Lecture 18

Metals and migration through ground water systems

1. **Radioactive**
2. **Heavy Metal Contamination**, i.e.. Pb, Hg, Cd - inorganic but toxic to mammalian life.

Factors:

Mobility in aqueous environments i.e. ground water, lakes, rivers, estuaries.

- Solubility of Metal → M^{2+}
- Adsorption → on clays or organic Carbon.

Metals:

- exist in ionic form (dissolved)
- exist in ligands
  - 1. Organic (Organic with attached metal)
  - 2. Hydroxo complexes, i.e. $Al(OH)^2$
- exist as aerosols i.e. Pb from coal fired power plants
- Volatile Compounds i.e. Methyl Mercury (becomes quite mobile)

  - Range and mobility are dependent on a number of factors.

* Solubility is a function of pH → it controls dissolution, H^+ exchange

Classification of elements into four groups on the basis of ionic charge (valence) and radius.

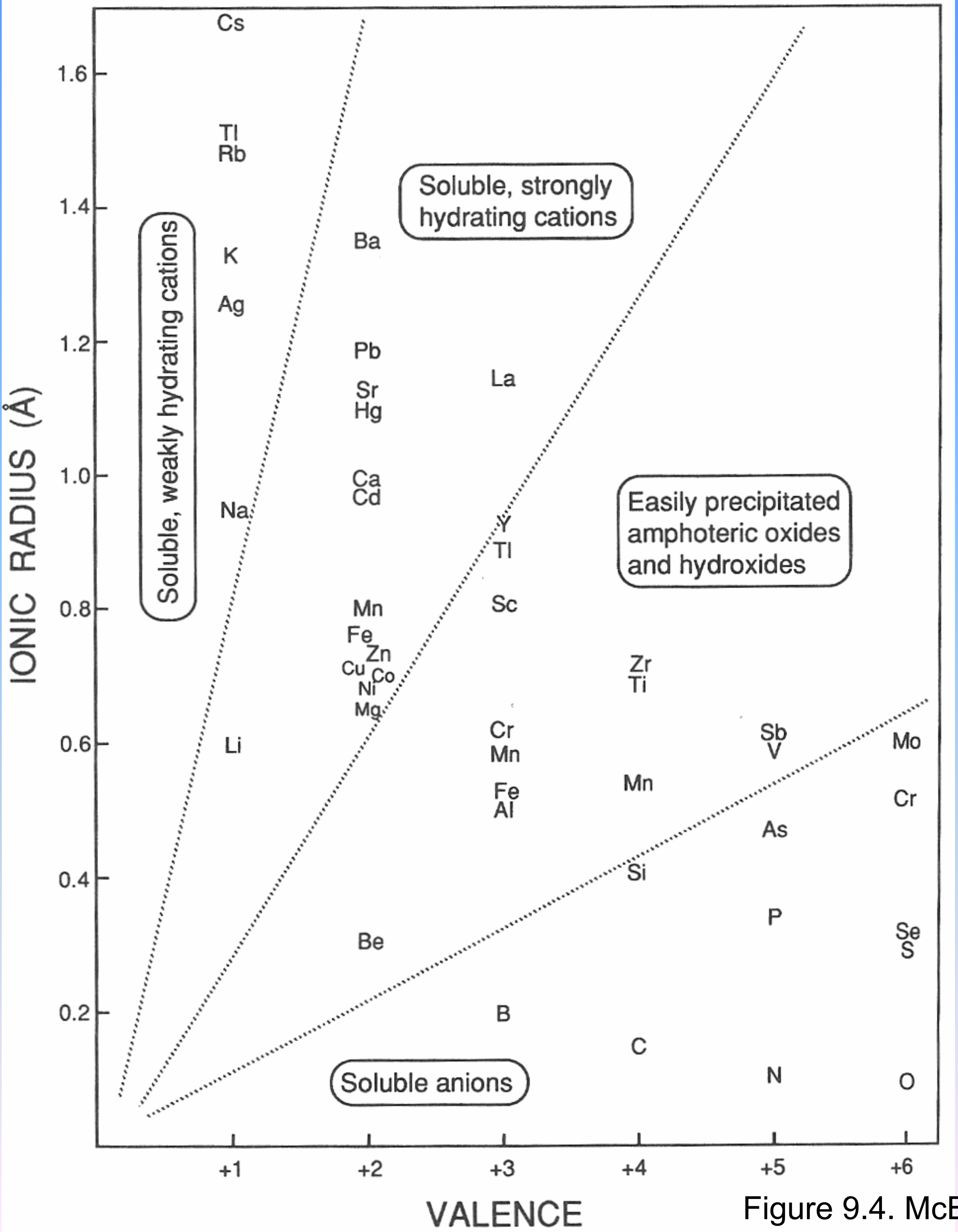
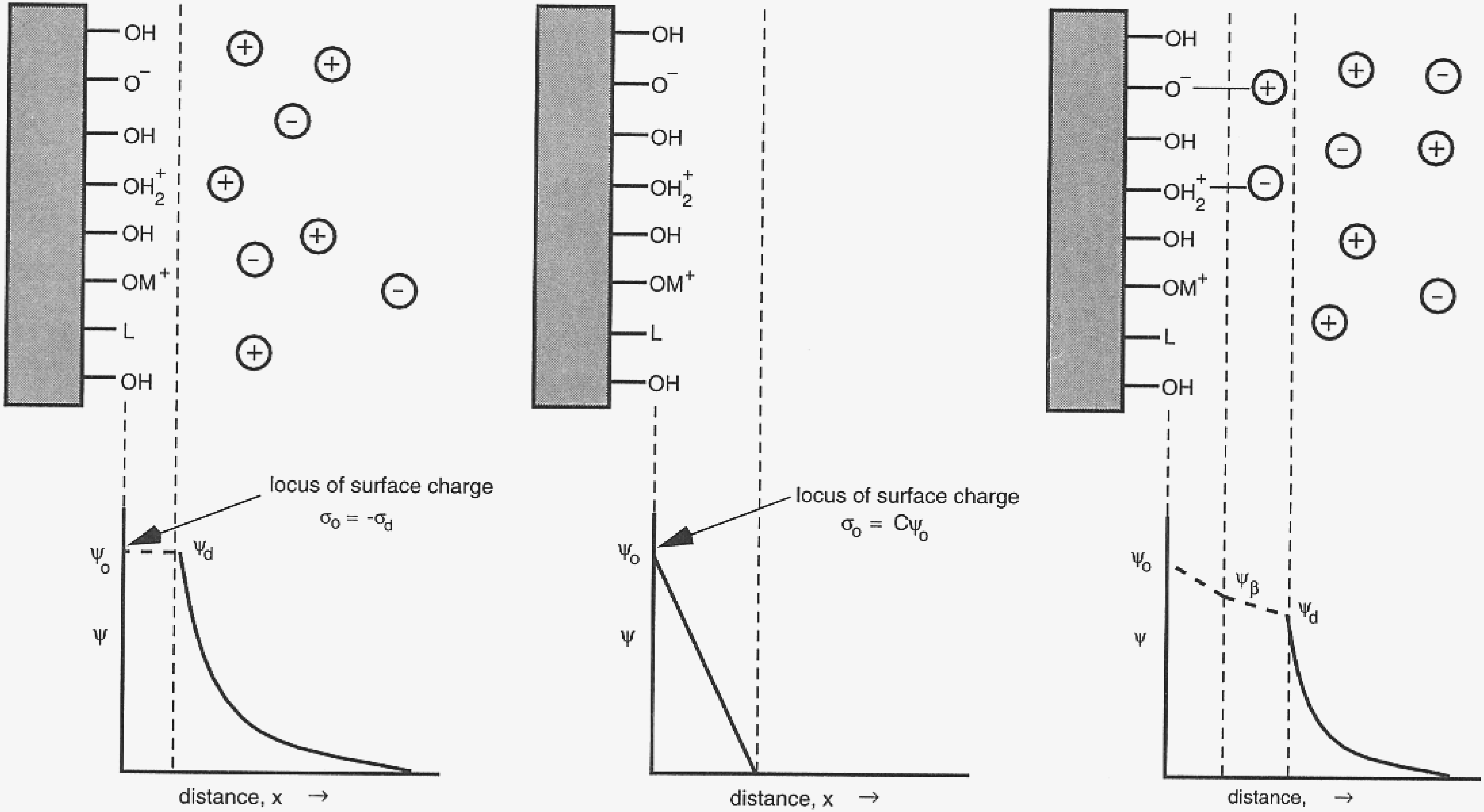


Figure 9.4. McBride. *Environmental Chemistry of Soils*



Diffuse-layer model

Constant capacitance model

Triple-layer model

FIGURE 5-10 Idealized distribution of electrical potential (ψ) in the vicinity of a hydrated oxide surface according to (a) the diffuse-layer model; (b) the constant capacitance model; (c) the triple-layer model (after Hayes et al., 1991).

Figure 5-10. Drever, *The Geochemistry of Natural Waters 3rd Edition*

Schematic representation of inner-sphere (phosphate, fluoride, copper) and outer-sphere (sodium, chloride) complexes. The labels on the layers correspond to the triple-layer model (after Stumm, 1992)

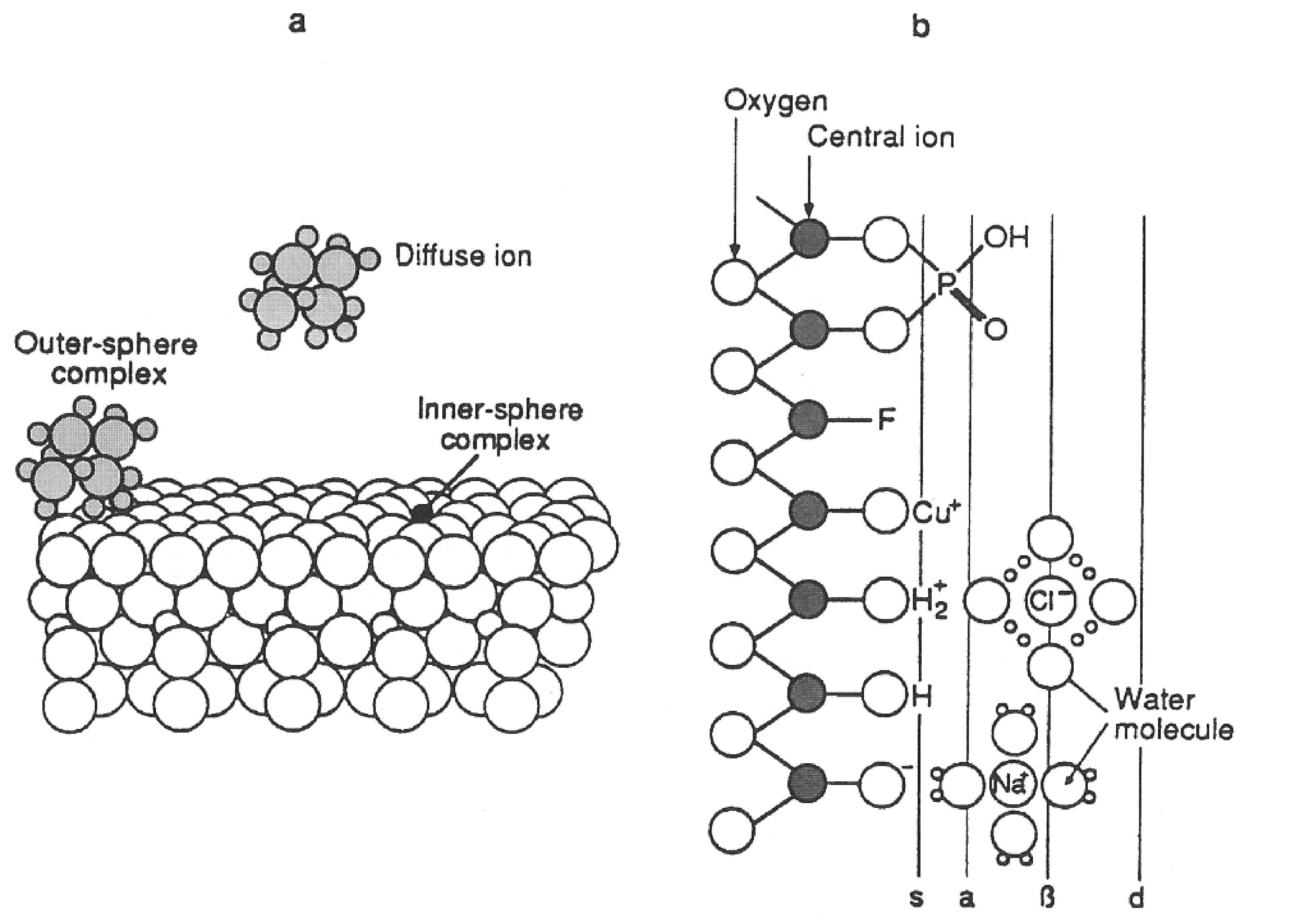


Figure 5-7. Drever, *The Geochemistry of Natural Waters 3rd Edition*

Dynamic interactive processes governing solubility, availability, and mobility of elements in soils

