Critical Minerals Workshop
of the southern Midcontinent

Prospecting for Critical Minerals and Recoverable Elements in southern Midcontinent Brines

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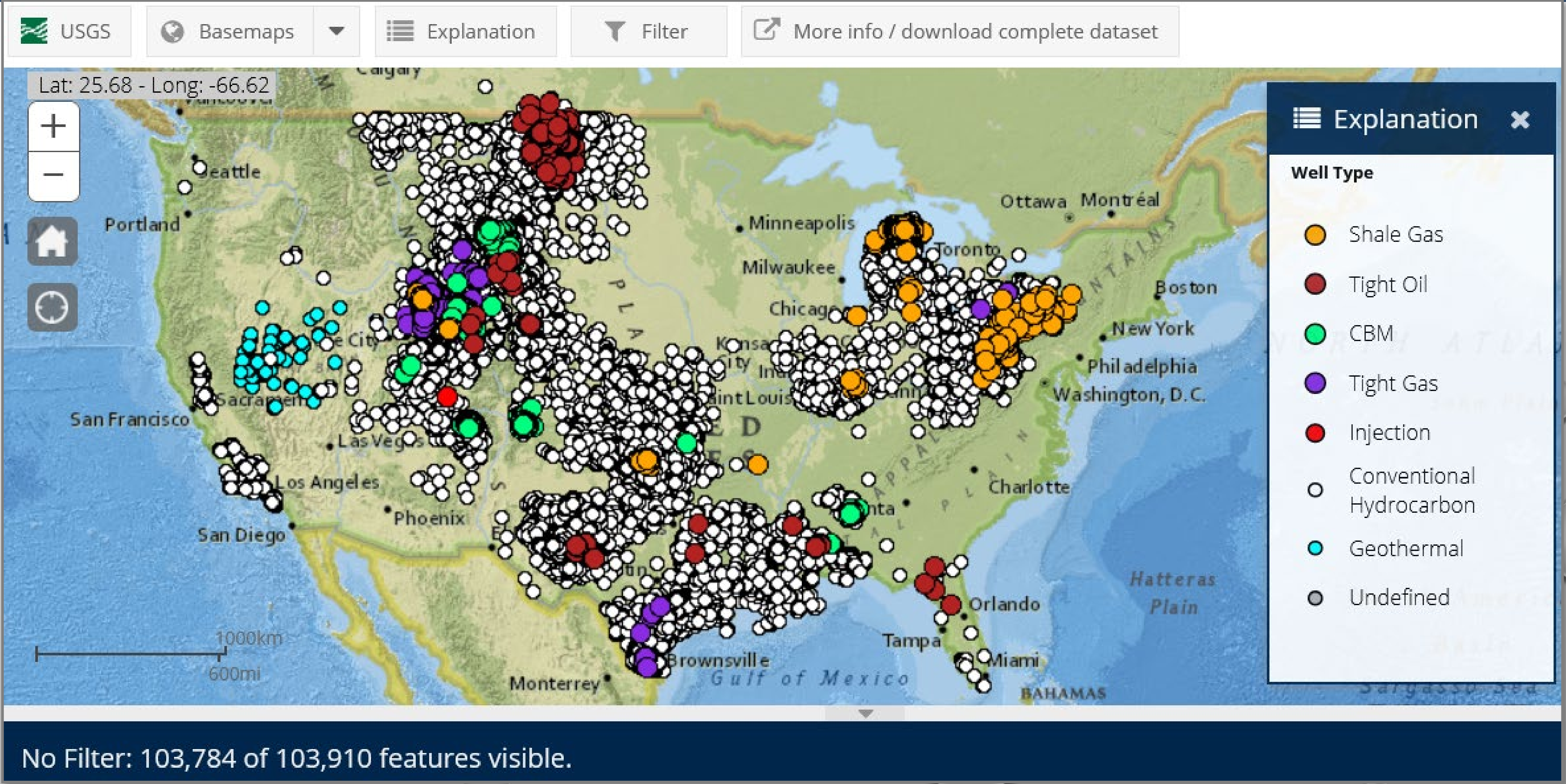
OKLAHOMA GEOLOGICAL SURVEY

OGS

1908

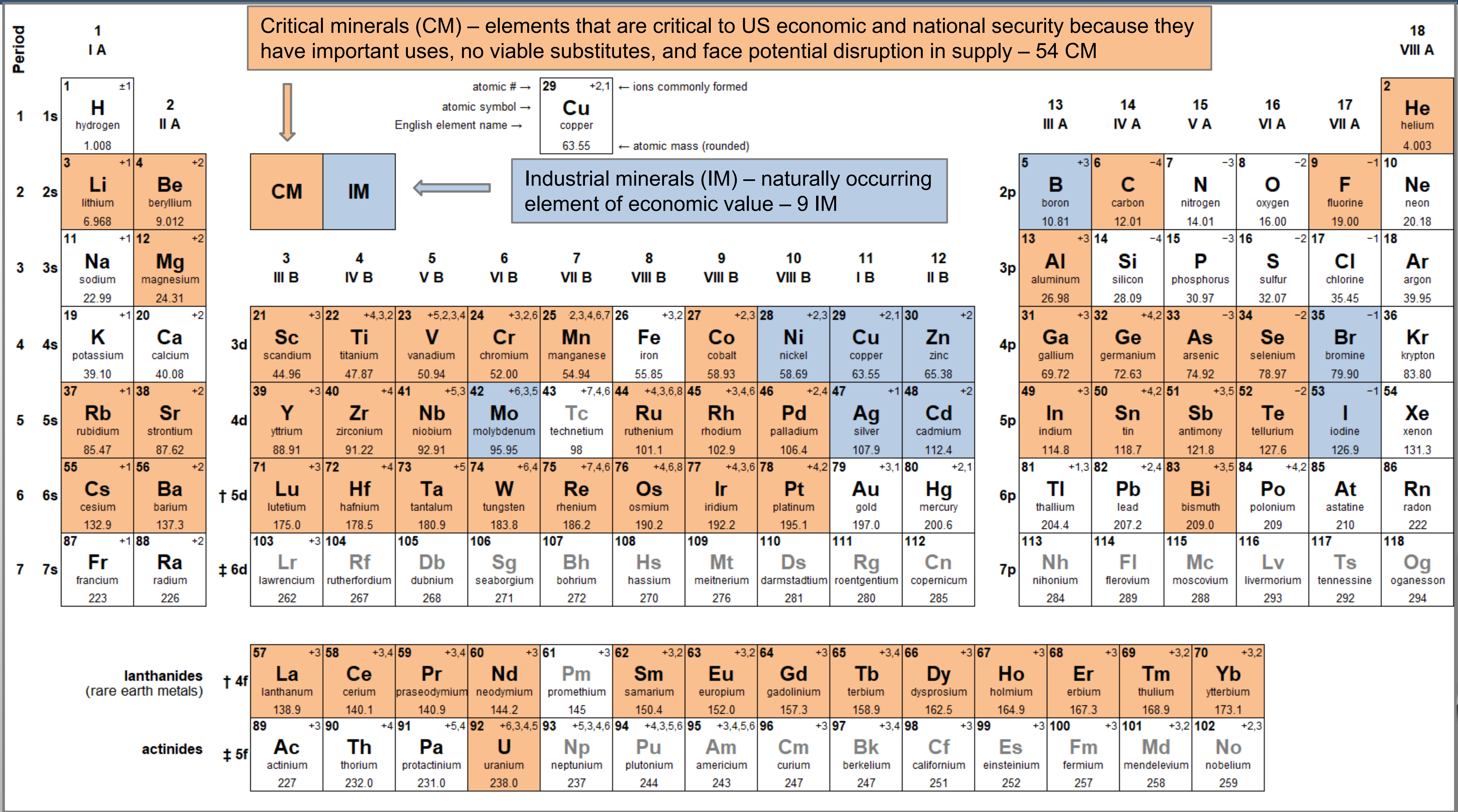
USGS Produced Waters Geochemical Database



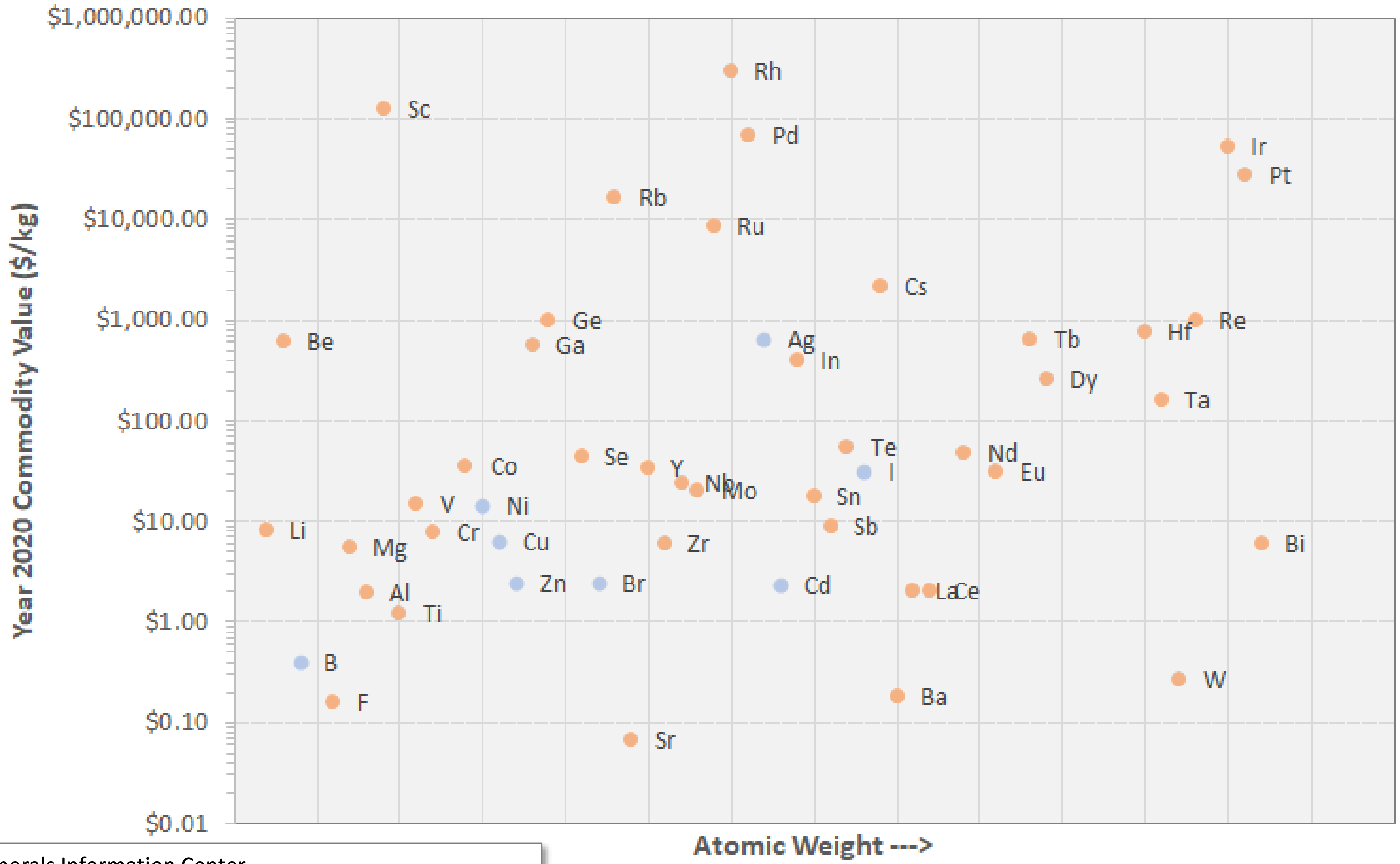
Critical and Industrial Minerals/Elements

Critical minerals (CM) – elements that are critical to US economic and national security because they have important uses, no viable substitutes, and face potential disruption in supply – 54 CM

Industrial minerals (IM) – naturally occurring element of economic value – 9 IM



Critical and Industrial Minerals/Elements



From USGS National Minerals Information Center
https://www.usgs.gov/centers/nmic/commodity-statistics-and-information#I

Example CM: Lithium

Table 2 World in-situ lithium resource

Deposit	*Country*	*Type*	*Average concentration (% Li)*	*In-situ resource (Mt Li)*
Uyuni	Bolivia	Brine	0.0532	10.2
Atacama[a]	Chile	Brine	0.14	6.3
Kings Mountain Belt	United States	Pegmatite	0.68	5.9
Qaidam[a]	China	Brine	0.03	2.02
Kings Valley	United States	Sedimentary rock	0.27	2.0
Zabuye[a]	China	Brine	0.068	1.53
Manono/Kitotolo	Congo	Pegmatite	0.58	1.145
Rincon	Argentina	Brine	0.033	1.118
Brawley	United States	Brine	–	1.0
Jadar Valley	Serbia	Sedimentary rock	0.0087	0.99
Hombre Muerto[a]	Argentina	Brine	0.052	0.8
Smackover	United States	Brine	0.0146	0.75
Gajika	China	Pegmatite	–	0.591
Greenbushes[a]	Australia	Pegmatite	1.59	0.56
Beaverhill	Canada	Brine	–	0.515
Yichun[a]	China	Pegmatite	–	0.325
Salton Sea	United States	Brine	0.02	0.316
Silver Peak[a]	United States	Brine	0.02	0.3
Kolmorzerskoe	Russia	Pegmatite	–	0.288
Maerking[a]	China	Pegmatite	–	0.225
Maricunga	Chile	Brine	0.092	0.22
Jiajika[a]	China	Pegmatite	0.59	0.204
Daoxian	China	Pegmatite	–	0.182
Dangxiongcuo[a]	China	Brine	0.04	0.181
Olaroz	Argentina	Brine	0.07	0.156
Other (producing)[a]	8 deposits in Brazil, Canada, China, Portugal	Pegmatite	–	0.147
Goltsovoe	Russia	Pegmatite	–	0.139
Polmostundrovskoe	Russia	Pegmatite	–	0.139
Ulug-Tanzek	Russia	Pegmatite	–	0.139
Urikskoe	Russia	Pegmatite	–	0.139
Koralpe	Austria	Pegmatite	–	0.1
Mibra	Brazil	Pegmatite	–	0.1
Bikita[a]	Zimbabwe	Pegmatite	1.4	0.0567[b]
Dead Sea	Israel	Brine	0.001	–
Great Salt Lake	United States	Brine	0.004	–
Searles Lake	United States	Brine	0.005	–
Total				38.68

Note: Li = lithium; Mt = million tonnes.
[a]Producing. [b]We used the lowest estimate in the literature, although some estimates for Bikita were over 100,000 tonnes Li.

