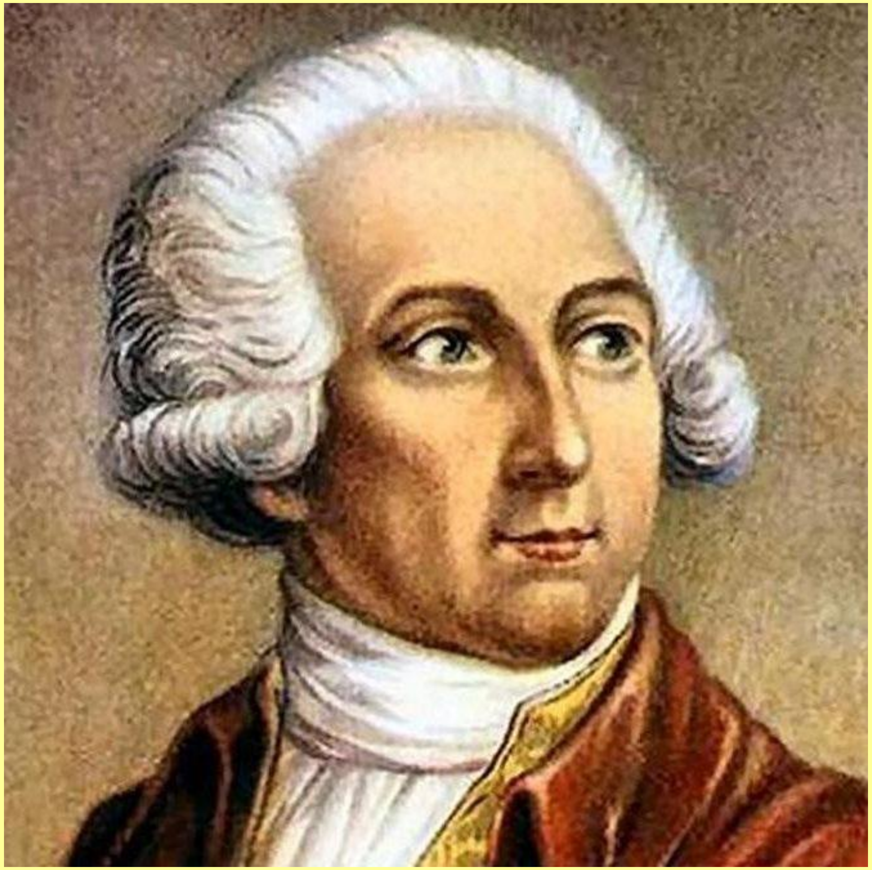
CAN SEAWEED CLEAN UP THE MESS LEFT BY YOUR CELL PHONE?

University of Maryland
CENTER FOR ENVIRONMENTAL SCIENCE
CHESAPEAKE BIOLOGICAL LABORATORY

Johan Schijf

UMCES Chesapeake Biological Laboratory

1794



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Mozart

Beethoven

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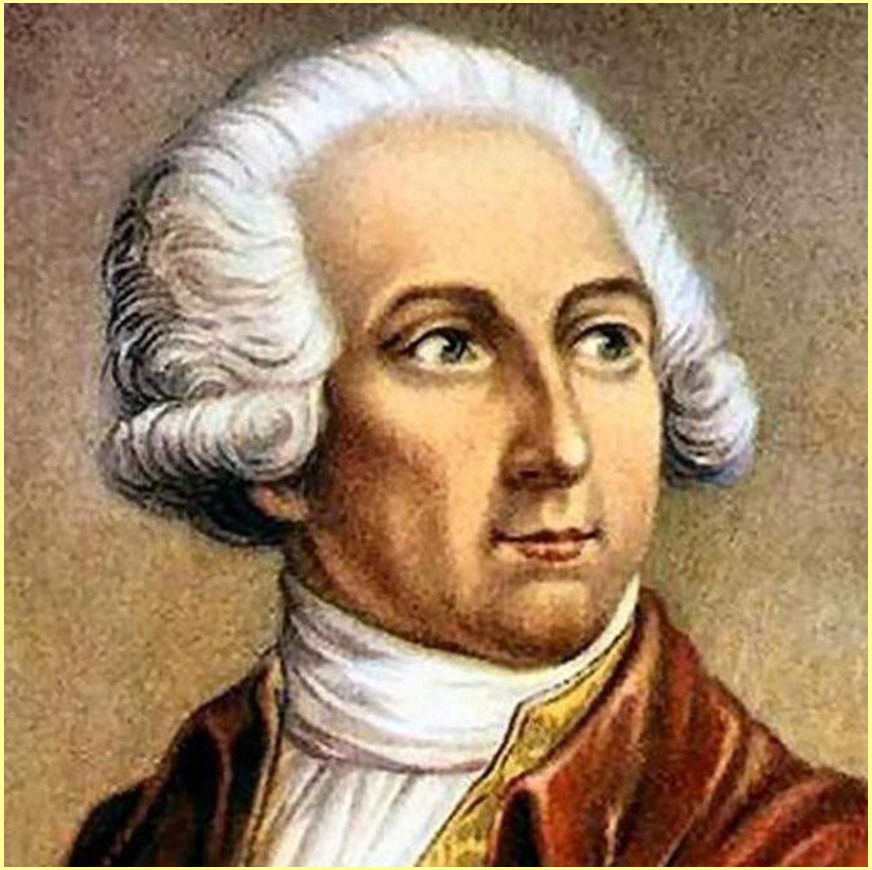
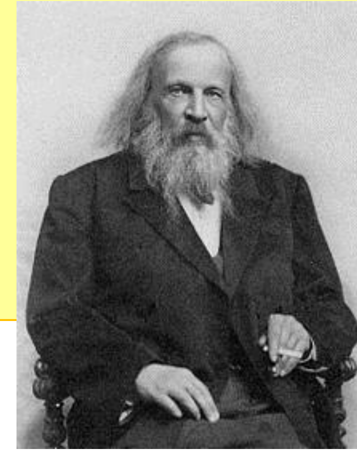


Antoine-Laurent de Lavoisier

Johan Gadolin

Formally proposed by Dmitri Ivanovich Mendeleev in 1869



Periodic Table of the Elements

Key: atomic number / Symbol / name / standard atomic weight

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H hydrogen 1.007 94(7)																	2 He helium 4.002 602(2)
3 Li lithium 6.941(2)	4 Be beryllium 9.012 182(3)											5 B boron 10.811(7)	6 C carbon 12.0107(8)	7 N nitrogen 14.0067(2)	8 O oxygen 15.9994(3)	9 F fluorine 18.998 4032(5)	10 Ne neon 20.1797(6)
11 Na sodium 22.989 770(2)	12 Mg magnesium 24.3050(6)											13 Al aluminium 26.981 538(2)	14 Si silicon 28.0855(3)	15 P phosphorus 30.973 761(2)	16 S sulfur 32.065(5)	17 Cl chlorine 35.453(2)	18 Ar argon 39.948(1)
19 K potassium 39.0983(1)	20 Ca calcium 40.078(4)	21 Sc scandium 44.955 910(8)	22 Ti titanium 47.867(1)	23 V vanadium 50.9415(1)	24 Cr chromium 51.9961(6)	25 Mn manganese 54.938 049(9)	26 Fe iron 55.845(2)	27 Co cobalt 58.933 200(9)	28 Ni nickel 58.6934(2)	29 Cu copper 63.546(3)	30 Zn zinc 65.409(4)	31 Ga gallium 69.723(1)	32 Ge germanium 72.64(1)	33 As arsenic 74.921 60(2)	34 Se selenium 78.96(3)	35 Br bromine 79.904(1)	36 Kr krypton 83.798(2)
37 Rb rubidium 85.4678(3)	38 Sr strontium 87.62(1)	39 Y yttrium 88.905 85(2)	40 Zr zirconium 91.224(2)	41 Nb niobium 92.906 38(2)	42 Mo molybdenum 95.94(2)	43 Tc technetium [98]	44 Ru ruthenium 101.07(2)	45 Rh rhodium 102.905 50(2)	46 Pd palladium 106.42(1)	47 Ag silver 107.8682(2)	48 Cd cadmium 112.411(8)	49 In indium 114.818(3)	50 Sn tin 118.710(7)	51 Sb antimony 121.760(1)	52 Te tellurium 127.60(3)	53 I iodine 126.904 47(3)	54 Xe xenon 131.293(6)
55 Cs caesium 132.905 45(2)	56 Ba barium 137.327(7)	57-71 lanthanoids	72 Hf hafnium 178.49(2)	73 Ta tantalum 180.9479(1)	74 W tungsten 183.84(1)	75 Re rhenium 186.207(1)	76 Os osmium 190.23(3)	77 Ir iridium 192.217(3)	78 Pt platinum 195.078(2)	79 Au gold 196.966 55(2)	80 Hg mercury 200.59(2)	81 Tl thallium 204.3833(2)	82 Pb lead 207.2(1)	83 Bi bismuth 208.980 38(2)	84 Po polonium [209]	85 At astatine [210]	86 Rn radon [222]
87 Fr francium [223]	88 Ra radium [226]	89-103 actinoids	104 Rf rutherfordium [261]	105 Db dubnium [262]	106 Sg seaborgium [266]	107 Bh bohrium [264]	108 Hs hassium [277]	109 Mt meitnerium [268]	110 Ds darmstadtium [271]	111 Rg roentgenium [272]							
		57 La lanthanum 138.9055(2)	58 Ce cerium 140.116(1)	59 Pr praseodymium 140.907 65(2)	60 Nd neodymium 144.24(3)	61 Pm promethium [145]	62 Sm samarium 150.36(3)	63 Eu europium 151.964(1)	64 Gd gadolinium 157.25(3)	65 Tb terbium 158.925 34(2)	66 Dy dysprosium 162.500(1)	67 Ho holmium 164.930 32(2)	68 Er erbium 167.259(3)	69 Tm thulium 168.934 21(2)	70 Yb ytterbium 173.04(3)	71 Lu lutetium 174.967(1)	
		89 Ac actinium [227]	90 Th thorium 232.0381(1)	91 Pa protactinium 231.035 88(2)	92 U uranium 238.028 91(3)	93 Np neptunium [237]	94 Pu plutonium [244]	95 Am americium [243]	96 Cm curium [247]	97 Bk berkelium [247]	98 Cf californium [251]	99 Es einsteinium [252]	100 Fm fermium [257]	101 Md mendelevium [258]	102 No nobelium [259]	103 Lr lawrencium [262]	