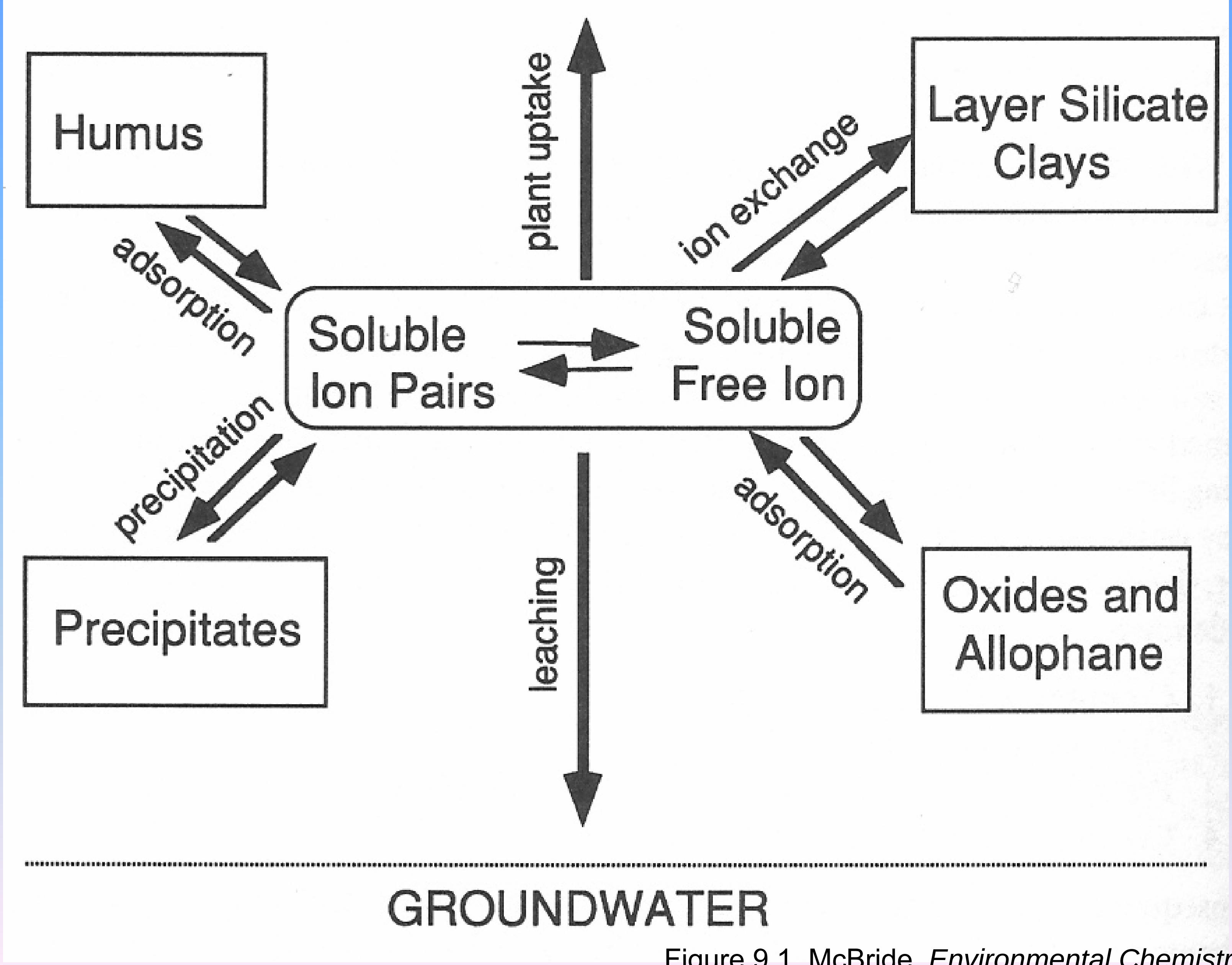


Figure 9.1. McBride. *Environmental Chemistry of Soils*

Adsorption of metal cations on hydrous ferric oxide as a function of pH

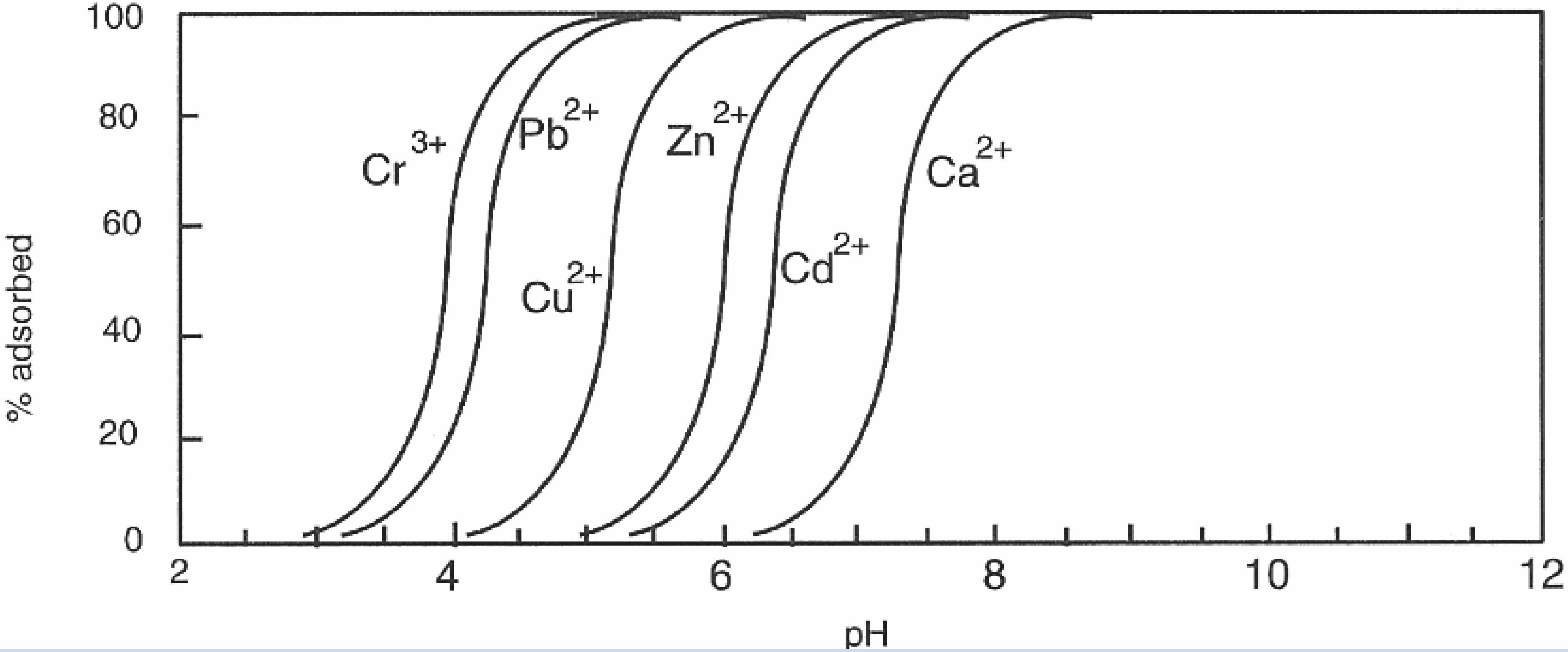


Figure 5-8. Drever, *The Geochemistry of Natural Waters 3rd Edition*

Adsorption of selected anions on hydrous ferric oxide as a function of pH

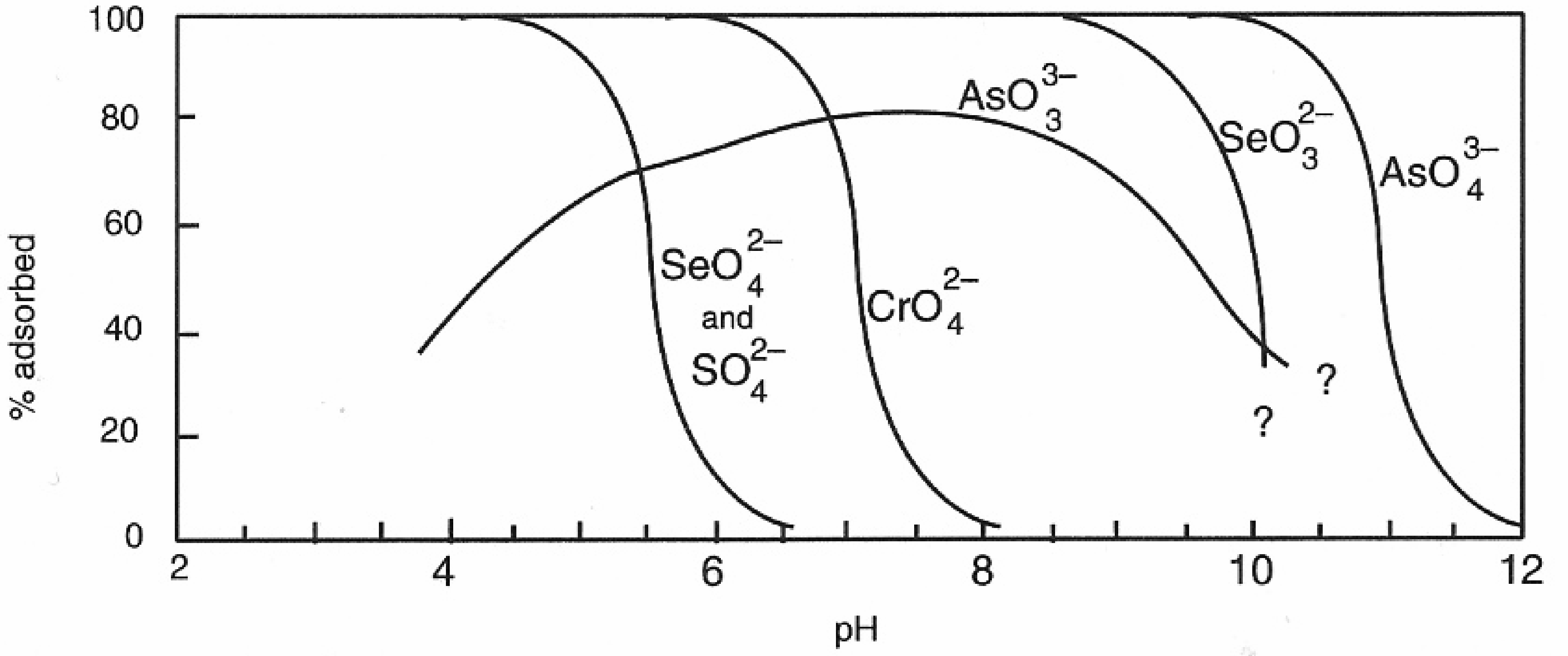


Figure 5-9. Drever, *The Geochemistry of Natural Waters 3rd Edition*

Relative Retention of some metals on goethite

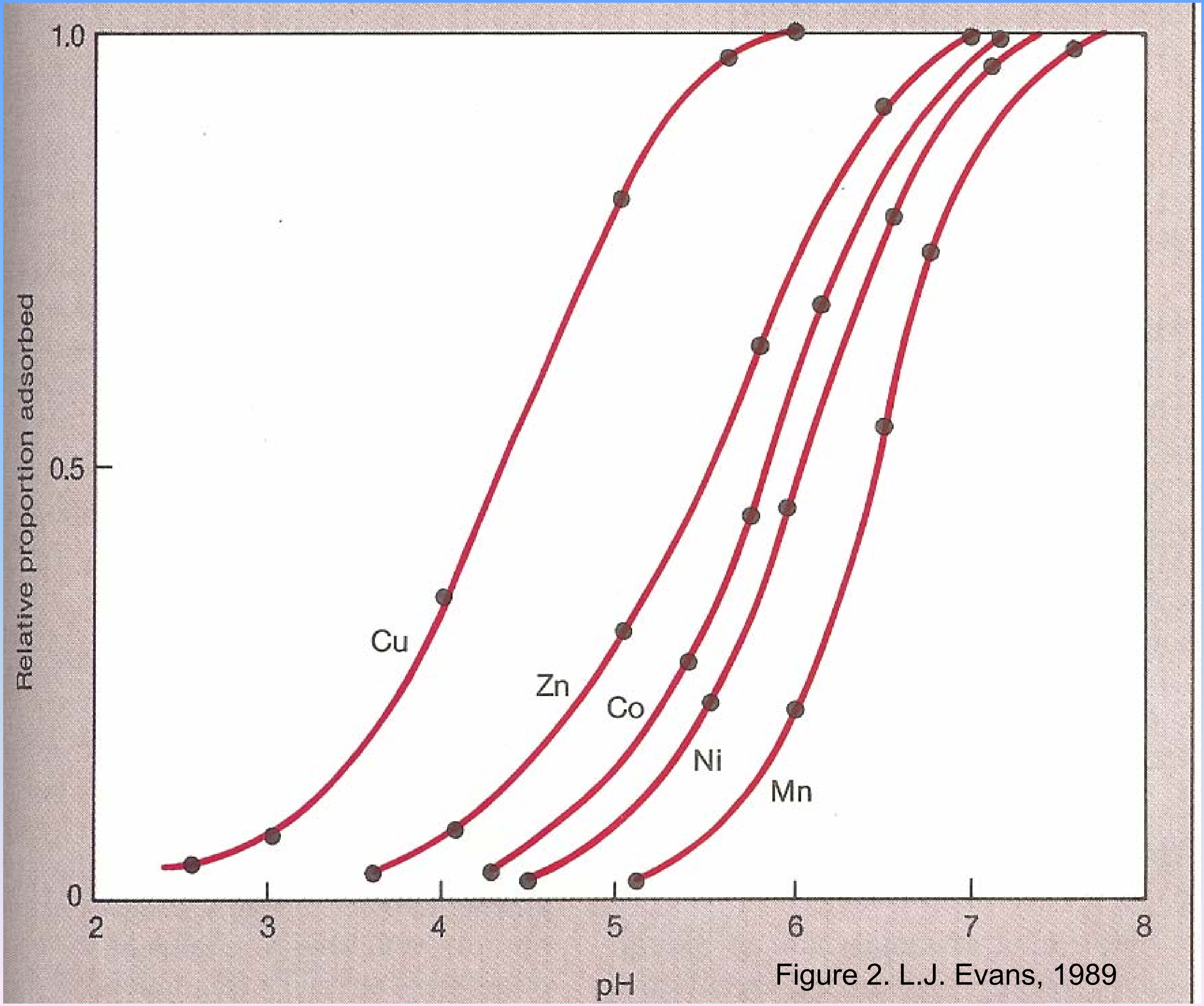
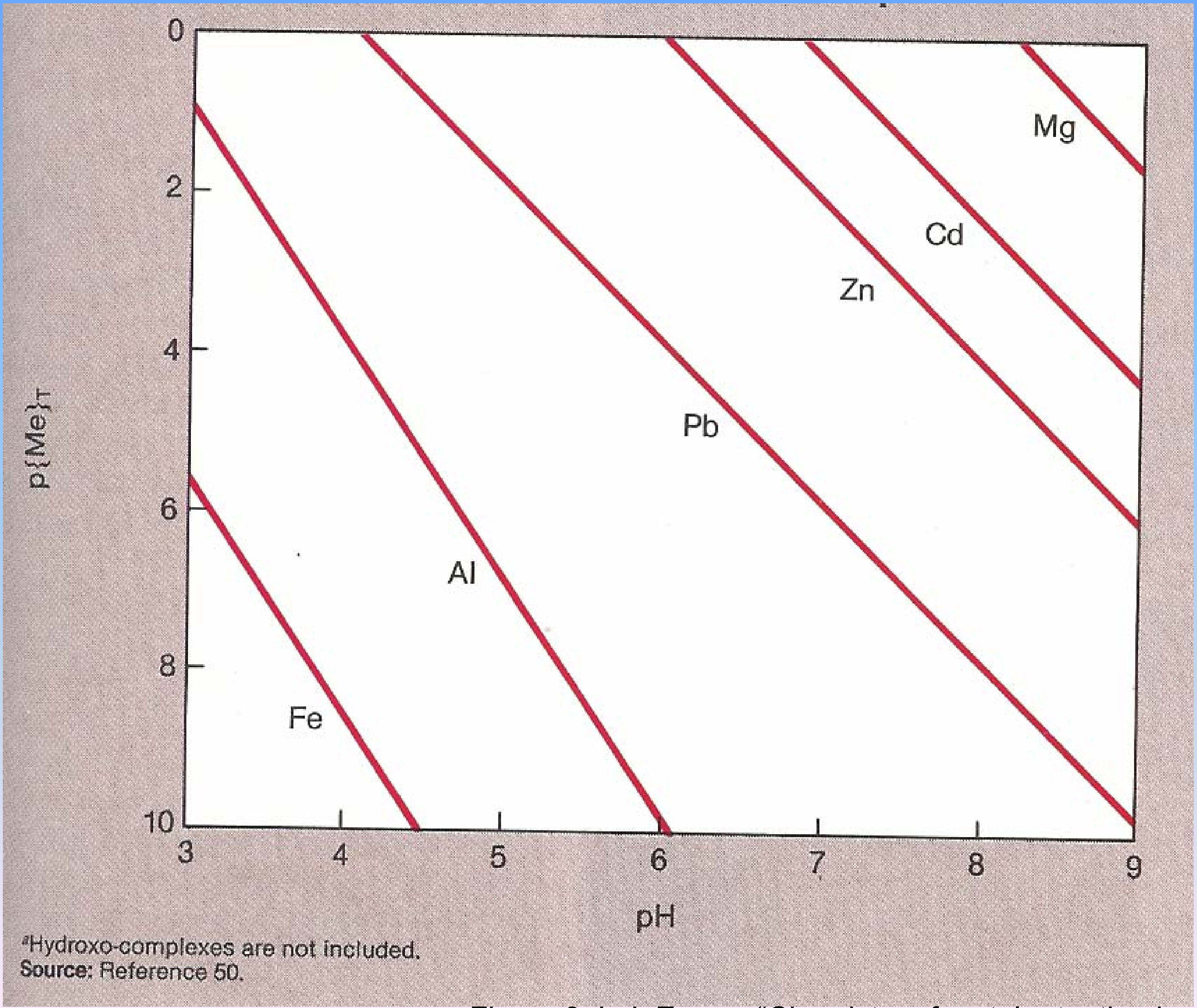


Figure 2. L.J. Evans, 1989

Dissolution of some metal hydroxides as a function of pH

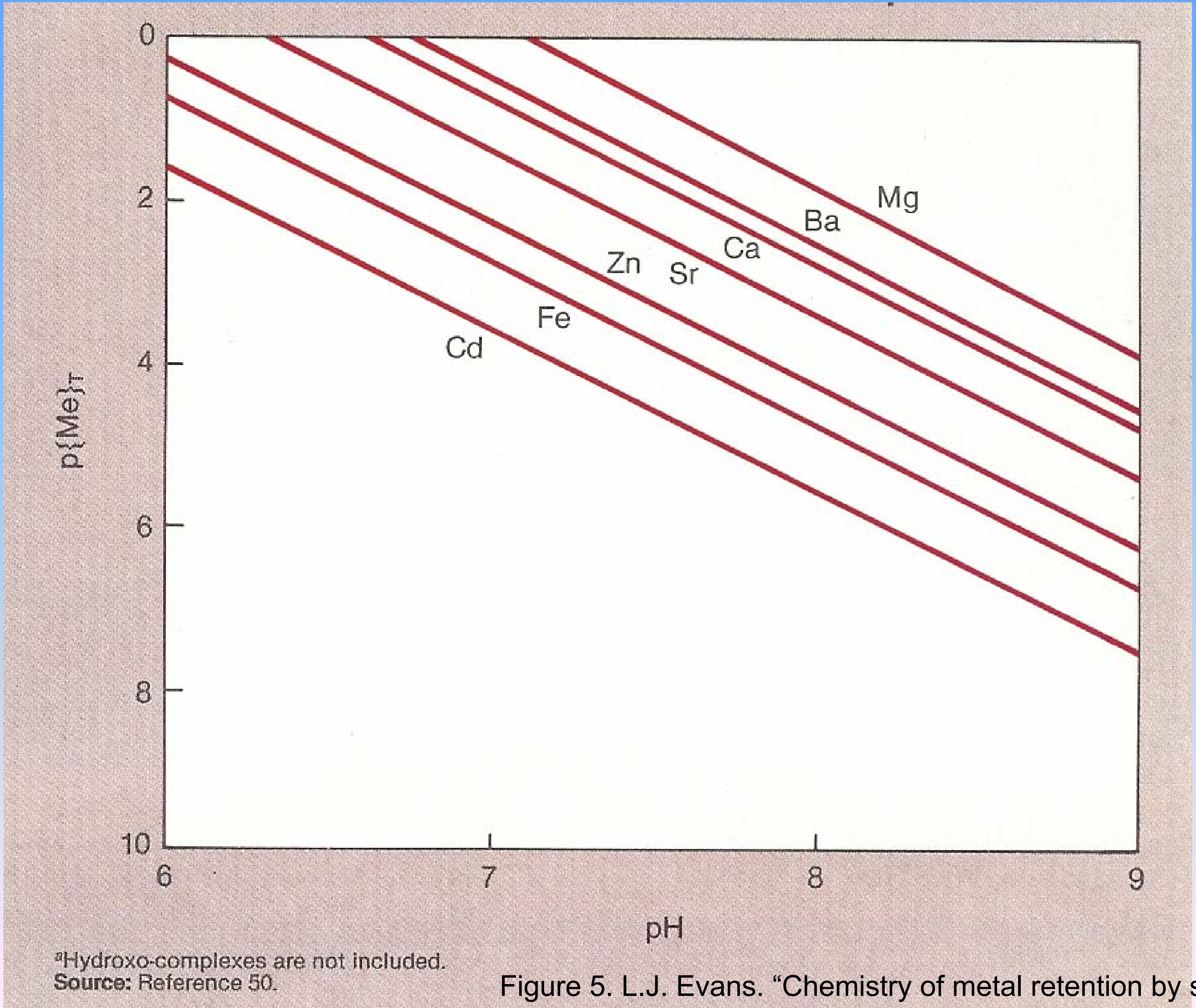


[a]Hydroxo-complexes are not included.

Source: Reference 50.

Figure 3. L.J. Evans. “Chemistry of metal retention by soils” 1989

Dissolution of some metal carbonates a s a function of pH



[a]Hydroxo-complexes are not included.
Source: Reference 50.

Figure 5. L.J. Evans. “Chemistry of metal retention by soils” 1989

- **Adsorption** - don't always behave as we think it should
  - In the presence of organic matter : Hg, Fe, Al > Cr > Cd > Ni, Zn > Co, moving from the most to least stable.
- Under oxidizing conditions, these are relatively immobile.

Radioactive

– **60Co, 90Sr, 137Cs** are all radioactive and are all related to nuclear weapon production (Co is a transition metal, while Sr is an alkali earth metal, and Cs is an alkali metal). **These metals have the ability to be strongly adsorbed- even in stream conditions.**

* Oak Ridge Natural Labs release a high amount of these contaminants

→Found that there were only traces of the contaminant every so often in the stream - occasional spikes.

* Behave as ”time release capsules” - even after input has stopped radionuclides are slowly released from sediments by equilibrium desorption

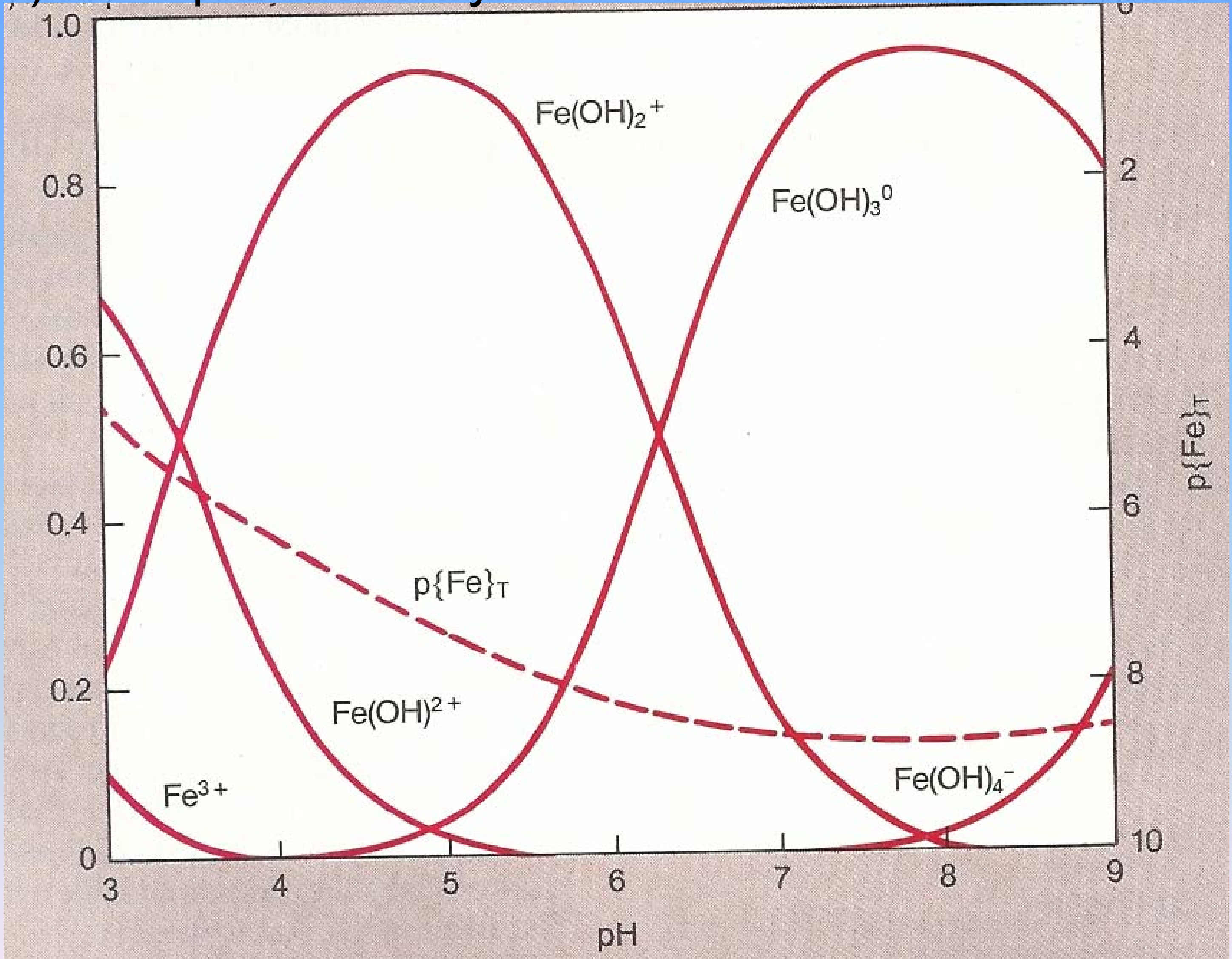
Testing the ground water proved it to be contaminated, however, downstream was showing relatively clean water. The contaminant had easily adsorbed onto the surfaces of the grains, even upon introduction to the stream. Th spikes would show occasional leakages of this.

Strongly adsorbed onto the surfaces in the stream- inorganic adsorption.

- It is hard to remediate because of this
- However, the half-life of these are on the order of 30 years- this may have time to degrade by the time the contaminant is able to move offsite.

Metal speciation and extent of dissolution

(a) Amorphous Fe-hydroxide



[a]As a function of pH; hydroxo-complexes are included.
Source: References 7 and 50.

Figure 4(b). L.J. Evans. “Chemistry of metal retention by soils” 1989

Red-Ox (Reduction- Oxidation) Reactions

EH (or pe = electron activity) is a way to represent the oxidation or reduction potential of a given environment.

- Mn, Fe can exist in many different valence states
- Fe^{0}, Fe^{2+}, Fe^{3+} in FeO(OH), $Fe^{2+}S$, $Fe^{2+}O$, etc.

Equivalence between electric energy and heat

1 Joule = 1 volt Coulomb

1 Watt = 1 Joule/second = 1 Amp*(volt)

(1 mole of e-)(1 volt) = 9.65×10^4 Joules = $\mathcal{F}$ (Faraday's number)

$$\Delta G = -q \mathcal{F} E_H$$

$Cu^{2+} + Fe \rightarrow Fe^{2+} + Cu$ $E_{H_o} = +.78$ v

This is the result of 2 half reactions:

$Cu^{2+} + 2e- \rightarrow Cu$ $E_H = .34$ v

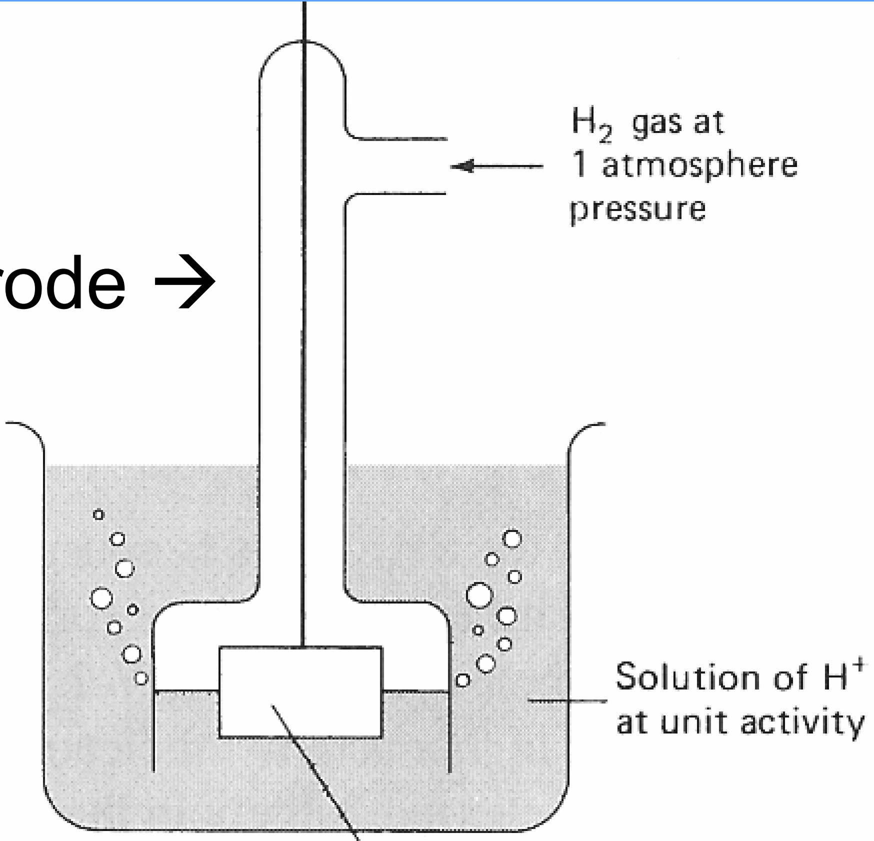
$Fe^{2+} + 2e- \rightarrow Fe$ $E_H = -.44$ v

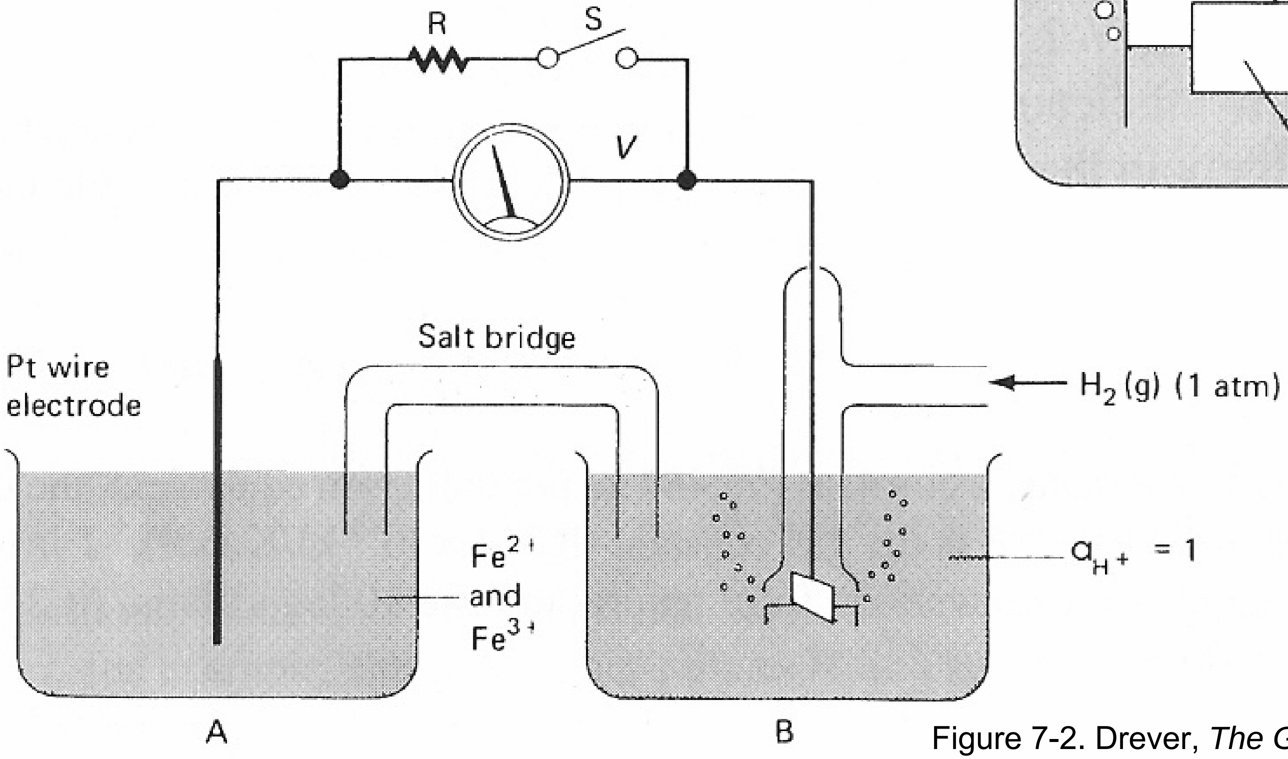
$E_H = V_{cathode} - V_{anode} \rightarrow + .78$

- All referenced to Hydrogen electrode
- Tabulated with e- on the left.
- **pe (electron activity) → minus log concentration of electrons**
- pe = $(16.8)E_H$ pe = $(\mathcal{F}/2.303RT)E_H$
- Relates Electrode potential to “moles of electrons

Figure 7-1. Drever, *The Geochemistry of Natural Waters 3rd Edition*

The standard hydrogen electrode →

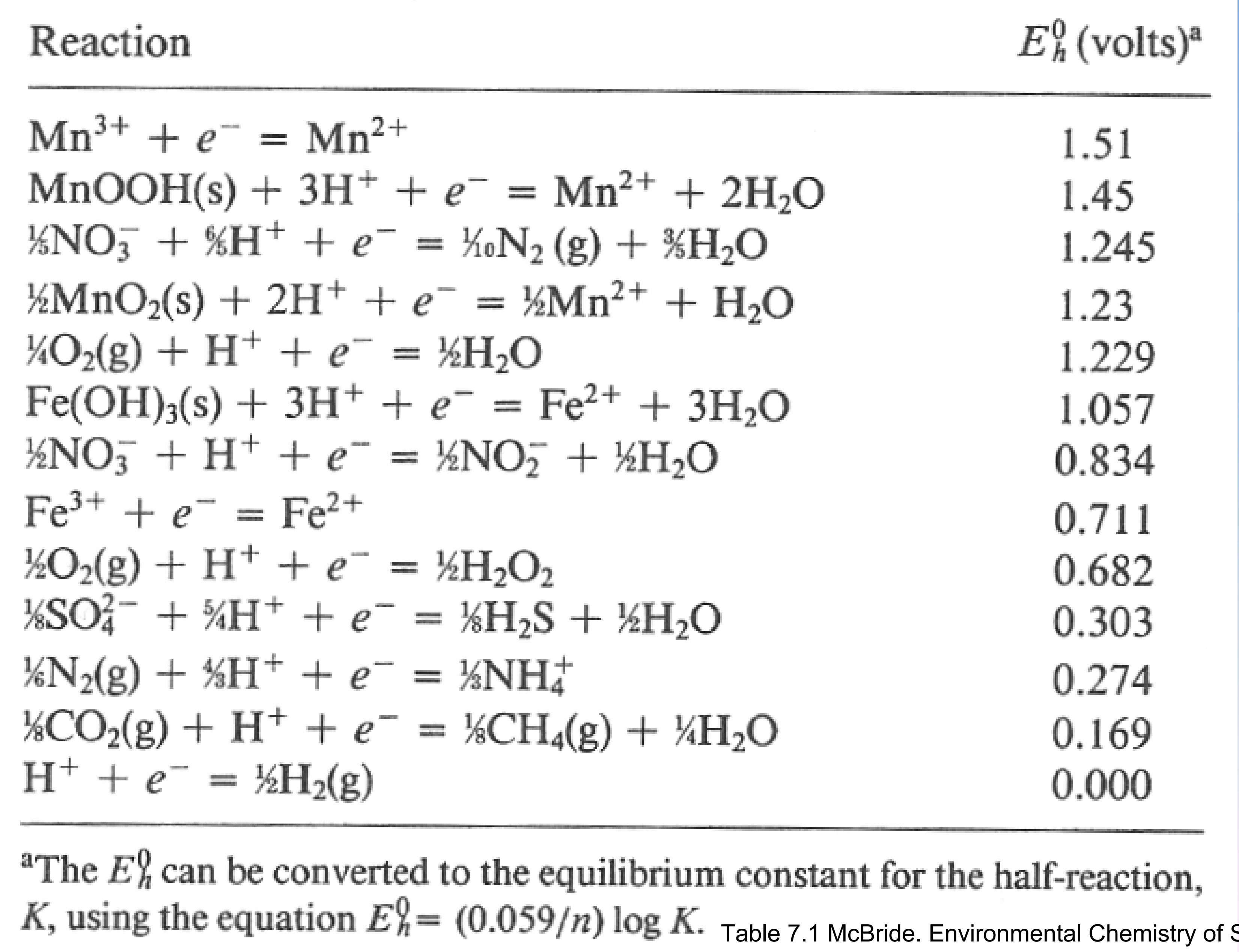




← Redox cell

Figure 7-2. Drever, *The Geochemistry of Natural Waters 3rd Edition*

Standard-State Reduction Potentials of Half-Reactions Involving Important Elements in Soils



Reaction	E_h^0 (volts)[a]
$Mn^{3+} + e^- = Mn^{2+}$	1.51
$MnOOH(s) + 3H^+ + e^- = Mn^{2+} + 2H_2O$	1.45
$\frac{1}{5}NO_3^- + \frac{6}{5}H^+ + e^- = \frac{1}{10}N_2(g) + \frac{3}{5}H_2O$	1.245
$\frac{1}{2}MnO_2(s) + 2H^+ + e^- = \frac{1}{2}Mn^{2+} + H_2O$	1.23
$\frac{1}{4}O_2(g) + H^+ + e^- = \frac{1}{2}H_2O$	1.229
$Fe(OH)_3(s) + 3H^+ + e^- = Fe^{2+} + 3H_2O$	1.057
$\frac{1}{2}NO_3^- + H^+ + e^- = \frac{1}{2}NO_2^- + \frac{1}{2}H_2O$	0.834
$Fe^{3+} + e^- = Fe^{2+}$	0.711
$\frac{1}{2}O_2(g) + H^+ + e^- = \frac{1}{2}H_2O_2$	0.682
$\frac{1}{8}SO_4^{2-} + \frac{5}{4}H^+ + e^- = \frac{1}{8}H_2S + \frac{1}{2}H_2O$	0.303
$\frac{1}{6}N_2(g) + \frac{4}{3}H^+ + e^- = \frac{1}{3}NH_4^+$	0.274
$\frac{1}{8}CO_2(g) + H^+ + e^- = \frac{1}{8}CH_4(g) + \frac{1}{4}H_2O$	0.169
$H^+ + e^- = \frac{1}{2}H_2(g)$	0.000

[a] The E_h^0 can be converted to the equilibrium constant for the half-reaction, K, using the equation $E_h^0 = (0.059/n) \log K$.

