Metals in Life or
The Inorganic Chemistry of Life
Chemistry 2211a

5) Geological and anthropogenic sources of metals

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1. Geological origins of metals
    a. Lithosphere
    b. Metal distribution between phases
    c. Geochemical-Biological interactions – distributing metals
2. Man's activities
    a. Mining
    b. Metal flow from extraction to the environment
    c. Metal deposition on soils
3. Natural materials – esp. Ca – calcite and hydroxyapatite & magnetite
4. Metals in rocks, seawater, cells
5. Tolerance levels and maximum levels - focus on Zn
6. But then there is toxic metal pollution Hg, As and Pb – focus on Hg

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On 2008-10-27 R07-4

1) Elements in the crust and water

We will look at a number of cartoons and tables, I will summarise at the end of these.

Constant flow of useful ions through biosphere, atmosphere, hydrosphere, lithosphere. We can trace the release of metals into the biosphere in the following way

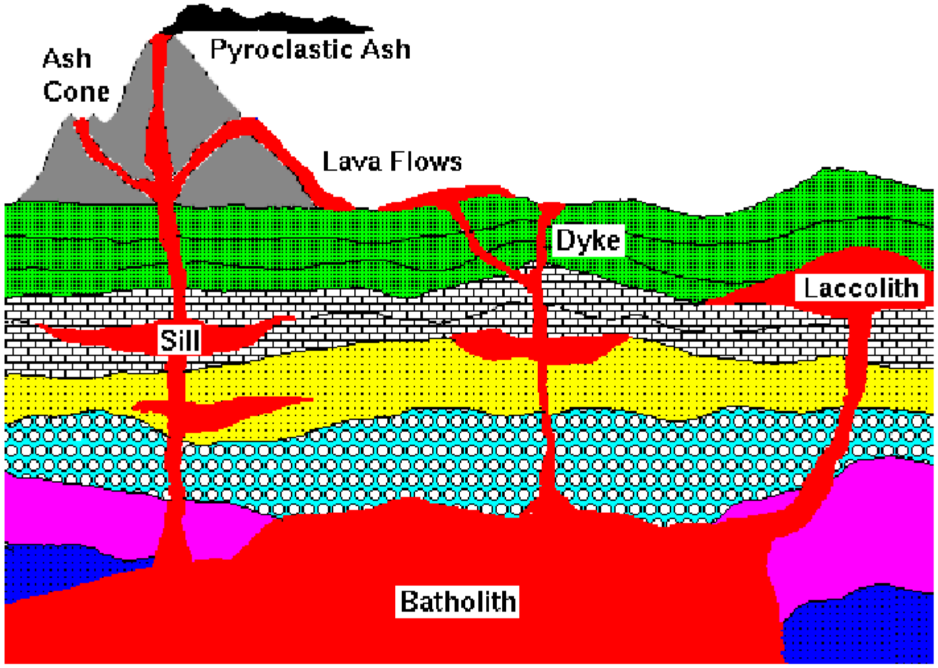
… first – release from the lithosphere

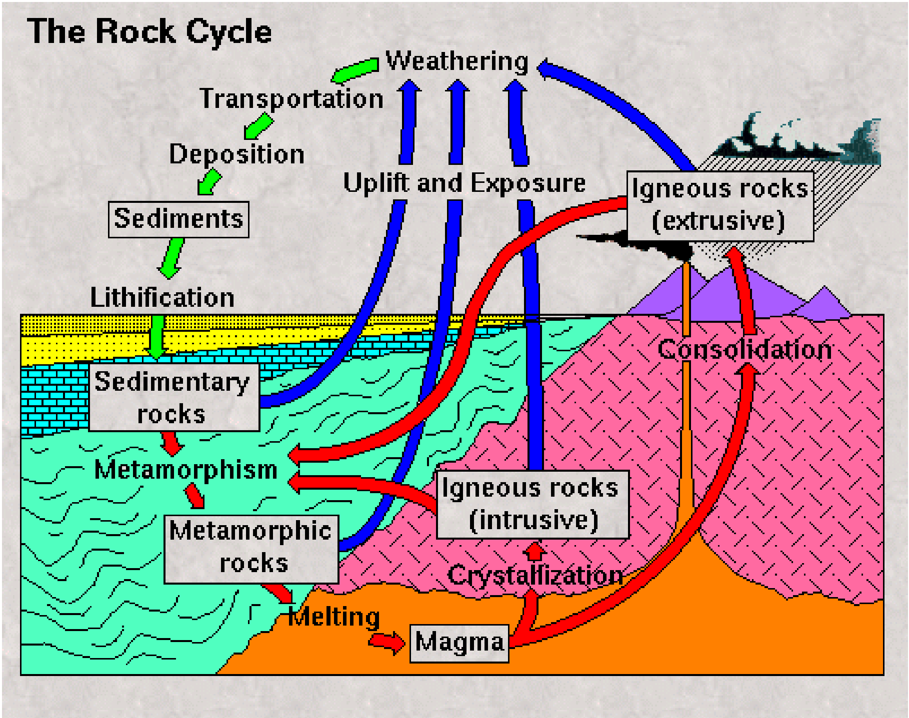
INTERACTIONS Generally - we can say that essentiaqlly-organic-based organisms, are in constant contact with the inorganic elements of 'their' environment from the air, the water-based hydrosphere and the mineral-based lithosphere

INCLUSION OF MINERALS The great concentration of all elements in the lithosphere and the mobilization of these elements through the hydrosphere and atmosphere (major sources are volcanoes and earthquakes; erosion both air and water) means that the biosphere was able to take advantage of chemistry not available from C, O and H alone

Interaction between elements on the planet and the biosphere - did organisms incorporate what was there and include no mechanisms for treating 'new' metals?

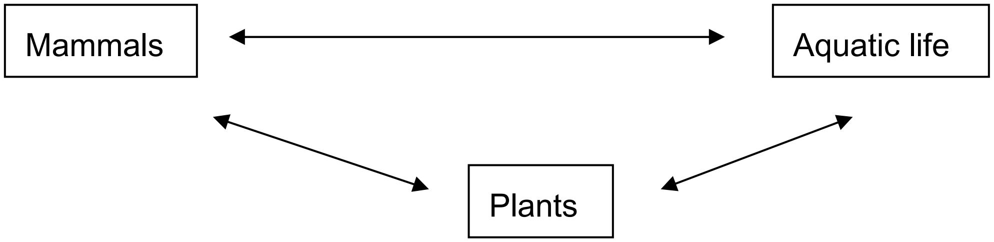
Hence toxicity?





http://science.cc.uwf.edu/sh/curr/rockcyc/rockcyc.htm

We can look at the distribution of elements in cellular systems compared with the abundance in the earth's crust.