Gruber et al, 2011

Kesler et al, 2012

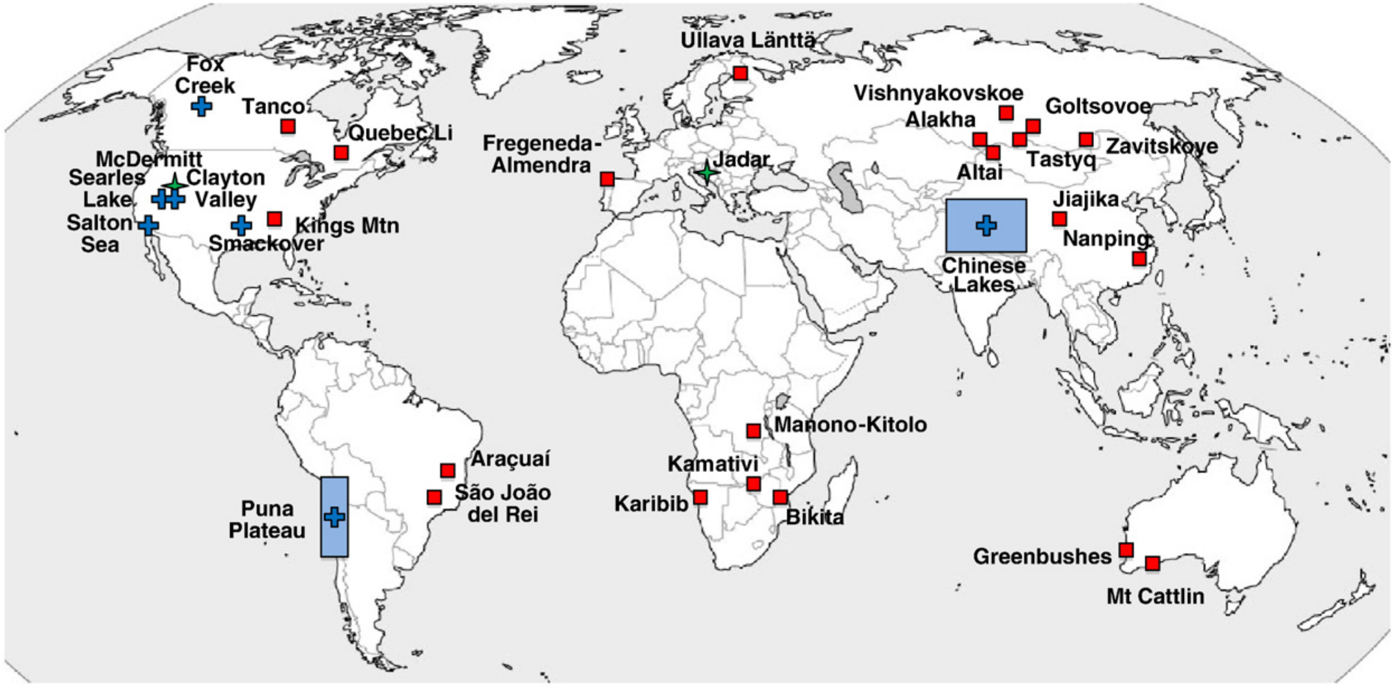
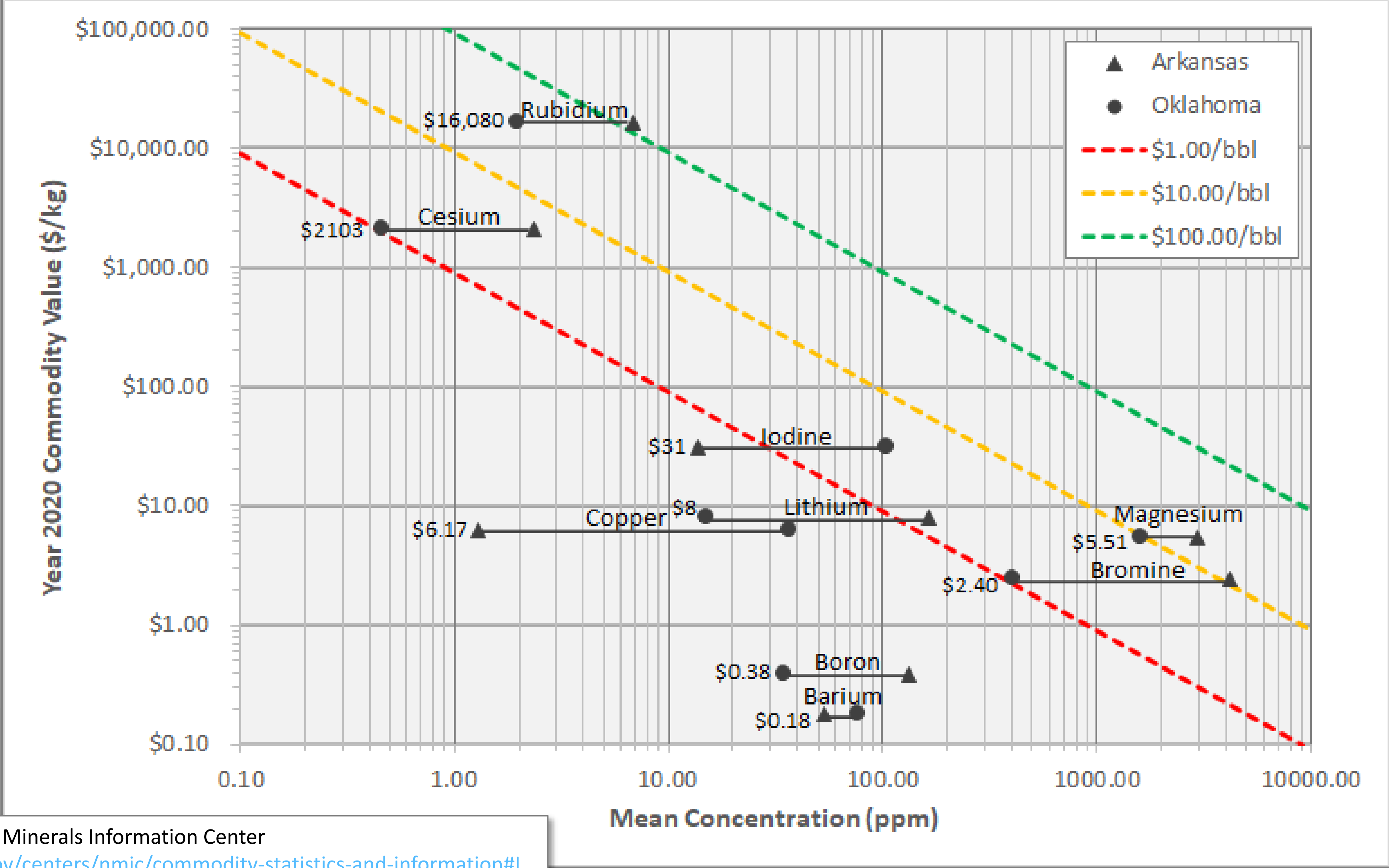


Fig. 2. Location of major lithium pegmatite (square) and brine (cross) deposits. Shaded rectangles are enlarged to show distribution of salars in the Puna Plateau (Chile–Argentina and China in Figs. 8 and 11, respectively.

Top Prospects in Brine of Oklahoma & Arkansas



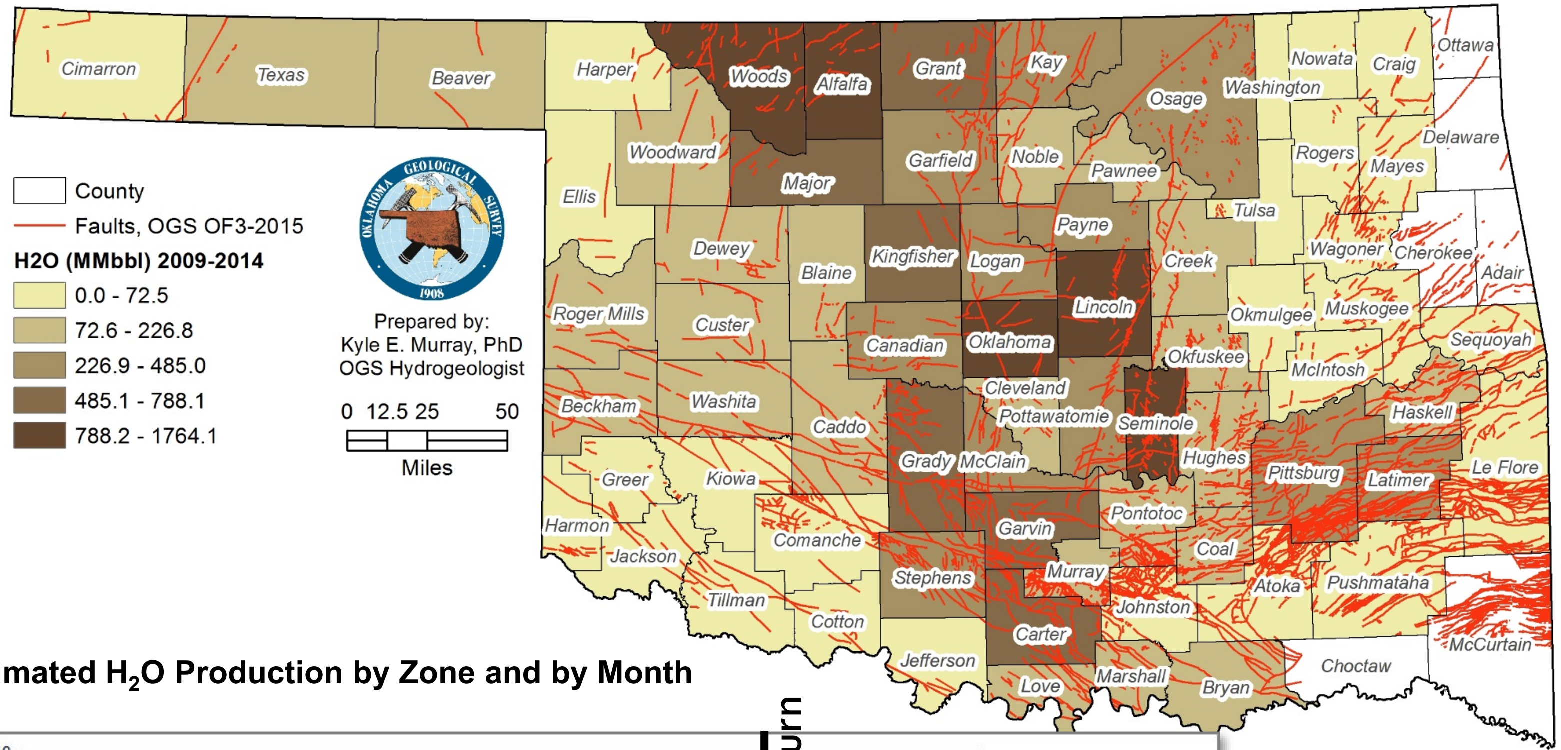
From USGS National Minerals Information Center
https://www.usgs.gov/centers/nmic/commodity-statistics-and-information#I