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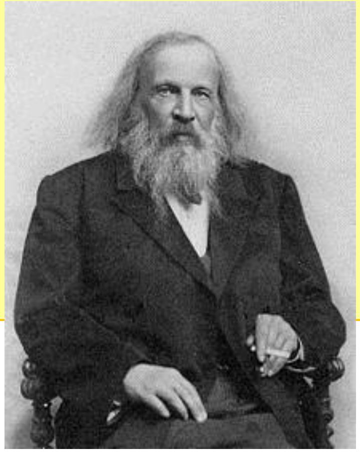

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			47 **Ag** silver 107.8682(2)		50 **Sn** tin 118.710(7)	51 **Sb** antimony 121.760(1)	
		78 **Pt** platinum 195.078(2)	79 **Au** gold 196.966 55(2)	80 **Hg** mercury 200.59(2)	82 **Pb** lead 207.2(1)		

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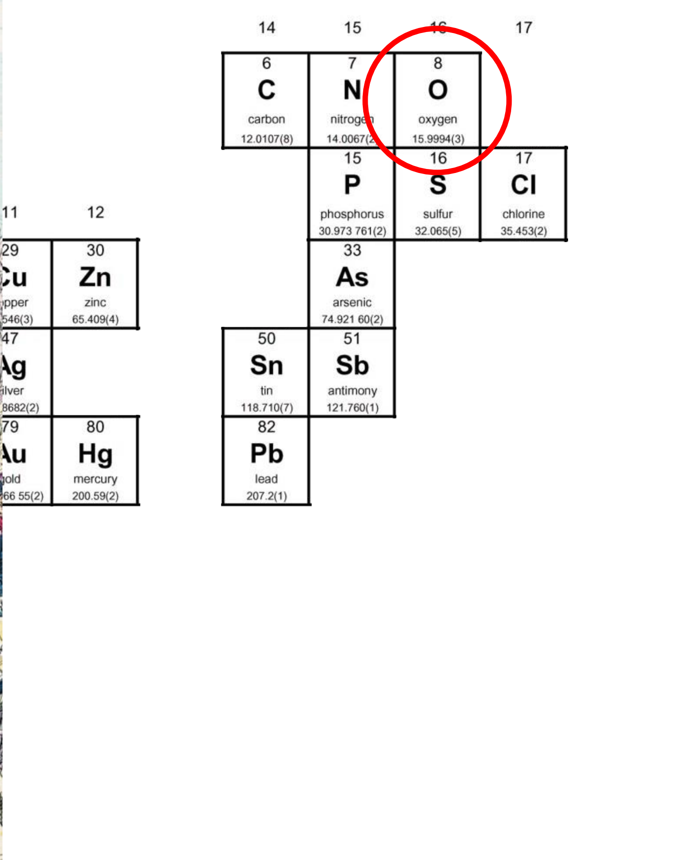

ents
14
15
16
17
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7
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O
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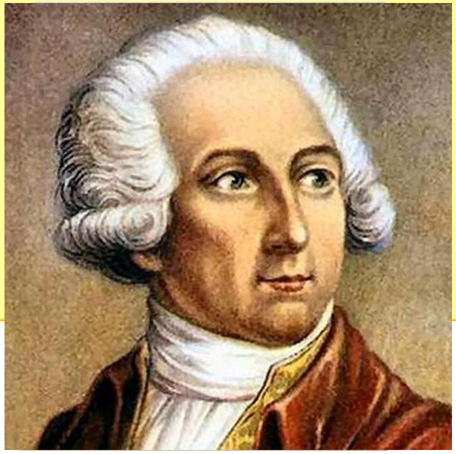

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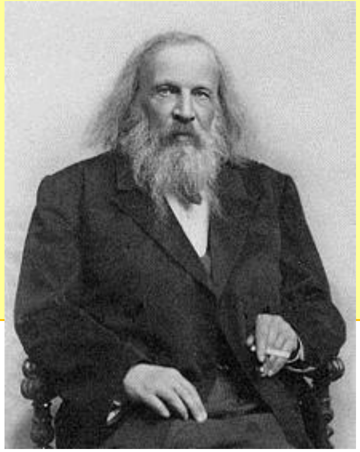

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37 **Rb** rubidium 85.4678(3)	38 **Sr** strontium 87.62(1)	39 **Y** yttrium 88.905 85(2)	40 **Zr** zirconium 91.224(2)	41 **Nb** niobium 92.906 38(2)	42 **Mo** molybdenum 95.94(2)		44 **Ru** ruthenium 101.07(2)	45 **Rh** rhodium 102.905 50(2)	46 **Pd** palladium 106.42(1)	47 **Ag** silver 107.8682(2)	48 **Cd** cadmium 112.411(8)	49 **In** indium 114.818(3)	50 **Sn** tin 118.710(7)	51 **Sb** antimony 121.760(1)	52 **Te** tellurium 127.60(3)	
55 **Cs** caesium 132.905 45(2)	56 **Ba** barium 137.327(7)			73 **Ta** tantalum 180.9479(1)	74 **W** tungsten 183.84(1)		76 **Os** osmium 190.23(3)	77 **Ir** iridium 192.217(3)	78 **Pt** platinum 195.078(2)	79 **Au** gold 196.966 55(2)	80 **Hg** mercury 200.59(2)	81 **Tl** thallium 204.3833(2)	82 **Pb** lead 207.2(1)	83 **Bi** bismuth 208.980 38(2)		
		57 **La** lanthanum 138.9055(2)	58 **Ce** cerium 140.116(1)							65 **Tb** terbium 158.925 34(2)			68 **Er** erbium 167.259(3)			
			90 **Th** thorium 232.0381(1)		92 **U** uranium 238.028 91(3)											

ld we care about the elements?

Bronze age (~3000–1200 BC)

High-Technology!

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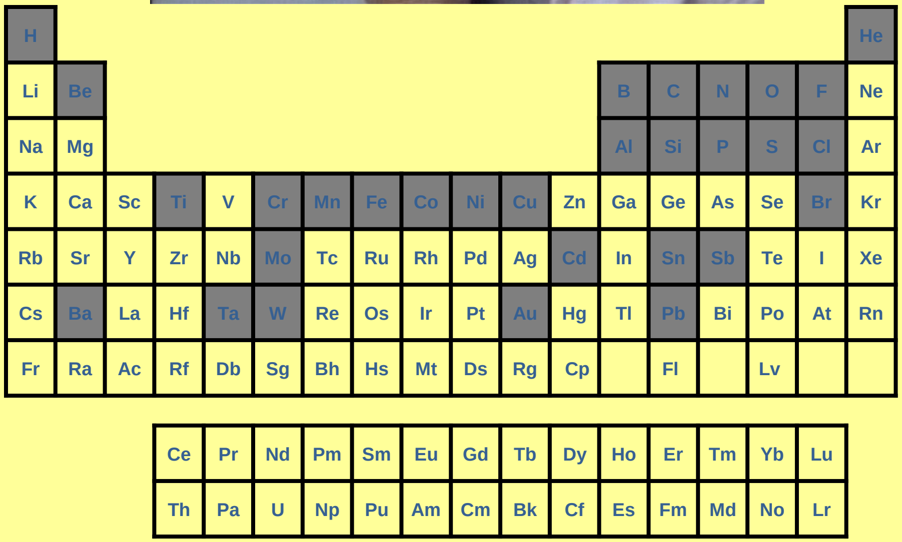
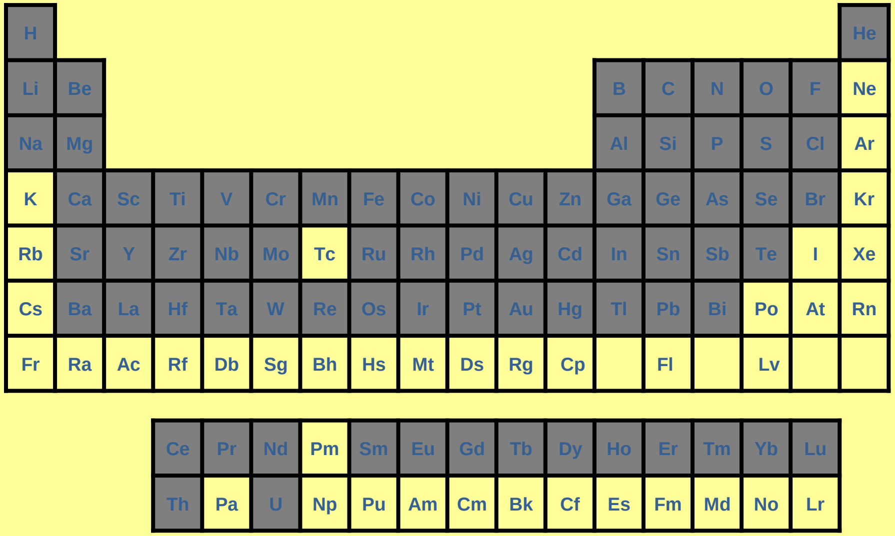
“Portable” phones

ca. 1980: ~30 elements

today: ~75 elements





Courtesy: Dr. Ron Eggert
Colorado School of Mines

Other emerging technologies

Automotive: rechargeable batteries, catalytic converters
(Ce, Co, Gd, La, Li, Mn,
Pb, Pd, Pt, Rh, V, Y)

Permanent magnets: wind turbines, electric vehicles
(Dy, Nd, Pr, Tb)