Mammals

Aquatic life

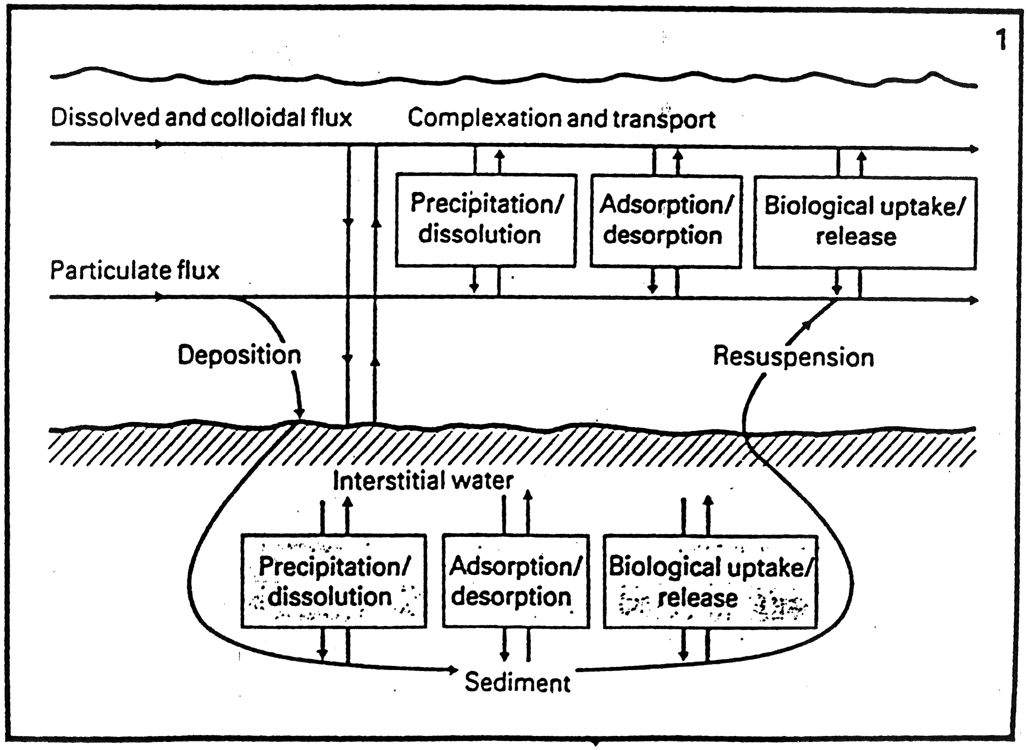
Plants

In rock: Fe – 62,000 ppm - what's that as a mass fraction?

But in seawater – 1×10^{-4} mM - hmmm so $\times 10^{-3}$ for M; in ppm?…..

But in serum – mainly bound iron is 2×10^{-2} mM that's 2×10^{-5} M

Fig. 1. Geochemical-biological interactions affecting trace metal speciation. (Reproduced with the permission of Martinus Nihoff.1)



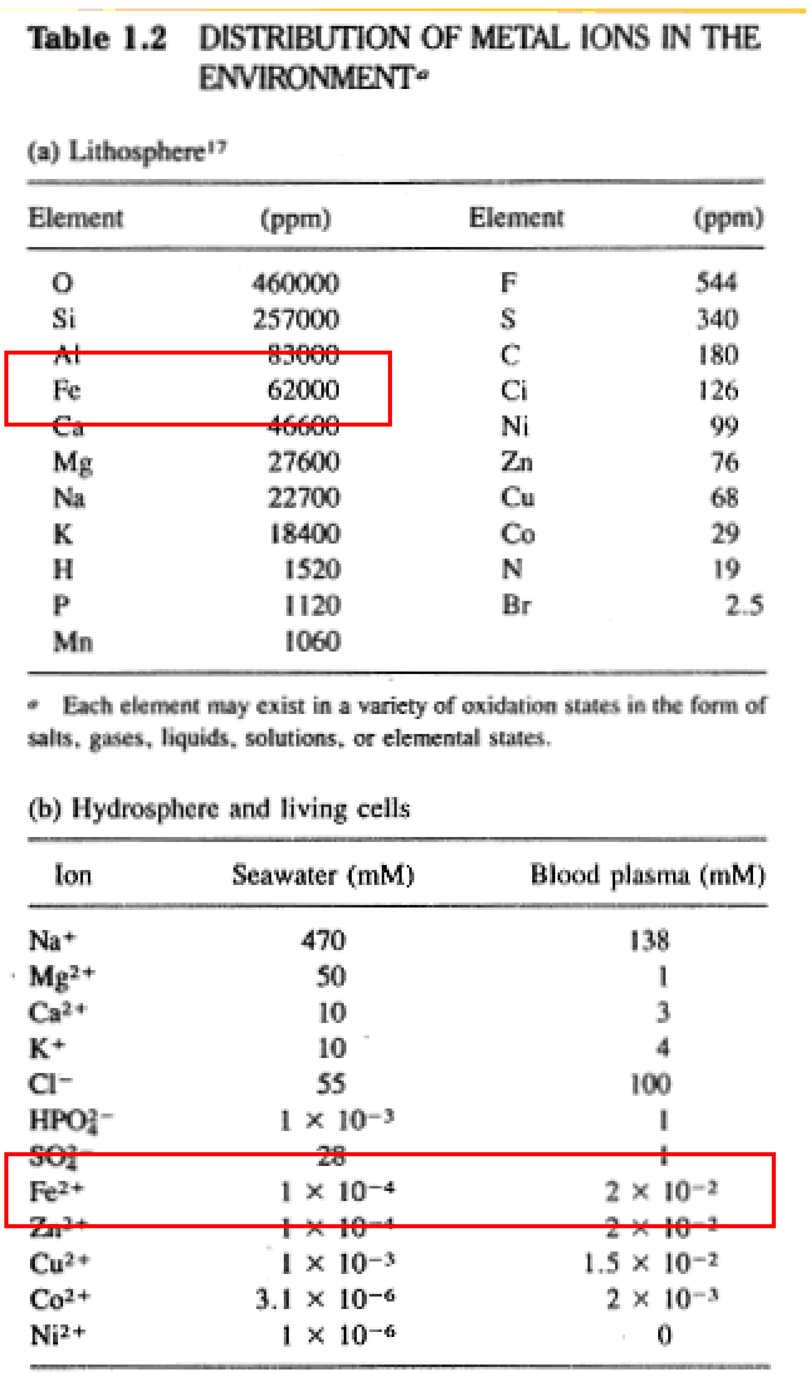


Table 1.2 DISTRIBUTION OF METAL IONS IN THE ENVIRONMENT[a]

(a) Lithosphere[17]

Element	(ppm)	Element	(ppm)
O	460000	F	544
Si	257000	S	340
Al	83000	C	180
Fe	62000	Cl	126
Ca	46600	Ni	99
Mg	27600	Zn	76
Na	22700	Cu	68
K	18400	Co	29
H	1520	N	19
P	1120	Br	2.5
Mn	1060		

[a] Each element may exist in a variety of oxidation states in the form of salts, gases, liquids, solutions, or elemental states.