Table 7.1 McBride. Environmental Chemistry of Soils, 1994.

How does this variation exist in natural waters?

$$2H^+ + 2e^- \rightarrow H_2(g)$$

$$O_2(g) + 4H^+ + 4e- \rightarrow 2H_2O(l)$$

These two reactions are never spontaneous in natural systems (although the same results can be found with different reactions). They set the boundary limits. They should also be a function of pH

$$E_H = E_{H^o} - 0.059\ pH$$

$2Fe_3O_4 + 1/2\ O_2 \rightarrow 3Fe_2O_3$

$2Fe_3O_4 + H_2O \rightarrow 3Fe_2O_3 + 2H+ + 2e^-$

- The 2e- represents the net result of $2Fe^{2+} \rightarrow 2Fe^{3+} + 2e^-$ where oxidation of iron releases electrons.

* This is different from acid/base reactions → valence state of metal will show how oxidizing or reducing the environment is.

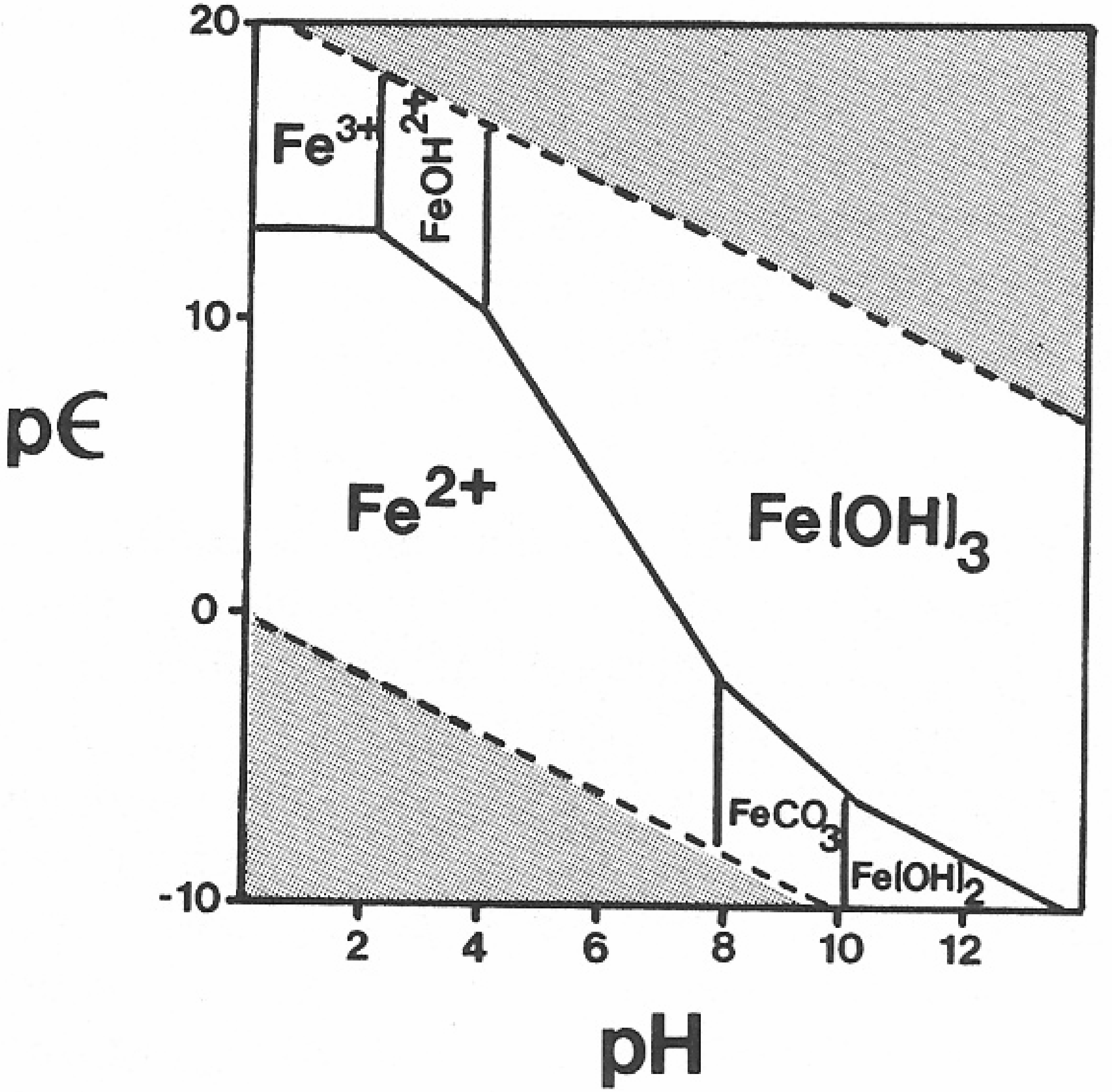
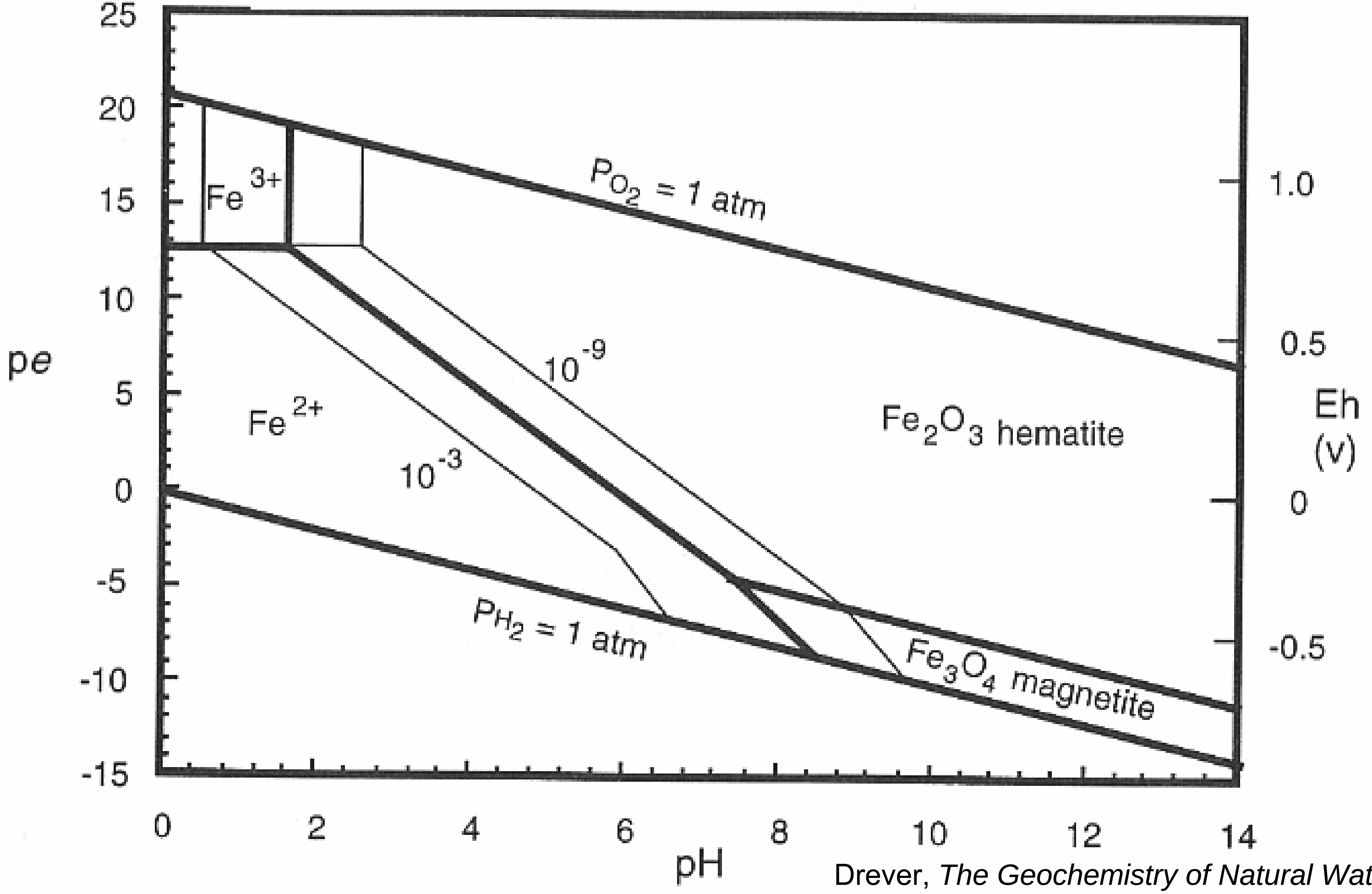


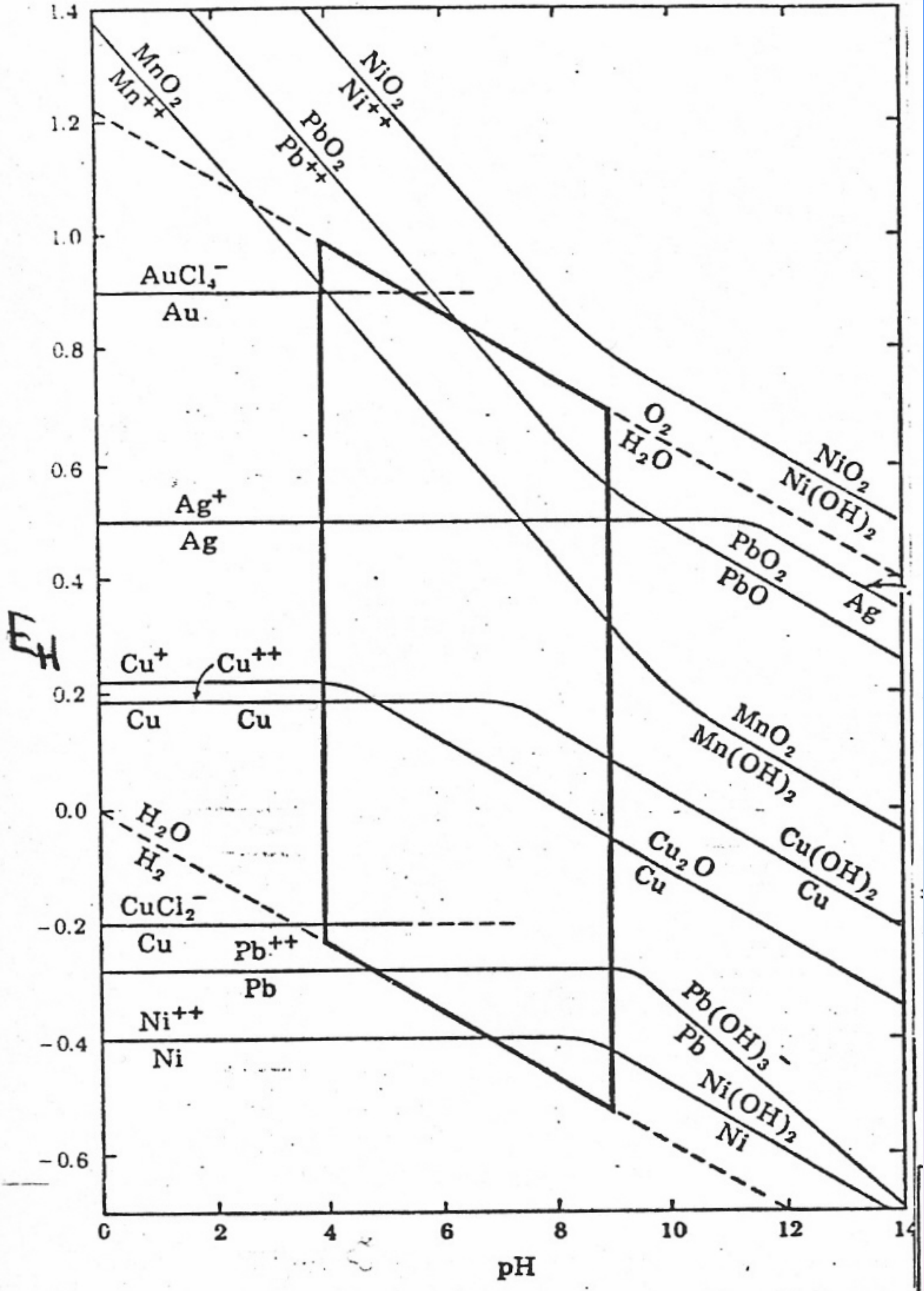
Figure 7.9. Stability field diagram for soluble and solid forms of Fe under a range of redox potential and pH conditions, assuming a dissolved CO_2 concentration of 10^{-3} *M*. Shaded areas delineate conditions that are unattainable because of water decomposition. (Adapted from W. Stumm and J. J. Morgan. 1981. *Aquatic Chemistry*. 2nd ed. New York: Wiley.)

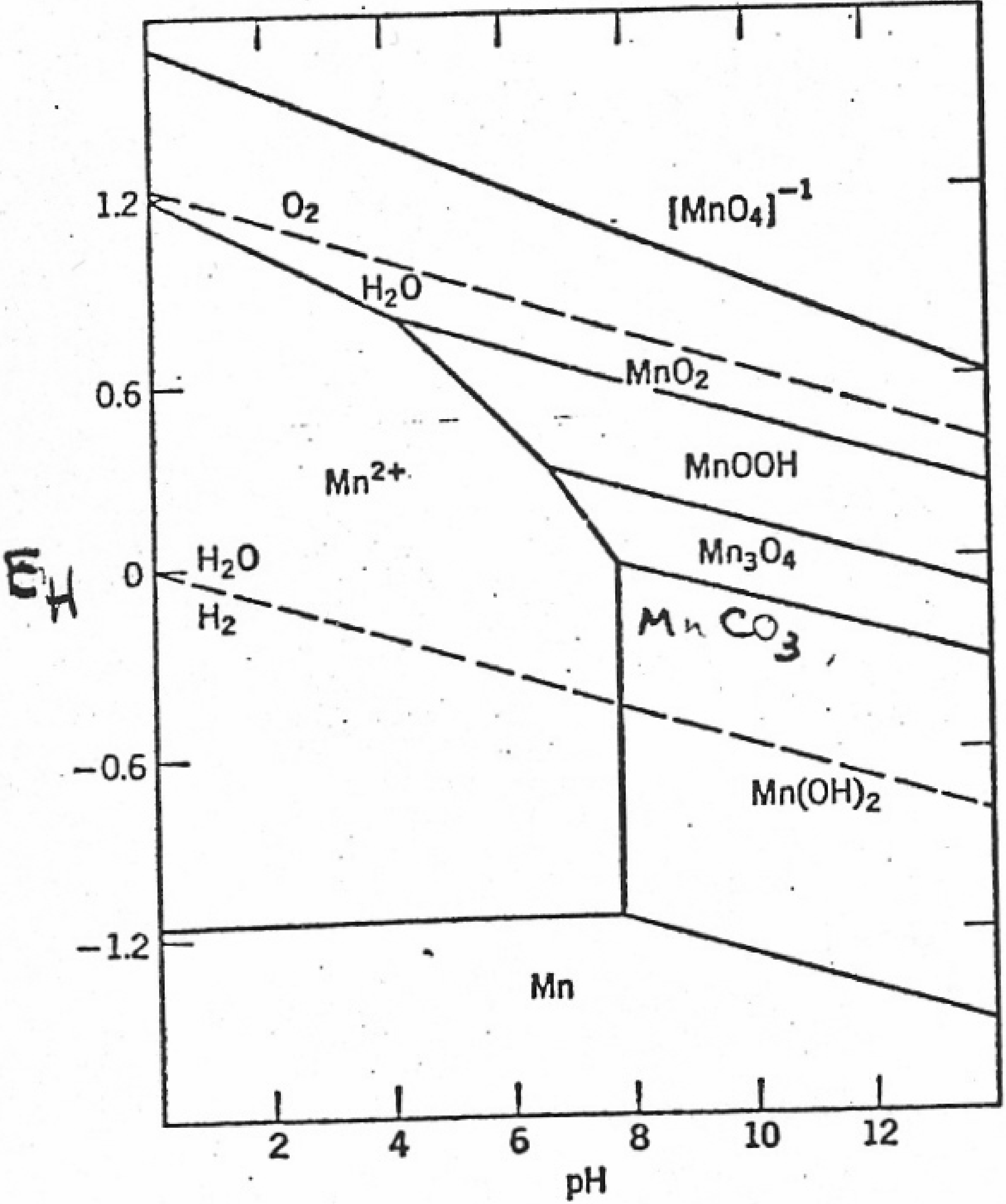
McBride. Environmental Chemistry of Soils, 1994.

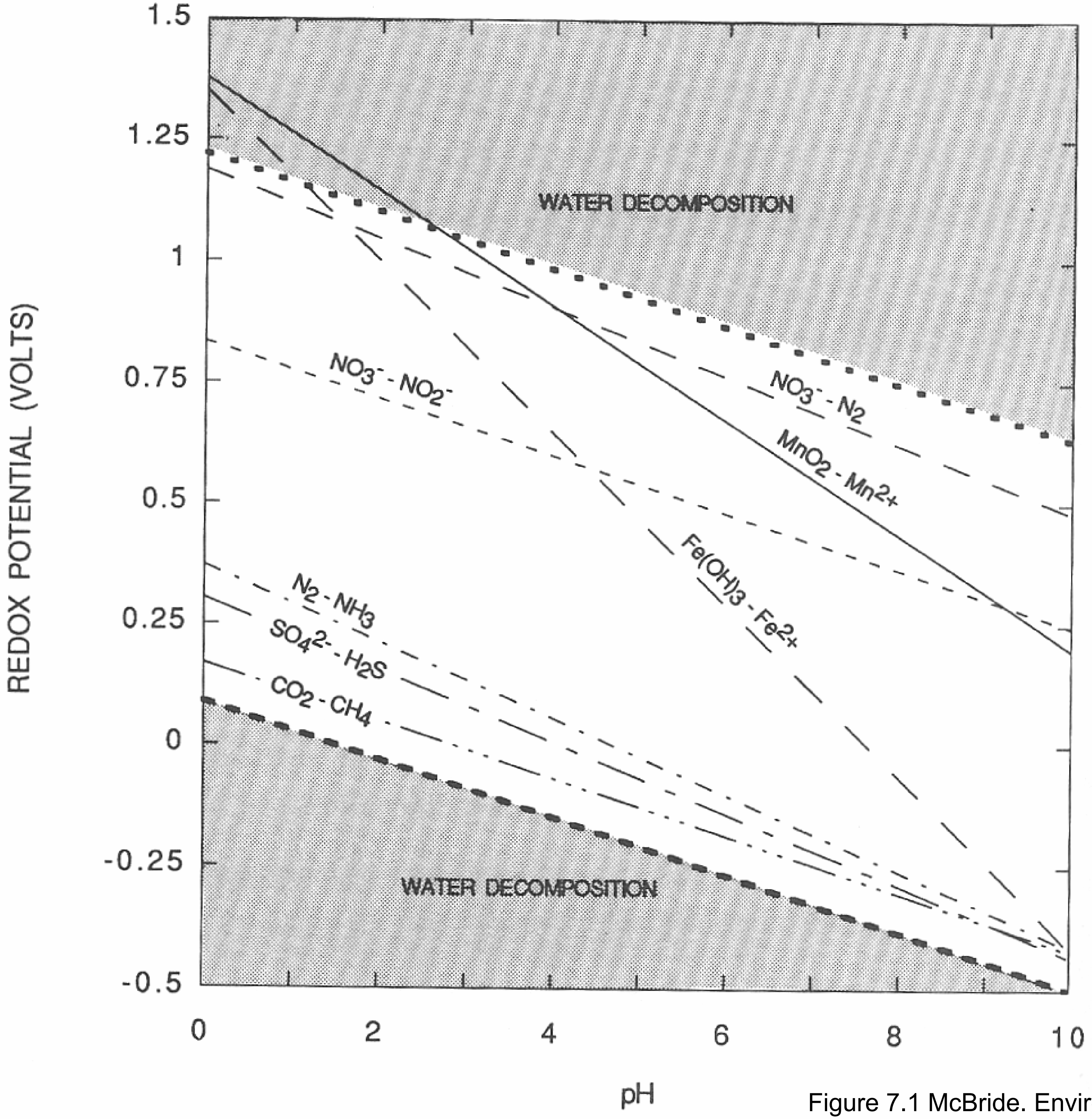
FIGURE 7-4 *pe*–pH diagram for the system Fe–O–H_2O at 25°C with hematite as the stable ferric oxide phase. The heavy lines are boundaries for $a_{Fe^{2+}} = 10^{-6}$. The light lines are boundaries for $a_{Fe^{2+}} = 10^{-3}$ and 10^{-9}.



Drever, *The Geochemistry of Natural Waters 3rd Edition*


1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
−0.2
−0.4
−0.6
E_H
0
2
4
6
8
10
12
14
pH
MnO_2
Mn^{++}
PbO_2
Pb^{++}
NiO_2
Ni^{++}
$AuCl_4^-$
Au
O_2
H_2O
NiO_2
$Ni(OH)_2$
Ag^+
Ag
PbO_2
PbO
Ag
Cu^+
Cu^{++}
Cu
Cu
MnO_2
$Mn(OH)_2$
H_2O
H_2
Cu_2O
Cu
$Cu(OH)_2$
Cu
$CuCl_2^-$
Cu
Pb^{++}
Pb
$Pb(OH)_3^-$
Pb
Ni^{++}
Ni
$Ni(OH)_2$
Ni


1.2
0.6
0
−0.6
−1.2
E_H
2
4
6
8
10
12
pH
O_2
H_2O
$[MnO_4]^{-1}$
MnO_2
MnOOH
Mn^{2+}
Mn_3O_4
H_2O
H_2
$MnCO_3$
$Mn(OH)_2$
Mn



The relationship of redox potential E_h, to pH for important half-cell reactions in water. The bold broken lines demote that E_h at which water is oxidized to O_2 (upper line) or reduced to H_2 (lower line).