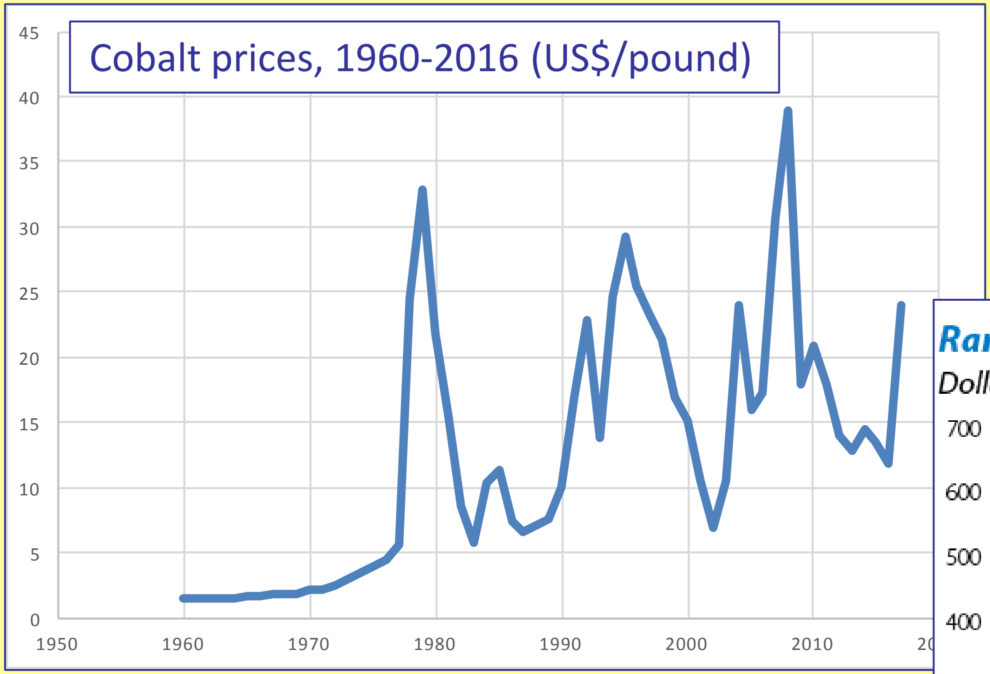
Advanced lighting: CFL and LED
(Ag, Ce, Eu, Ga, Ge, In, La, Mn, Sn, Tb, Y)

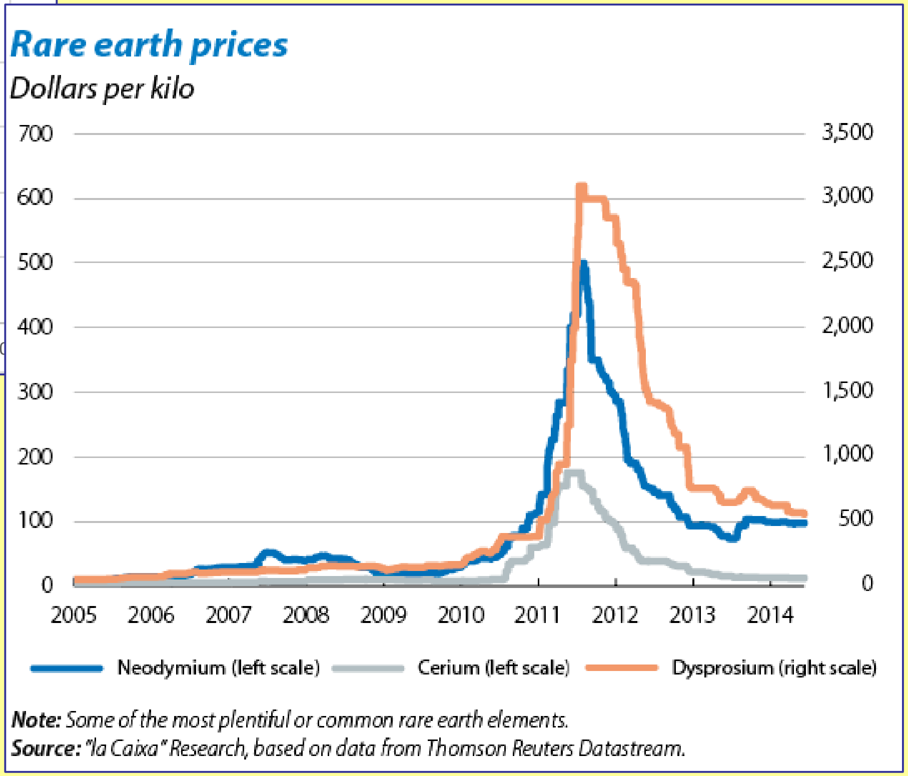
Solar panels (Ag, Ga, In, Ni, Se, Sn, Te)

Major concerns with regard to global resources of specialty metals

1. Unknown toxicity
2. Low economic incentive for production
3. High environmental impact from mining and refining

4. Small opaque markets and lack of supply chain diversity lead to high price volatility





Courtesy: Dr. Ron Eggert
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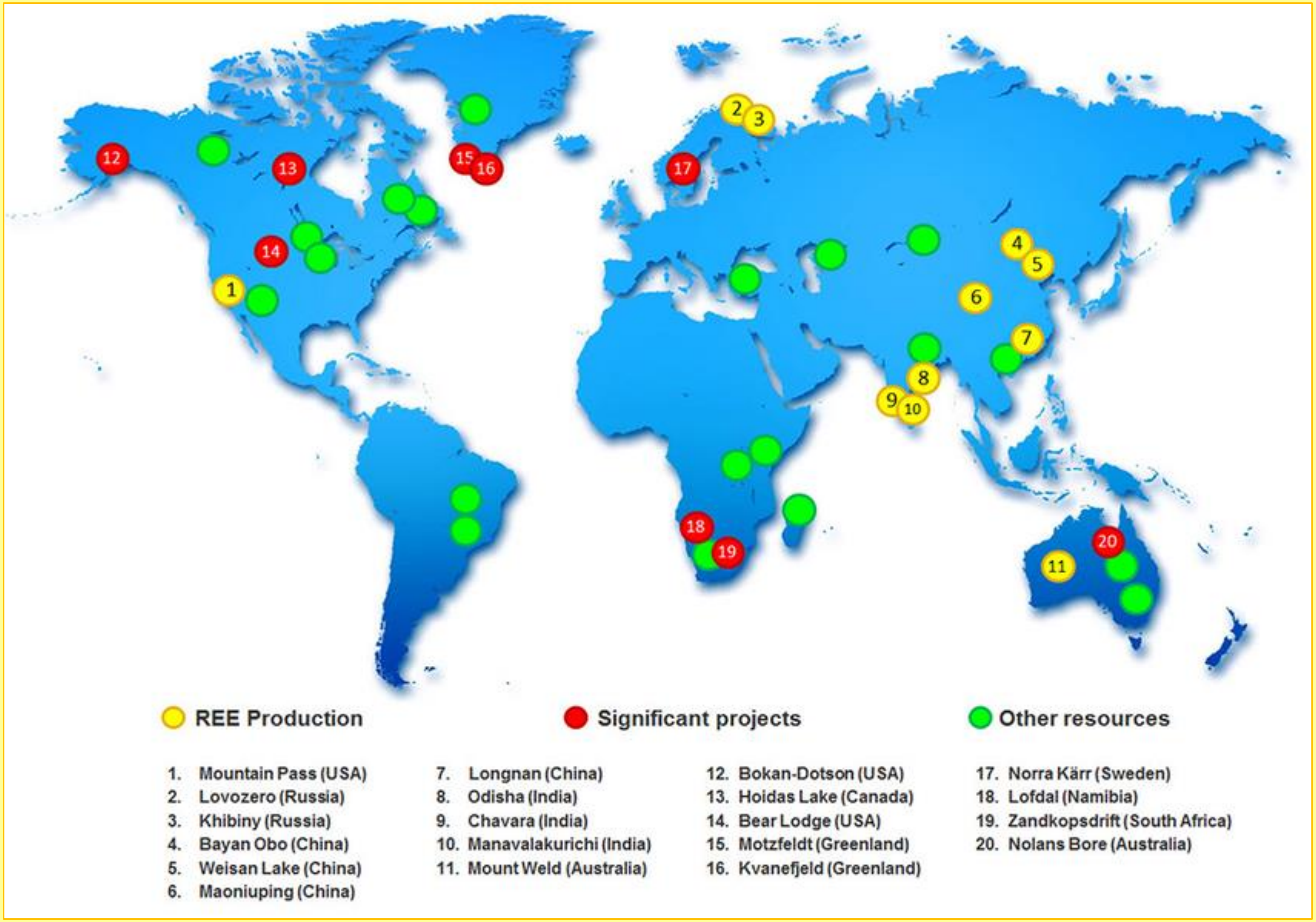
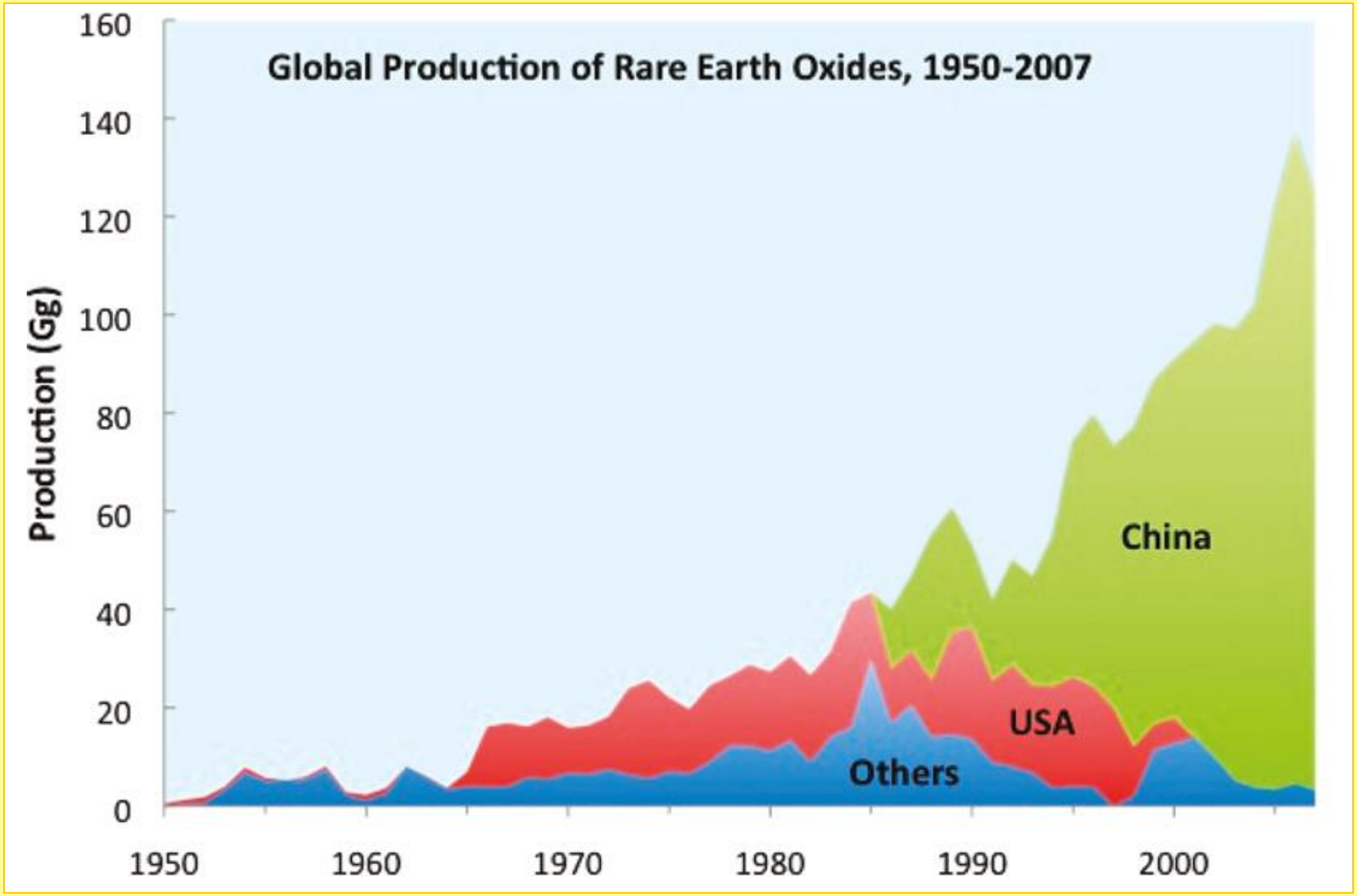
5. Ore deposits can be very unevenly distributed