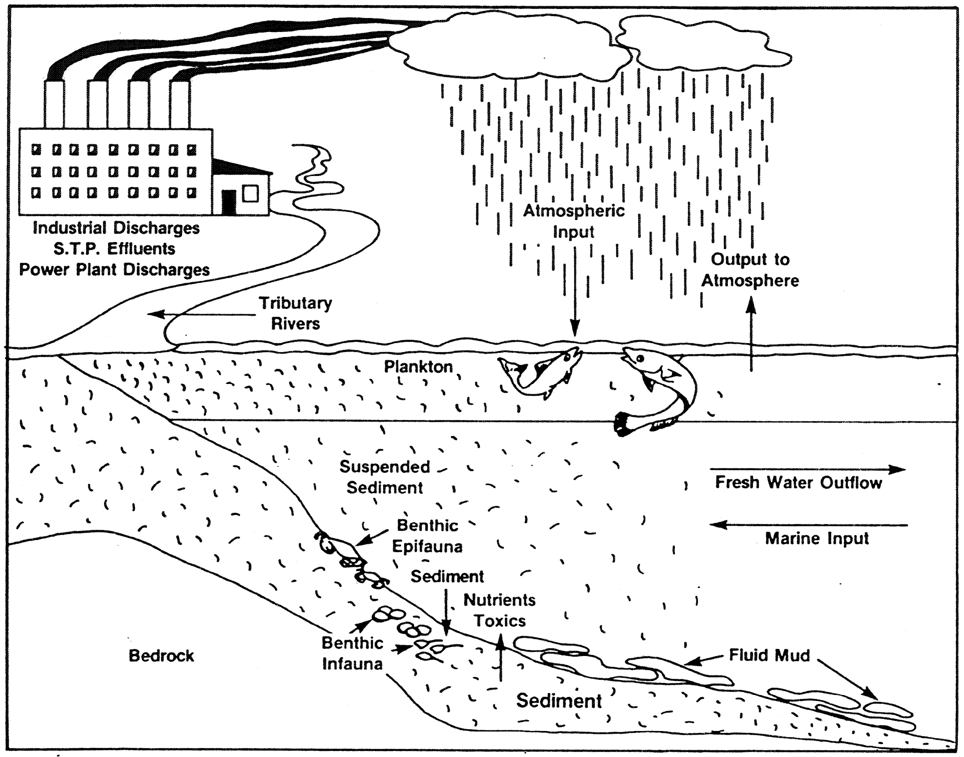
(b) Hydrosphere and living cells

Ion	Seawater (mM)	Blood plasma (mM)
Na^+	470	138
Mg^{2+}	50	1
Ca^{2+}	10	3
K^+	10	4
Cl^-	55	100
HPO_4^{2-}	1×10^{-3}	1
SO_4^{2-}	28	1
Fe^{2+}	1×10^{-4}	2×10^{-2}
Zn^{2+}	1×10^{-4}	2×10^{-2}
Cu^{2+}	1×10^{-3}	1.5×10^{-2}
Co^{2+}	3.1×10^{-6}	2×10^{-3}
Ni^{2+}	1×10^{-6}	0

2) Then there’s man …

Metals are extracted in amounts not proportional to their abundancies in the Earth’s crust – and many areas for increasing the environmental distribution – focus on – Fe, Zn-Pb-Hg

Tonnes/year: 10^8: Fe 10^7: Mg, Al 10^6: Cu, Zn, Pb
10^5: Ni, Sn 10^4: Mo, U, W, Co, Cd, V 10^3: Hg, Ag



Take-home message: simply extracting the metal results in potential major distribution of potetially toxic metals

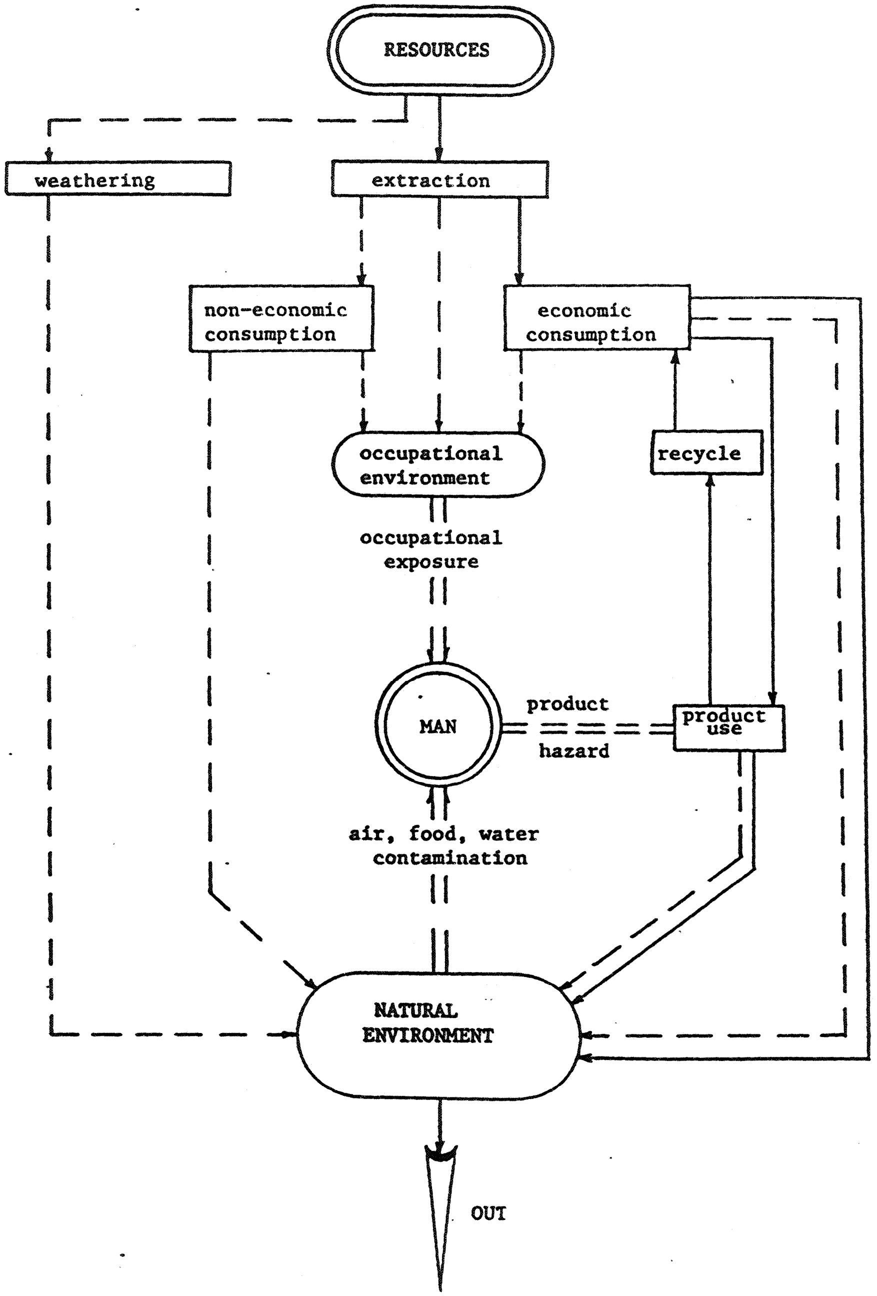
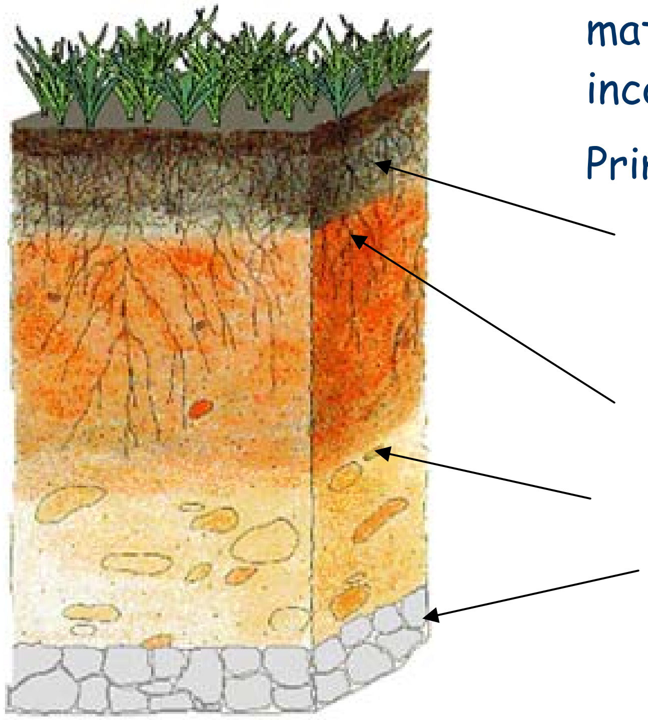