Figure 7.1 McBride. Environmental Chemistry of Soils, 1994

Fence Diagrams

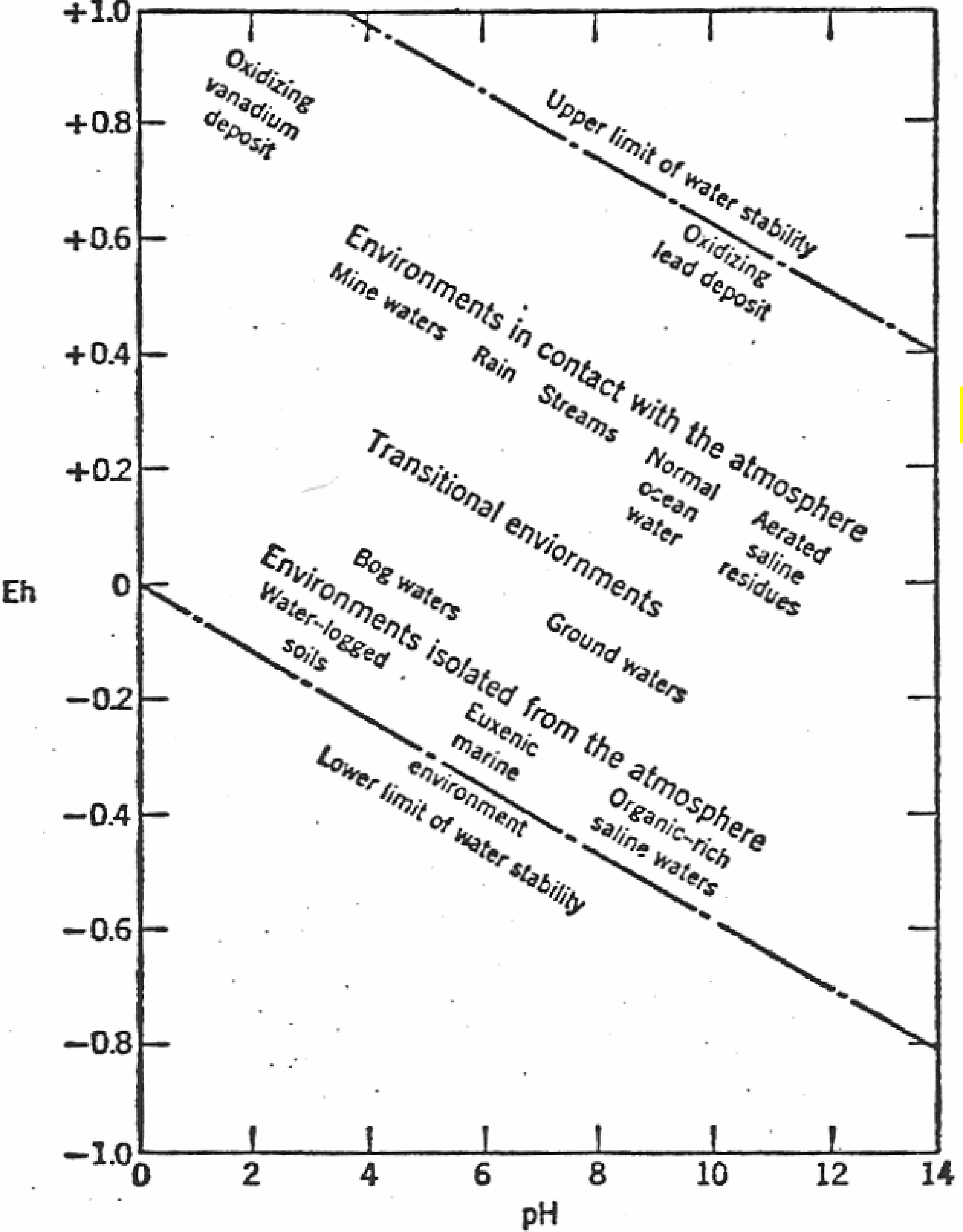
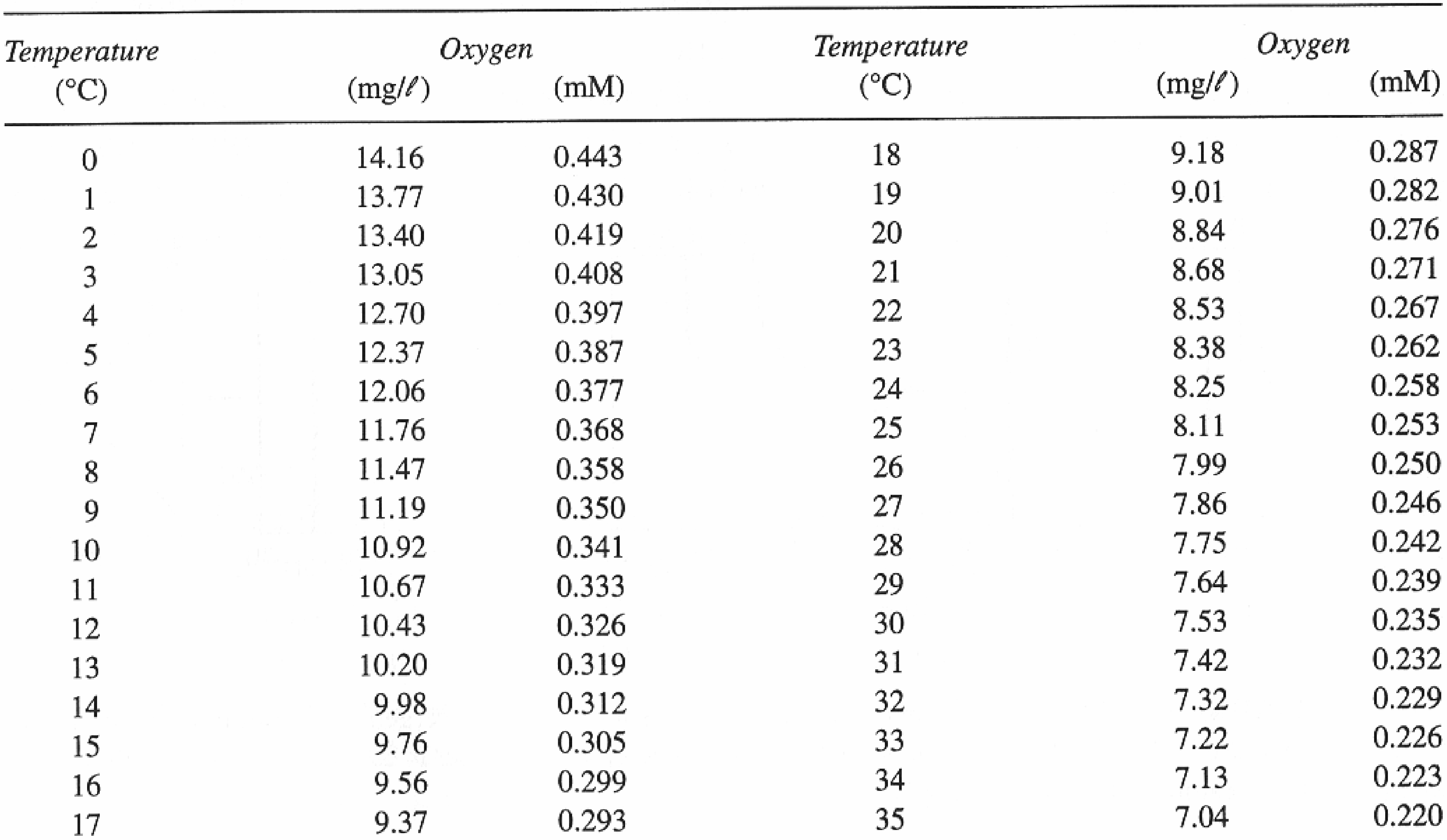
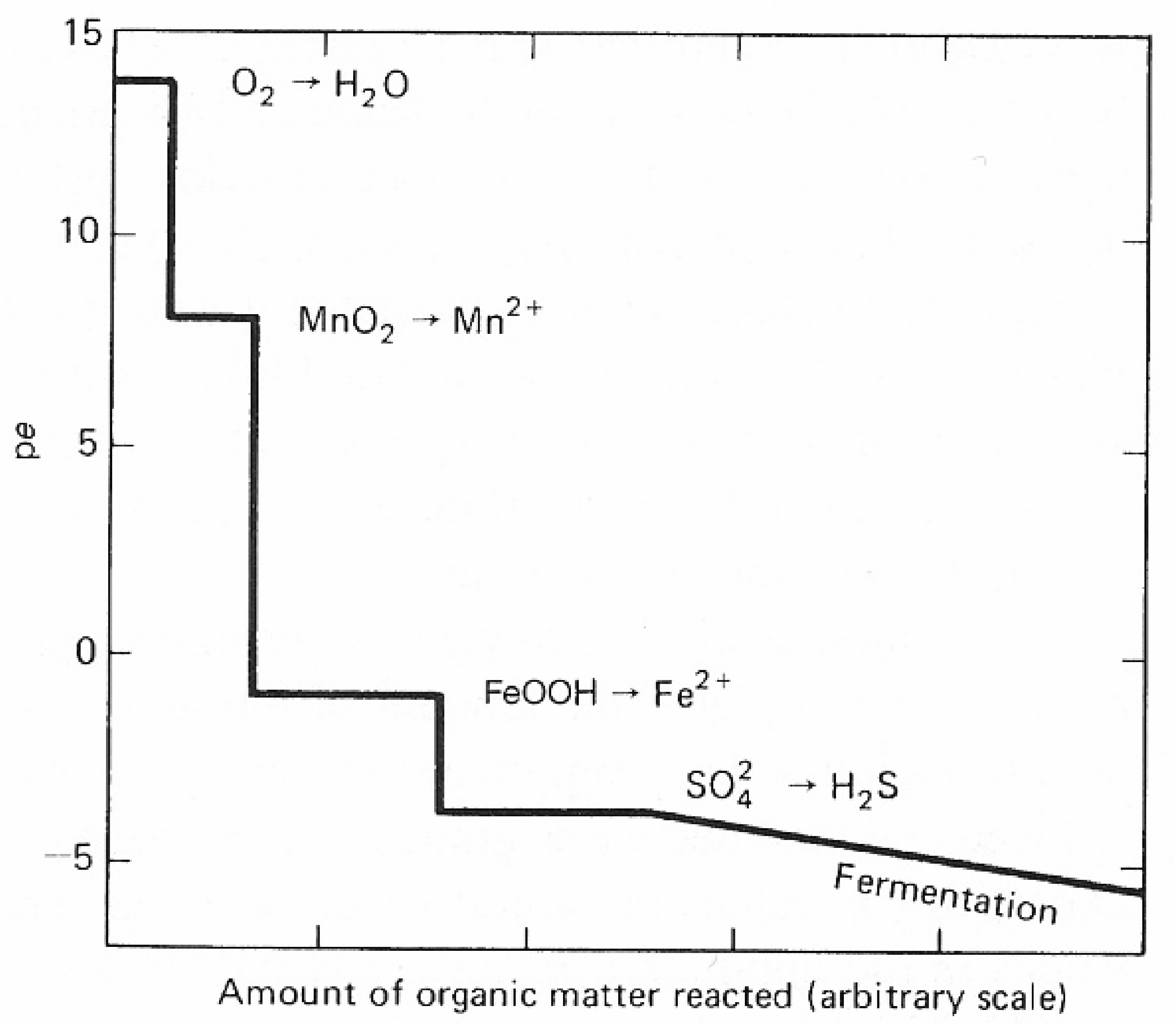


TABLE 8-1 **Concentration of Dissolved Oxygen in Water in Equilibrium with Air at a Total Pressure of 1 atm** (from data of Truesdale et al., 1955)



Temperature (°C)	*Oxygen* (mg/ℓ)	(mM)	*Temperature* (°C)	*Oxygen* (mg/ℓ)	(mM)
0	14.16	0.443	18	9.18	0.287
1	13.77	0.430	19	9.01	0.282
2	13.40	0.419	20	8.84	0.276
3	13.05	0.408	21	8.68	0.271
4	12.70	0.397	22	8.53	0.267
5	12.37	0.387	23	8.38	0.262
6	12.06	0.377	24	8.25	0.258
7	11.76	0.368	25	8.11	0.253
8	11.47	0.358	26	7.99	0.250
9	11.19	0.350	27	7.86	0.246
10	10.92	0.341	28	7.75	0.242
11	10.67	0.333	29	7.64	0.239
12	10.43	0.326	30	7.53	0.235
13	10.20	0.319	31	7.42	0.232
14	9.98	0.312	32	7.32	0.229
15	9.76	0.305	33	7.22	0.226
16	9.56	0.299	34	7.13	0.223
17	9.37	0.293	35	7.04	0.220

Drever, *The Geochemistry of Natural Waters 3rd Edition*



Change in pe of a fresh water in contact with sediment as a function of the amount of organic matter decomposed. The lengths of the various horizontal segments are arbitrary, depending on the amounts of specific solid phases available for reaction. pH is assumed constant at 7.0.

Figure 8-3. Drever, *The Geochemistry of Natural Waters 3rd Edition*

The reduction and oxidation sequence in soil solutions at pH 7

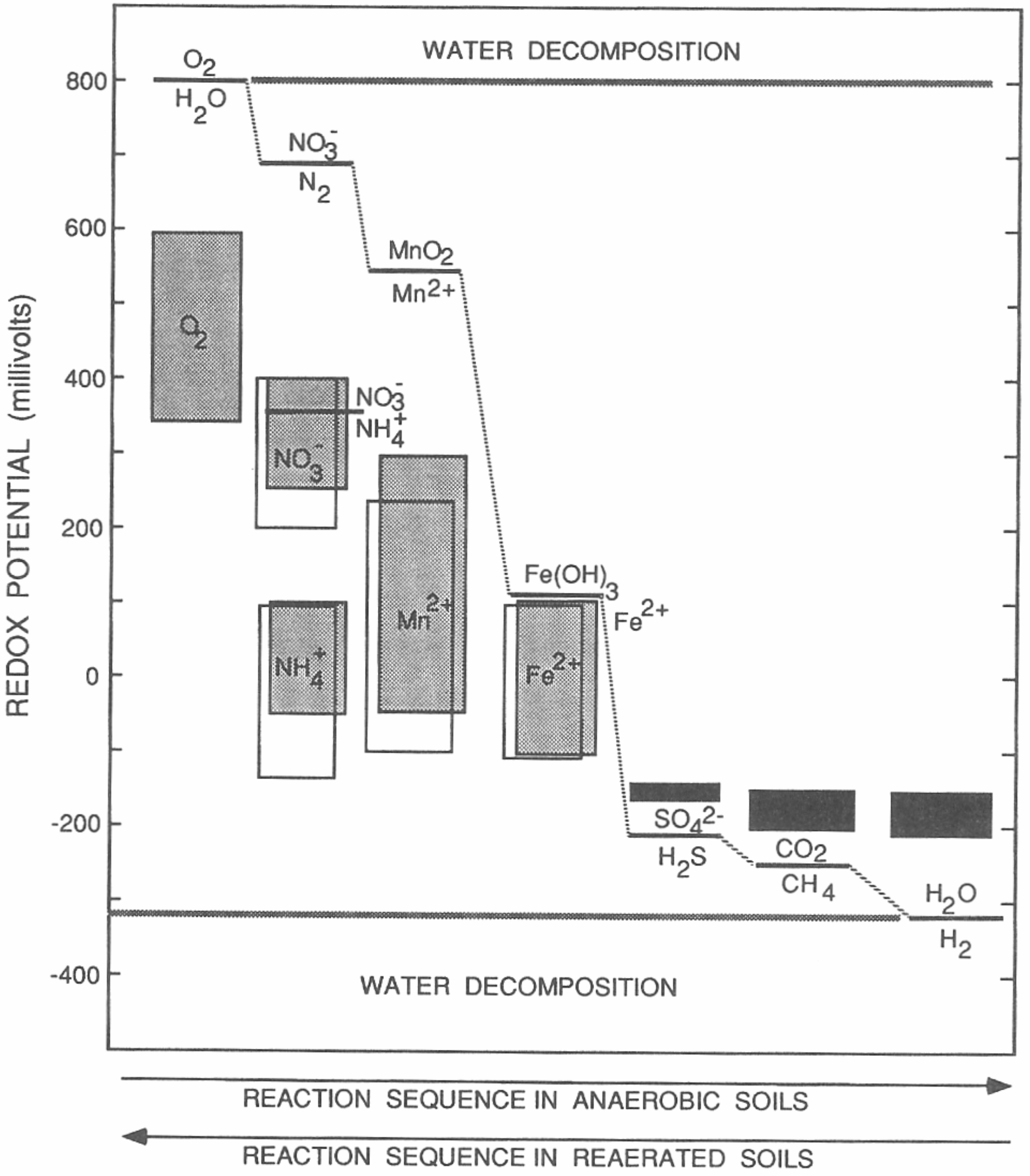


Figure 7.5. The reduction and oxidation sequence in soil solutions at pH 7. Theoretical potentials are indicated by solid lines, assuming equal activities of reduced and oxidized species unless otherwise noted (the pressure of H_2 is arbitrarily set at 10^{-3} atmosphere). Measured ranges of soil potentials over which the indicated species react (change concentration) during soil reduction and oxidation are specified by boxes (shaded for reduction, open for oxidation, black for initial appearance of the reduced form during reduction). (Data, in part, from W. H. Patrick and A.

McBride. Environmental Chemistry of Soils, 1994

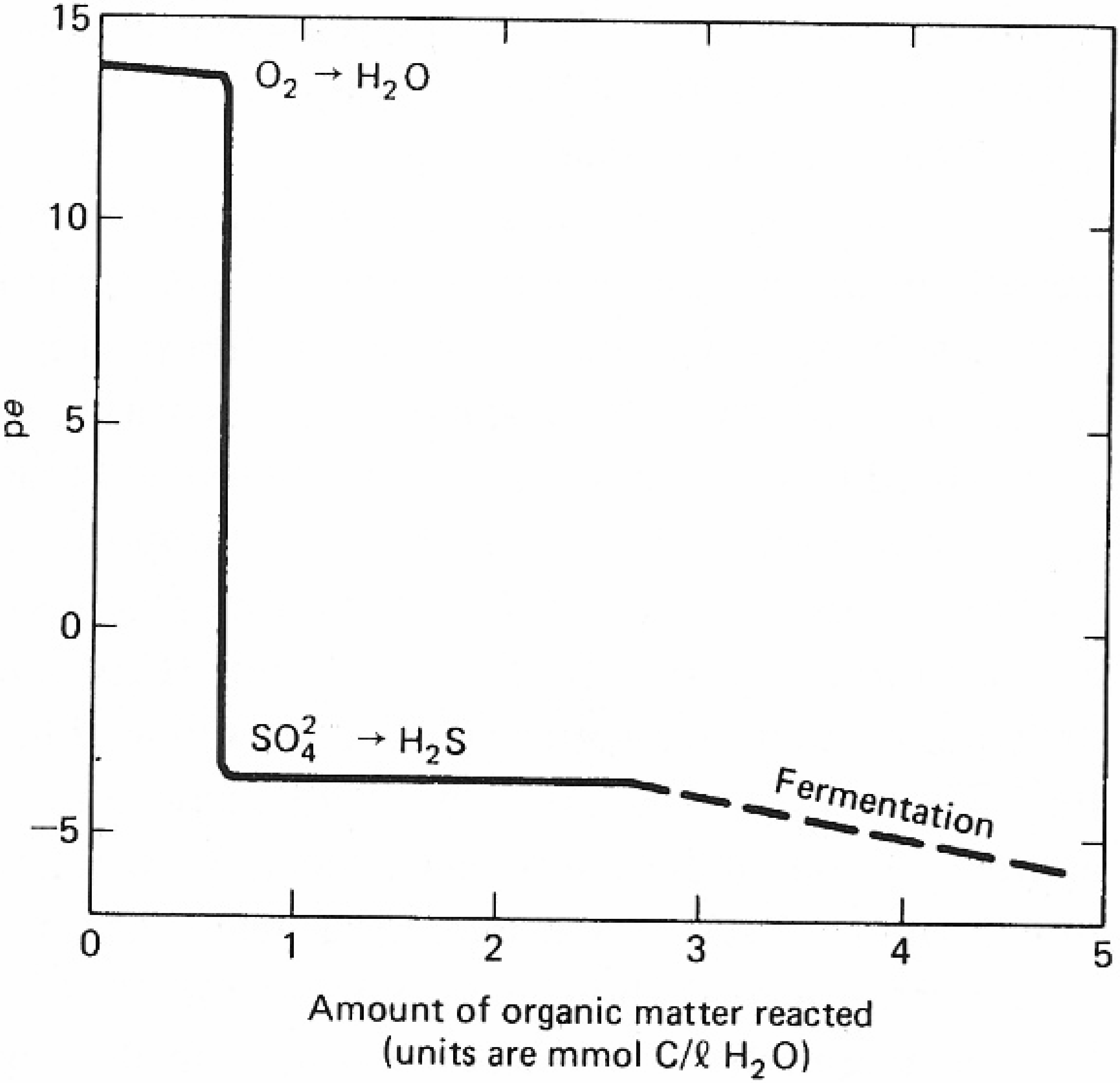


FIGURE 8-2 Change in p*e* of a fresh water (dissolved O_2 = 10 mg/ℓ, dissolved SO_4^{2-} = 96 mg/ℓ) as a function of the amount of organic matter decomposed. Reactions involving nitrogen compounds may provide a small amount of buffering between the O_2/H_2O and the SO_4^{2-}/H_2S levels. pH is assumed constant at 7.0.

Drever, *The Geochemistry of Natural Waters 3rd Edition*

Schematic description of ferrolysis in a soil with a perched water table

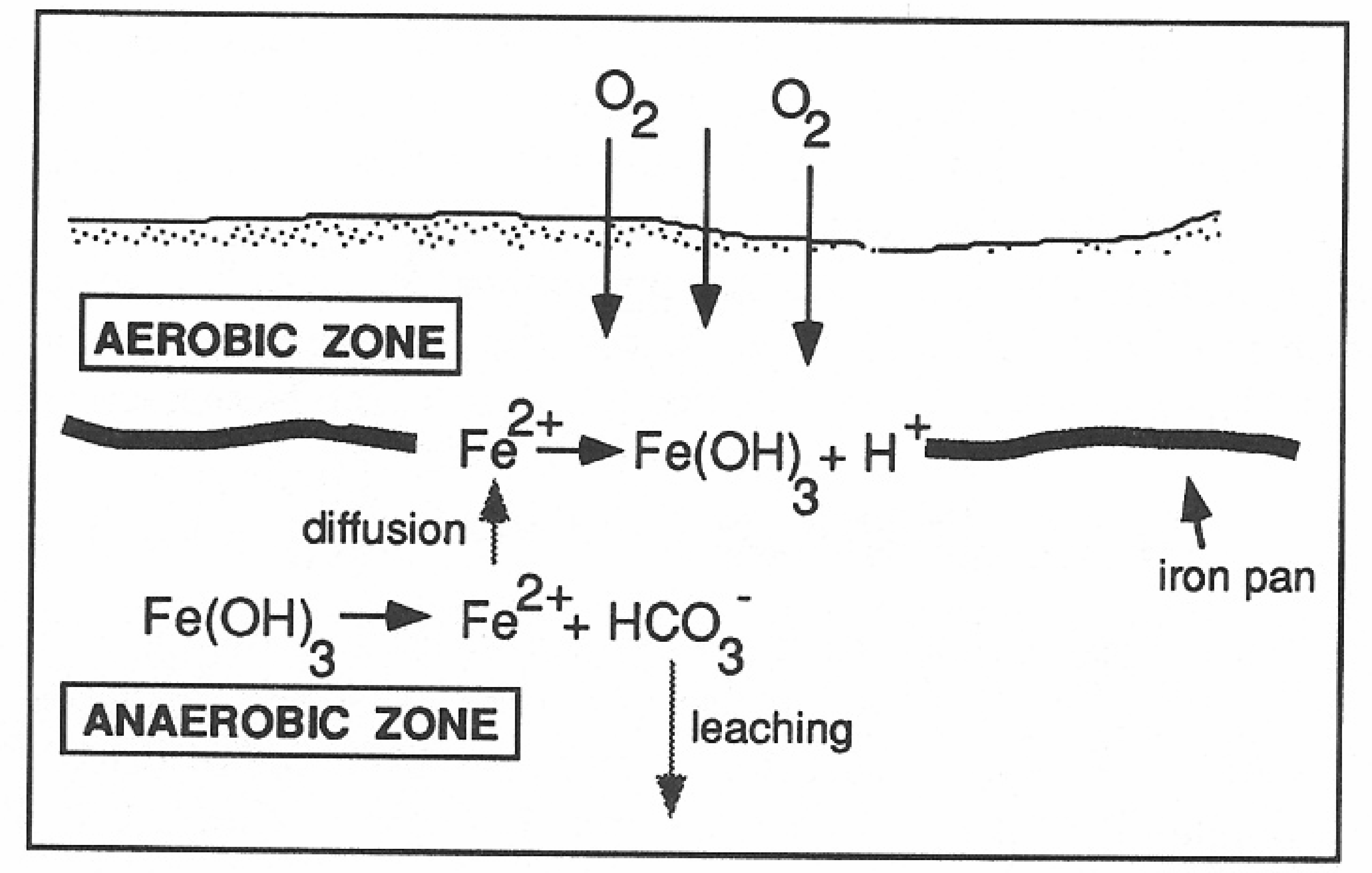
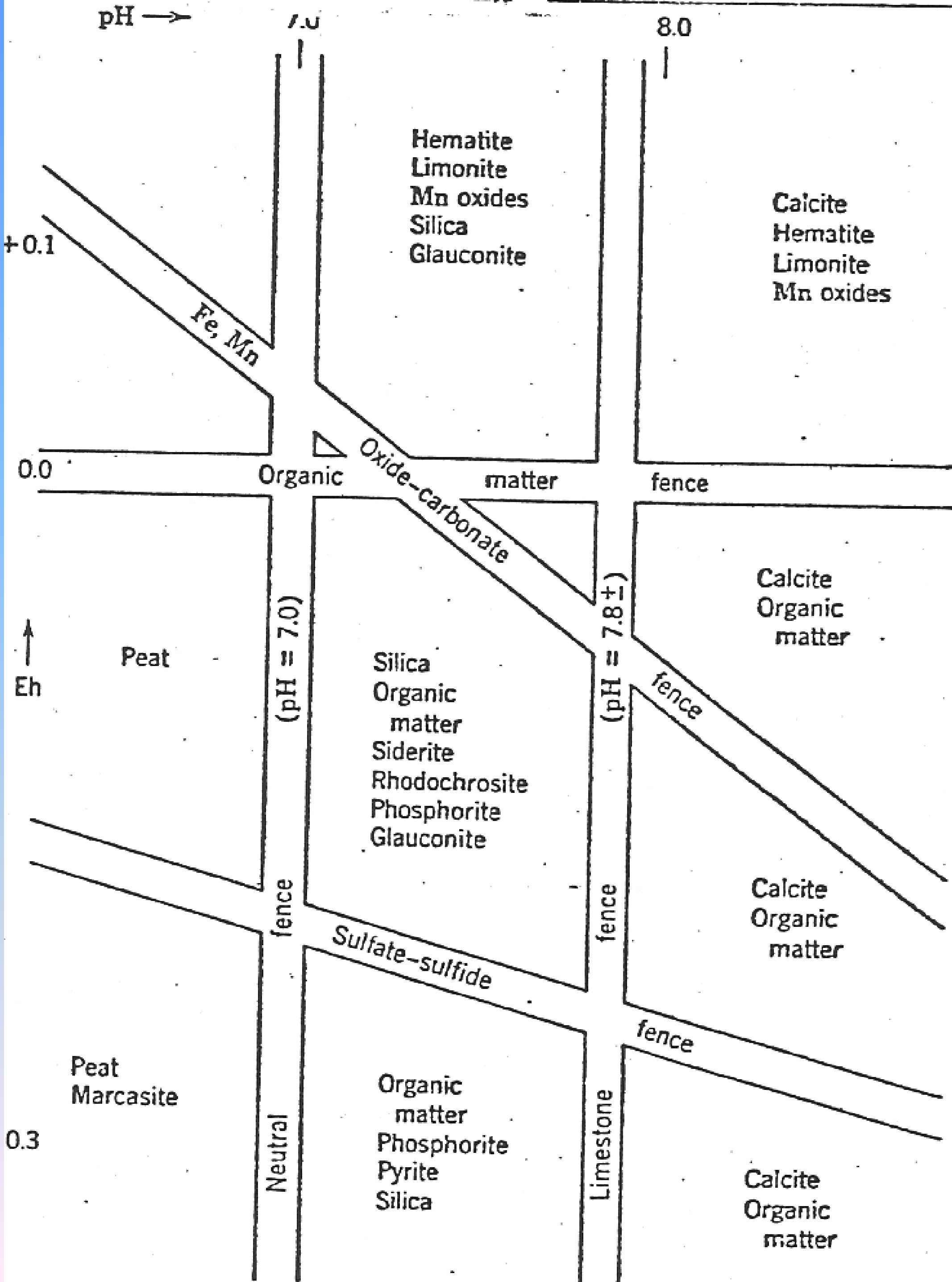


Figure 7.10 McBride. Environmental Chemistry of Soils, 1994

Fence Diagrams

- **<u>See Chapter 14, Drever</u>**
- See graphs or "Fence diagrams"- Notes are by the charts!