Produced H_2O by Zone and County

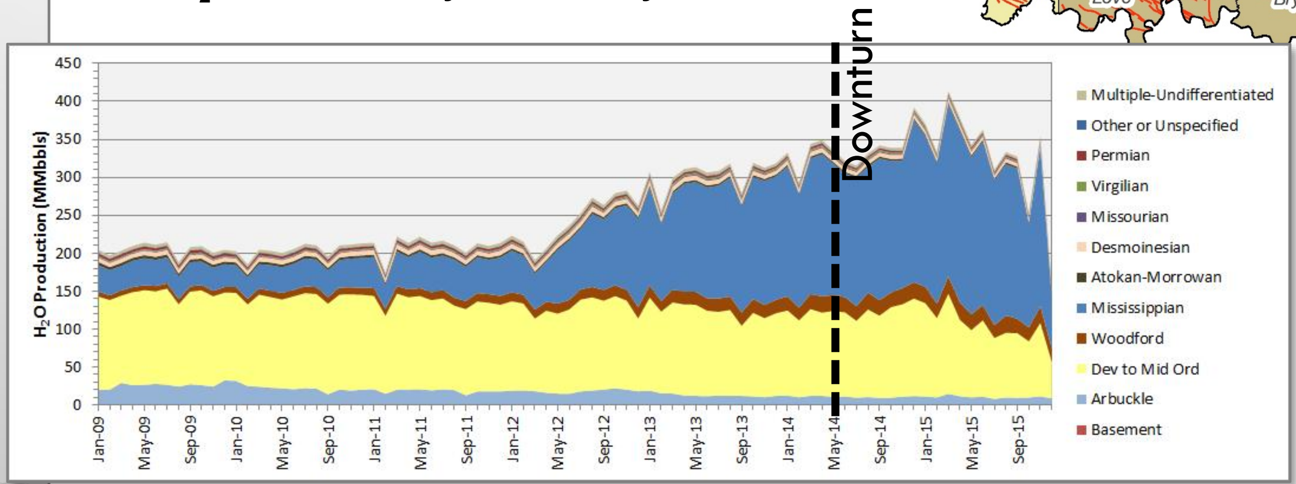
Zone	Group	Formation
Multiple-Undiff		
Other or Unspecified		
Permian		Garber
	Chase	Brown Dolomite
	Council Grove	Pontotoc
	Admire	Belveal
Virgilian	Wabaunsee	Cisco Lime
	Shawnee	Pawhuska
		Endicott
	Douglas	Tonkawa
Missourian	Hoxbar	Lansing
		Cottage Grove
		Kansas City
		Hogshooter
		Layton
		Cleveland
Desmoinesian	Marmaton - Deese	Oswego
	Cabaniss - Deese	Skinner
	Krebs - Deese	Red Fork
		Burbank
		Bartlesville
		Hartshorne
Atokan-Morrowan	Atoka	Gilcrease
		Dutcher
	Morrow	Cromwell
	Springer	Wamsley
Mississippian	Chester	Manning
		Caney
	Meramec	Miss Lime
		Miss Chat
		St. Louis
		Mayes
	Osage	Sycamore
	Kinderhook	Kinderhook
Woodford	Upper Devonian	Woodford
Dev to Mid Ord	Middle Devonian	Misener
	Hunton	Frisco
		Bois d'Arc
		Henryhouse
		Chimneyhill
	Cincinnatian	Sylvan
		Viola
	Simpson	Bromide
		Wilcox
		McLish
		Oil Creek
Arbuckle	Arbuckle Group	West Spring Creek
		Kindblade
		Cool Creek
		McKenzie Hill
		Butterly dolomite
		Signal mountain
		Royer dolomite
		Fort sill limestone
Basement & Crystalline Rock	Cambrian	Reagan
	Pre-Cambrian	Granite

Granite Wash

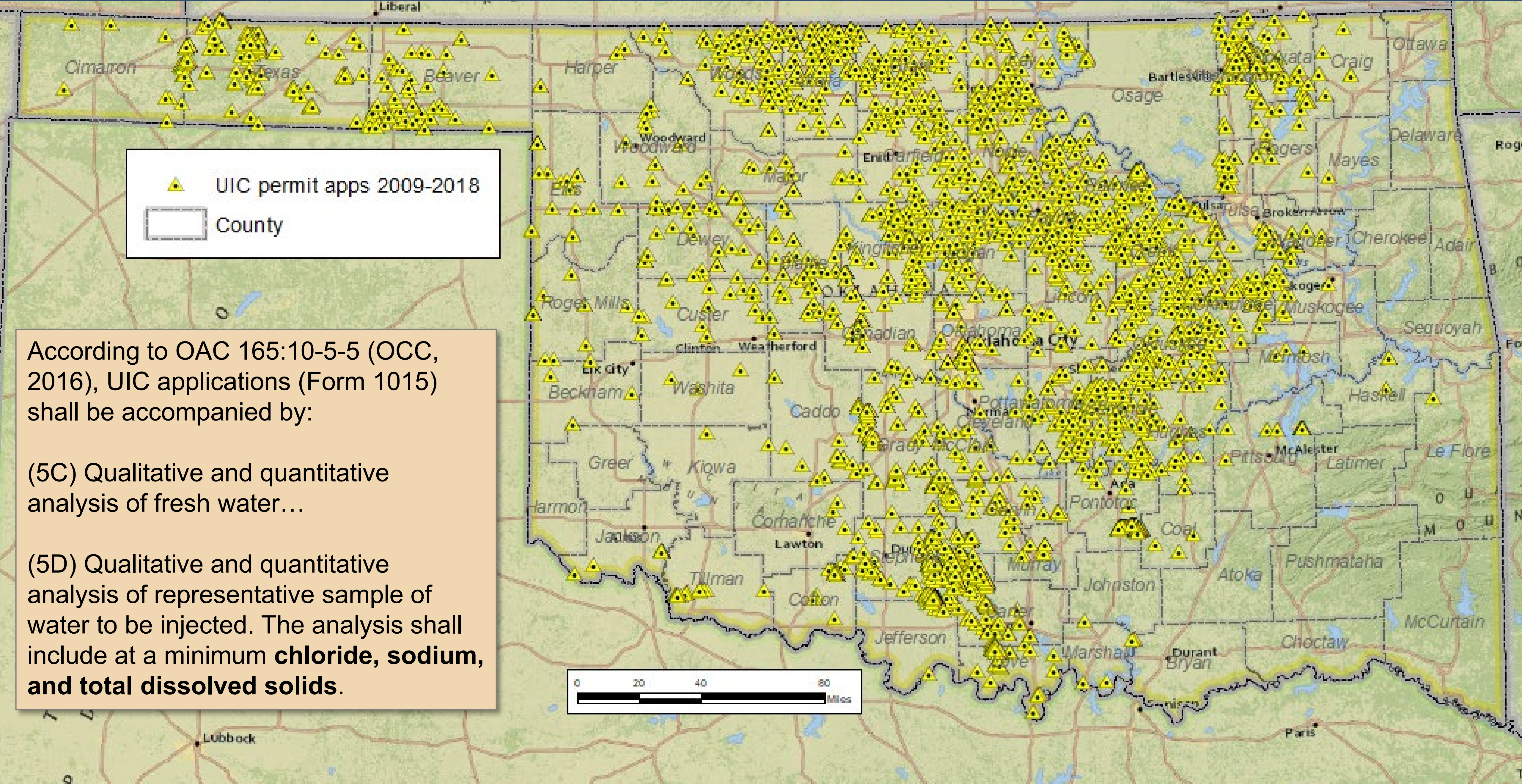
Key to Symbols
Sandstone
Carbonate
Shale
Coal
Granite



Estimated H_2O Production by Zone and by Month



Theoretically, there are about 15,000 PW samples/analyses

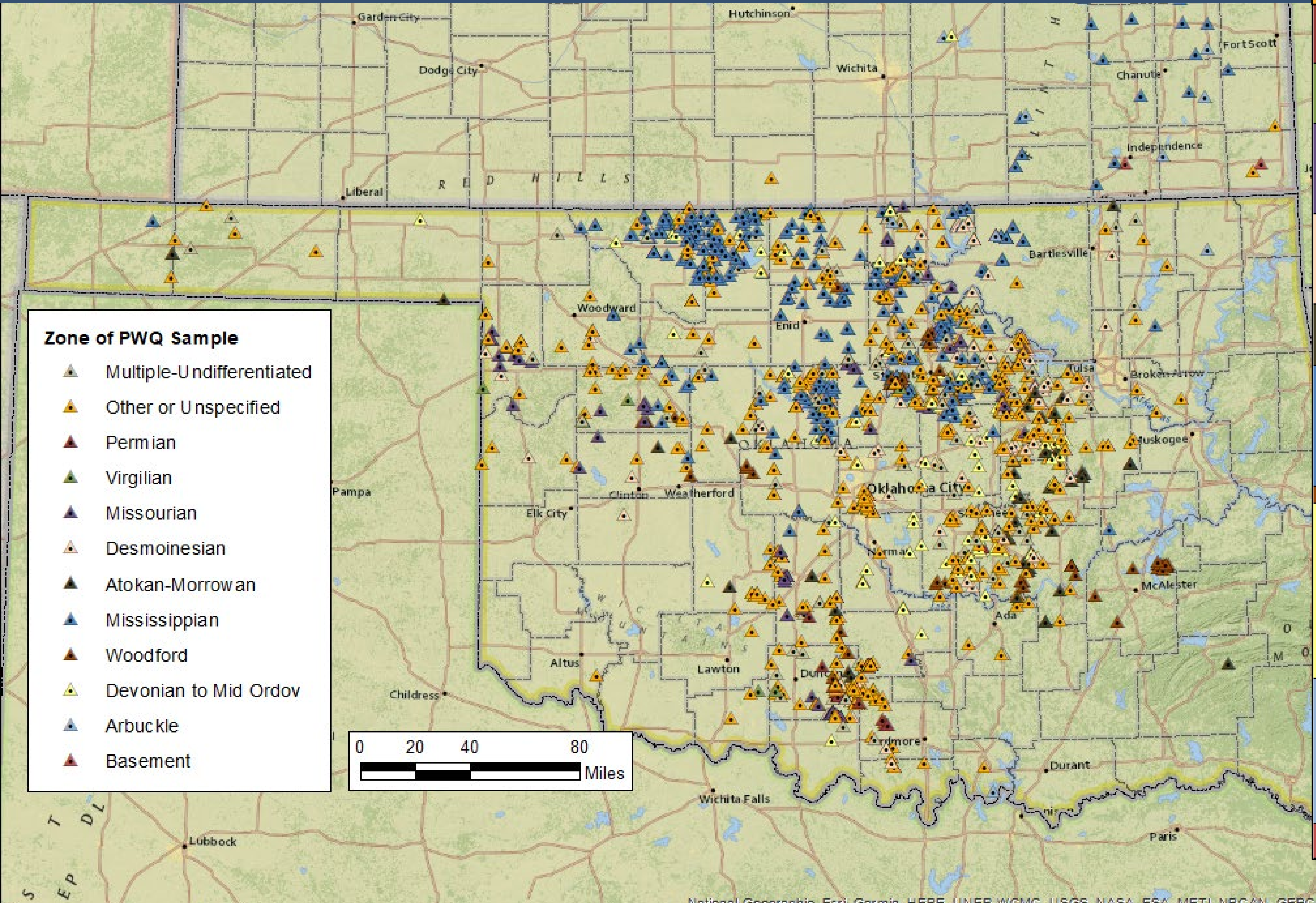


According to OAC 165:10-5-5 (OCC, 2016), UIC applications (Form 1015) shall be accompanied by:

(5C) Qualitative and quantitative analysis of fresh water…

(5D) Qualitative and quantitative analysis of representative sample of water to be injected. The analysis shall include at a minimum **chloride, sodium, and total dissolved solids**.