FIG. 1. Schematic metal flow (MacGregor [68]).

Many metals (Mg, Zn, Cu, Pb, Ni) are held by dead organic matter and clay minerals in the surface – available to be incorporated into new vegetation – esp. vegetables..

Primary layers of soil profile



A0 – humic material near surface: forest litter and partly decomposed plants.
A2 – bleached layer
B – enrichment layer
C – parent material

Sewage Sludge

Sludge originates from the process of treatment of waste water. Due to the physical-chemical processes involved in the treatment, the sludge tends to concentrate heavy metals and poorly biodegradable trace organic compounds as well as potentially pathogenic organisms (viruses, bacteria etc) present in waste waters. Sludge is, however, rich in nutrients such as nitrogen and phosphorous and contains valuable organic matter that is useful when soils are depleted or subject to erosion.

3) We are interested in …Ca in shells and bonds (hydroxyapatite) and Fe in (well, proteins) the storage protein ferritin (4500 atoms of Fe stored in one multiunit quaternary structure – 24 sub units).. Calcium carbonate – calcite – bones - magnets

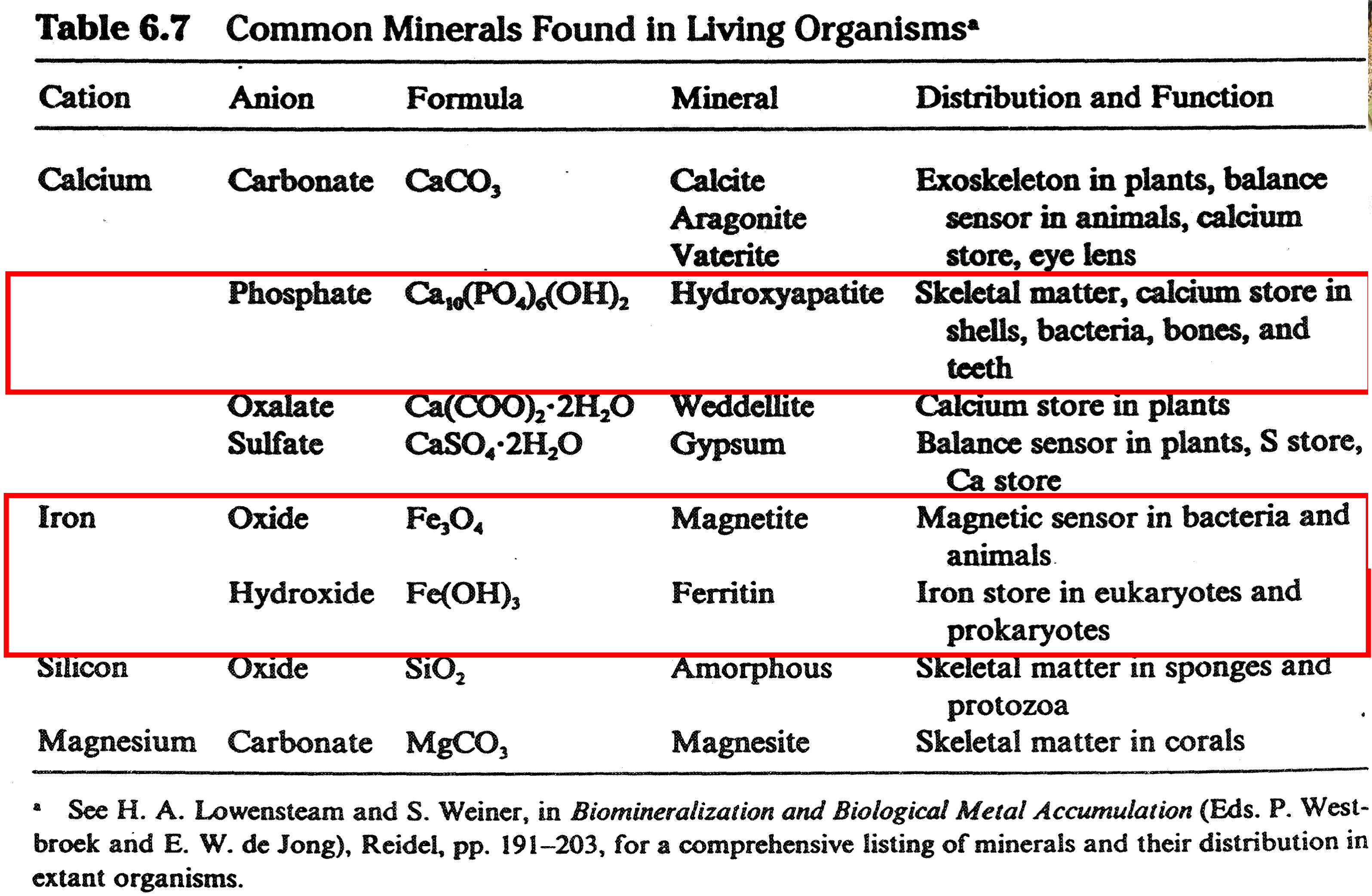
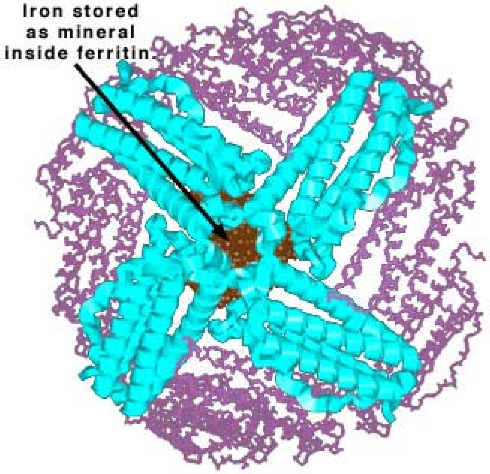
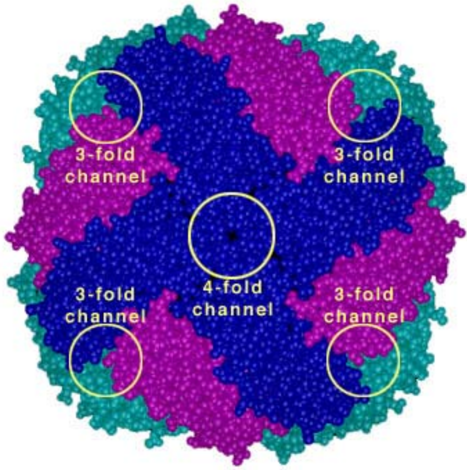