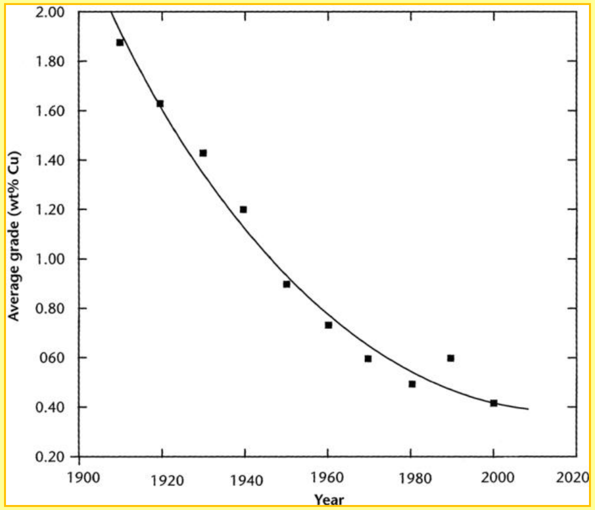


China completely controls the rare earths market



Du and Graedel (2011) *Environ. Sci. Technol.* **45,** 4096–4101.

Major concerns with regard to world resources of specialty metals (2)



Izatt, Izatt, Bruening, Izatt, and Moyer (2014)
Chem. Soc. Rev. **43,** 2451–2475.

6. Some specialty metals are exceedingly rare
7. Finite resource with no viable alternative
8. Significant losses in refining/manufacturing
9. e-Waste recycling is non-existent or currently unfeasible

Three vignettes from Johan’s research

1. The really toxic metal that you had never heard of and that is absolutely everywhere

2. How to use plants (and bacteria) to recover metals from waste and contaminated sites (phytoremediation)

3. How to use plants to estimate the amount of metal at a contaminated site over time (biomonitoring)

Gadolinium has been widely used all over the world to enhance contrast in medical magnetic resonance imaging (MRI) diagnostics since the late 1980s

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cp		Fl		Lv		

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

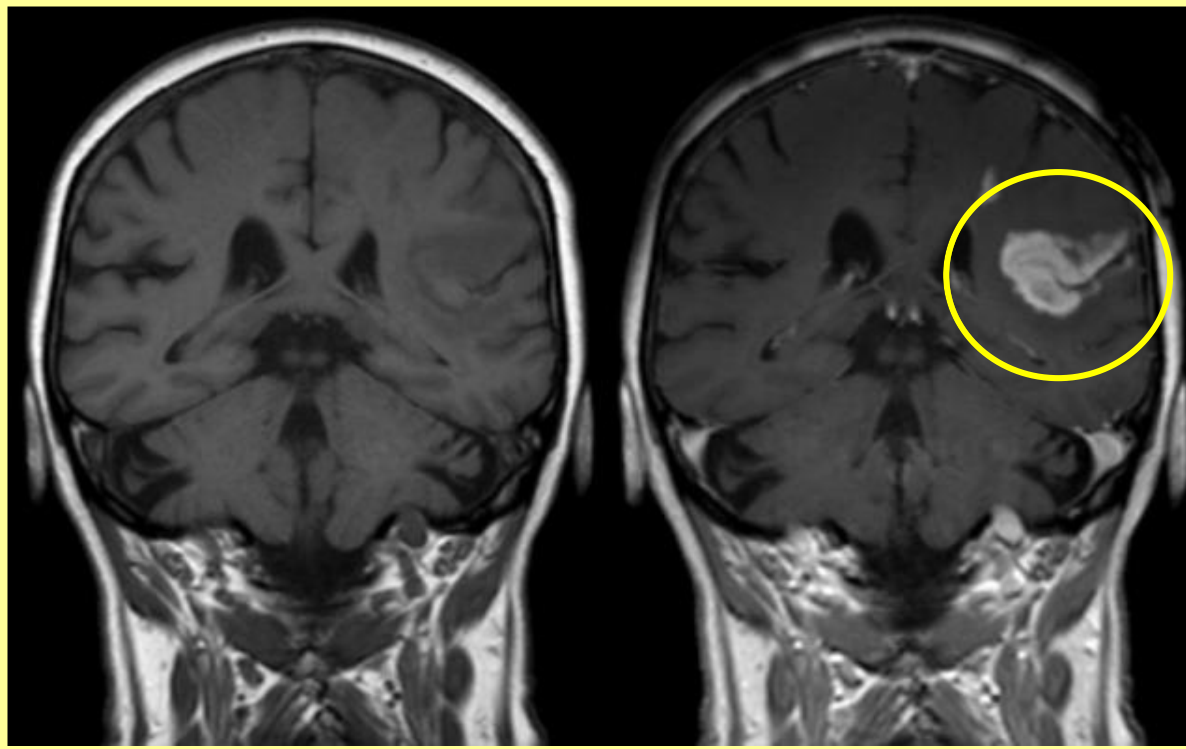


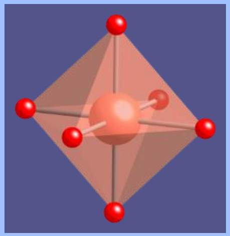
Image: Raleigh Radiology

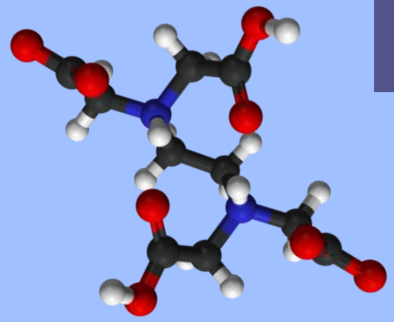
Image: Wikipedia

Here are some fun facts:

- Gd is highly toxic to humans

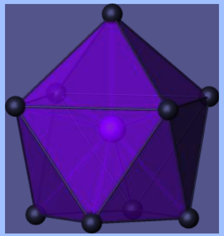
Mg, Ca, Fe

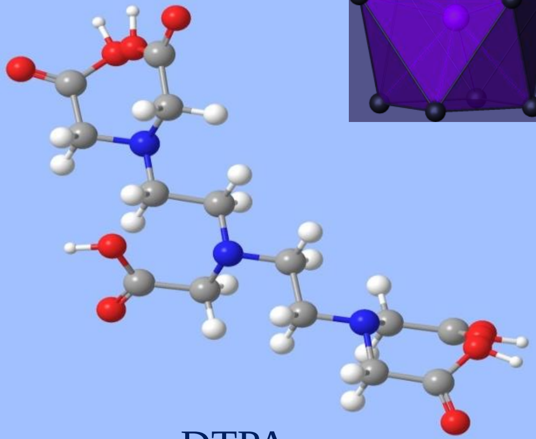




EDTA =
EthyleneDiamineTetraacetic Acid

Gd





DTPA =
DiethyleneTriaminePentaacetic Acid

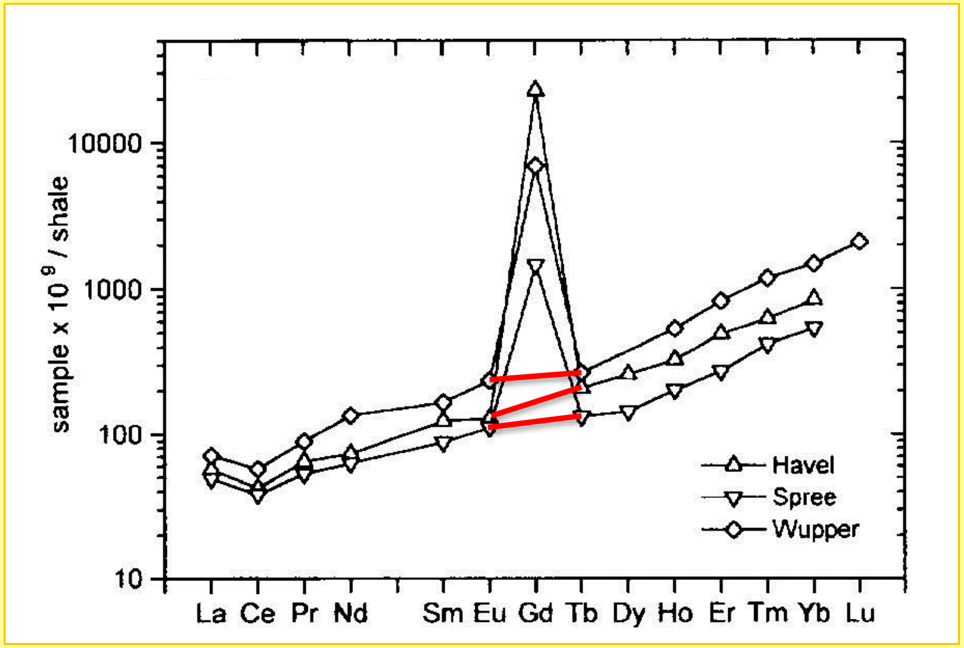
- Gd-DTPA is fully excreted via urine within hours after intake
- Typical administered dose is ~1 gram per patient per treatment
- Typical treatment rate is 5 patients per hospital per day
- Amount of *natural* Gd in 1 liter of river water is ~0.00000004 gram