OK PWQ Sample (2009-2018)



Zone	Group	Formation
Multiple-Undiff		
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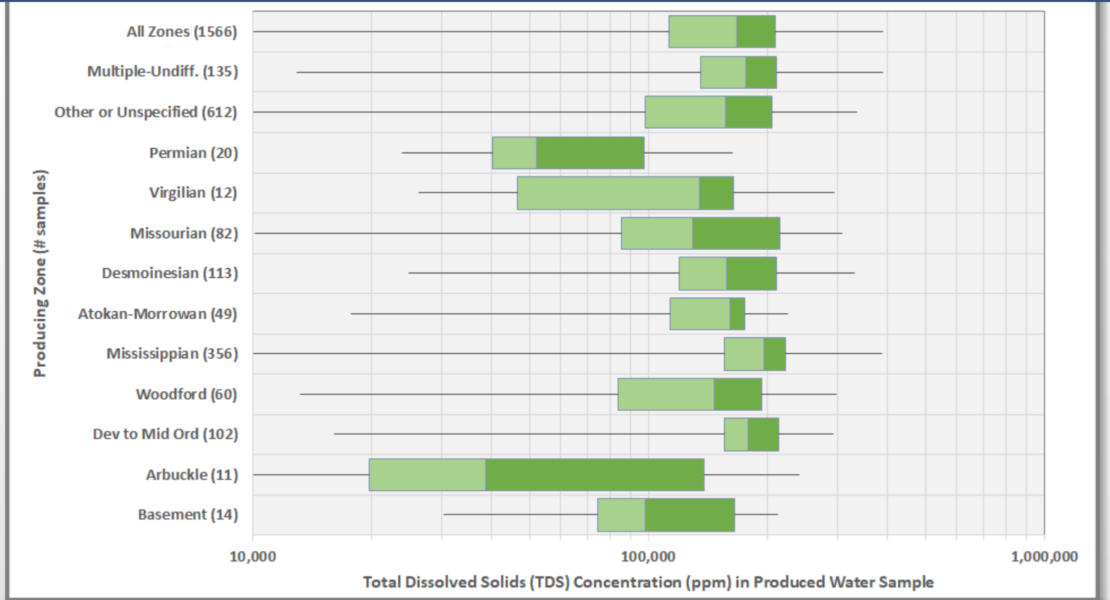
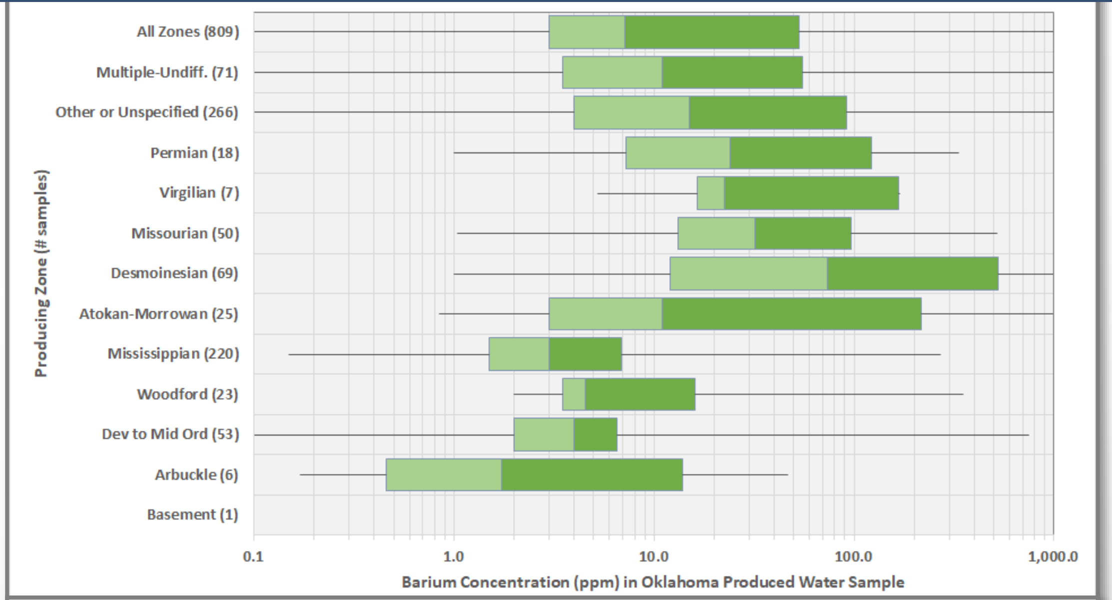
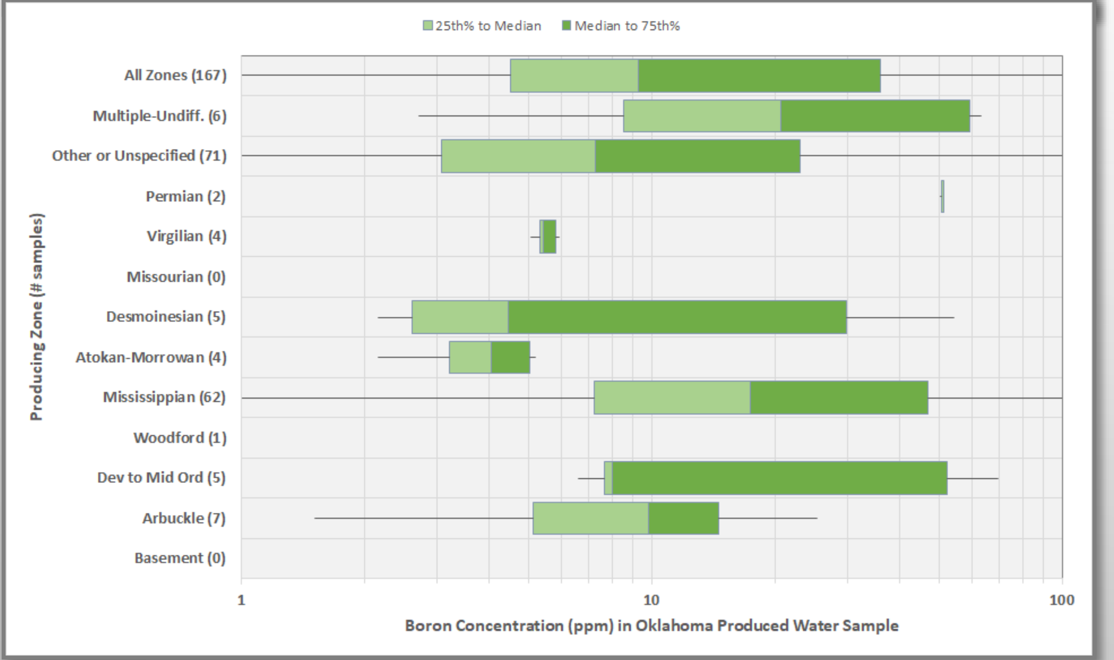
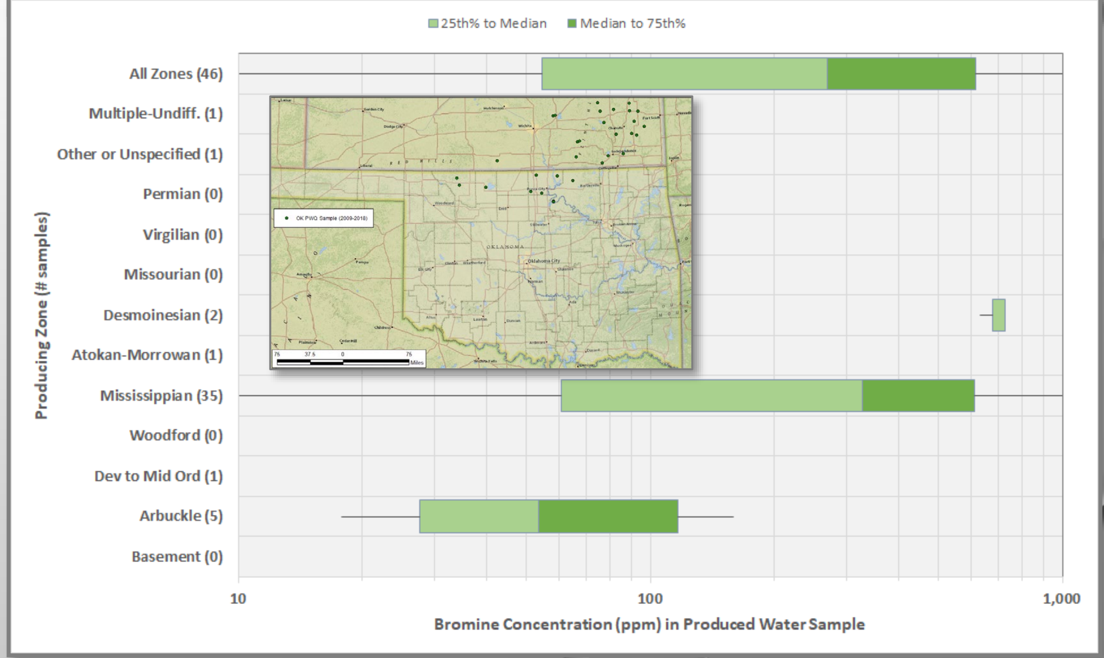
Permian		Garber
	Chase	Brown Dolomite
	Council Grove	Pontotoc
	Admire	Belveal
Virgilian	Wabaunsee	Cisco Lime
	Shawnee	Pawhuska
		Endicott
	Douglas	Tonkawa
Missourian	Hoxbar	Lansing
		Cottage Grove
		Kansas City
		Hogshooter
		Layton
		Cleveland
Desmoinesian	Marmaton - Deese	Oswego
	Cabaniss - Deese	Skinner
	Krebs - Deese	Red Fork
		Burbank
		Bartlesville
		Hartshorne
Atokan-Morrowan	Atoka	Gilcrease
		Dutcher
	Morrow	Cromwell
	Springer	Wamsley
Mississippian	Chester	Manning
		Caney
	Meramec	Miss Lime
		Miss Chat
		St. Louis
		Mayes
	Osage	Sycamore
	Kinderhook	Kinderhook
Woodford	Upper Devonian	Woodford
Dev to Mid Ord	Middle Devonian	Misener
	Hunton	Frisco
		Bois d'Arc
		Henryhouse
		Chimneyhill
	Cincinnatian	Sylvan
		Viola
	Simpson	Bromide
		Wilcox
		McLish
		Oil Creek
Arbuckle	Arbuckle Group	West Spring Creek
		Kindblade
		Cool Creek
		McKenzie Hill
		Butterly dolomite
		Signal mountain
		Royer dolomite
		Fort sill limestone
Basement & Crystalline Rock	Cambrian	Reagan
	Pre-Cambrian	Granite