Table 6.7 Common Minerals Found in Living Organisms[a]

Cation	Anion	Formula	Mineral	Distribution and Function
Calcium	Carbonate	$CaCO_3$	Calcite Aragonite Vaterite	Exoskeleton in plants, balance sensor in animals, calcium store, eye lens
	Phosphate	$Ca_{10}(PO_4)_6(OH)_2$	Hydroxyapatite	Skeletal matter, calcium store in shells, bacteria, bones, and teeth
	Oxalate	$Ca(COO)_2 \cdot 2H_2O$	Weddellite	Calcium store in plants
	Sulfate	$CaSO_4 \cdot 2H_2O$	Gypsum	Balance sensor in plants, S store, Ca store
Iron	Oxide	Fe_3O_4	Magnetite	Magnetic sensor in bacteria and animals
	Hydroxide	$Fe(OH)_3$	Ferritin	Iron store in eukaryotes and prokaryotes
Silicon	Oxide	SiO_2	Amorphous	Skeletal matter in sponges and protozoa
Magnesium	Carbonate	$MgCO_3$	Magnesite	Skeletal matter in corals

[a] See H. A. Lowensteam and S. Weiner, in *Biomineralization and Biological Metal Accumulation* (Eds. P. Westbroek and E. W. de Jong), Reidel, pp. 191–203, for a comprehensive listing of minerals and their distribution in extant organisms.





This brings us back to the beginning – the distribution of metals in the environment

Zn is our focus in a later unit so what are its parameters like? Very, very low in the lithosphere – therefore, low in the oceans – but nearly the same as iron in man? Then in plasma? 2x10^{-5}M – clearly 1000x more concentrated than sea water like Fe (note 2+ - 3+ is completely insoluble). Actually – very little Zn^{2+} in the plasma (<1% total) – most (>50%) in muscle (why???). In fact zinc is not very toxic. But even then NO FREE ZINC in cells! All in proteins. Highly regulated in/out across the membrane.

So, the levels of zinc in drinking water can be quite high. Units: µg/kg = ppb

Not necessary to memorize all these numbers (but, yes, you need to know – little Zn in the lithosphere (1000x less than Fe-same amount in seawater as Fe(II)).

First, though, the concentrations of metals in drinking water are controlled… then levels in foods are monitored.

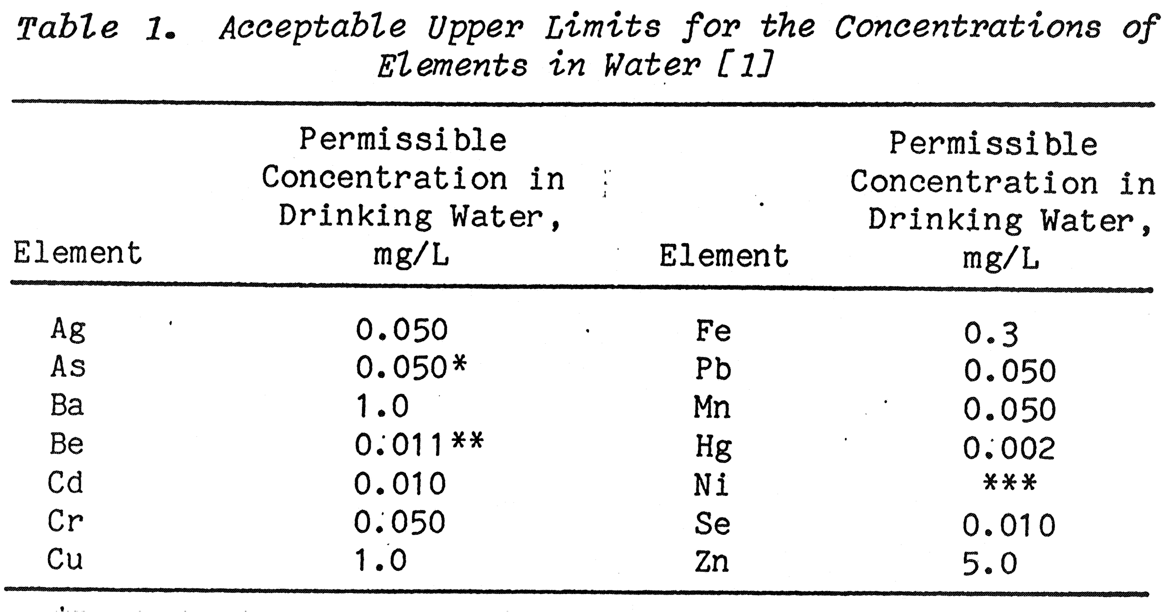
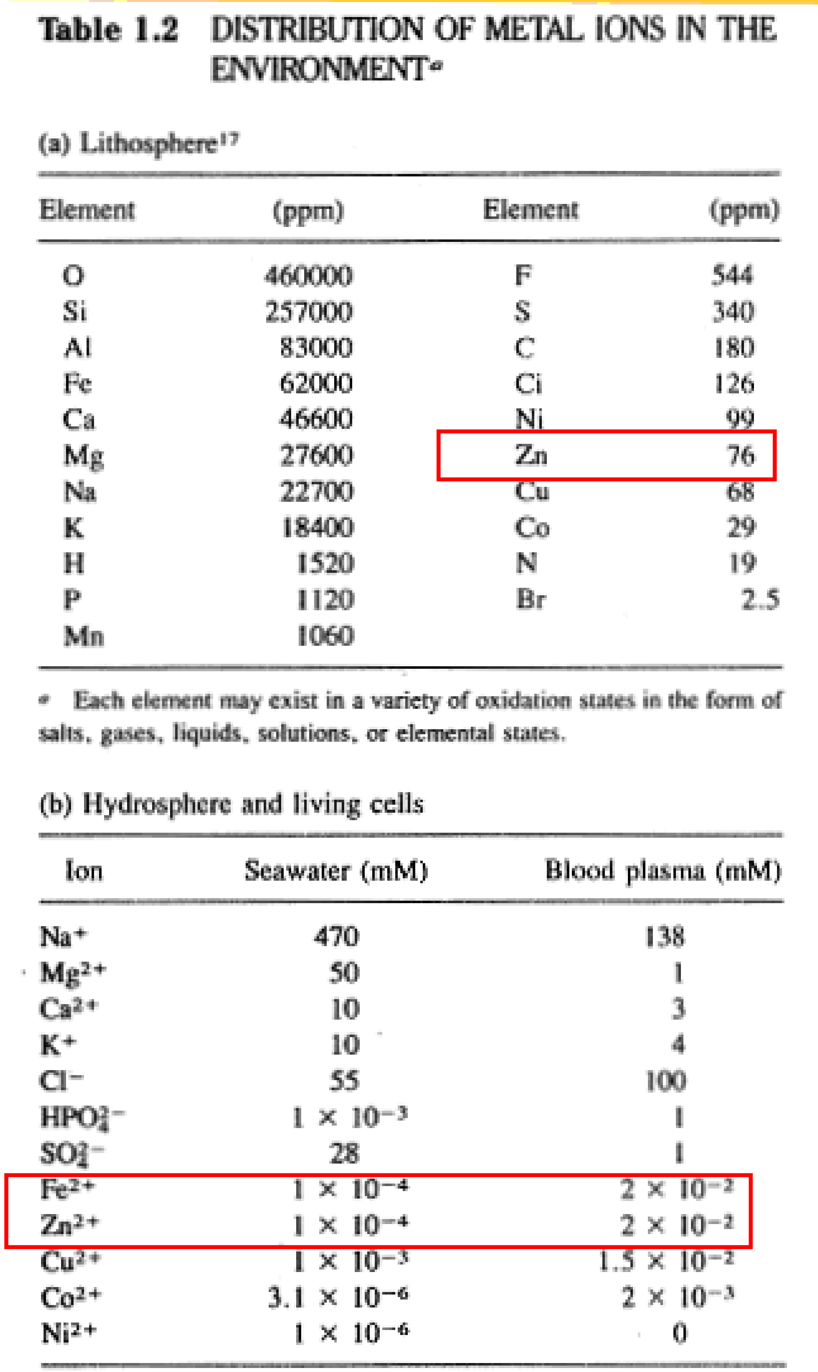