More fun facts:

- Gd-DTPA is NOT broken down and removed by: 1. bacteria; 2. UV radiation; 3. chlorination; 4. flocculation
- Consequently, it is impervious to advanced waste water treatment

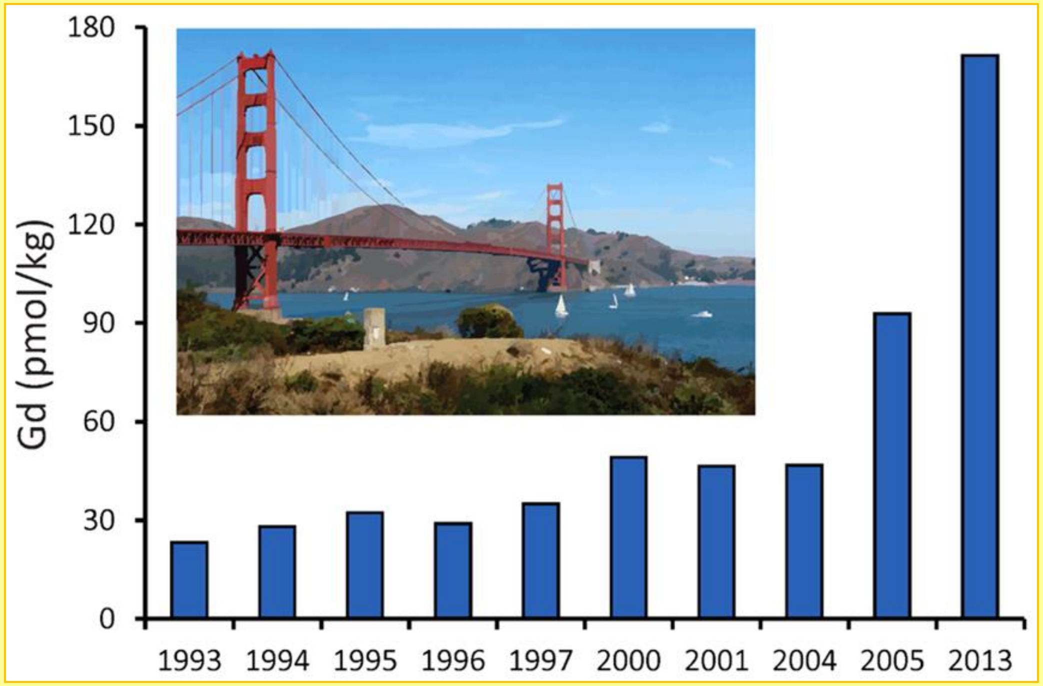
Gd contamination can be directly shown by using its Periodic Table neighbors

Bau and Dulski (1996) *Earth Planet. Sci. Lett.* **143,** 245–255.



- Gd contamination first reported in 1996 in German rivers downstream of wastewater treatment plants
- Ubiquitous in countries with well-developed healthcare systems
- So much Gd in rivers now that it is used as a wastewater tracer

Where does it all go? The ocean!



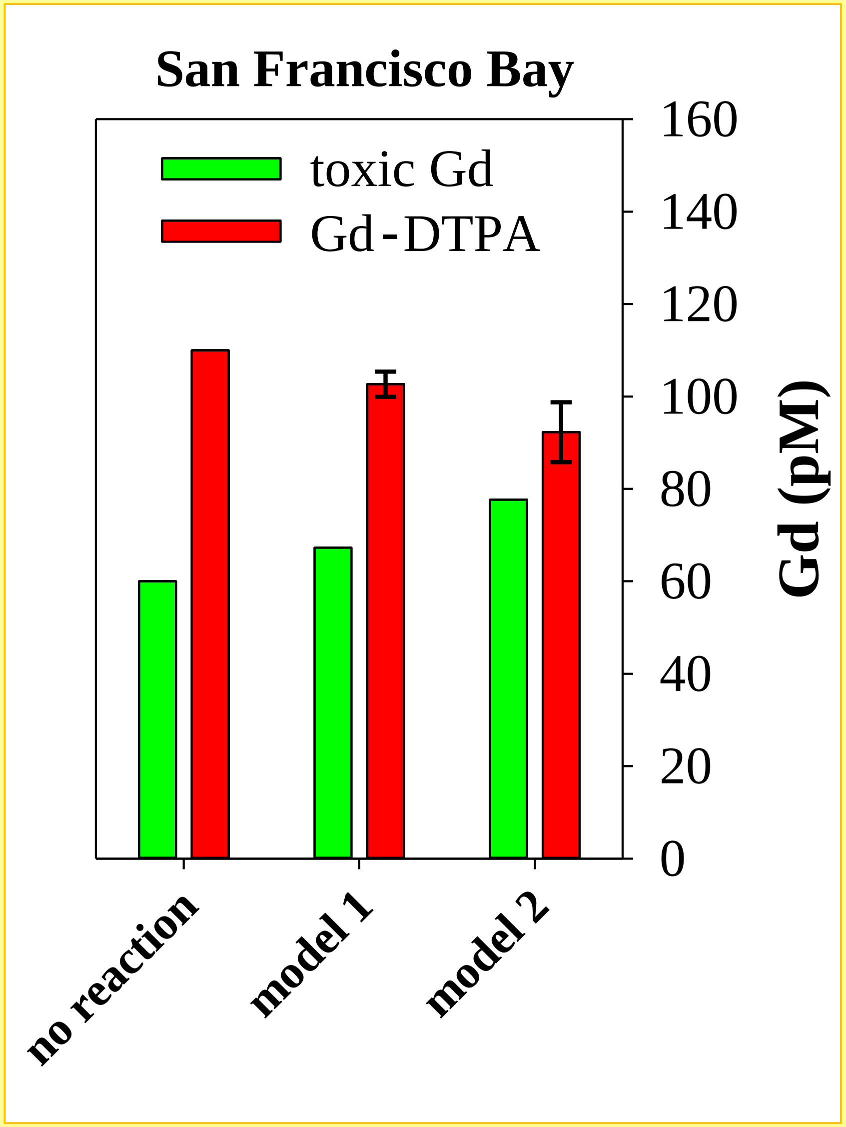
Gd concentrations have increased exponentially in San Francisco Bay since the late 1990s

Hatje, Bruland, and Flegal (2016) *Environ. Sci. Technol.* **50,** 4159–4168.

Magnesium and calcium in seawater may cause DTPA to let go of Gd by an exchange reaction (transmetalation):

$$\text{Gd-DTPA} + \text{Ca} \rightarrow \text{Ca-DTPA} + \text{Gd}$$

Our research question: Does mixing of river water with seawater in estuaries destabilize Gd-DTPA?



Our approach: potentiometric titration = measure the stability of Ca-DTPA and Mg-DTPA vs. Gd-DTPA and use a chemical model to estimate the effect

Our conclusions:

- Gd-DTPA is about a million times less stable in seawater than in river water
- As much as 16% of the total Gd-DTPA may break down in the ocean due to competition with Mg and Ca

frontiers in Marine Science

ORIGINAL RESEARCH
published: 10 April 2018
doi: 10.3389/fmars.2018.00111

Check for updates

Effect of Mg and Ca on the Stability of the MRI Contrast Agent Gd–DTPA in Seawater

Johan Schijf[1] and Isabel J. Christy[2]*

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Gadolinium diethylenetriaminepentaacetic acid (Gd–DTPA) is widely applied as a contrast

Sea Grant Maryland

NSF

Work done together with Isabel Christy, Whitman College, Walla Walla, WA (2016 REU student)

Phytoremediation: the use of plants to remove metal contaminants from soil or water

The plant can be disposed of, or processed to recover metals for recycling

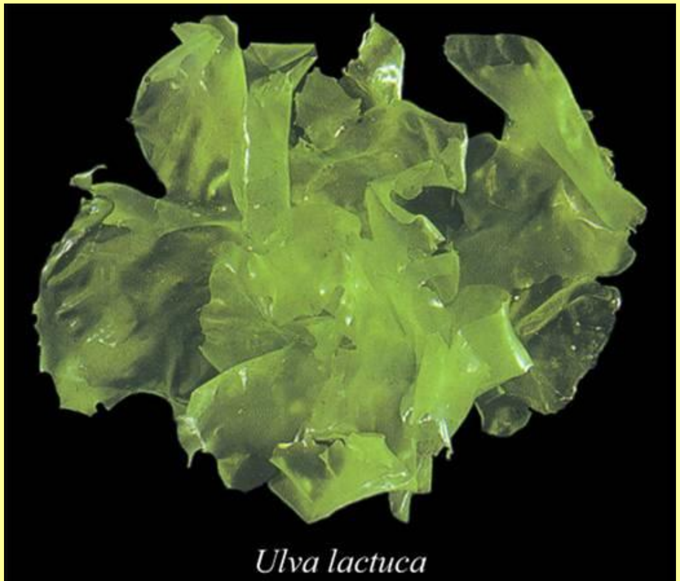
Certain bacteria can also be used to make metals more or less soluble

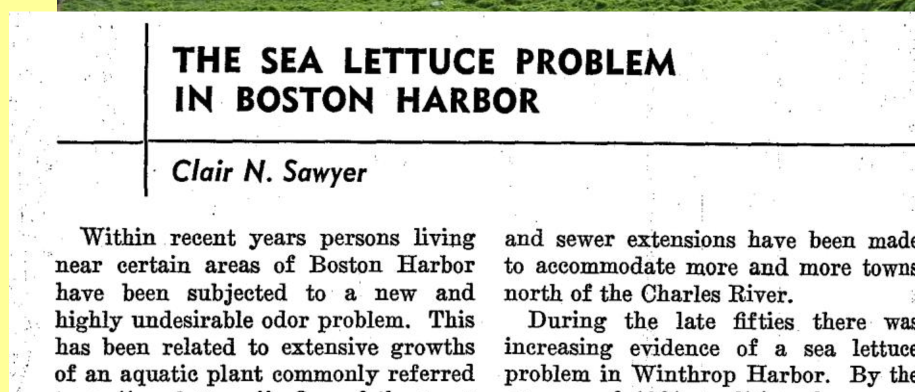
To be a good phytoremediator, a plant must:

- Strongly take up the metal of interest
- Be easy to grow in many places
- Grow quickly and abundantly
- Be easy to harvest
- Not be killed by the metal
- Be selective if possible

Our research question:

Can sea lettuce (saltwater) and common duckweed (freshwater) be used to remove rare earths from their environment?