In Summary:

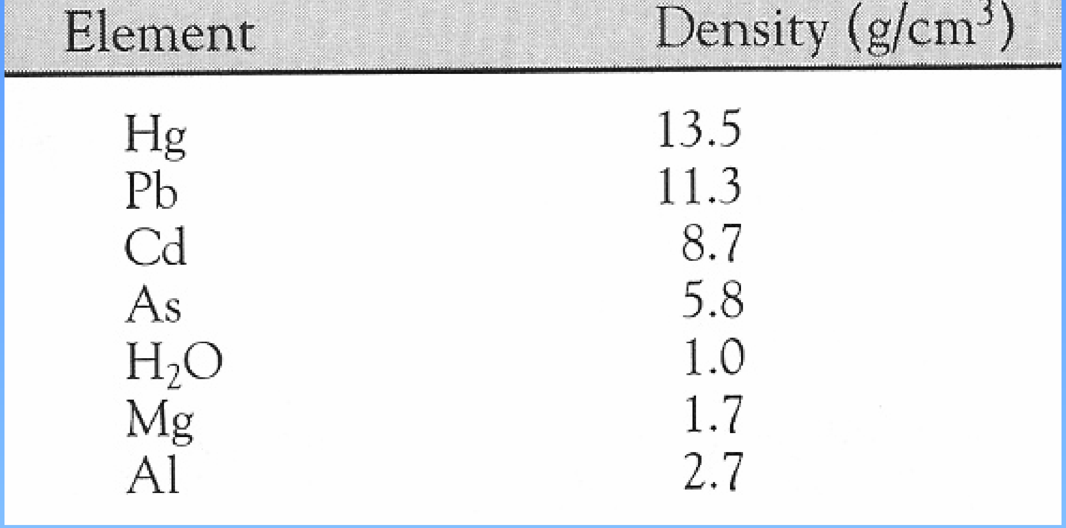
- Red-Ox conditions in natural water
- oxygen supply from atmosphere
- supply versus consumption determines what oxidation state the environment is in
- Other control of red-ox conditions in water such as reduction of ferric hydroxide
    - May form FeS, Mn which can act an inorganic buffers of reduction state.
- Flow length or time of flow is important.

Lecture 19

Heavy Metals

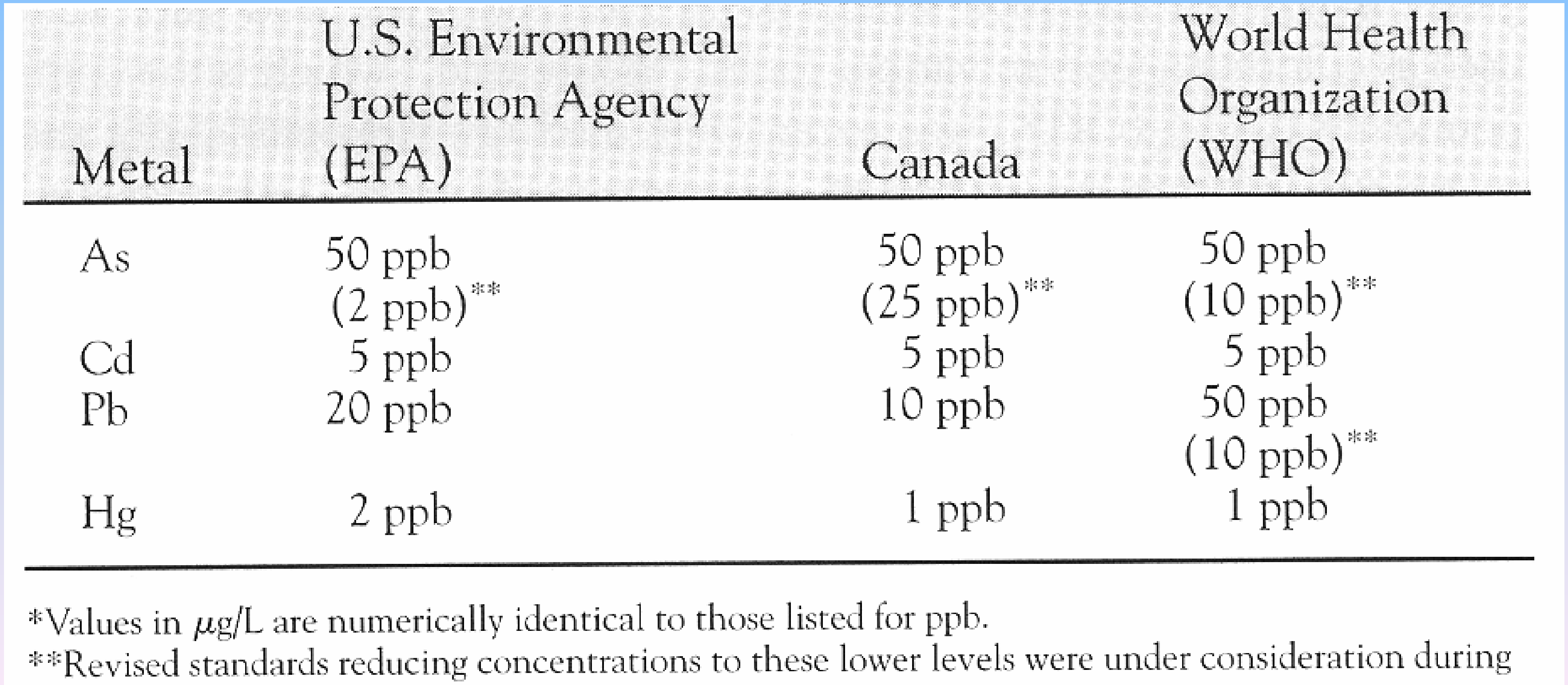
http://www.epa.gov/seahome/child/mercury/merc_m.htm

Densities of Some Important Heavy Metals and Important Substances



Element	Density (g/cm^3)
Hg	13.5
Pb	11.3
Cd	8.7
As	5.8
H_2O	1.0
Mg	1.7
Al	2.7

Drinking Water Standards for Heavy Metals



Metal	U.S. Environmental Protection Agency (EPA)	Canada	World Health Organization (WHO)
As	50 ppb (2 ppb)**	50 ppb (25 ppb)**	50 ppb (10 ppb)**
Cd	5 ppb	5 ppb	5 ppb
Pb	20 ppb	10 ppb	50 ppb (10 ppb)**
Hg	2 ppb	1 ppb	1 ppb

*Values in μg/L are numerically identical to those listed for ppb.

**Revised standards reducing concentrations to these lower levels were under consideration during the writing of this book, and may now be in place.

Tables 9-1,2. Baird, *Environmental Chemistry*, 1995 http://www.city.palo-alto.ca.us/cleanbay/graphics/mercury.jpg

Mercury Hg

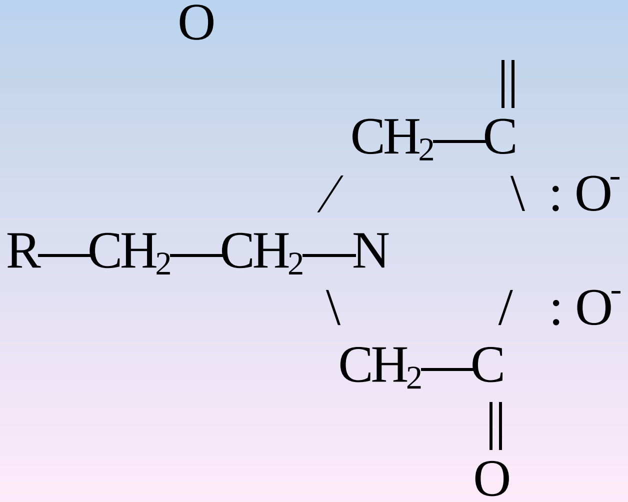
- ❖ very volatile:liquid at room T (b.p. 300°C)
- ❖ *Natural origins*: volcanoes
- ❖ *Man Made*: incineration of HgO in batteries, coal combustion, loss of Hg_0 in industrial processes
- ❖ Toxic: as Hg_0 (vapor) ; methylmercury

* Sulfhydryl group in enzymes that control metabolic Rx :

$$2R\text{-}SH + M^{2+} \rightarrow R—S—M—S—R + 2H\uparrow$$

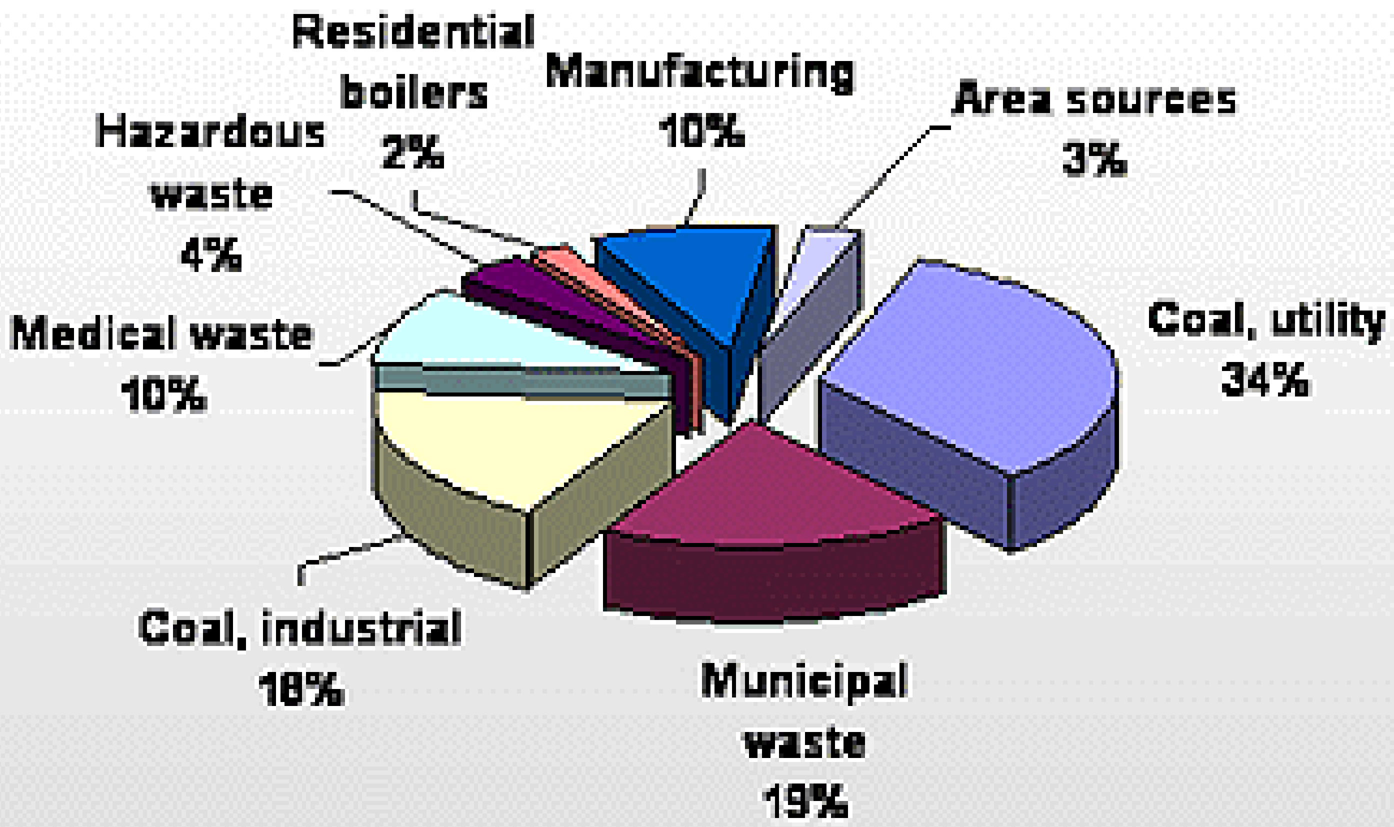
* to treat metal toxicity:

Chelation → EDTA , binds with metal in body



← binds to cationic metals

Figure 1: Combustion Sources of Mercury in the U.S.



http://www.epa.gov/owow/oceans/airdep/air2.html

Combustion sources account for 86% of total mercury emissions in the U.S. Of those sources, coal-fired utility boilers account for 34% of the total emissions. Other significant sources include coal-fired industrial boilers, incineration of municipal, medical, and hazardous waste, and certain manufacturing processes. Minor sources include residential boilers, and "area sources" which are small sources such as laboratory and home products (see Mercury Study Report to Congress 1997).

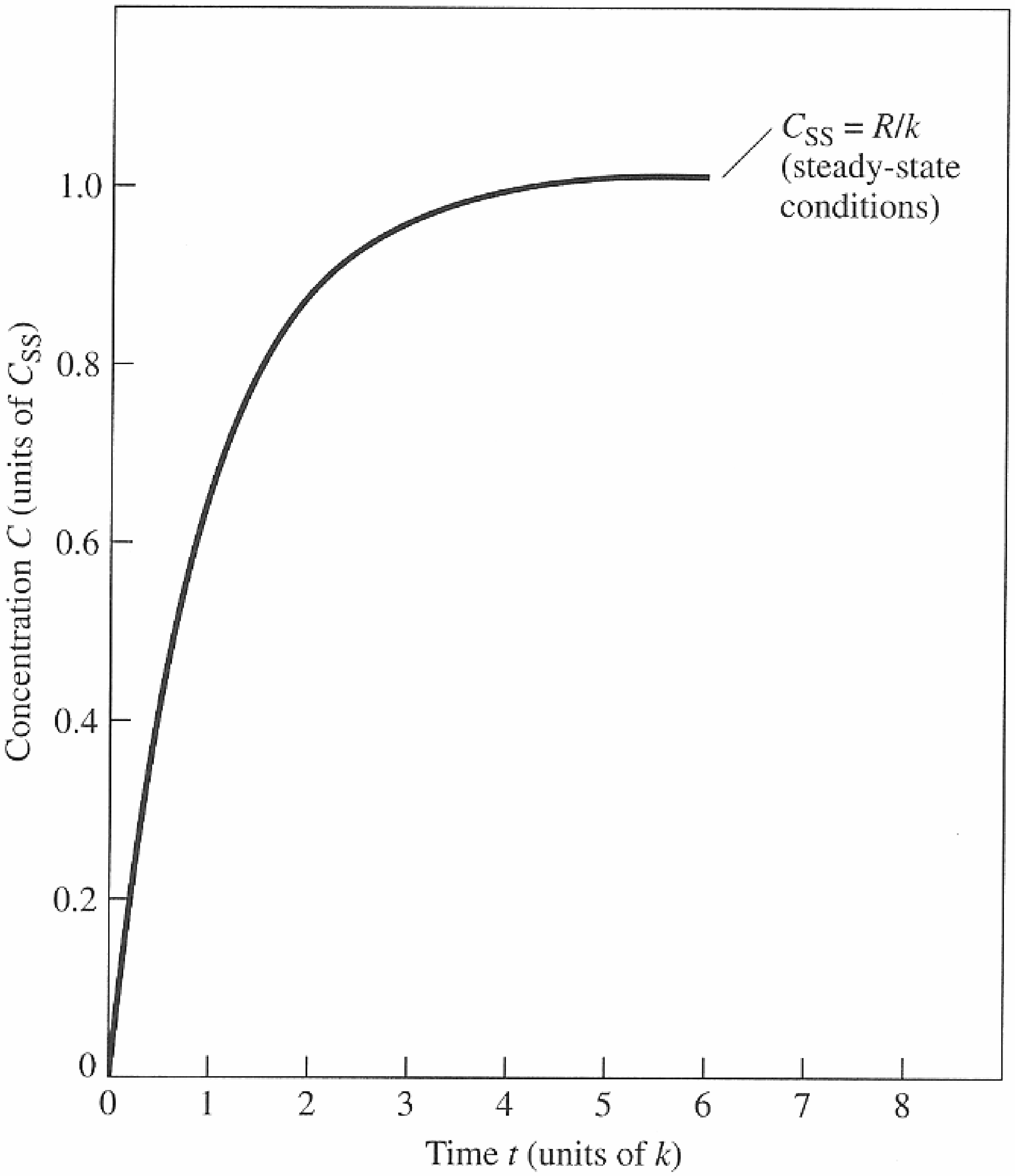
* *Mercury Hg*

* Residence time τ in bioaccumulation varies as a function of species and builds up

* Rate of ingestion = R excretion = kC → curve to steady state R = kC

→ unfortunately, acute toxicity often occurs (Toxicity = steady state)

- EX. Hg poisoning in Minamata, Japan from fish (~ 10-50 ppm Hg)
- Lake Ontario → fish are 0.5 ppm (and are recommended to be eaten max. of 1-2x per month)



Increase in mercury concentrations with time to steady-state level, C_{ss}

Baird, *Environmental Chemistry*, 1995

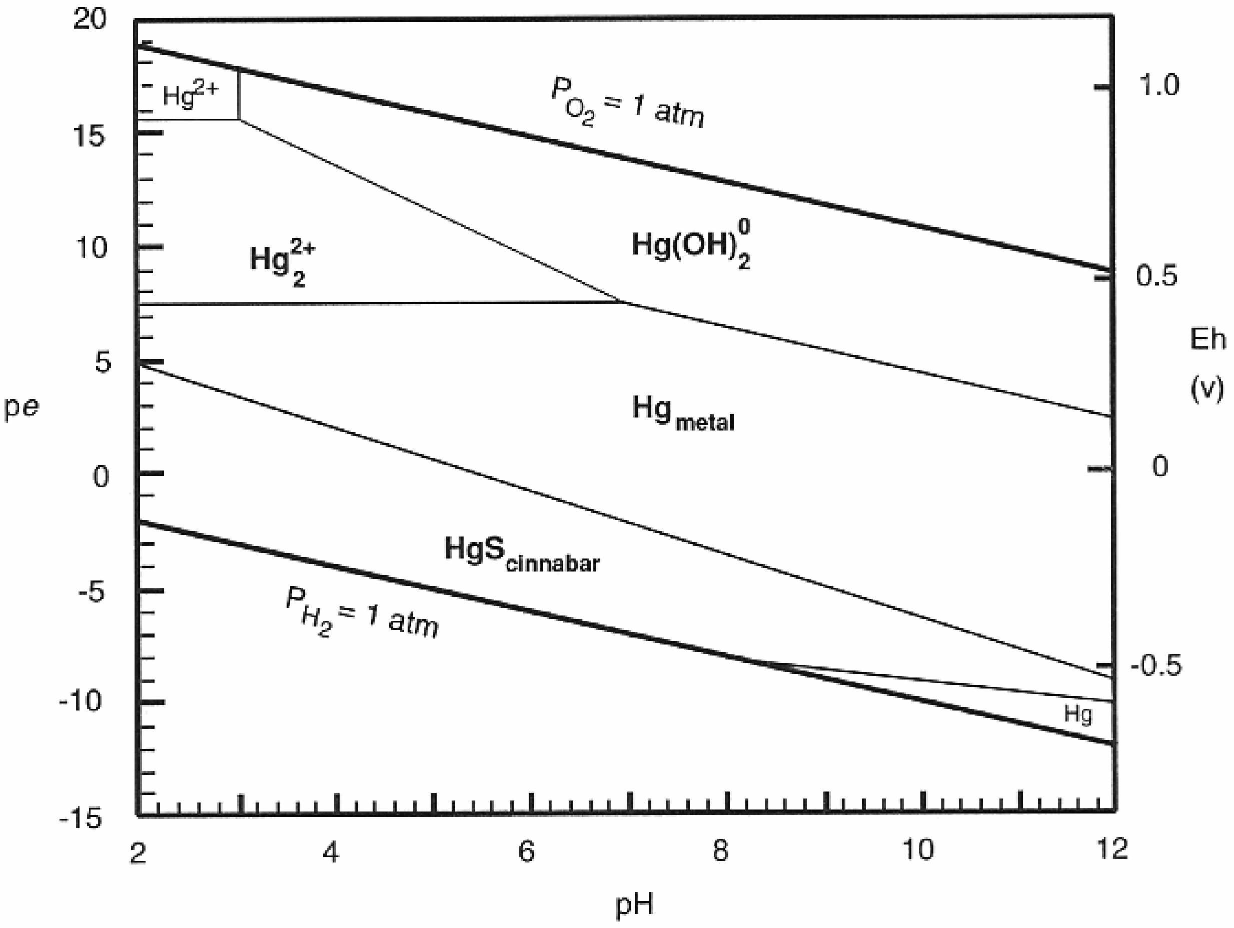
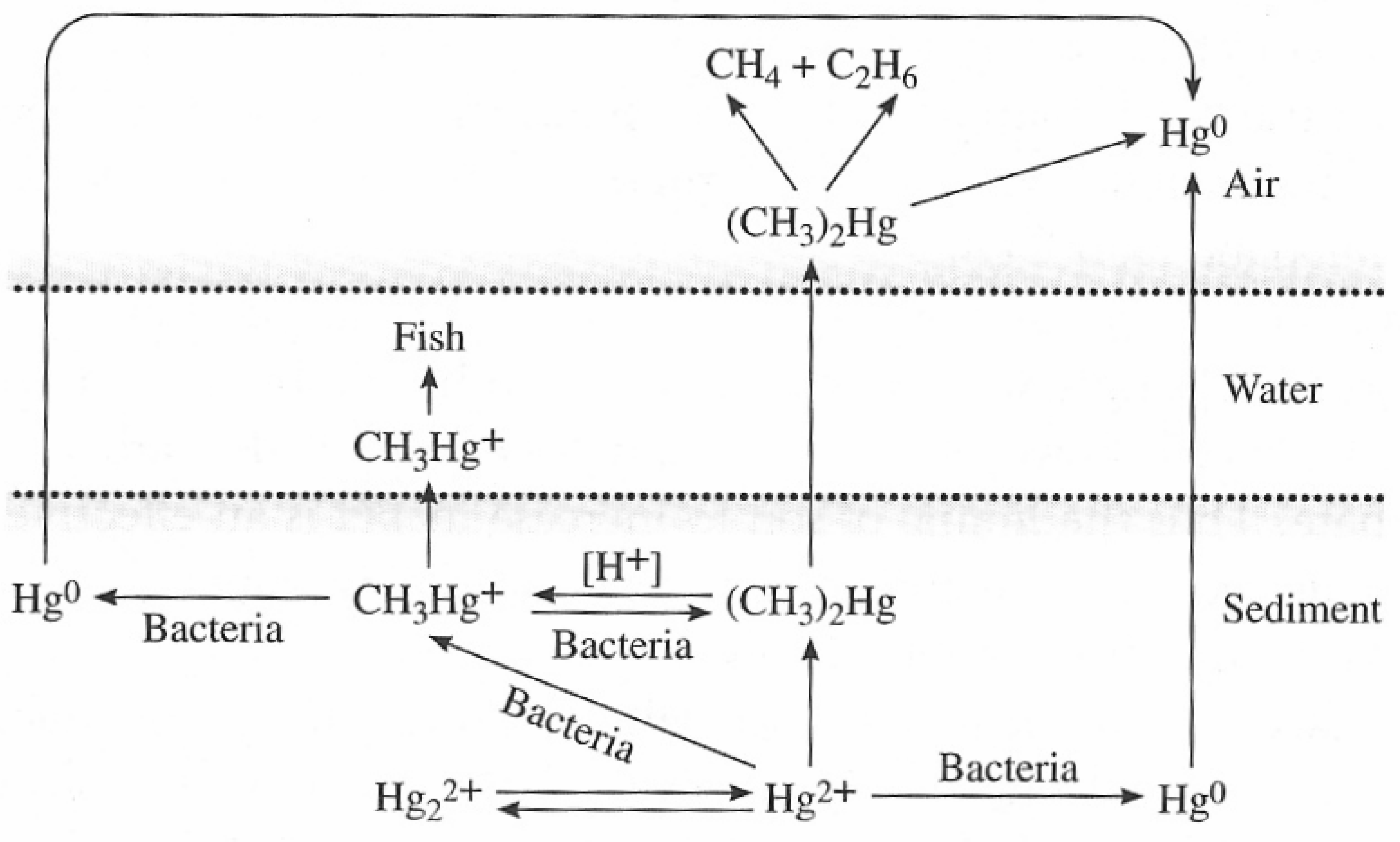


FIGURE 9-22 pe–pH diagram for the system Hg–S–O–H_2O at 25°C and one atm. Solubility is defined as a dissolved Hg activity of 10^{-6}. Total activity of sulfur species = 10^{-2}. The diagram is the same in the absence of S species, with the HgS (cinnabar) field replaced by Hg (metal). In the presence of chloride, the Hg_2^{2+} may be replaced by the insoluble mercurous chloride (calomel). Data are consistent with Allison et al. (1991).