Table 1. Acceptable Upper Limits for the Concentrations of Elements in Water [1]

Element	Permissible Concentration in Drinking Water, mg/L	Element	Permissible Concentration in Drinking Water, mg/L
Ag	0.050	Fe	0.3
As	0.050*	Pb	0.050
Ba	1.0	Mn	0.050
Be	0.011**	Hg	0.002
Cd	0.010	Ni	***
Cr	0.050	Se	0.010
Cu	1.0	Zn	5.0



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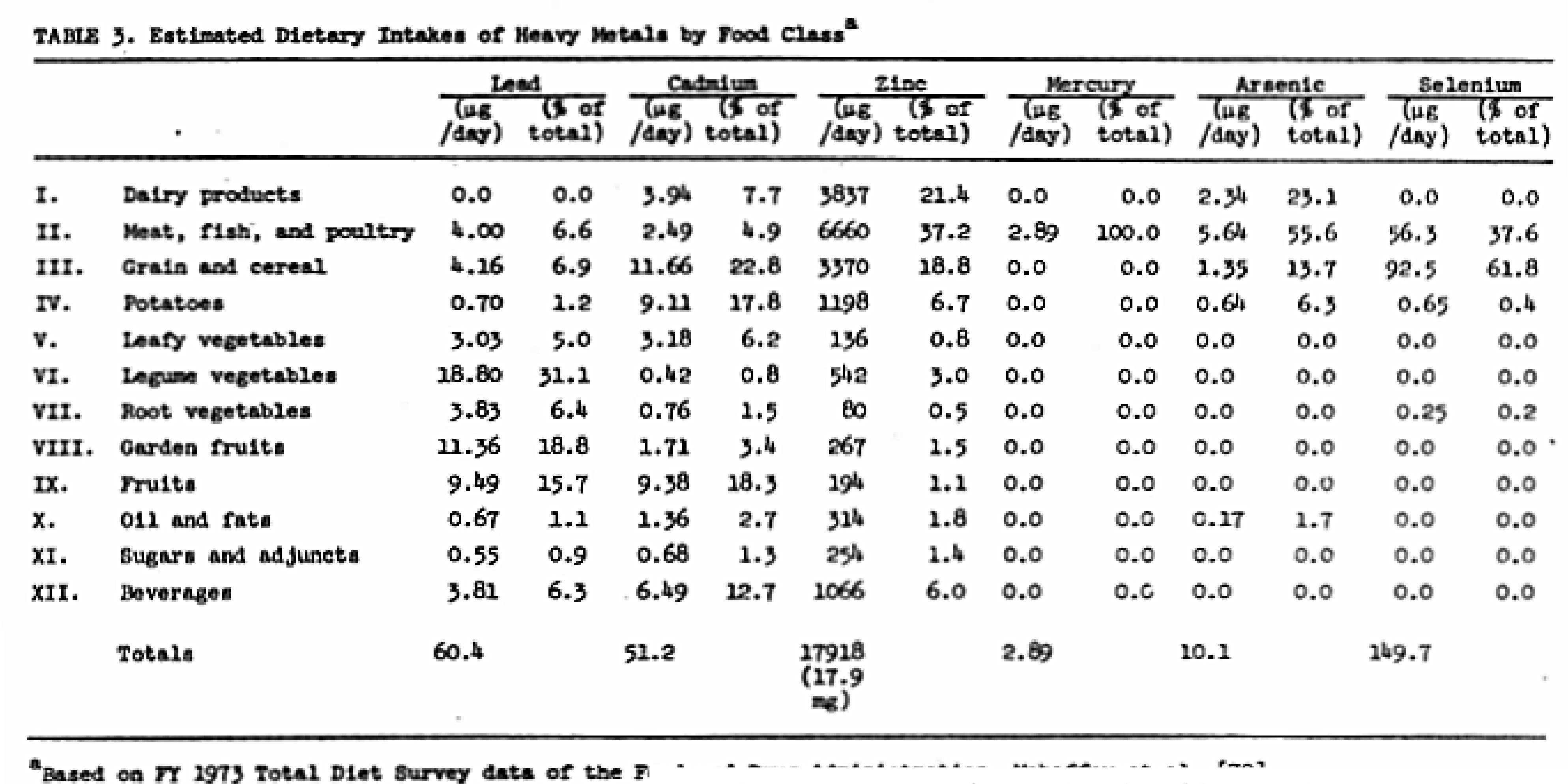


