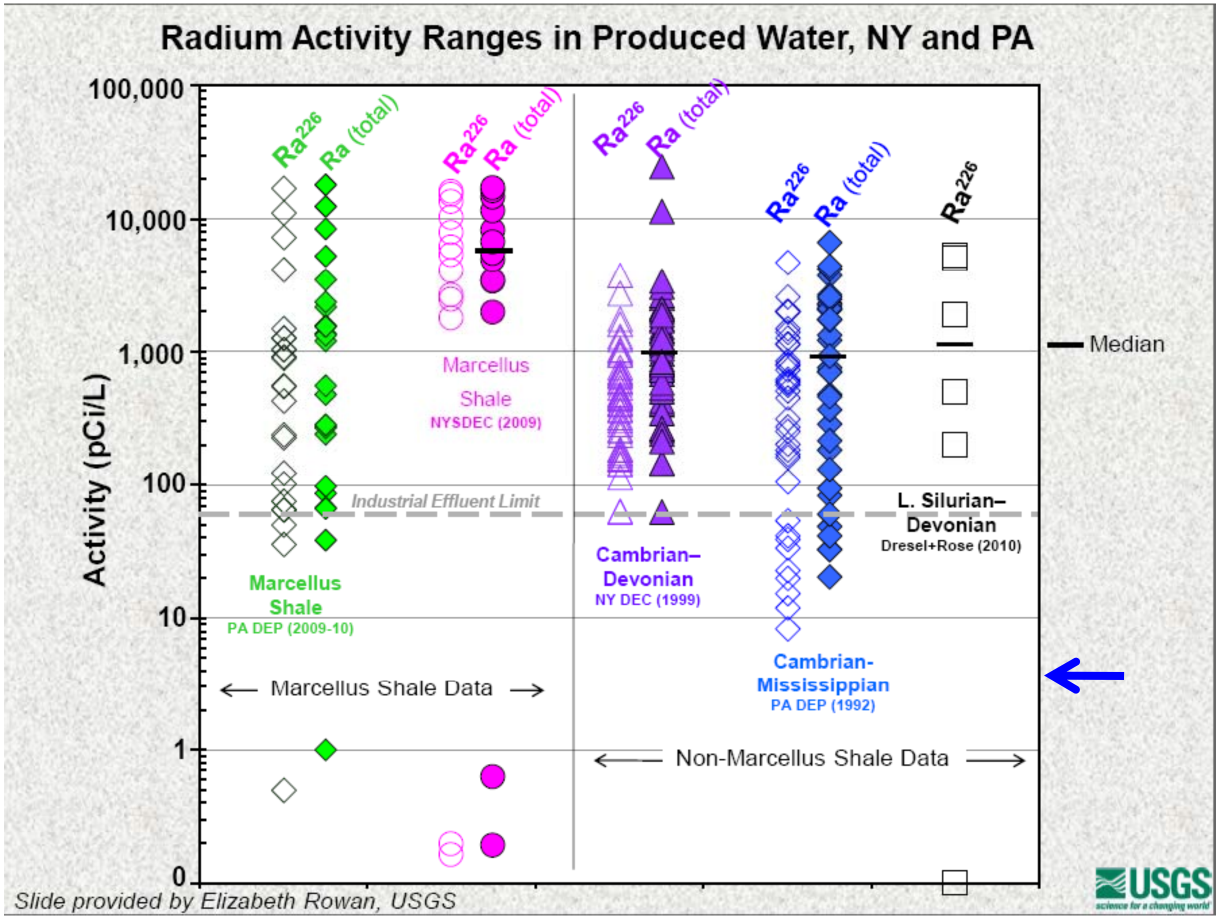


1 cubic ft = 7.48 gallons
1cfs = 0.24x10^9 gallons per year

Pad development scenario is from a presentation by Art Pierce in Lansing June 29, 2011

Fracking chemicals less serious than dissolved Minerals like Ra

Radium is an issue that must be managed



Slide provided by Elizabeth Rowan, USGS

- Managed at existing wells
- Can be detected and precipitated at well head
- Can be removed in drinking water treatment facilities