THE SEA LETTUCE PROBLEM IN BOSTON HARBOR

Clair N. Sawyer

Within recent years persons living near certain areas of Boston Harbor have been subjected to a new and highly undesirable odor problem. This has been related to extensive growths of an aquatic plant commonly referred

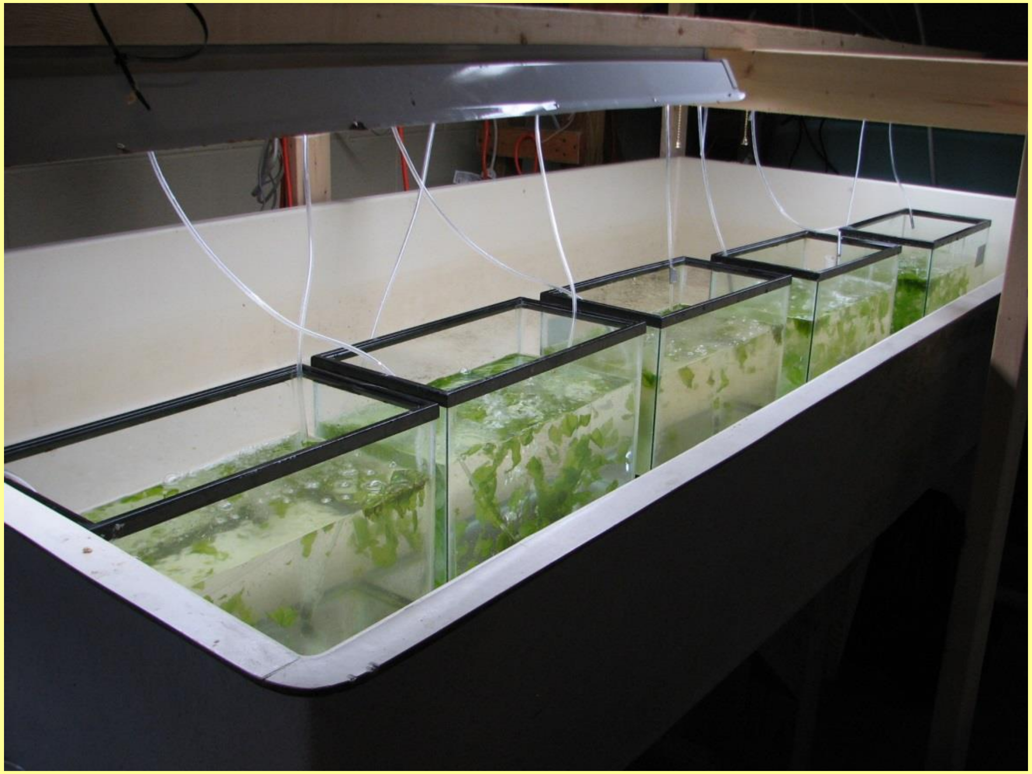
and sewer extensions have been made to accommodate more and more towns north of the Charles River.

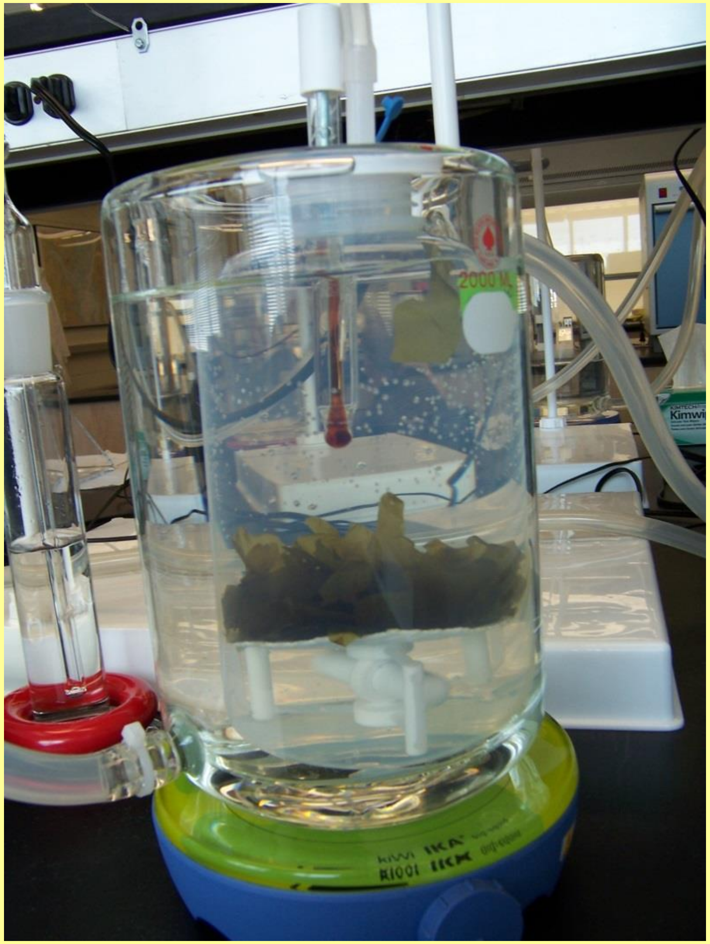
During the late fifties there was increasing evidence of a sea lettuce problem in Winthrop Harbor. By the

Sawyer (1965) *J. Water Poll. Contr. Fed.* **37,** 1122–1123.

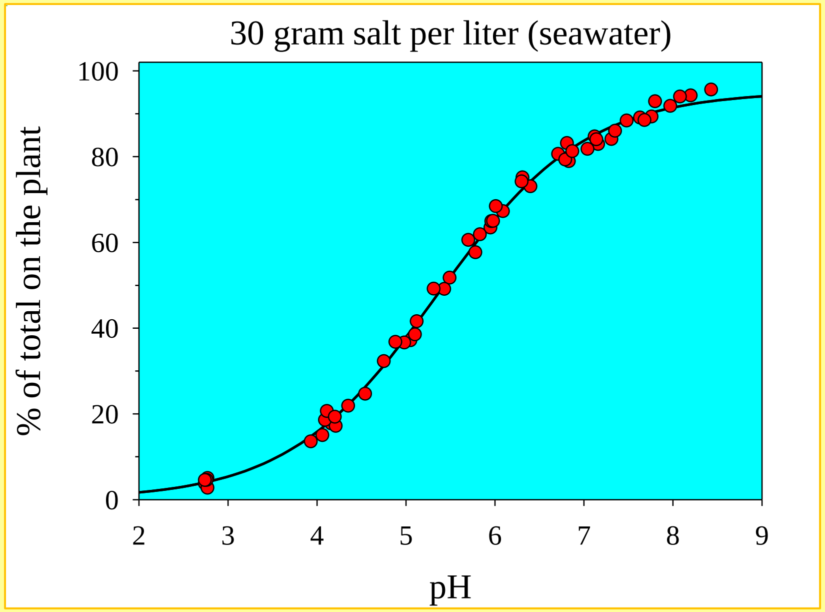
Our approach:

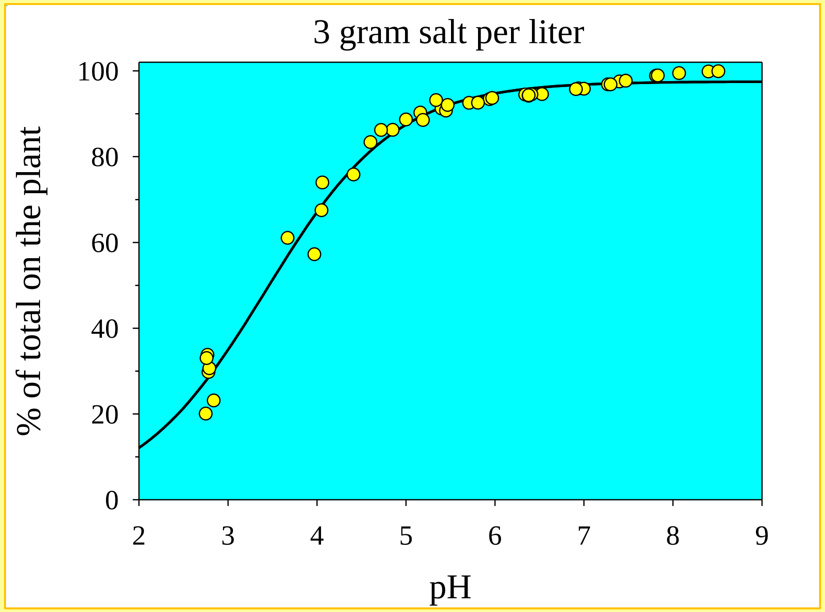
Grow the plants in culture, expose them to rare earths under controlled conditions and measure how much they take up

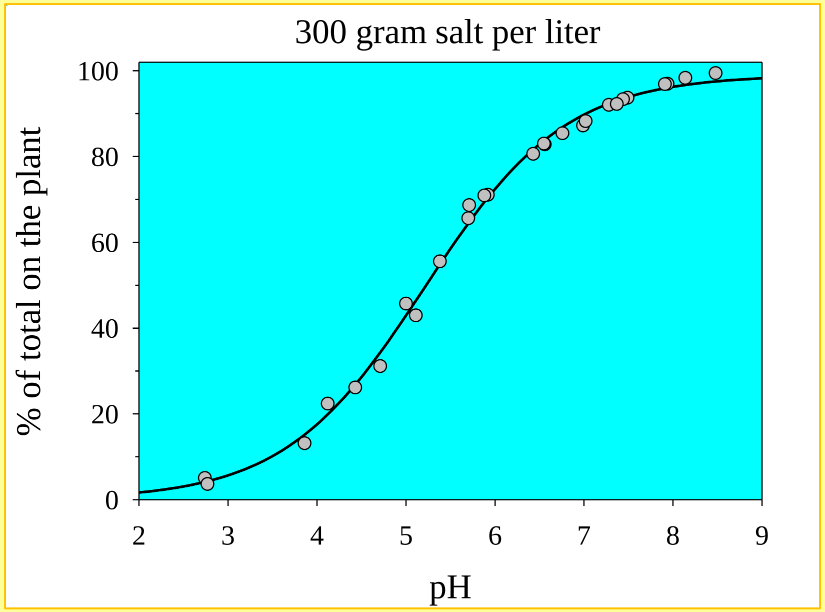




Our conclusion: A definite maybe!