TABLE 3. Estimated Dietary Intakes of Heavy Metals by Food Class[a]

		Lead		Cadmium		Zinc		Mercury		Arsenic		Selenium	
		(µg /day)	(% of total)	(µg /day)	(% of total)	(µg /day)	(% of total)	(µg /day)	(% of total)	(µg /day)	(% of total)	(µg /day)	(% of total)
I.	Dairy products	0.0	0.0	3.94	7.7	3837	21.4	0.0	0.0	2.34	23.1	0.0	0.0
II.	Meat, fish, and poultry	4.00	6.6	2.49	4.9	6660	37.2	2.89	100.0	5.64	55.6	56.3	37.6
III.	Grain and cereal	4.16	6.9	11.66	22.8	3370	18.8	0.0	0.0	1.35	13.7	92.5	61.8
IV.	Potatoes	0.70	1.2	9.11	17.8	1198	6.7	0.0	0.0	0.64	6.3	0.65	0.4
V.	Leafy vegetables	3.03	5.0	3.18	6.2	136	0.8	0.0	0.0	0.0	0.0	0.0	0.0
VI.	Legume vegetables	18.80	31.1	0.42	0.8	542	3.0	0.0	0.0	0.0	0.0	0.0	0.0
VII.	Root vegetables	3.83	6.4	0.76	1.5	80	0.5	0.0	0.0	0.0	0.0	0.25	0.2
VIII.	Garden fruits	11.36	18.8	1.71	3.4	267	1.5	0.0	0.0	0.0	0.0	0.0	0.0
IX.	Fruits	9.49	15.7	9.38	18.3	194	1.1	0.0	0.0	0.0	0.0	0.0	0.0
X.	Oil and fats	0.67	1.1	1.36	2.7	314	1.8	0.0	0.0	0.17	1.7	0.0	0.0
XI.	Sugars and adjuncts	0.55	0.9	0.68	1.3	254	1.4	0.0	0.0	0.0	0.0	0.0	0.0
XII.	Beverages	3.81	6.3	6.49	12.7	1066	6.0	0.0	0.0	0.0	0.0	0.0	0.0
	Totals	60.4		51.2		17918 (17.9 mg)		2.89		10.1		149.7	

[a]Based on FY 1973 Total Diet Survey data of the F

This is an old table, but note the uneven distribution of metal contamination

Concentrate on: Pb (vegetables & fruit); Cd (grains & liver); Zn (everything – but esp. meat) ; Hg (fish mainly); As (fish)

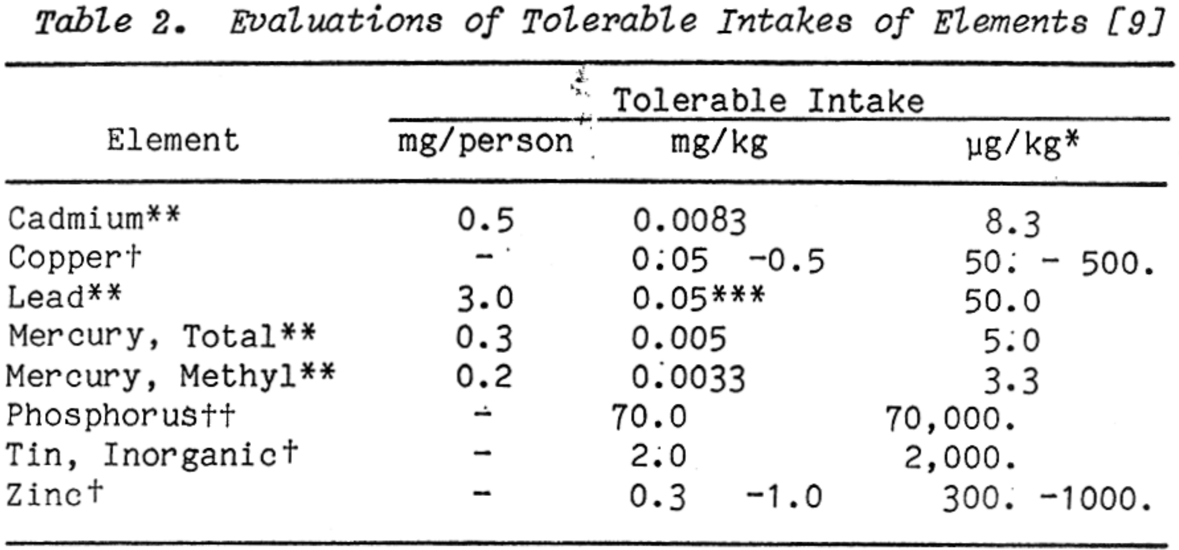


Table 2. Evaluations of Tolerable Intakes of Elements [9]

Element	Tolerable Intake		
	mg/person	mg/kg	µg/kg*
Cadmium**	0.5	0.0083	8.3
Copper†	–	0.05 -0.5	50. - 500.
Lead**	3.0	0.05***	50.0
Mercury, Total**	0.3	0.005	5.0
Mercury, Methyl**	0.2	0.0033	3.3
Phosphorus††	–	70.0	70,000.
Tin, Inorganic†	–	2.0	2,000.
Zinc†	–	0.3 -1.0	300. -1000.

Sea waters – now do not represent sea/fresh waters because of salt formation – salts precipitate. Drinking water (and most foods) contain a mix of metals but we try to define a 'tolerable' level so that daily consumption is less.