•Drever. *The Geochemistry of Natural Waters 3rd Edition*

- Sediment: Hg^{2+} , Hg -anaerobic bacteria → methylate mercury → CH_3—Hg—CH_3 = soluble in water, volatile, τ (residence time) in body = 70 days
- methyl & phenyl mercury were once used as fungicide for pulp & paper, and seeds



The biogeochemical cycle of bacterial methylation and demethylation of mecury in sediments

- Figure 9-8. Baird, *Environmental Chemistry*, 1995

Biological and chemical transformations of mercury in the soil

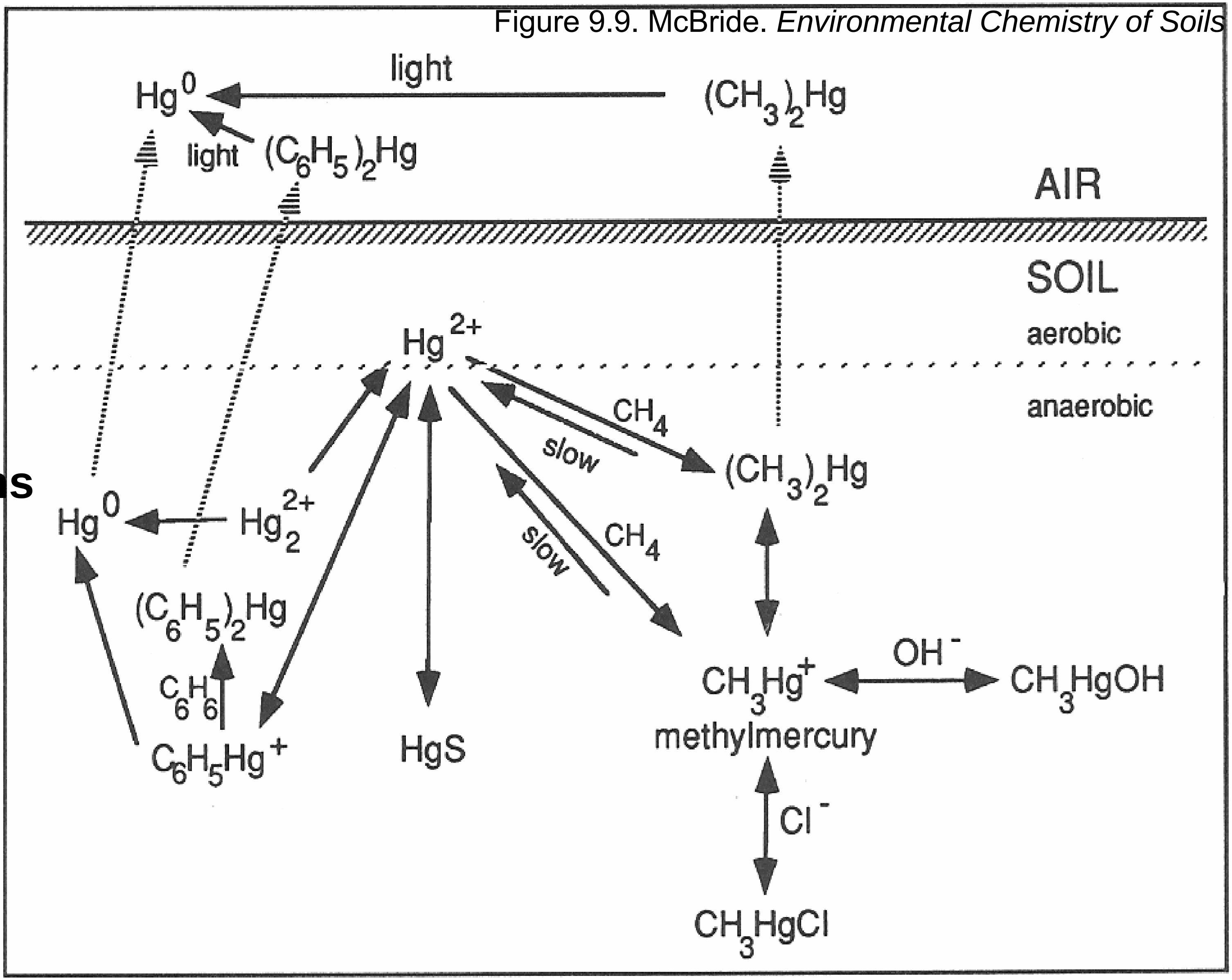
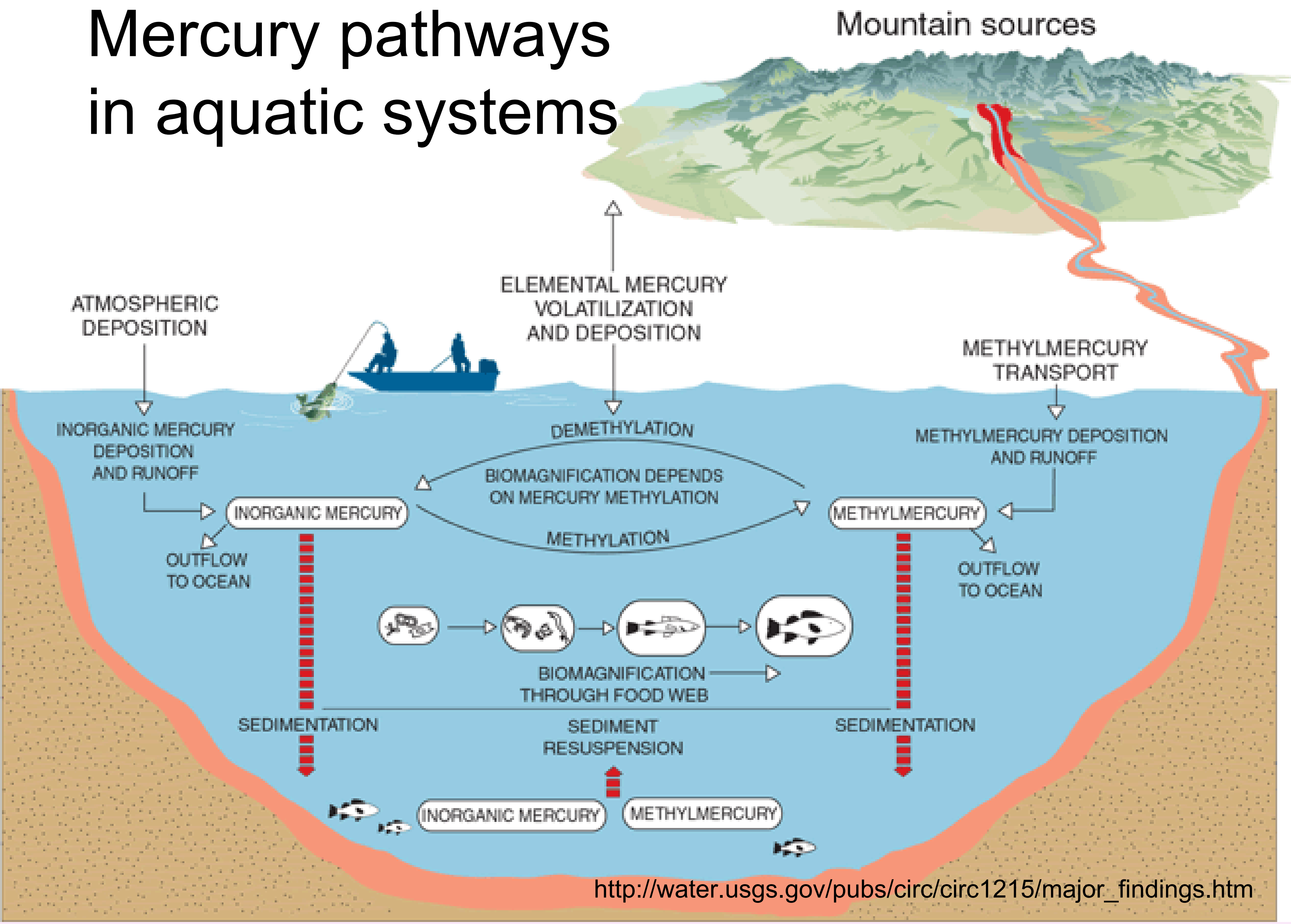


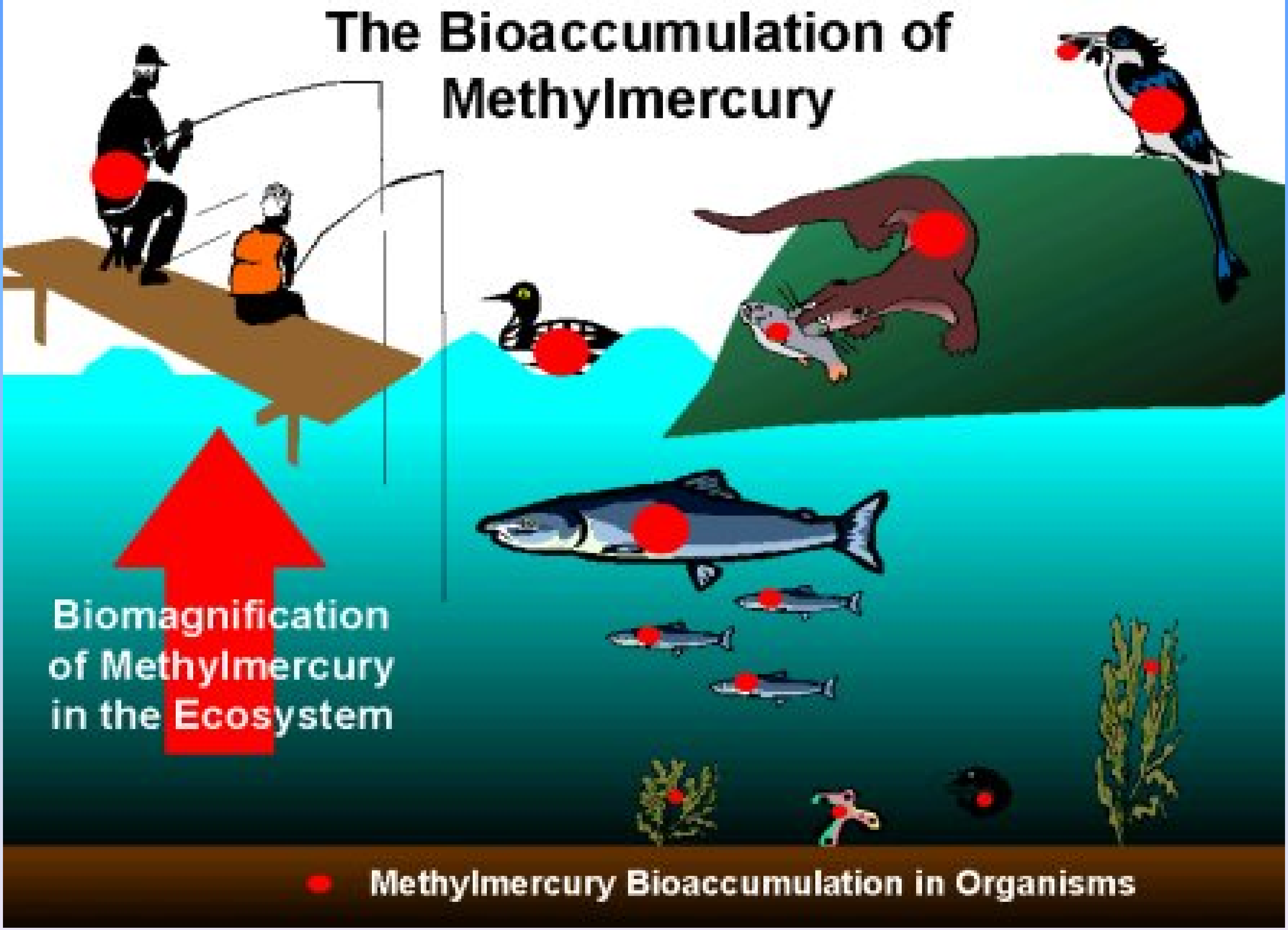
Figure 9.9. McBride. *Environmental Chemistry of Soils*

Figure 9.9. Biological and chemical transformations of mercury in the soil. Broken arrows denote the loss of volatile forms of Hg to the atmosphere or the air-filled pores of the soil. (Modified from B. E. Davies. 1980. Trace element pollution. In B. E. Davies (ed.), *Applied Soil Trace Elements*. New York: Wiley.)

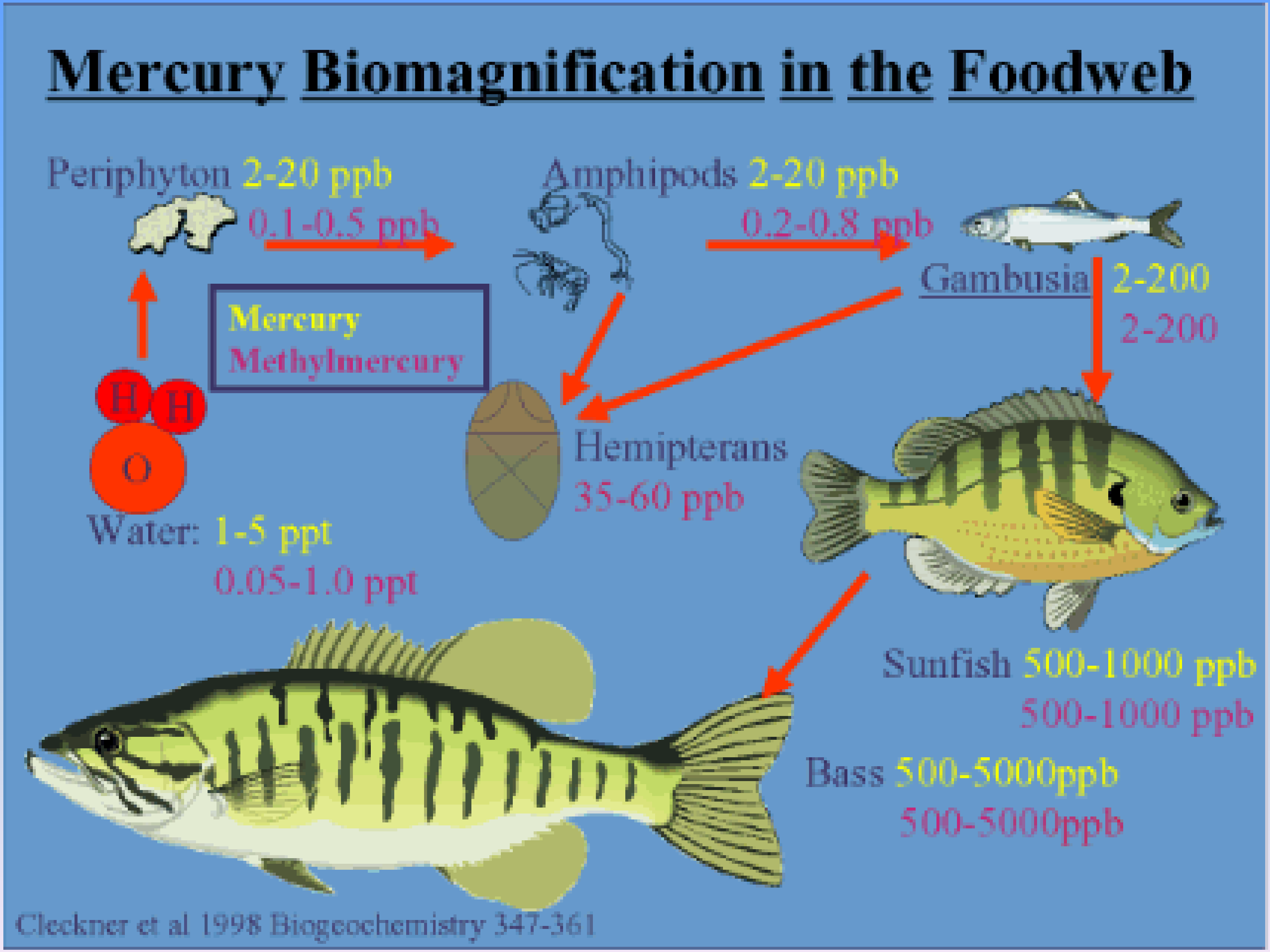
Mercury pathways in aquatic systems



http://water.usgs.gov/pubs/circ/circ1215/major_findings.htm



http://www.ec.gc.ca/MERCURY/EN/bf.cfm



Mercury Biomagnification in the Foodweb

Mercury
Methylmercury

Periphyton 2-20 ppb
0.1-0.5 ppb

Amphipods 2-20 ppb
0.2-0.8 ppb

Gambusia 2-200
2-200

Hemipterans
35-60 ppb

Water: 1-5 ppt
0.05-1.0 ppt

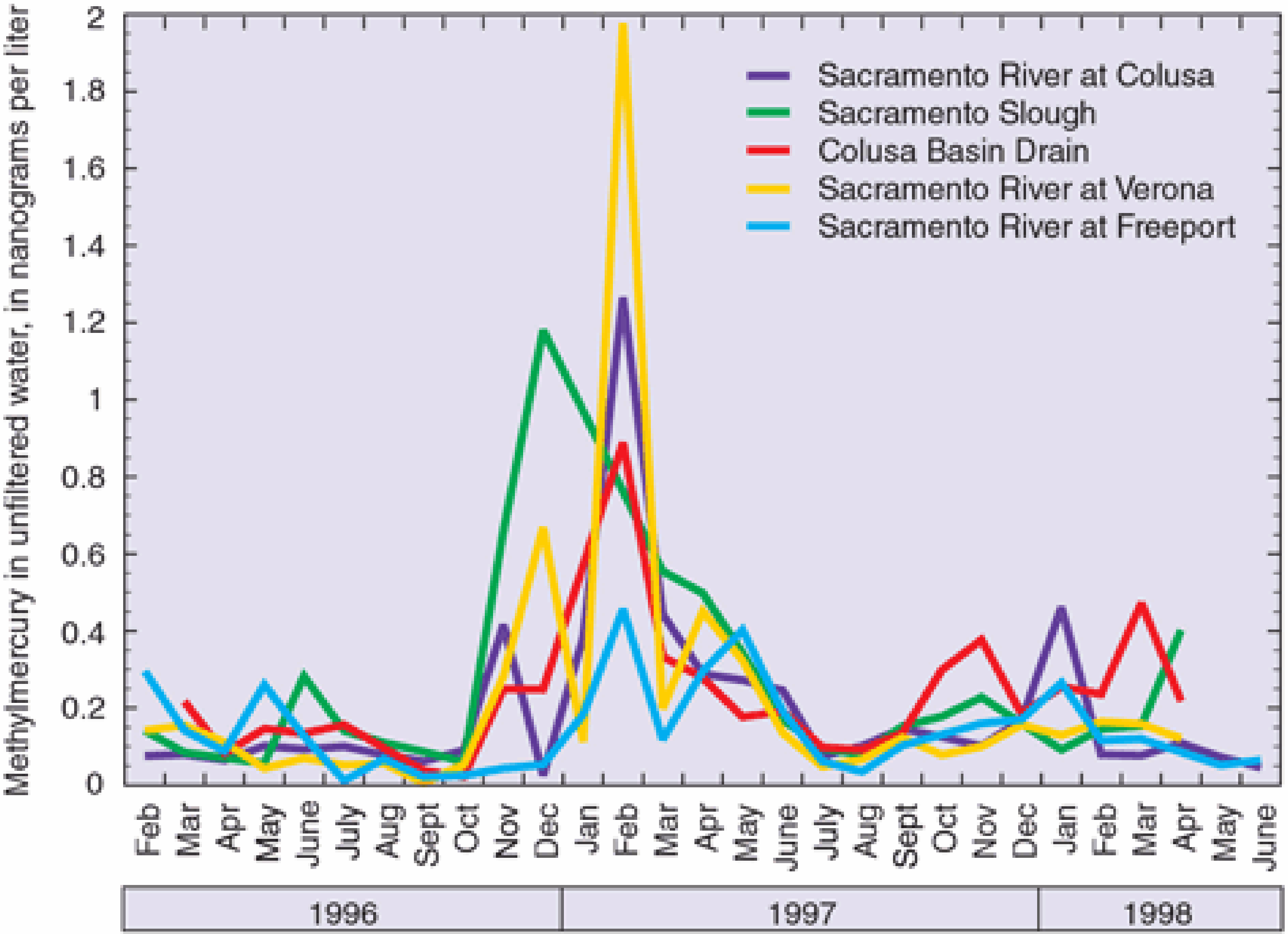
Sunfish 500-1000 ppb
500-1000 ppb

Bass 500-5000ppb
500-5000ppb

Cleckner et al 1998 Biogeochemistry 347-361

http://sofia.usgs.gov/sfrsf/rooms/acme_sics/acme/how.html

Seasonal changes of methylmercury concentrations. The highest concentrations were measured during high streamflow and following rainfall.



http://water.usgs.gov/pubs/circ/circ1215/major_findings.htm

Annual variation of mercury concentrations in walleye fish from Lake Saint Clair

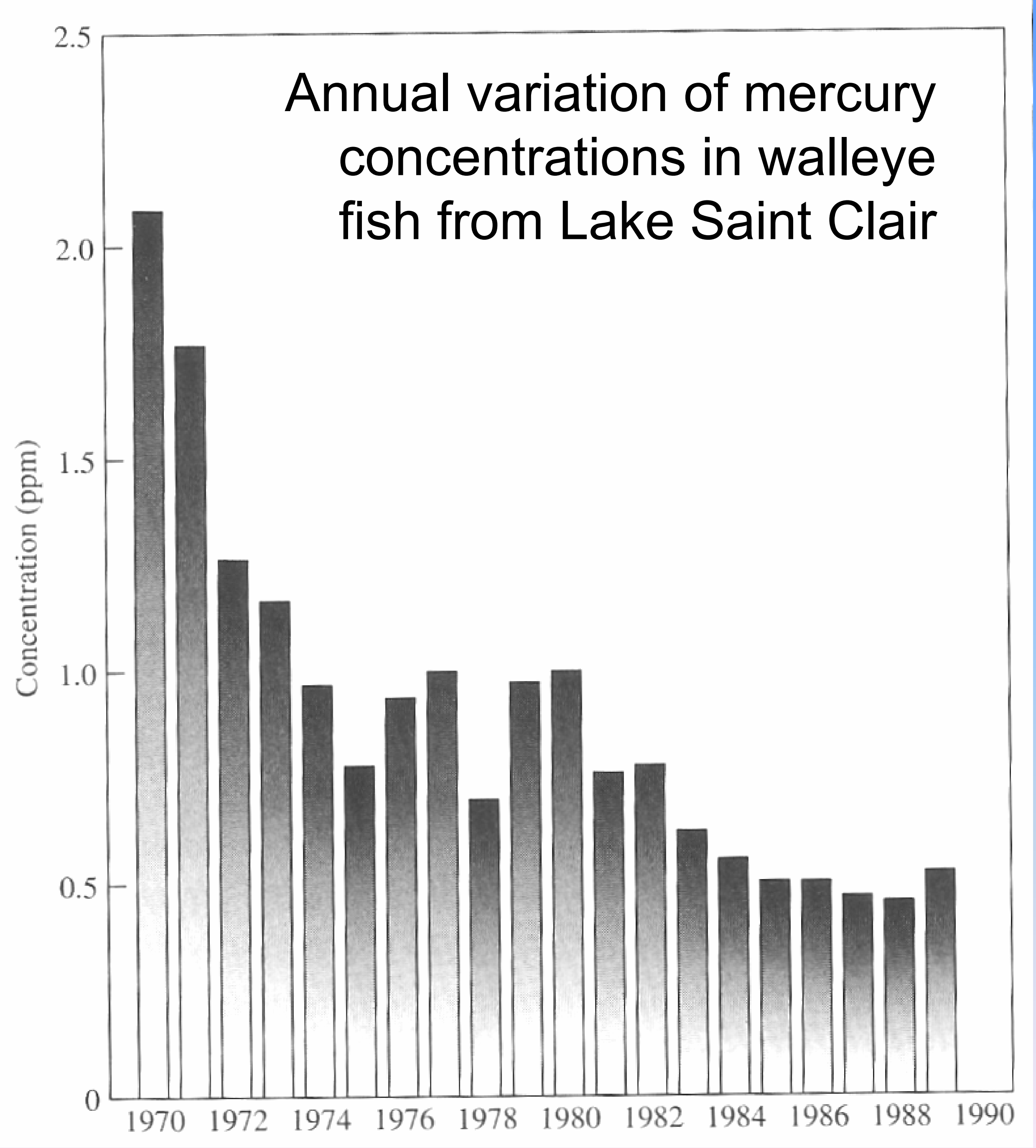
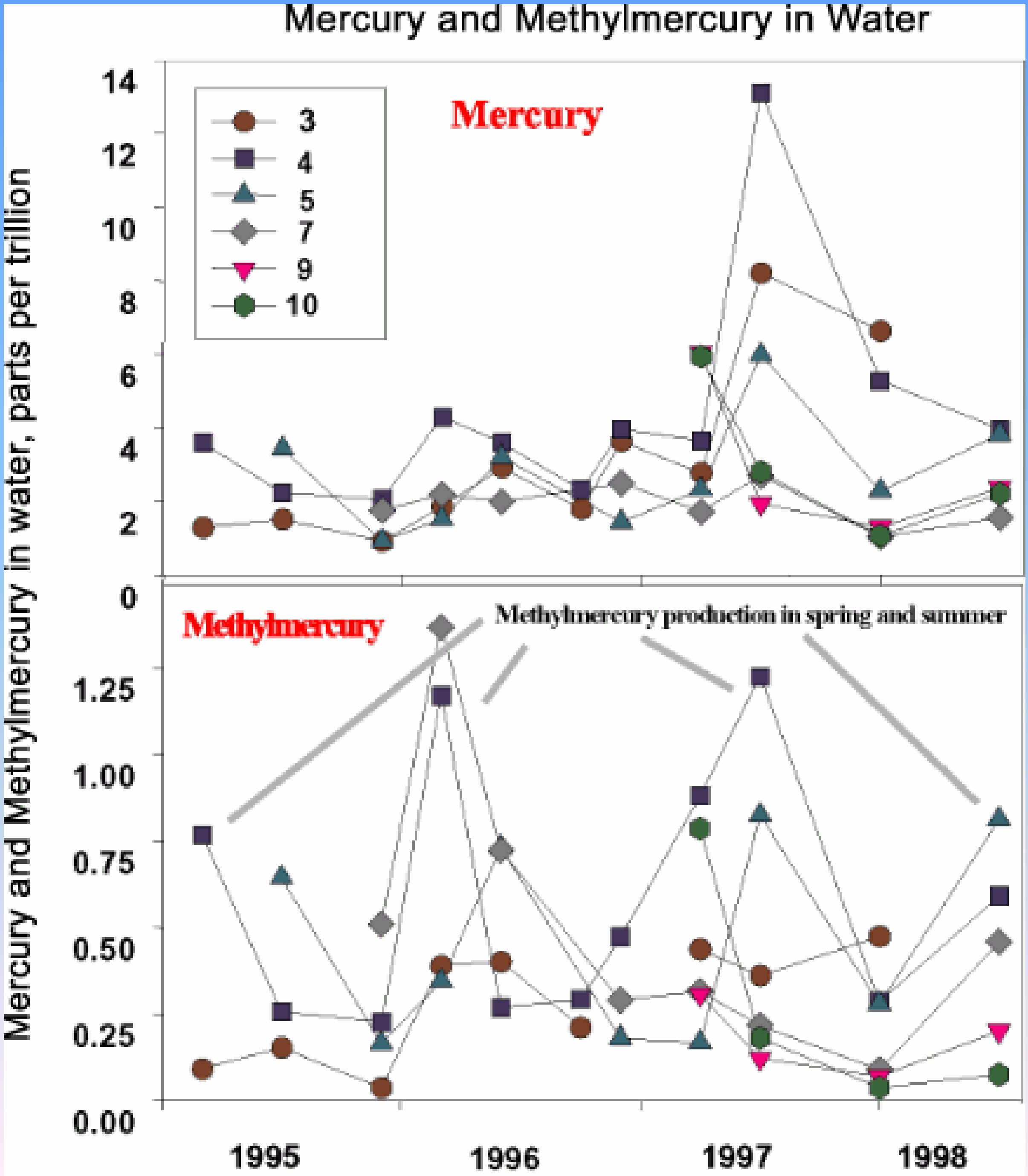