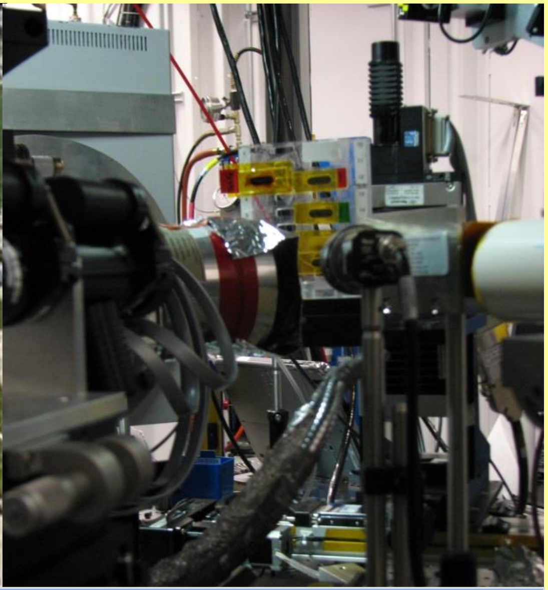


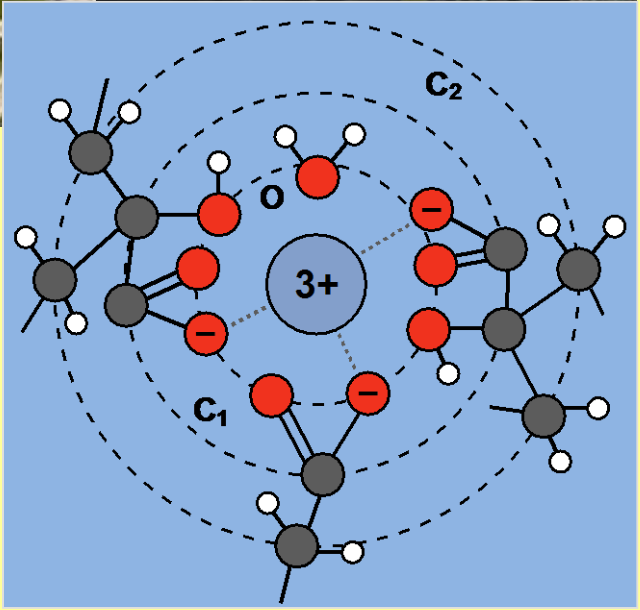
Uptake of dysprosium, used in magnets (computers, audio systems, cars, wind turbines)

0.5 gram seaweed per liter
500 microgram Dy per liter
1 hour uptake time

A quick glimpse of my scientific tinkering

Argonne National Laboratory (near Chicago)
synchrotron particle accelerator





$$\log {}_{i}K_S = \log\left[\frac{1}{3}\times\sum_{j=1}^{3}\left\{\frac{10^{(\log {}_{Lj}\beta_1 - pK_{aj} + pH)}}{1+10^{(pK-pK_{aj})}}\right\} + \frac{10^{(\log {}_{L3}\beta_1^{*} + \log\beta_1^{*} - pK_{a3} + 2\times pH)}}{3\times\left[1+10^{(pK-pK_{a3})}\right]}\right]$$

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www.elsevier.com/locate/gca

A surface complexation model of YREE sorption on *Ulva lactuca* in 0.05–5.0 M NaCl solutions

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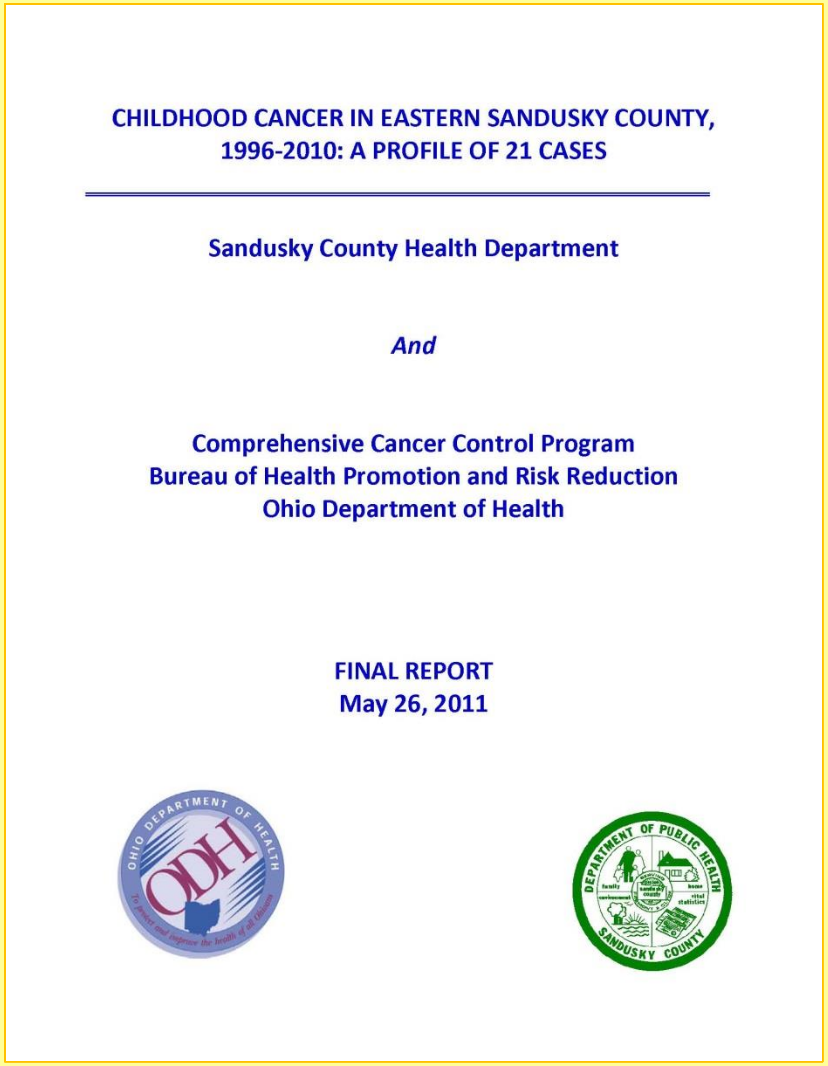
Biomonitoring


CHILDHOOD CANCER IN EASTERN SANDUSKY COUNTY, 1996-2010: A PROFILE OF 21 CASES

Sandusky County Health Department

And

Comprehensive Cancer Control Program
Bureau of Health Promotion and Risk Reduction
Ohio Department of Health

FINAL REPORT
May 26, 2011


Friday

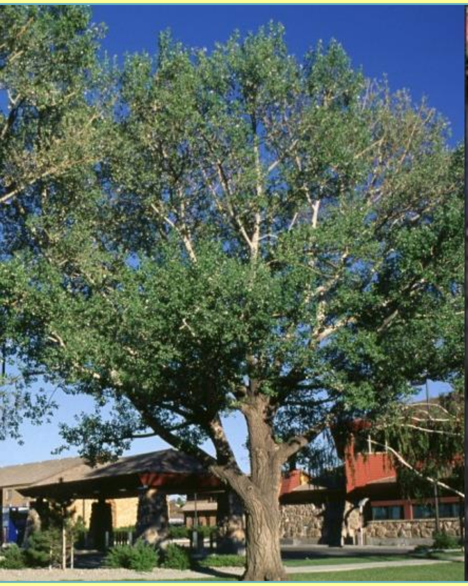
The News-Messenger

Brown third to die in cancer cluste

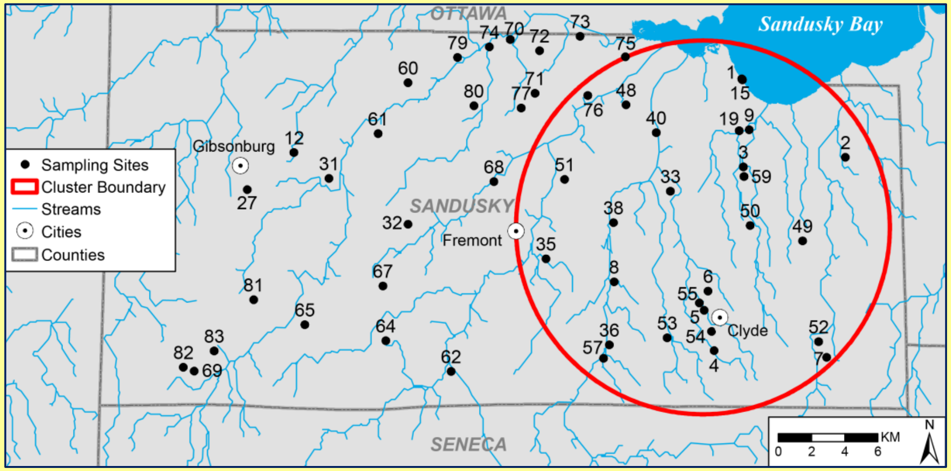
- There has been a childhood cancer cluster around the city of Clyde, OH
- At least 35 cases of rare cancers in children 19 years and younger since 1996; 7 victims have died since 2007
- Environmental contaminants are thought to be the most likely cause of childhood cancer clusters
- Ohio EPA has found no definitive common cause in Clyde despite years of intensive environmental testing

Our research question:

Can we use tree rings to get an historical record of contaminants that the sick children may have been exposed to, via groundwater or the soil, several decades ago?