Critical and Industrial Minerals/Elements in OK dbase

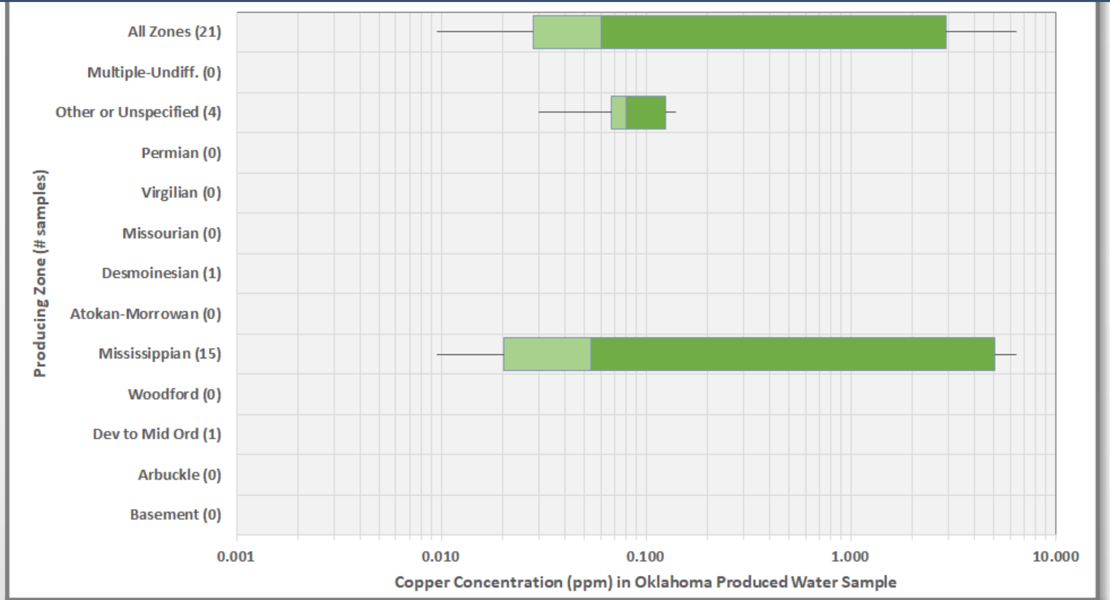








Critical and Industrial Minerals/Elements in OK dbase



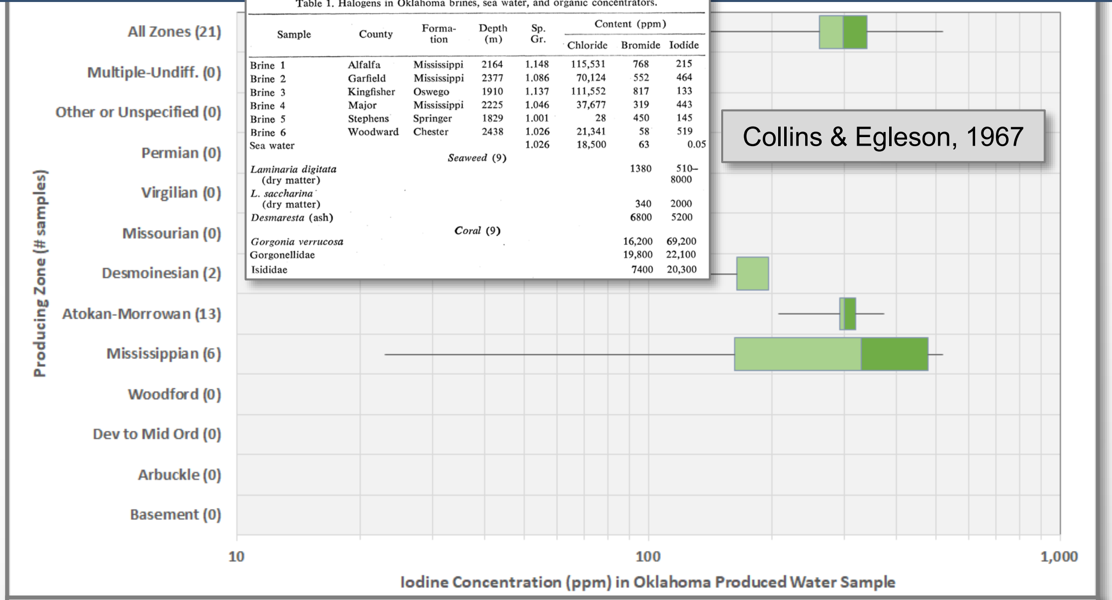
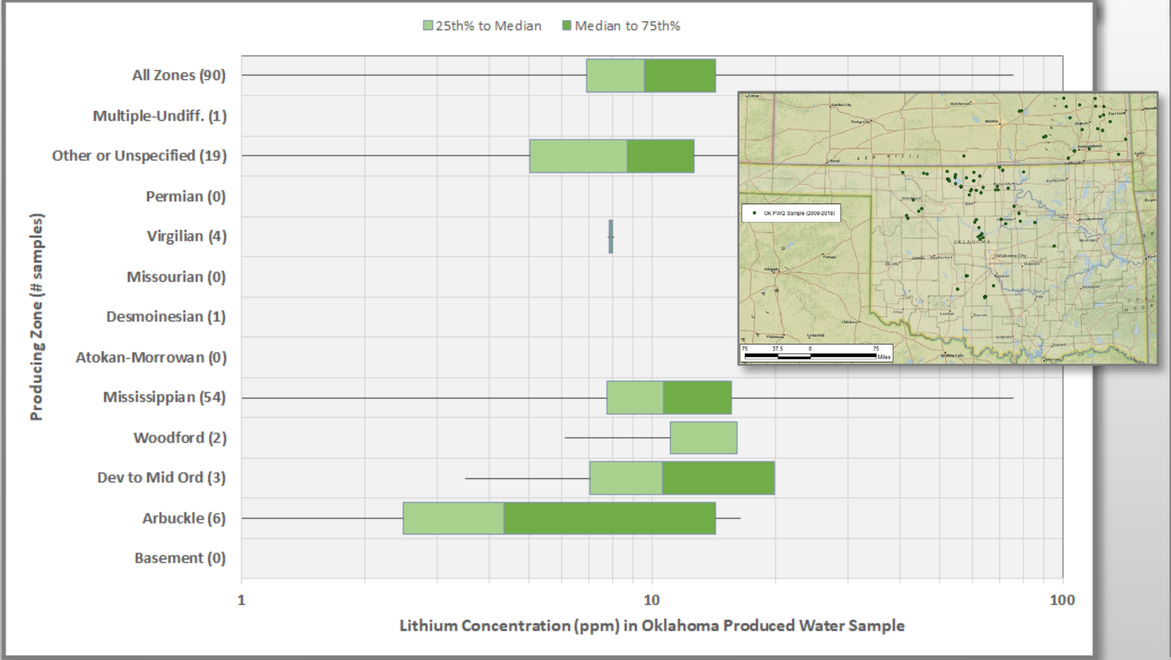
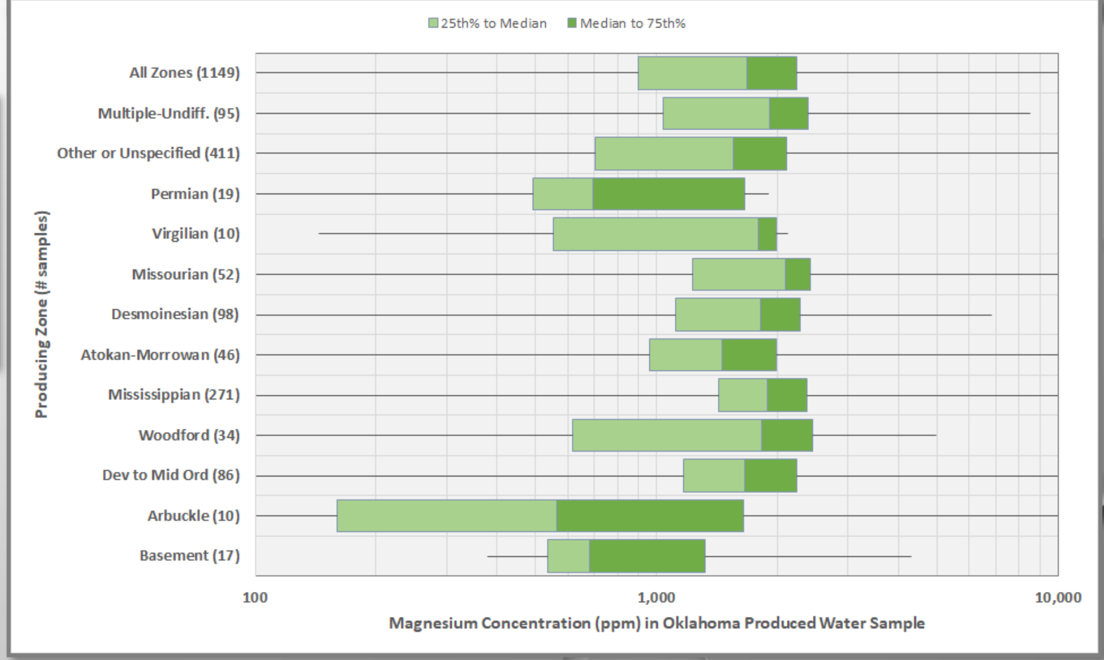


Table 1. Halogens in Oklahoma brines, sea water, and organic concentrators.

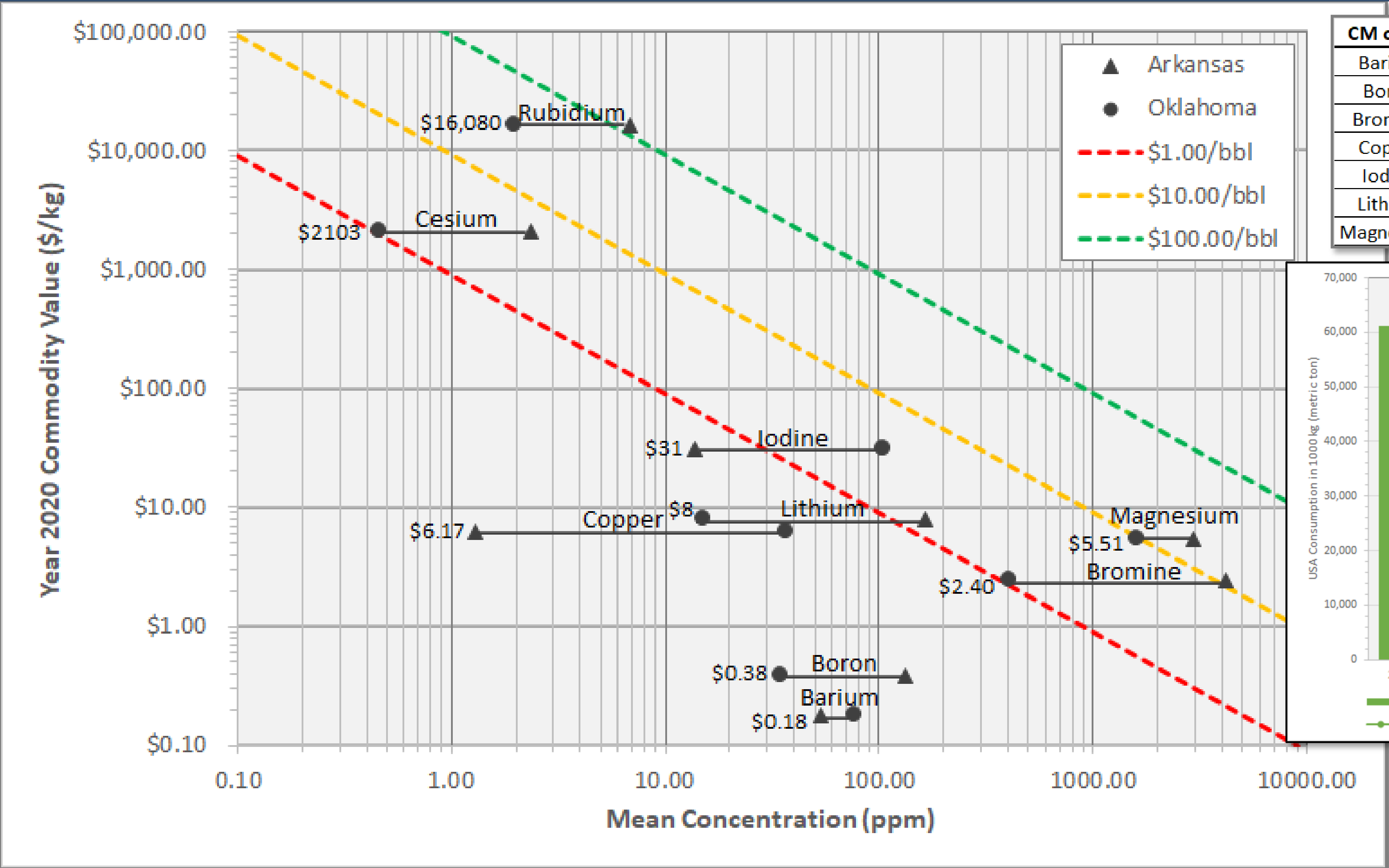
Sample	County	Formation	Depth (m)	Sp. Gr.	Content (ppm) Chloride	Bromide	Iodide
Brine 1	Alfalfa	Mississippi	2164	1.148	115,531	768	215
Brine 2	Garfield	Mississippi	2377	1.086	70,124	552	464
Brine 3	Kingfisher	Oswego	1910	1.137	111,552	817	133
Brine 4	Major	Mississippi	2225	1.046	37,677	319	443
Brine 5	Stephens	Springer	1829	1.001	28	450	145
Brine 6	Woodward	Chester	2438	1.026	21,341	58	519
Sea water				1.026	18,500	63	0.05
		Seaweed (9)					
Laminaria digitata (dry matter)						1380	510–8000
L. saccharina (dry matter)						340	2000
Desmaresta (ash)						6800	5200
		Coral (9)					
Gorgonia verrucosa						16,200	69,200
Gorgonellidae						19,800	22,100
Isididae						7400	20,300

Collins & Egleson, 1967

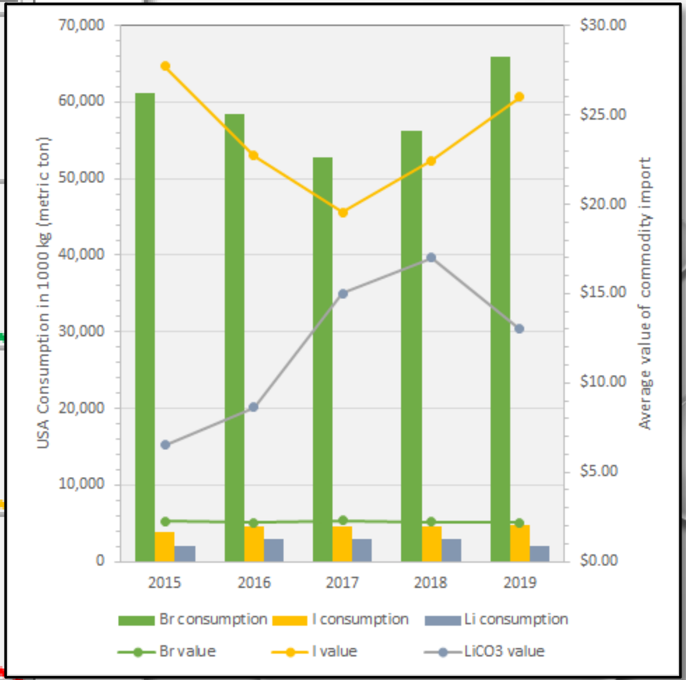




Critical and Industrial Minerals/Elements



CM or IM	Zone	Median (ppm)
Barium	Basement	80
Boron	Woodford	70
Bromine	Desmoinesian	724
Copper	Desmoinesian	0.8
Iodine	Mississippian	329
Lithium	Woodford	16
Magnesium	Missourian	2092



O&G H_2O Management Flowchart: Water Reclamation

Key

- FreshH_2O
- SaltH_2O
- Treated H_2O
- Approach

Well Drilling and Hydraulic Fracturing

Flowback and Produced H_2O

Pre-treatment (aka treat to clean brine)