Figure 9-2. Baird, *Environmental Chemistry*, 1995

http://sofia.usgs.gov/sfrsf/rooms/acme_sics/acme/how.html

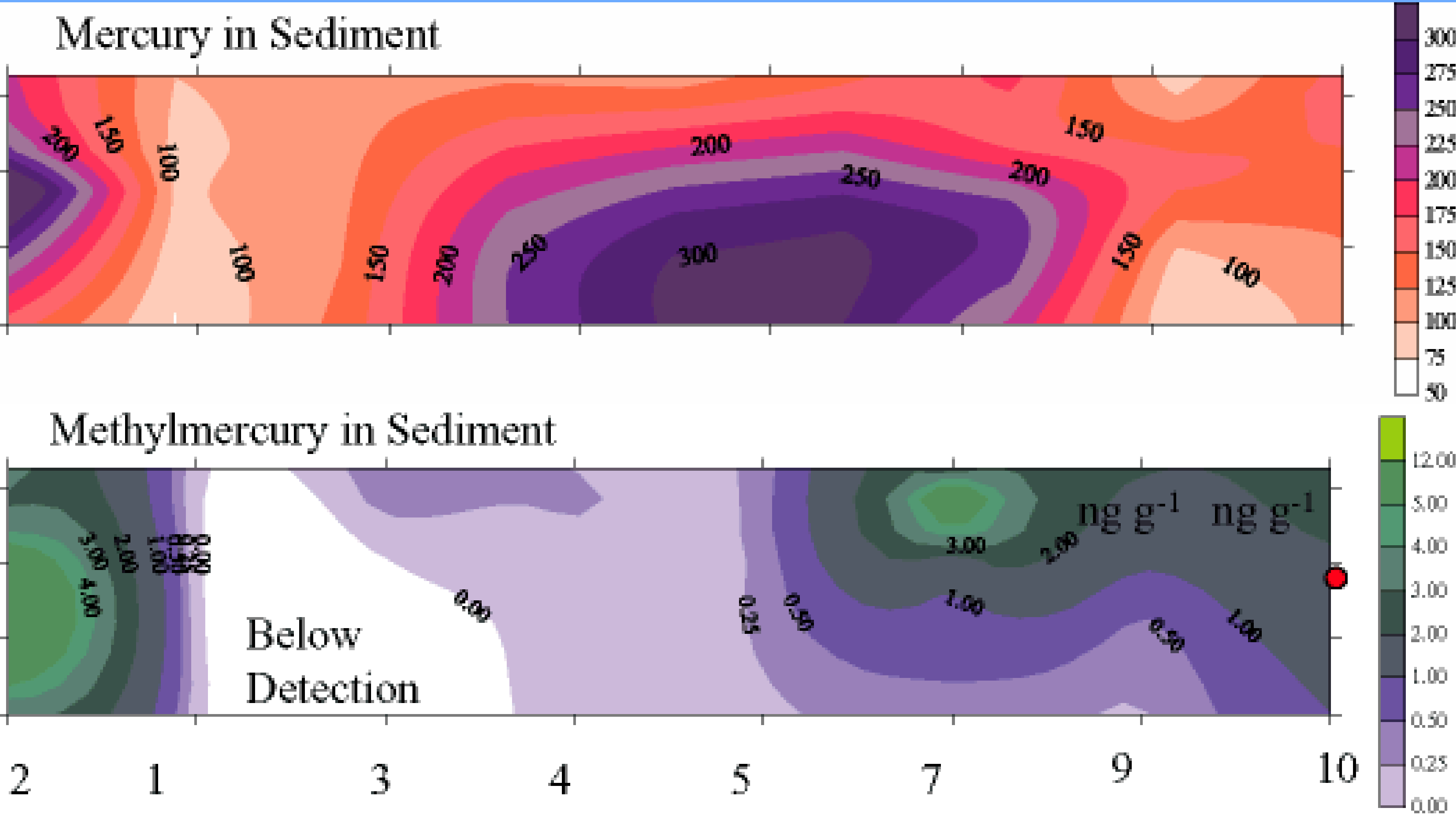
Mercury and Methylmercury in the South Florida Everglades



← **Mercury and Methylmercury in Water**

Water, a more rapidly changing sample media, shows distinct variations in time.

Sediments integrate environmental conditions over time, and shows distinct spatial differences.

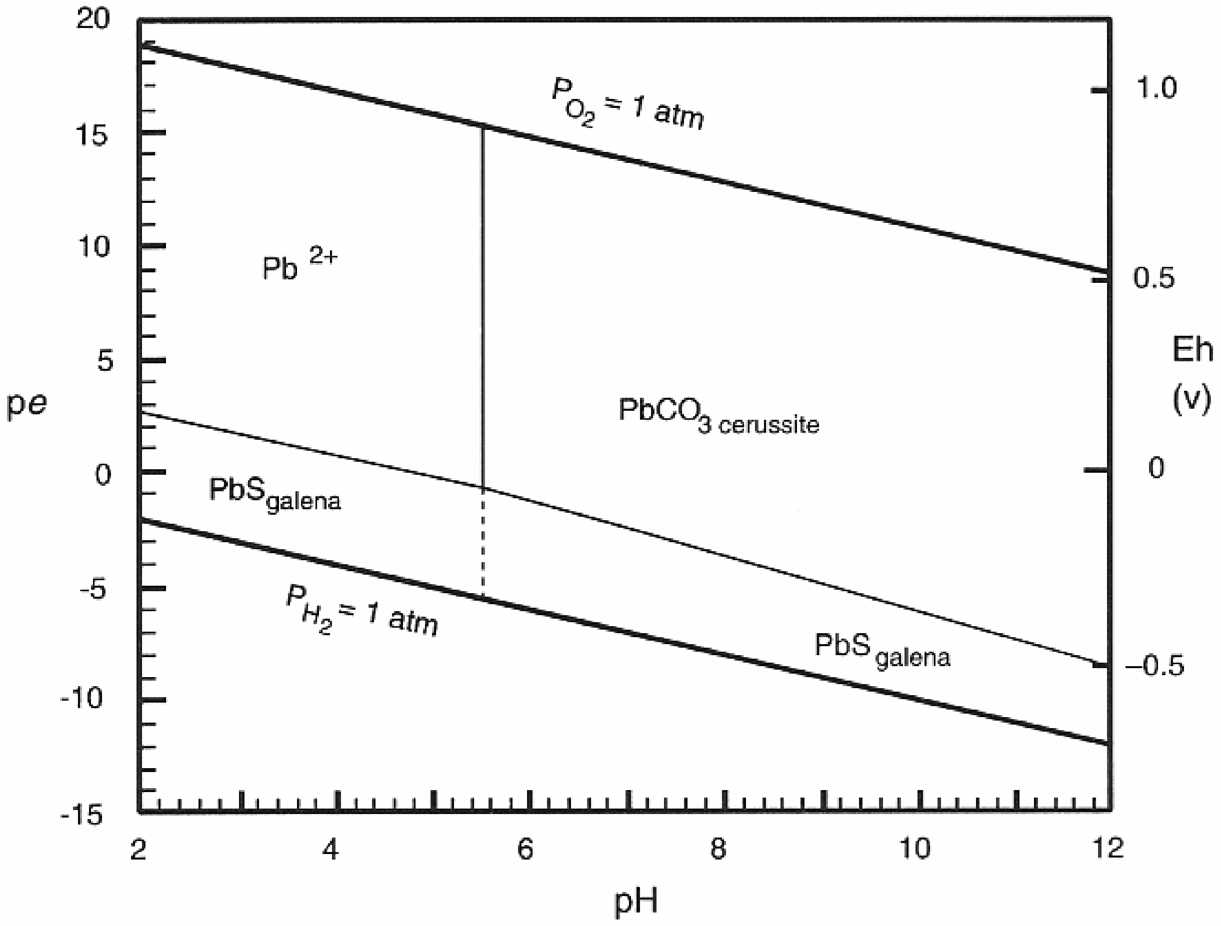


http://sofia.usgs.gov/sfrsf/rooms/acme_sics/acme/how.html

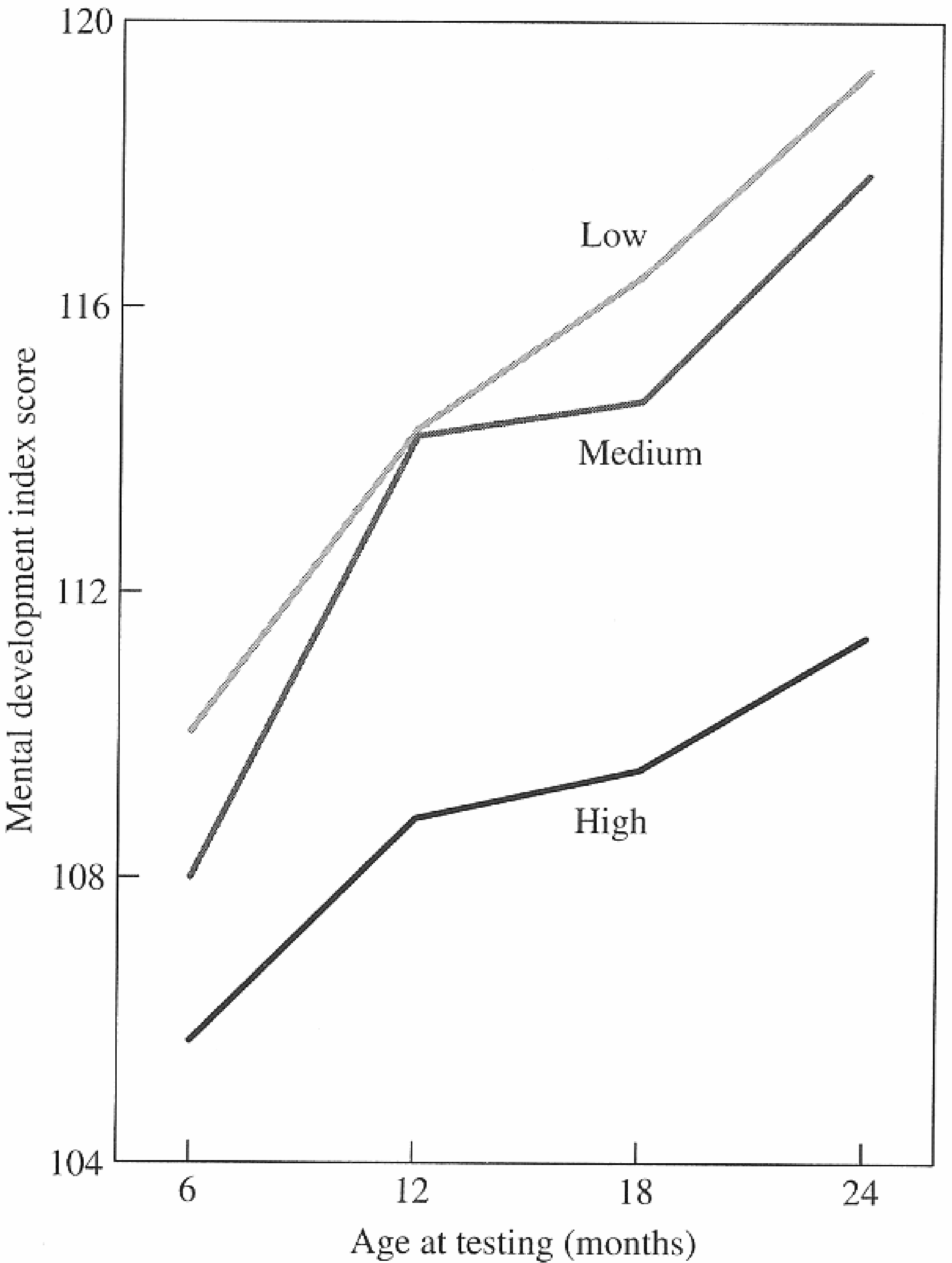
Lead Pb

- low melting point: 327°C
- Natural sources: formation in hydrothermal processes (with S source and high temperatures→ reducing environment)
- Anthropogenic: paint, pipes, solder of Pb & Sn

FIGURE 9-15 Simplified *pe*–pH diagram for the system Pb–CO_2–S–O–H_2O at 25°C and 1 atm. Solubility is defined as a dissolved Pb activity of 10^{-6}. Total activity of sulfur species = 10^{-2}, $P_{CO_2} = 10^{-2}$ atm. The P_{CO_2} has to be very low for the oxide, PbO (litharge) to be stable relative to the carbonate. Solid lines are solubility in the presence of S species, and the dashed line is solubility of the carbonate in the absence of S species. Data are consistent with Appendix III.



Drever. *The Geochemistry of Natural Waters 3rd Edition*



The effect of prenatal exposure to lead upon the mental development of infants. Lead exposure is measured by its concentration in the blood of the umbilical cord. “Low” corresponds to <3 µg /dL, “medium” to an average of 6.7 µg/dL, and “high” to >10 µg/dL.

Figure 9-5. Baird, *Environmental Chemistry*, 1995

Annual variation in lead concentrations in human blood and lead usage in gasoline for selected U.S. cities

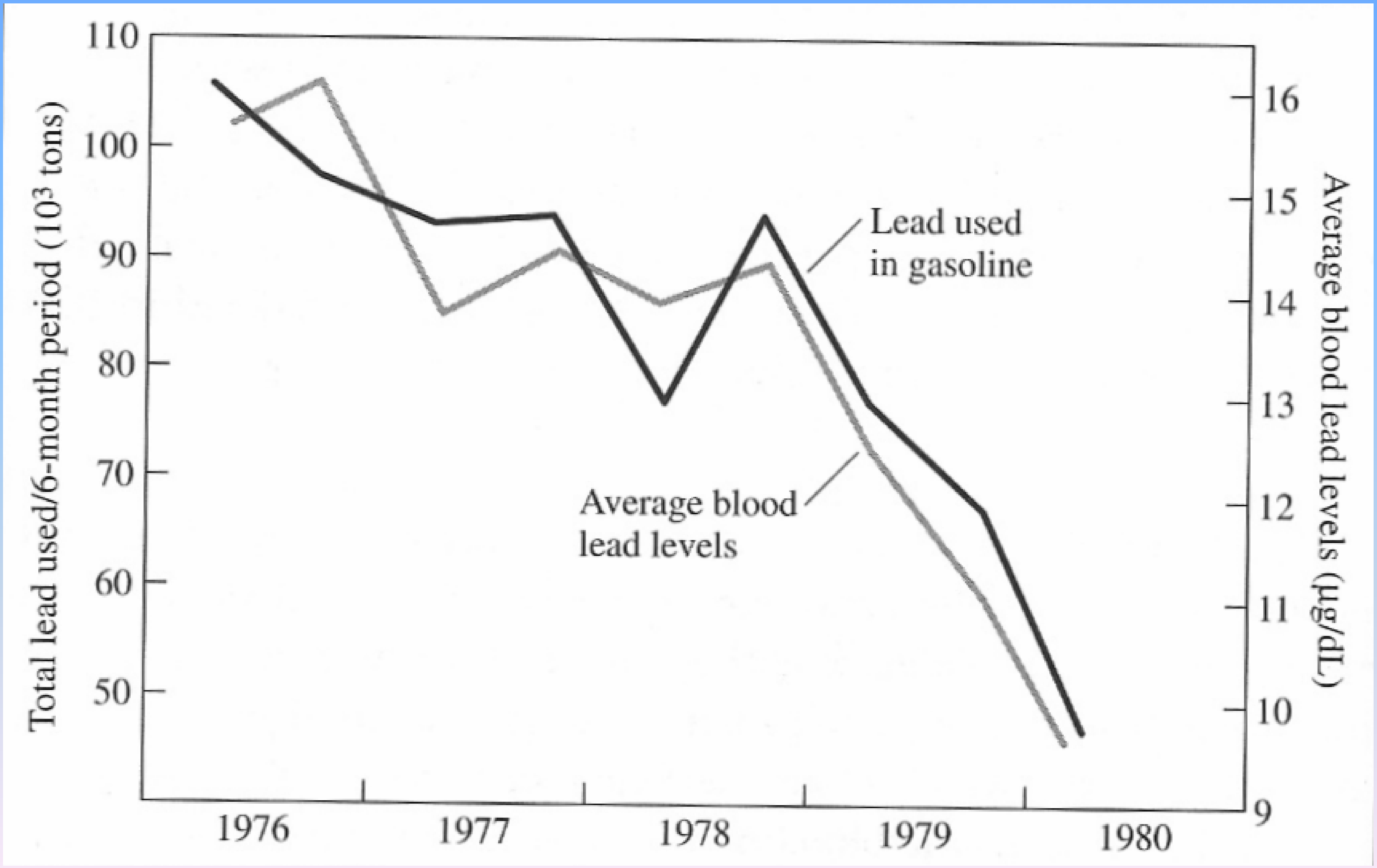


Figure 9-4. Baird, *Environmental Chemistry*, 1995

- Forms:

  * Pb^{2+}, PbS (galena)

  * Pb → Pb^{2+} in solution

  * Toxicity:

  Ex. Tuna Fish Scare—lead is ubiquitous in the environment (→ very easy to have lab contamination in measurements)

Lead Pb

Ex. Tuna Fish Scare—

It was seen in the following concentrations:

- 0.1-0.5ppm in the oceans & 0.5-1ppm in the cans.

- Clair Patterson at Cal Tech, using very careful Pb-isotope analysis, measured:

Fresh tuna: 5-10 ppb ; can: 0.5-1ppm

HUGE DIFFERENCE

→ in new pressed cans, 50 ppb.

*** Lead Sources :**

- Drinking water: Pb from solder in domestic plumbing & Pb in distribution pipes
  - $Pb^{2+} + CO_3^{2-} \rightarrow PbCO_3$ under alkaline conditions
  - 20 ppb maximum allowable limit.

Lead and mercury concentrations in the sediments of Halifax Harbor versus depth (and therefore year).

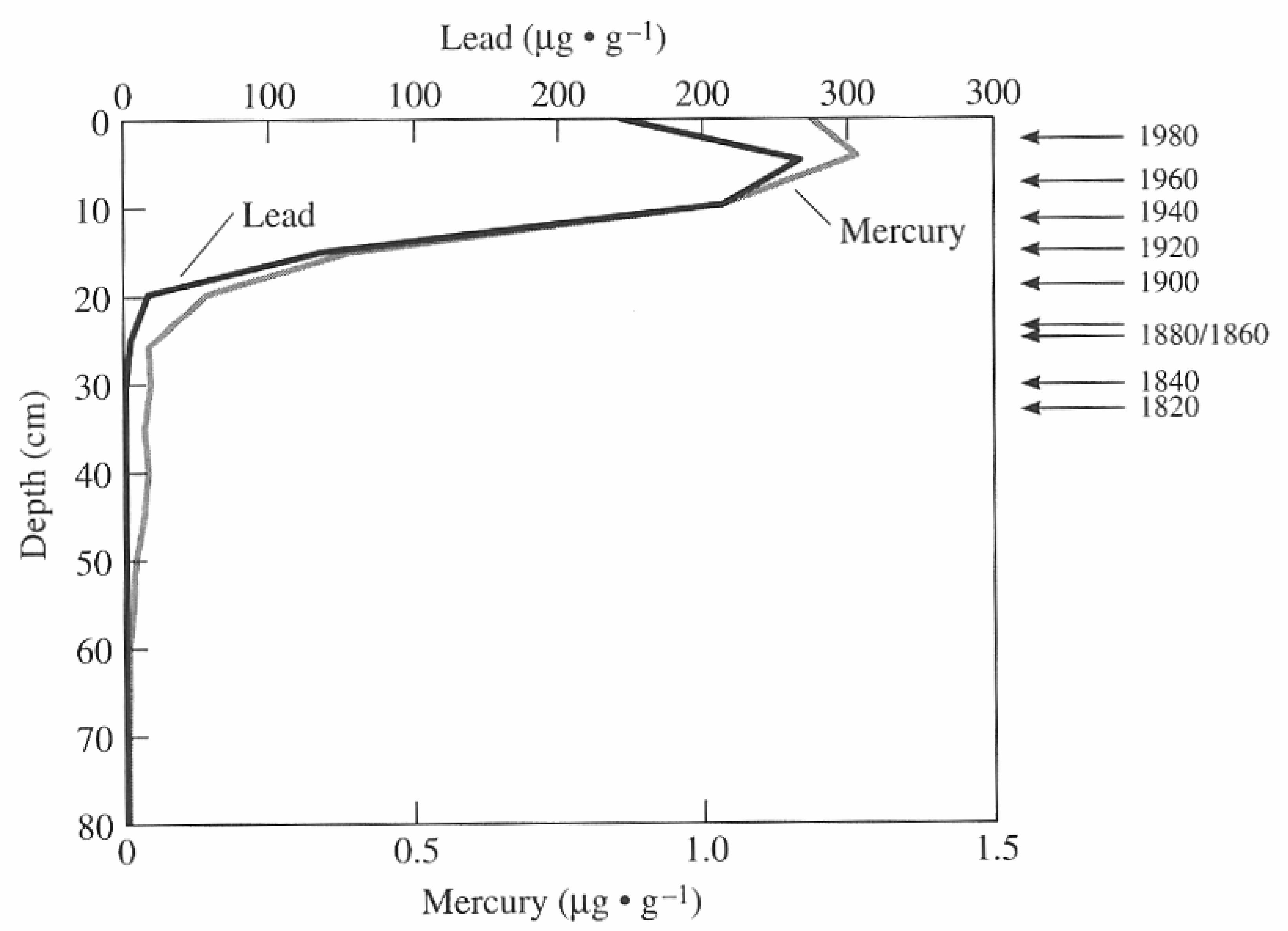


Figure 9-9. Baird, *Environmental Chemistry*, 1995

Diagnostic Tracers - Isotopic tracers

Isotopic systems to trace metals. Lead is not only used in concentrations but has a more complex isotopic history. Used in nature or in the human body.

- 238U ---> 206Pb 4.5 billion year half-life
- 235U ---> 207Pb 0.7 billion year half-life
- 232Th ---> 208Pb 12 billion years

Diagnostic Tracers – Pb isotopes

- Therefore, with different half-lives, there should be different amounts of these lead isotopes with different times in history.
- 206Pb/207Pb has moved from low to high through time.
- Ratio of the radio-isotopes with a stable isotope 204Pb.
- The ratio of 206Pb/204Pb was varied through time.
- Mexico, Chile, Peru : 1.2, 1.3 = lead from young igneous hydrothermal system less than 100 million years old.
- Canada, Australia: .9, 1.1 = old system greater than 1 billion year.

→ **Since these areas have characteristic lead isotope concentrations, one can trace the source of pollution by finding out what the ratio of the isotopes of lead are**

Diagnostic Tracers - by radioactive tracers

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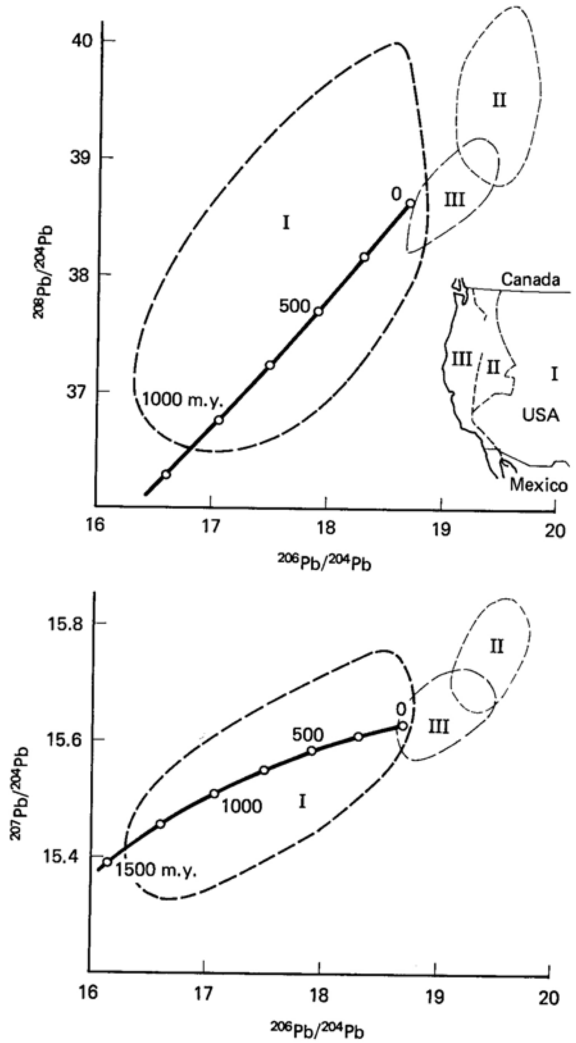


Figure 12.16 Lead isotopic ratios of young igneous rocks of the western United States (see inset map) define three metallogenic provinces I, II, and III. Calculated lead evolution curves (labelled with time in m.y.) demonstrate that these variations cannot be explained by *in situ* decay of U and Th after crystallization of these rocks. (Modified from Zartman 1974.)

URANIUM-THORIUM-LEAD SYSTEMATICS

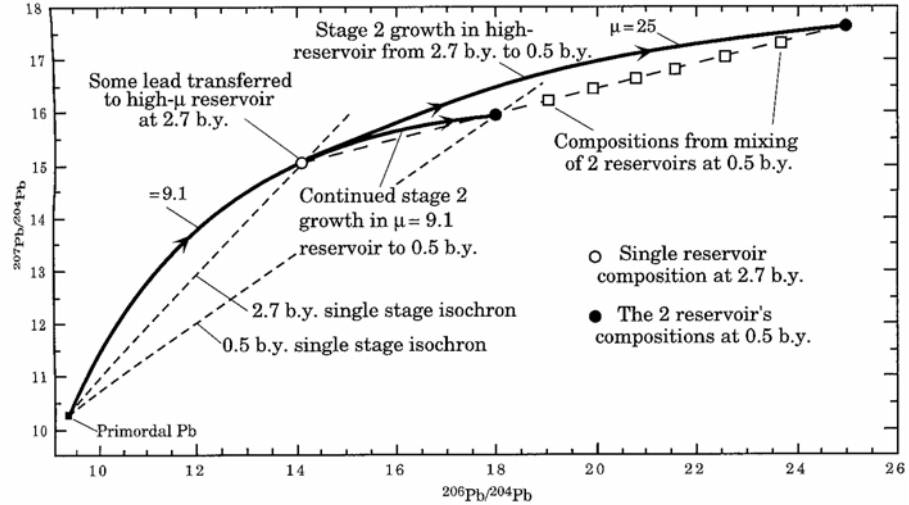


FIGURE 10-12 A two-stage Holmes-Houterman diagram for the development of common lead with stage 1 to 2.7 b.y. and stage 2 to 0.5 b.y. Note that the measured values occur to the right of a single stage 0.5 b.y. isochron. (From Long, 1999.)