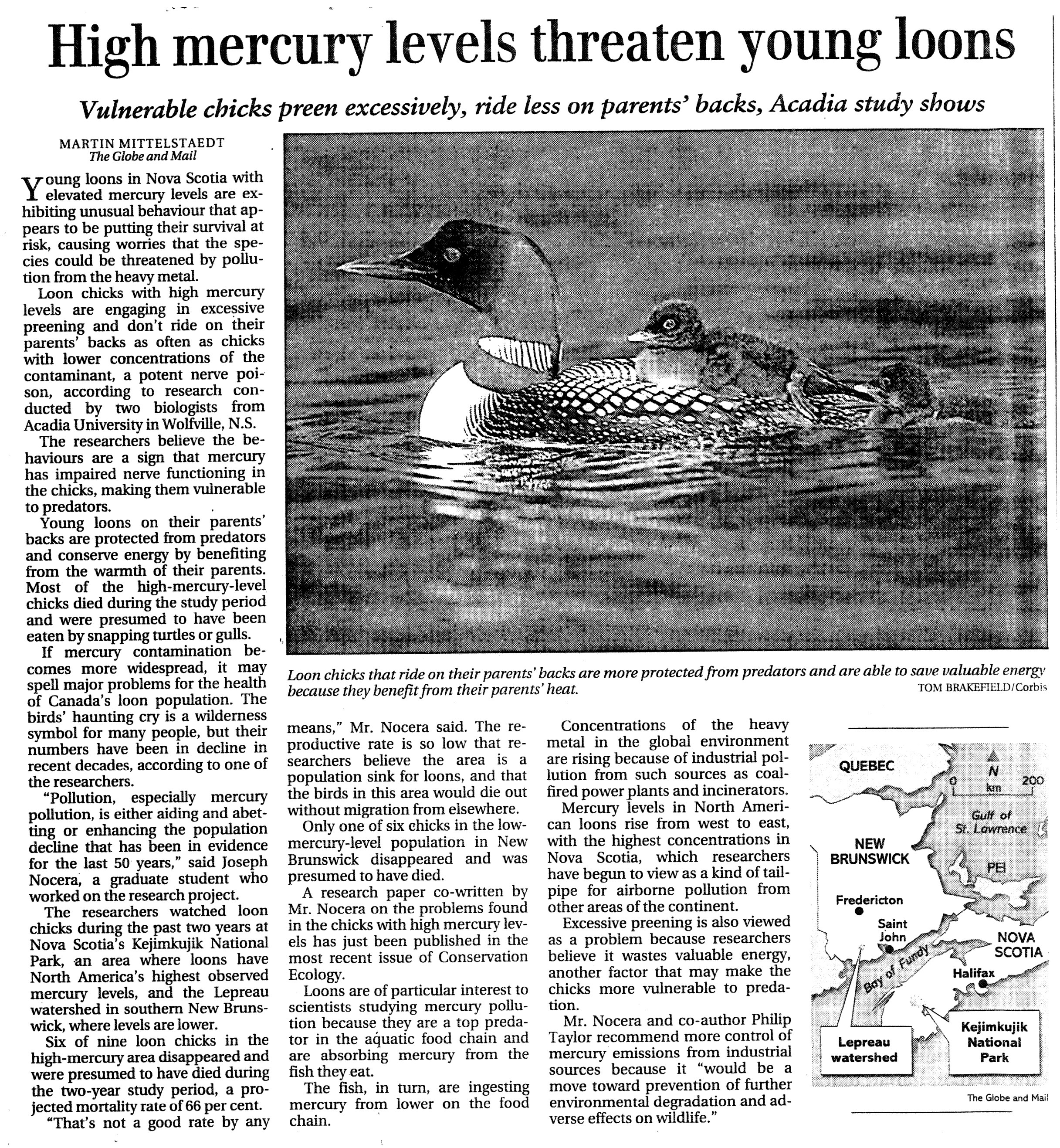
It is clear now that many elements exert biological activity at concentrations below the measurement levels of even the recent decade so were largely ignored in models that connect metals with changes in biological activity.

See the obvious neurological effects of mercury on loons →.

But many metals are found in all organisims, esp. man, – does this make them essential?

At an ultra-trace level?

Dietary intake is not restricted to 'good' elements. We see that the concentration from foods of toxic metals is not all that close to zero.



High mercury levels threaten young loons

Vulnerable chicks preen excessively, ride less on parents' backs, Acadia study shows

MARTIN MITTELSTAEDT
The Globe and Mail

Young loons in Nova Scotia with elevated mercury levels are exhibiting unusual behaviour that appears to be putting their survival at risk, causing worries that the species could be threatened by pollution from the heavy metal.

Loon chicks with high mercury levels are engaging in excessive preening and don't ride on their parents' backs as often as chicks with lower concentrations of the contaminant, a potent nerve poison, according to research conducted by two biologists from Acadia University in Wolfville, N.S.

The researchers believe the behaviours are a sign that mercury has impaired nerve functioning in the chicks, making them vulnerable to predators.

Young loons on their parents' backs are protected from predators and conserve energy by benefiting from the warmth of their parents. Most of the high-mercury-level chicks died during the study period and were presumed to have been eaten by snapping turtles or gulls.

If mercury contamination becomes more widespread, it may spell major problems for the health of Canada's loon population. The birds' haunting cry is a wilderness symbol for many people, but their numbers have been in decline in recent decades, according to one of the researchers.

"Pollution, especially mercury pollution, is either aiding and abetting or enhancing the population decline that has been in evidence for the last 50 years," said Joseph Nocera, a graduate student who worked on the research project.

The researchers watched loon chicks during the past two years at Nova Scotia's Kejimkujik National Park, an area where loons have North America's highest observed mercury levels, and the Lepreau watershed in southern New Brunswick, where levels are lower.

Six of nine loon chicks in the high-mercury area disappeared and were presumed to have died during the two-year study period, a projected mortality rate of 66 per cent.

"That's not a good rate by any means," Mr. Nocera said. The reproductive rate is so low that researchers believe the area is a population sink for loons, and that the birds in this area would die out without migration from elsewhere.

Only one of six chicks in the low-mercury-level population in New Brunswick disappeared and was presumed to have died.

A research paper co-written by Mr. Nocera on the problems found in the chicks with high mercury levels has just been published in the most recent issue of Conservation Ecology.

Loons are of particular interest to scientists studying mercury pollution because they are a top predator in the aquatic food chain and are absorbing mercury from the fish they eat.

The fish, in turn, are ingesting mercury from lower on the food chain.

Concentrations of the heavy metal in the global environment are rising because of industrial pollution from such sources as coal-fired power plants and incinerators.

Mercury levels in North American loons rise from west to east, with the highest concentrations in Nova Scotia, which researchers have begun to view as a kind of tailpipe for airborne pollution from other areas of the continent.

Excessive preening is also viewed as a problem because researchers believe it wastes valuable energy, another factor that may make the chicks more vulnerable to predation.

Mr. Nocera and co-author Philip Taylor recommend more control of mercury emissions from industrial sources because it "would be a move toward prevention of further environmental degradation and adverse effects on wildlife."

Loon chicks that ride on their parents' backs are more protected from predators and are able to save valuable energy because they benefit from their parents' heat.

TOM BRAKEFIELD/Corbis

The Globe and Mail

Key points from this unit	
1	Distribution of metals ‘naturally’ and by man
2	‘Man’ has decided we can exist in the presence of metals at a certain level = ‘tolerance’ in our diet.
3	Man’s activities might change the natural levels – eg Hg and the loons

Key questions to consider on this unit	Ch 1 in LB & KS – ‘what do we mean by the interface between inorganic chemistry and biology?’. Give a definition of bioinorganic chemistry – yes, repeated but we are looking in more detail now. So, geological distribution is fairly straightforward – volcanoes etc. Extraction by man … Metals in biology are involved in enzymes, proteins, structure and … materials…where are metal-based materials in the natural world? Which specific foods do you know (find) concentrate different metals? Fe? Co? Hg? As? Shells, bones, teeth, and then there are the ‘odd’ ones, magnetite Know the names of the calcite and hydroxyapatite (phosphate – hydroxide mixture) We see that Fe is high in the crust, and quite high in man, but see Fig 2.2, p 9 in K&S, Fe is very low in seawater today. Explain this. How did mammals evolve to use Fe then? Account for the properties of the atmosphere. Reducing then, oxidizing now. How is vitB12 connected with the toxicity of mercury – related to those loons, Yes? Yes.