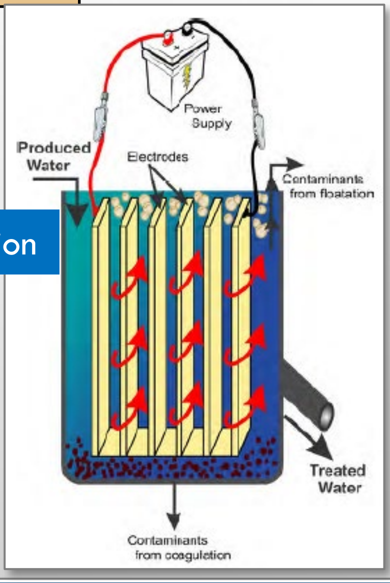
Treat & Desalinate to FreshH_2O

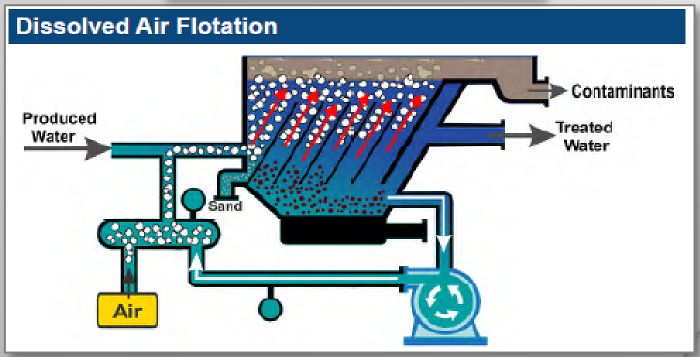
FreshH_2O User

Pretreatments Include:
*Bag Filter
*Settling Pond
*Gravity Separation Tank
*Biocide
Micro/Ultra Filtration
Electrocoagulation
Hydrocyclone
Dissolved Air Flotation
Nanotechnology
Bioreactors
*before all HF jobs

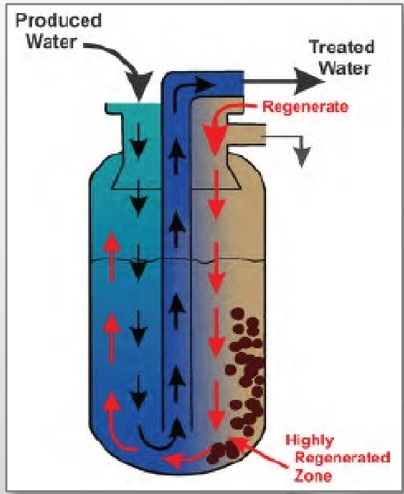
Desalination Systems Include:
Evaporation
Reverse/Forward Osmosis
Ion Exchange
Membrane Distillation
Multi-Effect Distillation
Multi-Stage Flash Distillation
Mechanical Vapor Compression

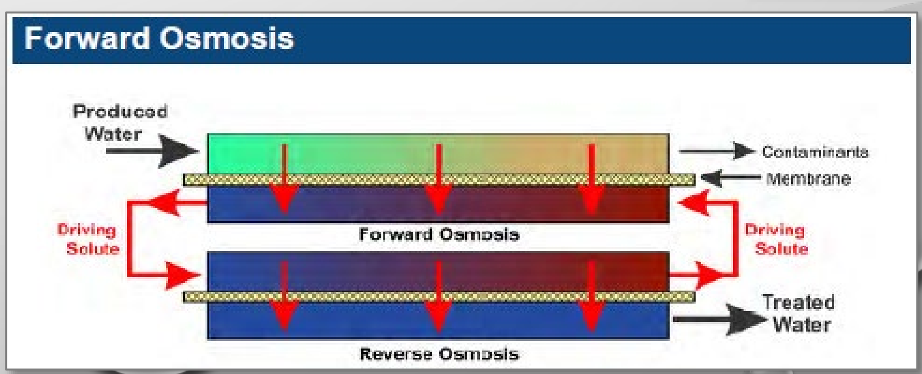
Electrocoagulation





Ion Exchange





Treatment and Concentrated Brine

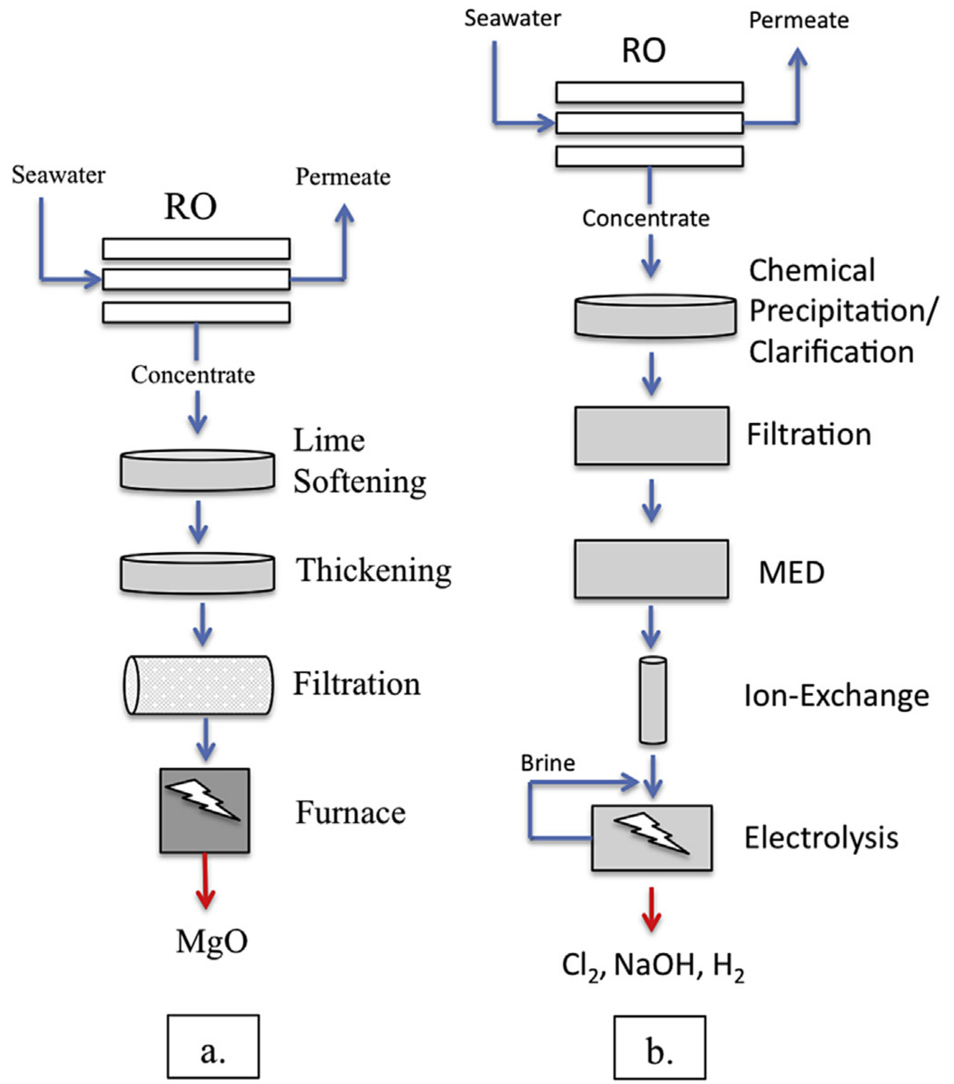


Fig. 2. Proposed schemes for extraction of constituents from RO brine/concentrate. (a) the common production method for producing magnesia (MgO) from seawater. (b) process based on literature by Melian-Martel et al. (2011).

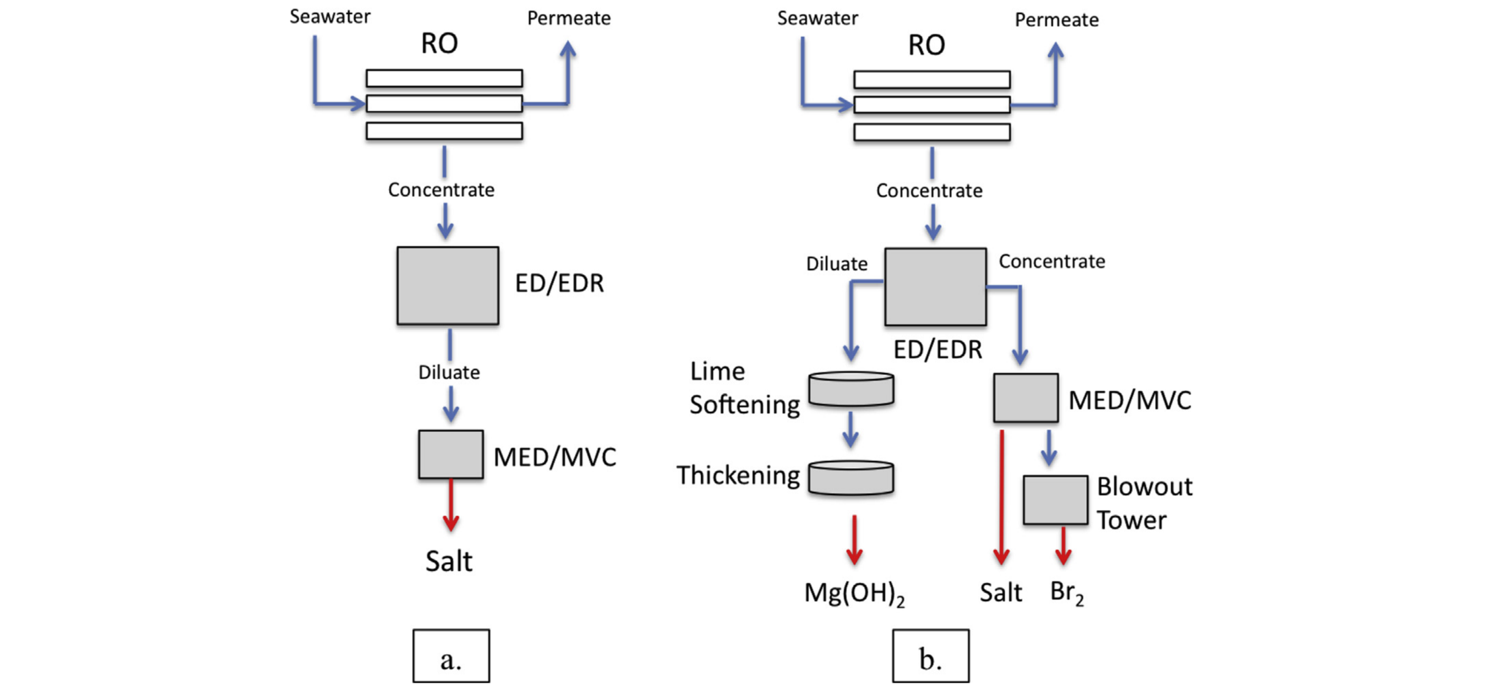


Fig. 3. Proposed schemes for extraction of constituents from RO brine/concentrate. (a) from literature by Tanaka et al. (2003), and Turek (2003) and, (b) from literature by Davis (2006).