5 pCi/L = USEPA drinking water standard

Environmental Levels of Radium in Water of Central New York, Thomas F. Kraemer U.S. Geological Survey, Reston, VA, Finger Lakes Research Conference, December 4, 2010

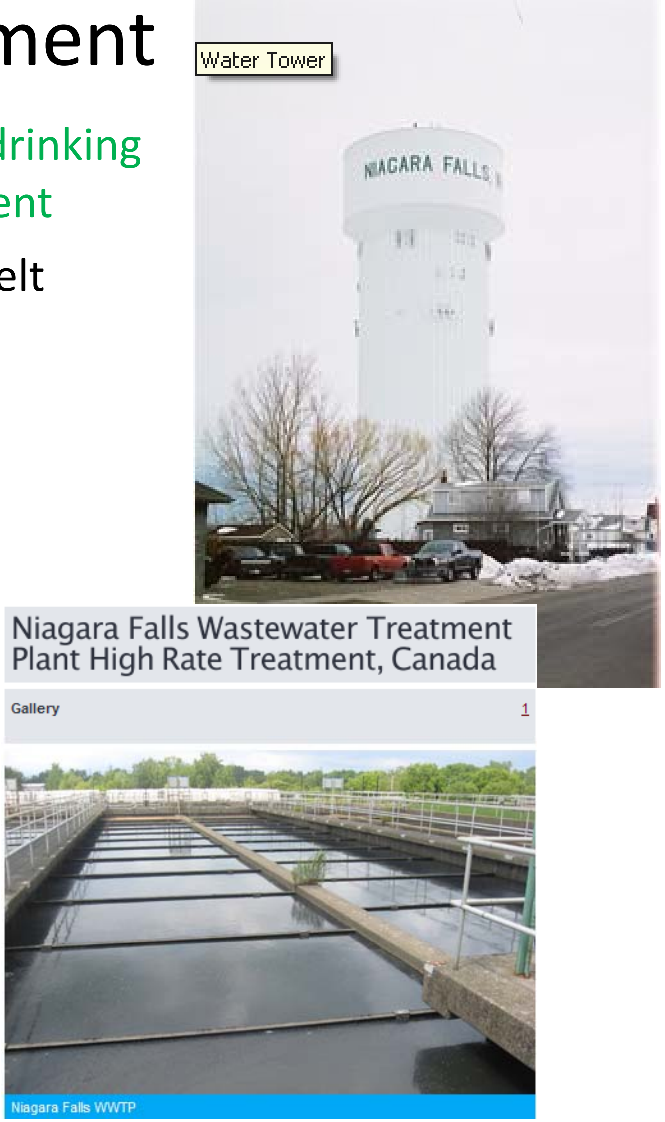
Return water can be treated

Niagra Falls Wastewater Treatment

Not same as drinking water treatment

- Screen for large solids
- Remove grit is settling ponds
- flocculate with $FeCl_3$ and polymer -> thickeners , belt dewater, disposal
- Flow through carbon beds
- Treat with peroxide and Na hyperchlorite
- dispose Niagra River
- capacity 136 ML/d = 55 cfs

- 21 pads generate 1 cfs return water
- Niagra plant could treat 1100 pads per year



Niagara Falls Wastewater Treatment Plant High Rate Treatment, Canada

Gallery 1

Niagara Falls WWTP

http://nfwb.org/customer/faq.php

http://www.water.mottmac.com/waterprojects/?mode=type&id=327912

Propane fracking eliminates water problems, cuts trucks by 5x, and does not impair resource

- no water injected
- no capillary seals
- no contaminants returned (Ra, metals)
- recycle 80% propane
- propane uniform chemistry→gelation chemistry simple (P-ester, Fe+++ SO4 linker, MnO breaker)
- no flaring at startup
- Fewer trucks (30 vs 947)
- Fewer frac jobs (because all fractures good)
- Lower cost because more effective

Technological innovation can address issues

Robert Lestz, Gasfrac Energy Services Inc
Cornell Lectures March 1 and 2, 2010

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