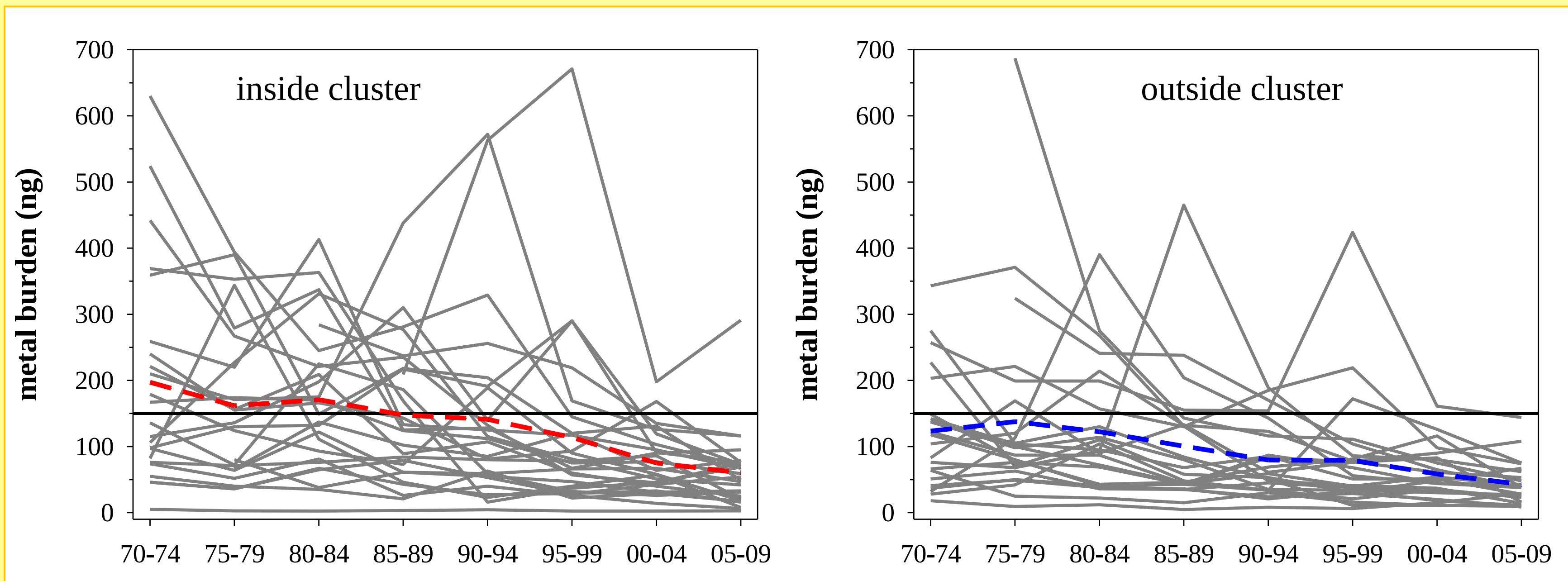


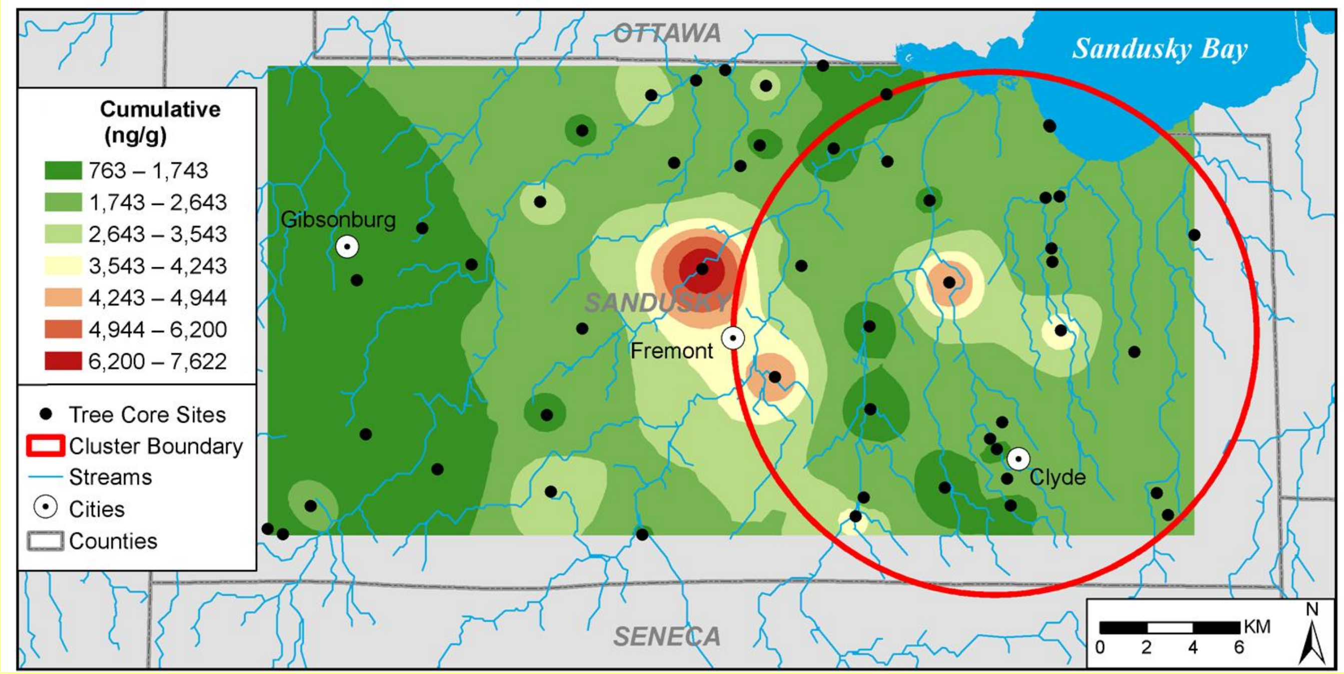
Our approach:



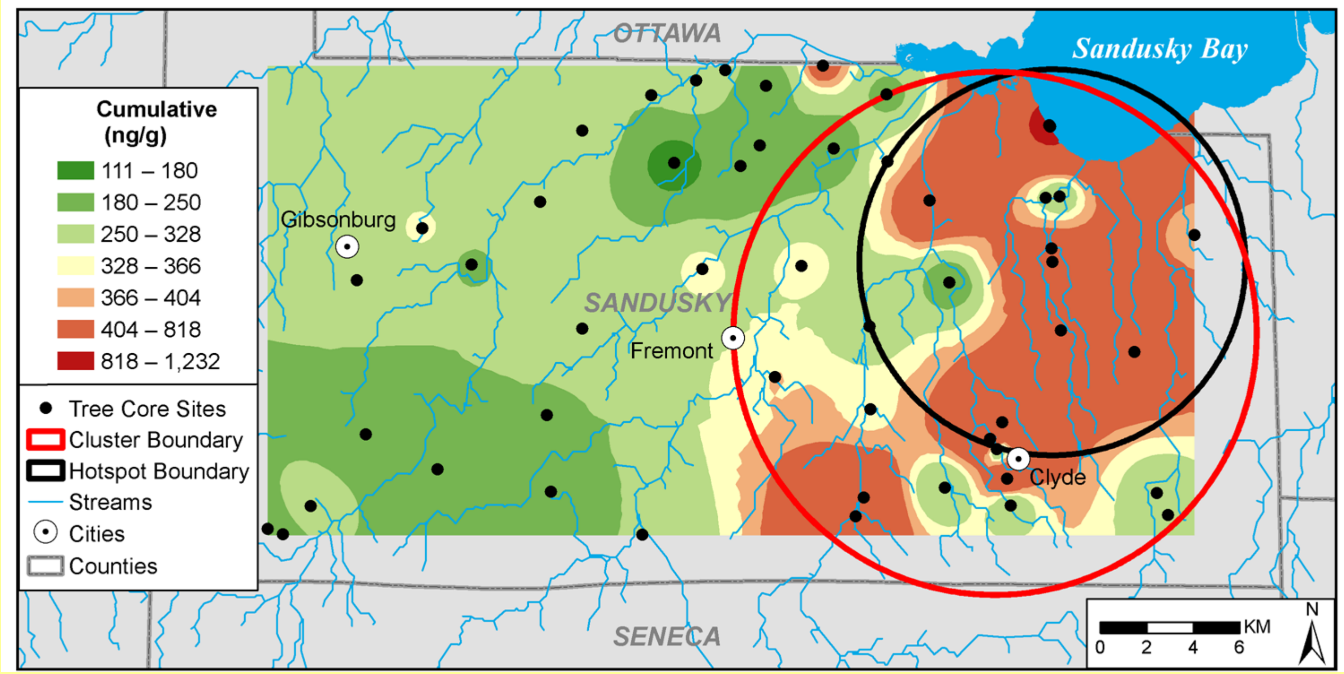
We cored more than 80 eastern cottonwood around Clyde, about half inside the cancer cluster

Each core was analyzed for nine trace metals via ICP-MS in eight 5-year increments (1970–2009)





OTTAWA
Sandusky Bay
Cumulative (ng/g)
763 – 1,743
1,743 – 2,643
2,643 – 3,543
3,543 – 4,243
4,243 – 4,944
4,944 – 6,200
6,200 – 7,622
Tree Core Sites
Cluster Boundary
Streams
Cities
Counties
Gibsonburg
SANDUSKY
Fremont
Clyde
SENECA
KM
0 2 4 6
N



OTTAWA
Sandusky Bay
Cumulative (ng/g)
111 – 180
180 – 250
250 – 328
328 – 366
366 – 404
404 – 818
818 – 1,232
Tree Core Sites
Cluster Boundary
Hotspot Boundary
Streams
Cities
Counties
Gibsonburg
SANDUSKY
Fremont
Clyde
SENECA
KM
0 2 4 6
N

Our (partial) conclusions:

- For certain metals, eastern cottonwood trees inside the cancer cluster have accumulated significantly more from the soil than those on the outside, during the period 1970–2009
- For other metals, no difference was found
- This observation is NOT PROOF that metals had anything to do with the childhood cancers, but it does make them candidates for further study

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Validation and application of a new microwave-digestion/ICP-MS method for the analysis of trace metals in tree increment cores

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A method is presented for the routine analysis of eight trace metals (As, Cd, Co, Cr, Cu, Ni, Pb, V)

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Mary Garvin, Oberlin College
Alynne Bayard, CBL (GIS)
Dong Liang, CBL (statistics)

What can YOU do?

1. RECYCLE all your batteries (household, car, phone)
2. RECYCLE all your light bulbs (CFL and LED)
3. RECYCLE your electronics (TVs, computers, toys)
4. Be an educated consumer!
   No more MRI scans!
5. Please donate to support our great graduate students

THANK YOU!