Shamansouri et al, 2015

Resource Recovery

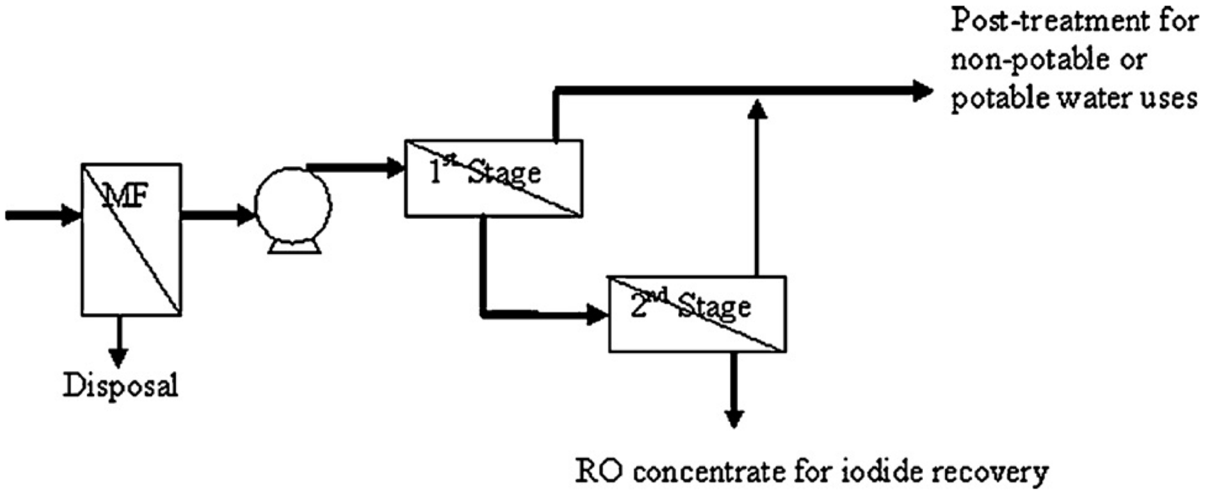
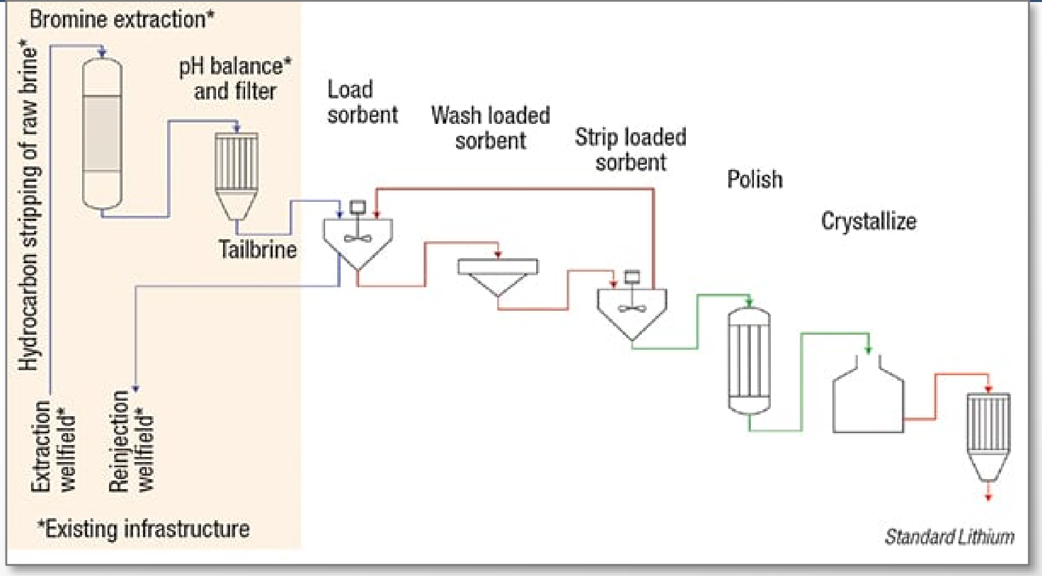
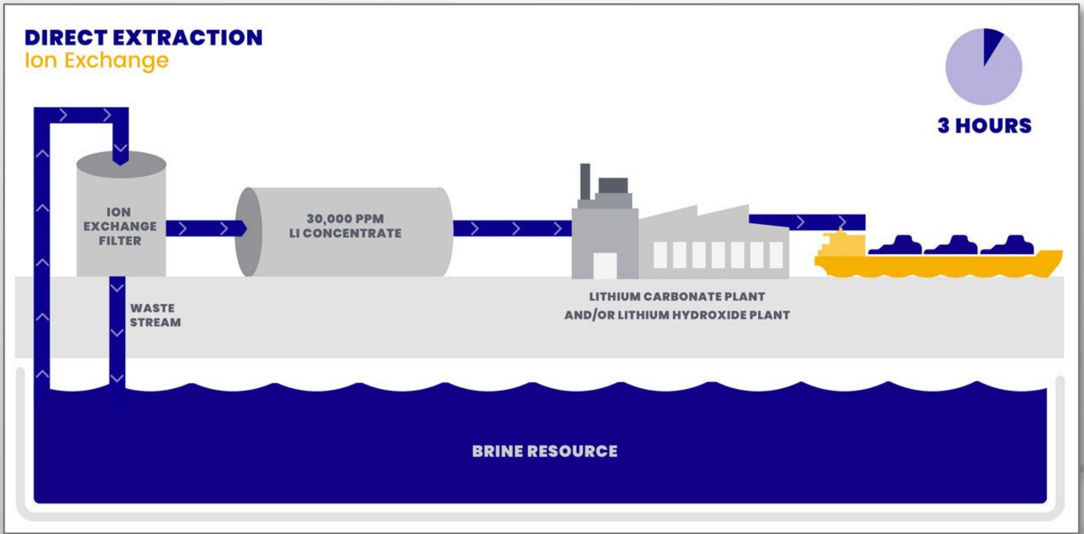


Fig. 5. Proposed MF and two-stage RO or NF membrane treatment. Reprinted with permission from Ref. [109].





Ahmadun et al, 2009

Naturally Occurring Radioactive Materials (NORM)

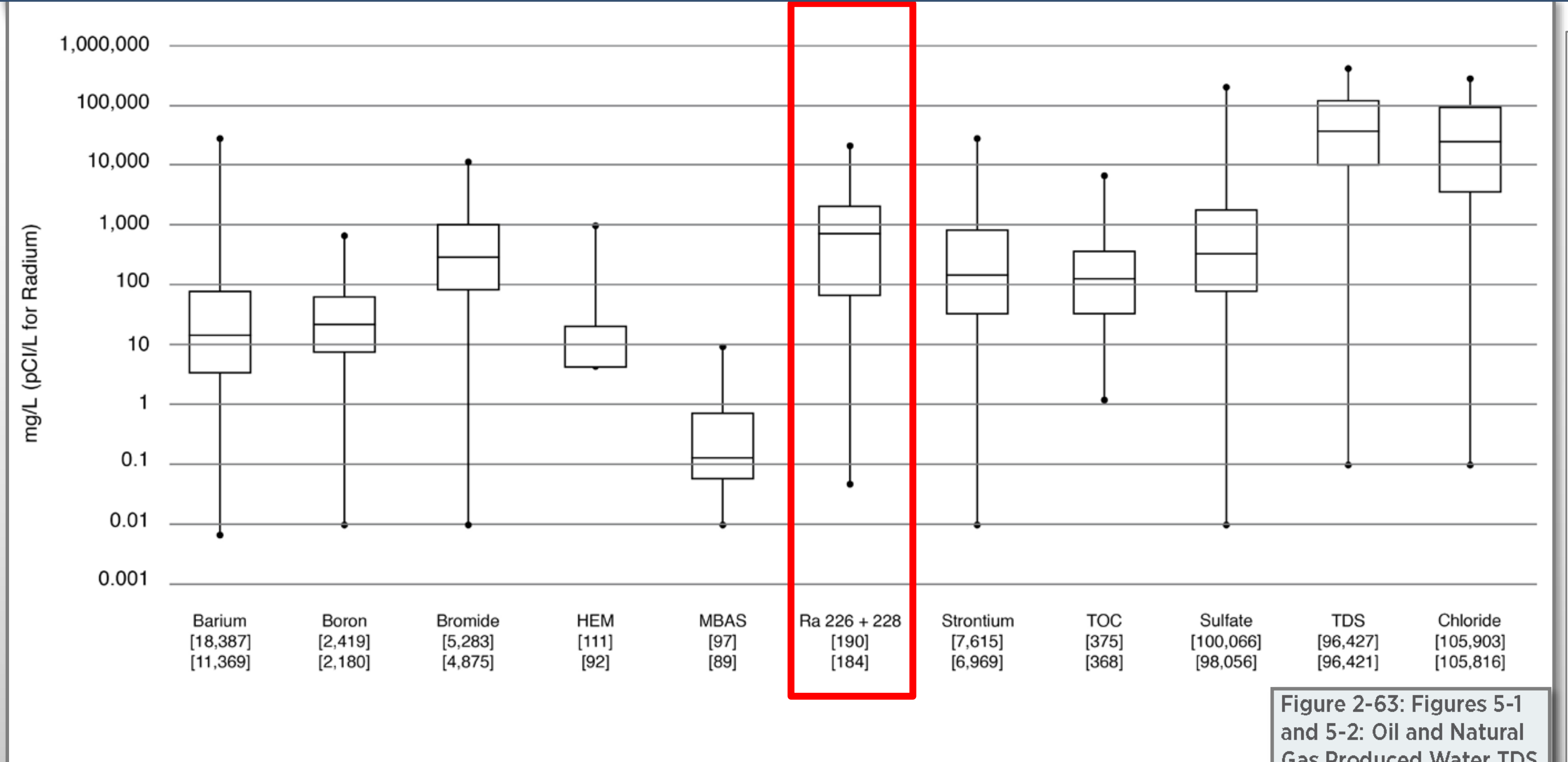


Figure 5-1. Oil and Gas Produced Water Constituent Concentration Data (USGS National Produced Waters Geochemical Database, V2.2)

GWPC, 2020

Figure 2-63: Figures 5-1 and 5-2: Oil and Natural Gas Produced Water TDS Concentration by Basin

Source: USGS National Produced Waters Geochemical Database, V2.2

* USEPA, *Detailed Study of the Centralized Waste Treatment Point Source Category for Facilities Managing Oil and Gas Extraction Wastes*, EPA-821-R-18-004, May 2018, 262 pp., https://www.epa.gov/sites/production/files/2018-05/documents/cwt-study_may-2018.pdf

What are the median and 75th% concentrations for total Radium?

How do they compare to MCL

Because of the human health risks associated with the ingestion of Ra and inhalation of its daughter products (e.g., Rn), total Ra activity (226Ra + 228Ra) for public water supplies is not to exceed 5 pCi/L or ~11.1 disintegrations per minute per kilogram (dpm/kg).

Naturally Occurring Radioactive Materials (NORM)

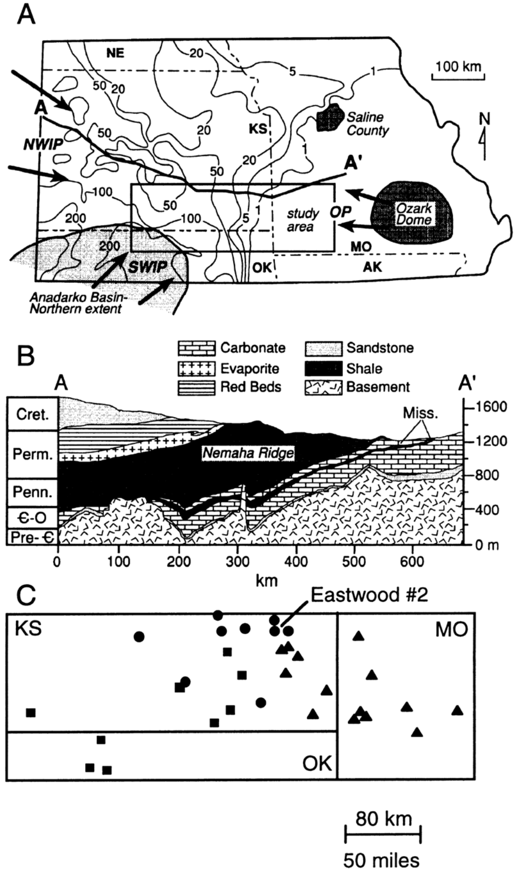


Fig. 1. (A) Map showing location of study area in southwestern Missouri, southeastern Kansas, and northeastern Oklahoma (also shown is area in Saline County, Missouri, from which four samples are included in this study). Contours of regional distribution of ground water salinities in Cambrian-Ordovician rocks expressed in g l^{-1} of total dissolved solids. Prevailing flow directions of regional ground water in the northern western interior plains aquifer (NWIP), the southern western interior plains aquifer (SWIP), and the Ozark Plateaus aquifer (OP) shown by arrows. (B) West-east geologic cross-section showing schematic stratigraphy. (C) Enlargement of study area from Fig. 1(A) showing fluid sampling localities [symbols based on geographic-geochemical correlations of Musgrove and Banner (1993) as summarized in Table 1: triangles, group 1; circles, group 2; squares, group 3]. This figure is adapted from Musgrove and Banner (1993).

Table 2
Compositional data for ground waters and brines[a]

Sample	Date[b]	Group/type[c]	TDS (mg l^{-1})	Ca (mg l^{-1})	Sr (mg l^{-1})	Ba (mg l^{-1})	(^{226}Ra) dpm kg^{-1}	(^{228}Ra/^{226}Ra)
Southwestern Missouri								
Lamar	910623	1/MWS	294	32	0.16	0.29	4.0 ± 0.4	0.22 ± 0.05
Webb City ♯7	891104	1/MWS	372	59	0.09	0.14	2.4 ± 0.4	0.18 ± 0.17
Fairview ♯11	910621	1/MWS	286	38	0.09	0.14	2.2 ± 0.4	0.26 ± 0.06
Miller ♯2	910622	1/MWS	278	36	0.04	0.01	0.8 ± 0.4	0.12 ± 0.12
Carthage ♯7	910622	1/MWS	568	101	0.22	0.11	4.3 ± 0.4	0.74 ± 0.04
Carthage ♯11	910622	1/MWS	303	39	0.09	0.14	2.4 ± 0.4	0.32 ± 0.05
Aurora ♯4	910625	1/MWS	328	42	0.06	0.04	0.7 ± 0.4	0.43 ± 0.22
Nevada ♯4	910713	1/MWS	1320	75	2.03	0.08	11.9 ± 0.4	0.20 ± 0.02
Saline County, Missouri								
Sweet Spring	891105	1/AW	4680	333	7.89	0.04	69 ± 2	0.12 ± 0.02
McCallister	891105	1/NS	6300	306	9.81	0.50	94 ± 2	0.20 ± 0.01
Blue Lick	891105	2/NS	25,500	1330	40.4	0.04	380 ± 10 397 ± 13[d]	0.31 ± 0.01
Boone's Lick	891105	2/AW	21,600	1120	36.4	0.03	322 ± 8 315 ± 8[d]	0.095 ± 0.005
Southeastern Kansas								
Pittsburg ♯10	910620	1/MWS	609	63	0.88	0.18	5.8 ± 0.4	0.24 ± 0.03
Columbus ♯4	910626	1/MWS	666	48	1.37	0.12	10.5 ± 0.4	0.19 ± 0.02
Elmer	910627	1/OWS	2870	19	1.10	0.15	11.5 ± 0.4	0.27 ± 0.01
Campbell ♯2	910621	1/OWS	6720	110	5.14	0.71	59.4 ± 0.4	0.27 ± 0.01
Nelson	891104	1/OWS	3470	77	0.03	0.16	40.2 ± 1.0	0.26 ± 0.01
McCoy	910628	1/OWS	14,100	208	15.3	1.26	186 ± 1	0.32 ± 0.01
Althouse ♯1	910706	2/OP	22,200	1140	43.7	0.08	1060 ± 20	0.08 ± 0.02
Koenig ♯2A	910707	2/OP	26,300	794	54.7	3.25	258 ± 11	0.62 ± 0.10
Perkins ♯2	910704	2/OP	63,200	3400	86.8	0.18	1520 ± 20	0.14 ± 0.02
Fuller ♯15	910623	2/OP	45,300	1635	103	4.28	783 ± 14	0.22 ± 0.03
Kimbell ♯1	891103	2/OP	42,900	1721	83.0	2.17	1310 ± 30 1303 ± 39[d]	0.11 ± 0.01
Eastwood ♯2	891102	2/OWS	18,400	444	30.4	2.05	208 ± 5 202 ± 5[d]	0.80 ± 0.01
Minckley A	910627	2/OWS	13,300	262	15.3	2.93	179 ± 1	0.20 ± 0.01
Love 1W	910703	2/OWS	9400	173	9.41	0.65	113 ± 1	0.17 ± 0.01
Perry	910704	2/OWS	25,300	937	27.5	3.02	331 ± 12	0.21 ± 0.07
Hyde ♯18	910704	3/OP	137,000	8132	1050	1.76	728 ± 14	0.12 ± 0.04
Short	910711	3/OP	114,000	5400	197	0.88	431 ± 9	0.33 ± 0.04
Clubine	910629	3/OWS	68,800	2530	124	43.5	1743 ± 4	0.105 ± 0.003
Sheik	910701	3/GP	79,200	2940	163	32.0	1260 ± 20	0.14 ± 0.02
Peck	910701	3/OP	62,300	2280	136	45.3	590 ± 13	1.48 ± 0.06
Louk 1W	910703	3/OWS	72,900	2800	137	3.31	4190 ± 30	0.096 ± 0.007
Northern Oklahoma								
Jenkins ♯1	910709	3/OP	249,000	25,900	1510	6.04	2150 ± 20	0.22 ± 0.01
E. McCullough	910710	3/OP	229,000	16,100	813	35.0	474 ± 13	1.14 ± 0.06
Shoffner ♯1	910710	3/OP	138,000	8850	283	2.16	7660 ± 50	0.057 ± 0.004

[a] Data for TDS, Ca, Sr, and Ba concentrations for southwestern MO, southeastern KS, and northern OK samples from Musgrove (1993), and for central Missouri samples from Banner et al. (1989).
[b] Date format is yymmdd.
[c] Groups 1,2 and 3 defined in Table 1; fluid sources: MWS = municipal water supply; OWS = oilfie[...] duction well; GP = gas production well; AW = artesian well; NS = natural spring.
[d] Replicate analysis by Rn emanation method (Lucas, 1977).

Sturchio, 2001

Naturally Occurring Radioactive Materials (NORM)

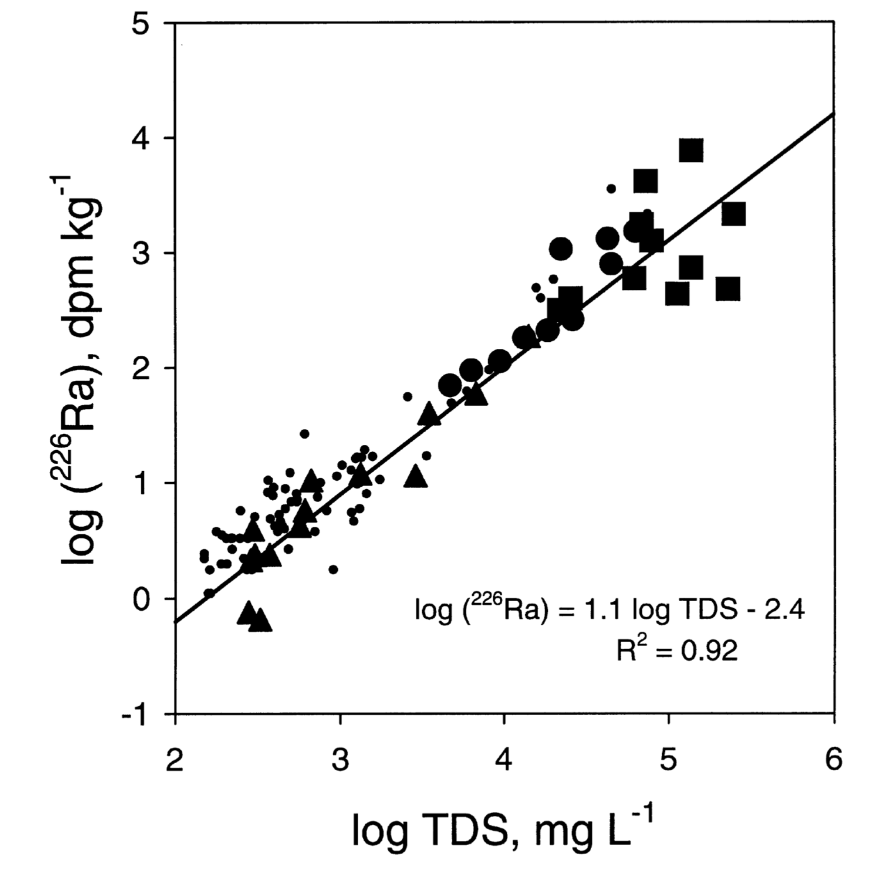


Fig. 2. Log (^{226}Ra) (dpm kg^{-1}) vs salinity (log TDS in mg l^{-1}) for ground water samples. Solid line shows positive correlation. Symbols represent ground water groups as in Fig. 1(C). Also shown (small filled circles), but not used to define the correlation line, are data from Macfarlane and Hathaway (1987).

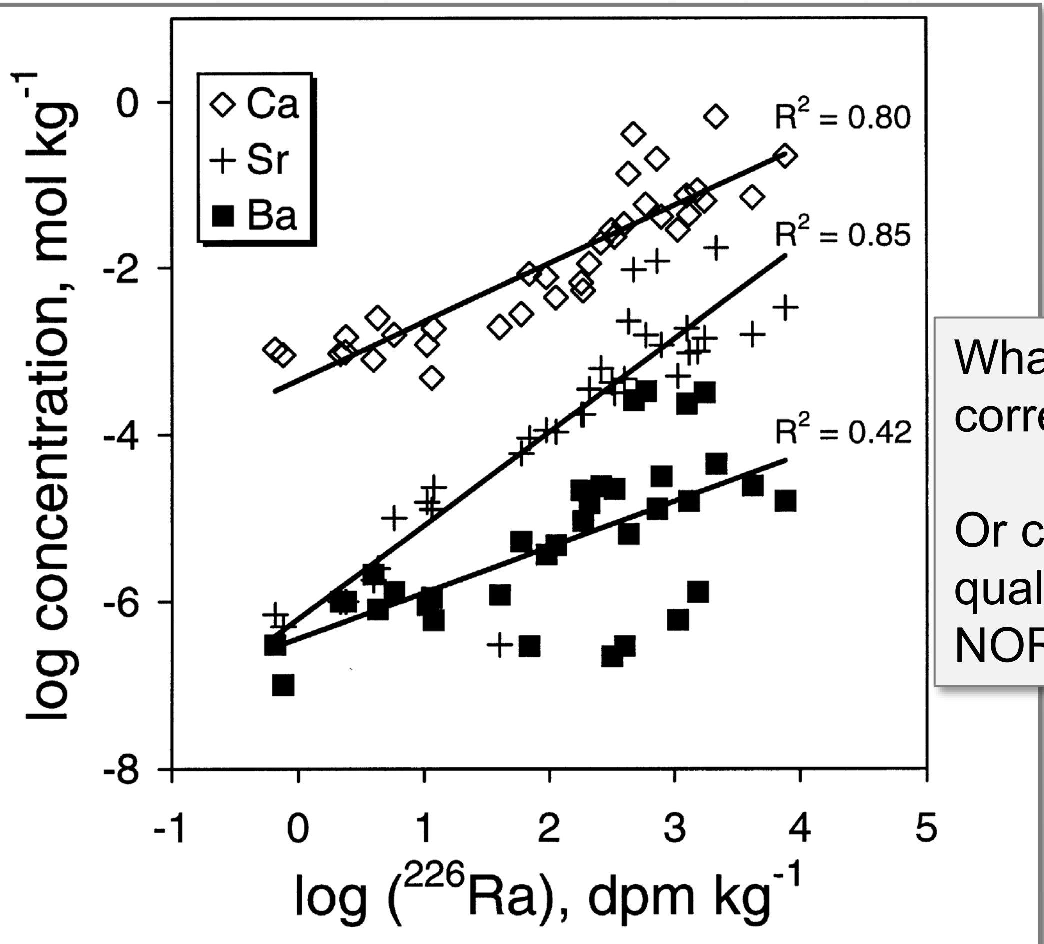


Fig. 3. Log Ca, Sr, and Ba (molar) vs log (^{226}Ra) (dpm kg^{-1}) for ground water samples, illustrating positive correlation among all elements.

What has the strongest correlation with ^{226}Ra?

Or could be used to qualitatively assess NORM?

Sturchio, 2001

Naturally Occurring Radioactive Materials (NORM)

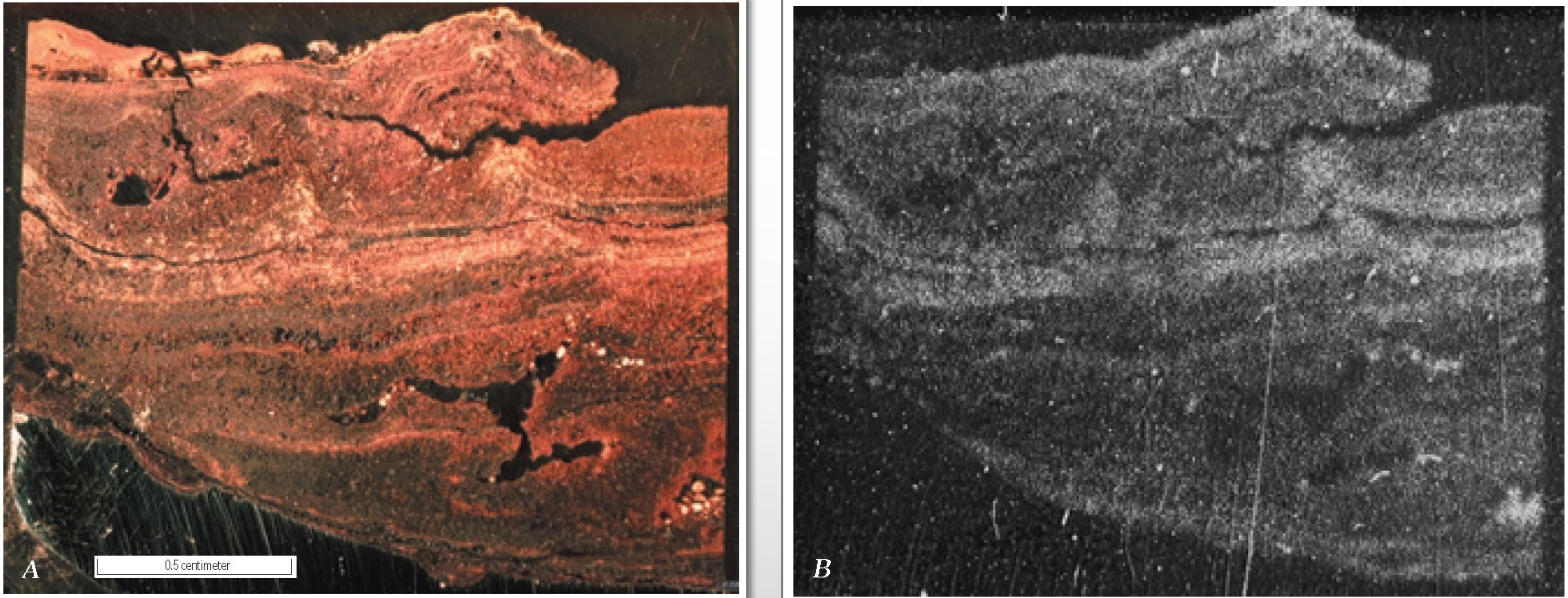


Figure 2. Radioactive scale deposits inside oil-field pipe (*A*) and the distribution of alpha-particle-emitting radium and radium decay products in the same sample (*B*). Brighter regions on the alpha emission image indicate areas of scale with higher concentrations of radioactive elements.

USGS, 1999

Summary

- Numerous Critical and Industrial Minerals/Elements (CM/IM) are present in produced water or brine at concentrations with potential for resource recovery
- Data collection, compilation, and reporting on PW quality would help for development of domestic “recoverable elements”
- Research on the why – origin and enrichment of CM/IM in brine – is needed

Pairing produced water treatment with resource recovery:

- CM/IM are already concentrated by treatment processes
- NORM are also concentrated in brine, scale deposits, and solid waste – so must be carefully managed for health and safety