RADIOACTIVE ISOTOPE GEOCHEMISTRY

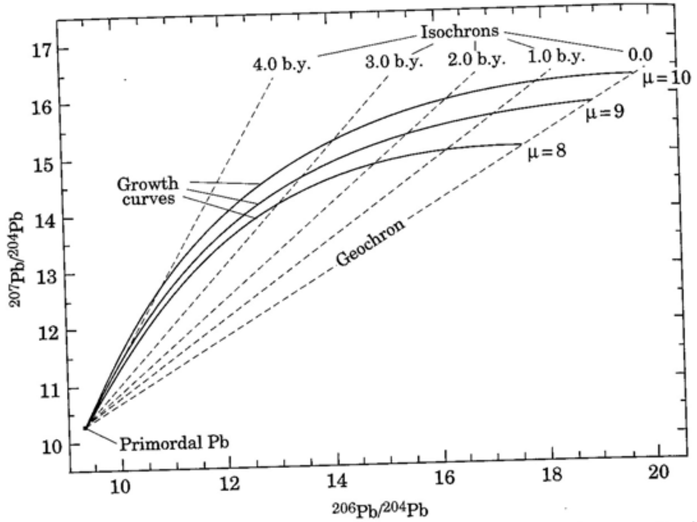
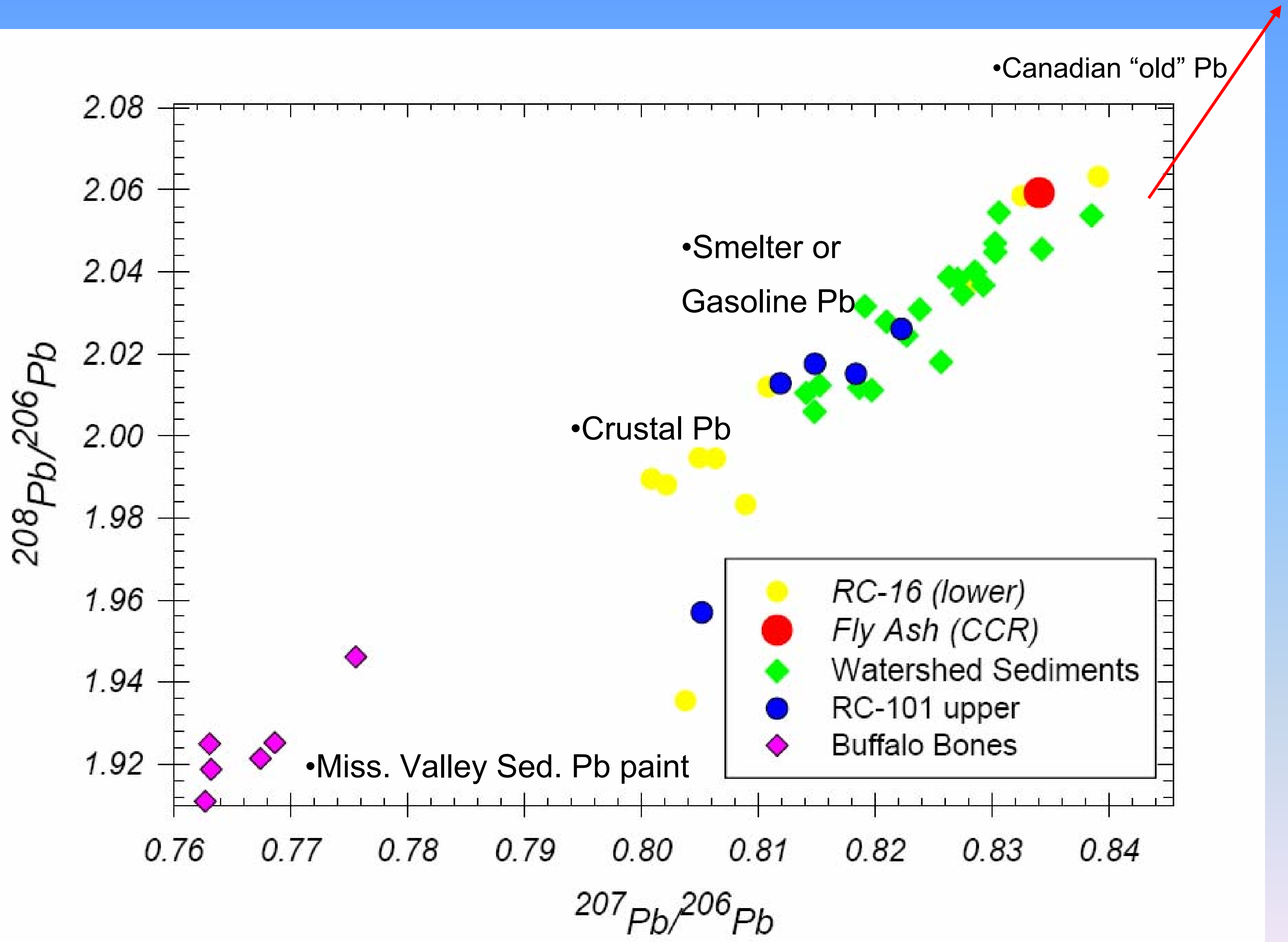


FIGURE 10-11 Holmes-Houterman diagram indicating the growth of common Pb isotope ratios from primordial values to predicted present day values for three different present day values of $\mu = {}^{238}U/{}^{204}Pb$.

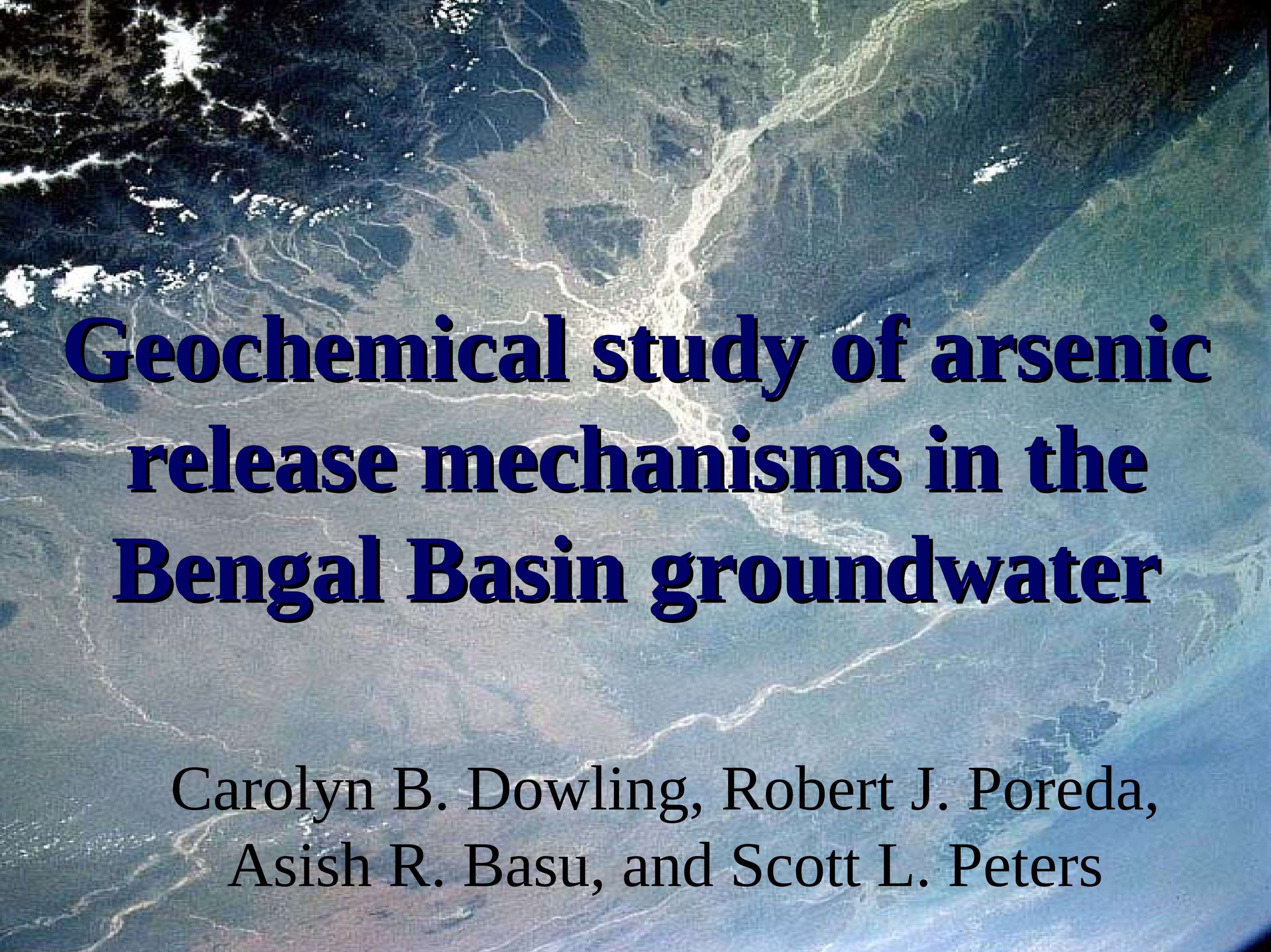


•Canadian “old” Pb

•Smelter or Gasoline Pb

•Crustal Pb

•Miss. Valley Sed. Pb paint



Geochemical study of arsenic release mechanisms in the Bengal Basin groundwater

Carolyn B. Dowling, Robert J. Poreda,
Asish R. Basu, and Scott L. Peters

Research Questions?

- Why do we care about Arsenic in groundwater?
- Is it a problem in the Bengal Basin?
- Which wells are contaminated by Arsenic?
  - Where are the wells located? What are their depths?
- Does As correlate with other elements?
- What are the sources of As?
  - Sediments? Industrial pollution? Agricultural pollution?
- Why is it a problem in the Bengal Basin?

Some Answers

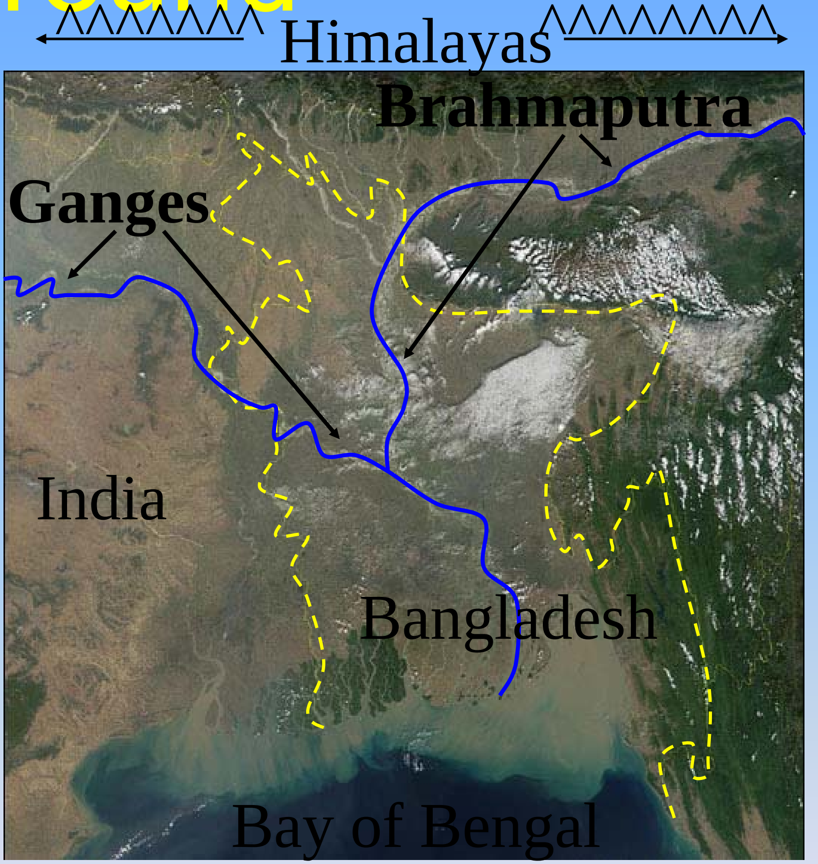
- Arsenic contamination is a real issue
- Source is natural
- Bulk sediments supplies As to the groundwater
  - Microbial mediated reduction of iron oxy-hydroxides
  - a.k.a. the microbial breakdown of FeOOH

Time Line

- World Health Organization (WHO)
  - Until 1970s, population used polluted rivers
  - Drilled 2 million groundwater wells
- Most wells are contaminated with arsenic (As)
  - Levels are greater than WHO maximum contaminant level (MCL) of 0.01 ppm or 0.13 μM
  - Symptoms of Arsenic poisoning develop slowly
  - 30-60% of the population is affected

Background

- Bangladesh and West Bengal State, India
- Quaternary deposits
  - Ganges-Brahmaputra
  - Himalayas
- Sea level changes and river migration
  - Complex stratigraphy of coarse and fine-grained sediment.



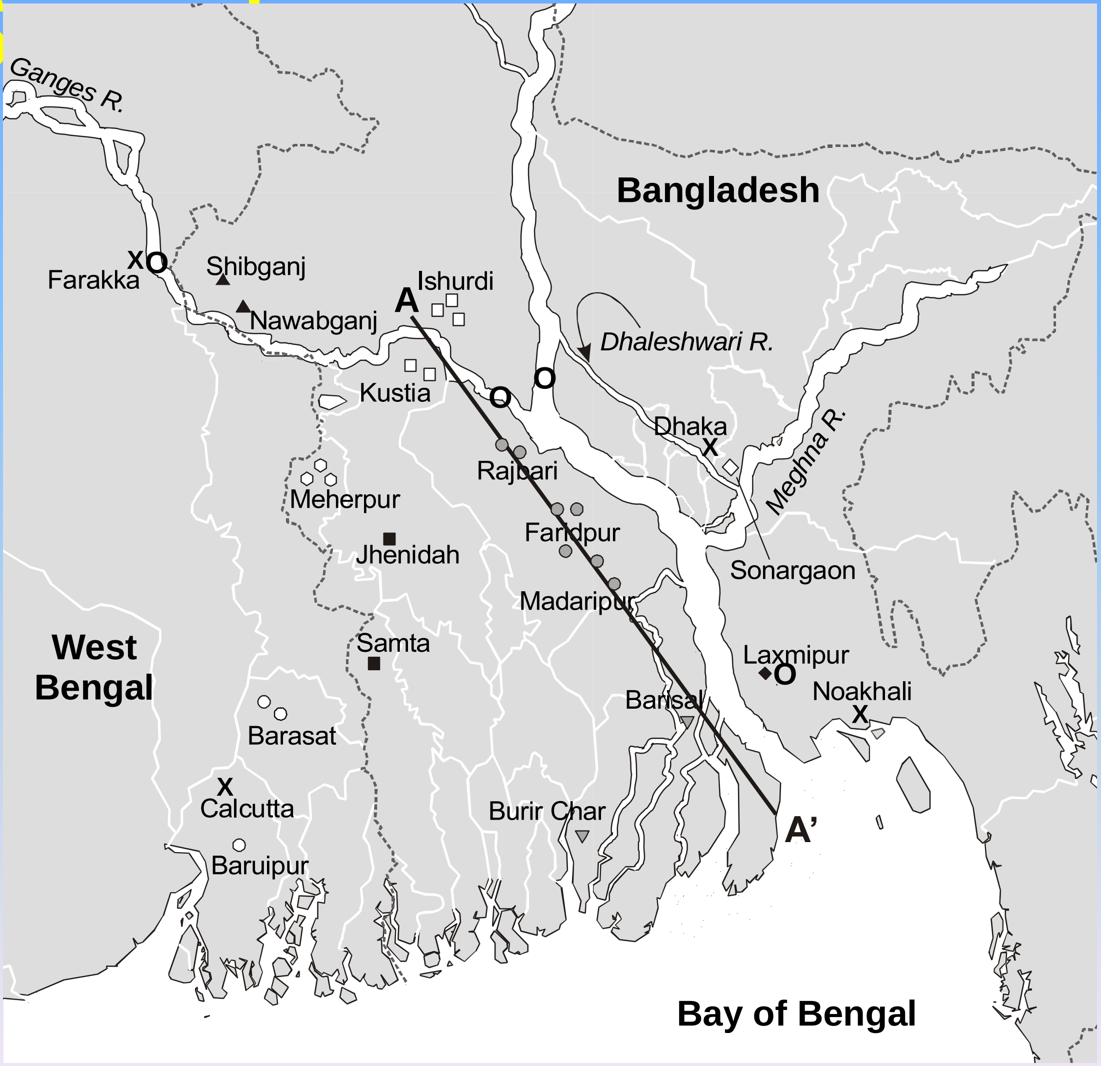
(Modified from http://www.geoexplorer.co.uk)

Sampling

- Where is the Arsenic located?
  - Groundwater chemistry
- Is the Arsenic coming from the sediments?
  - Sediment chemistry
- What is the watershed hydrology?
  - Groundwater flow

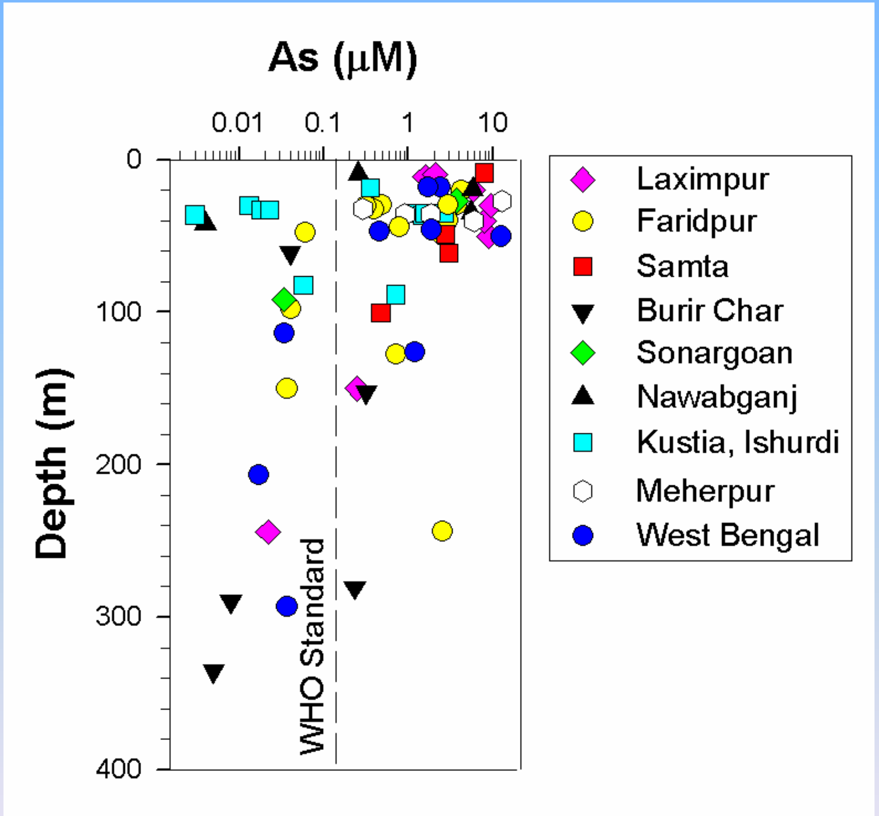
S

- Sixty-eight groundwater samples
  - Bangladesh
  - West Bengal (India)
- Sediment
  - Drill core
  - River



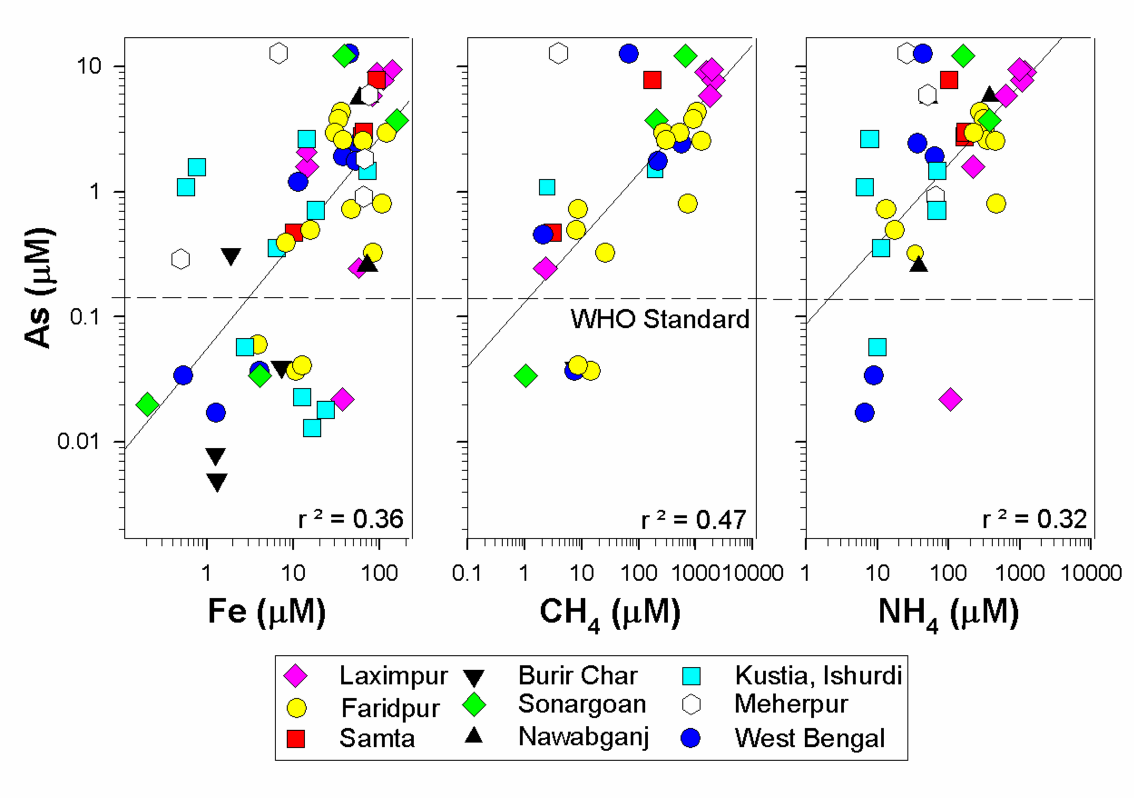
Groundwater Depth Profile

- Is As a problem?
  - More than 60% of samples above 0.13 μM
- Where are the wells?
  - Throughout the country
- What are the depths?
  - Highest levels of As at shallow depths (< 60 m)



Does As correlate with others?

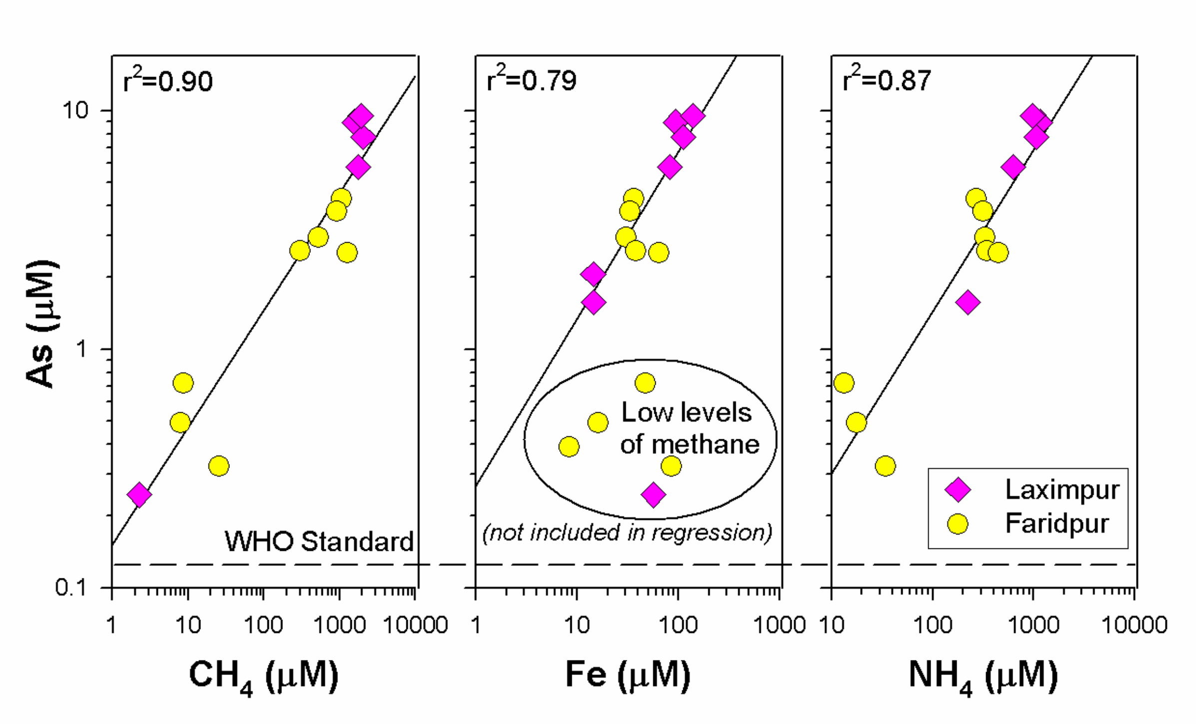
- Iron (Fe)
  - Previous studies link As and Fe
  - Weak correlation between As and Fe (r^2=0.37)
- Methane (CH_4) & Ammonia (NH_4)
  - Microbial activity
  - Weak to modest correlation (r^2: 0.39-0.55)



Correlations with Arsenic

Faridpur and Laxmipur

- As-rich areas
  - Faridpur
  - Laxmipur
- Strong correlations with CH_4, Fe, & NH_4 (r^2: 0.8-0.9)



Existing Theories of As Release

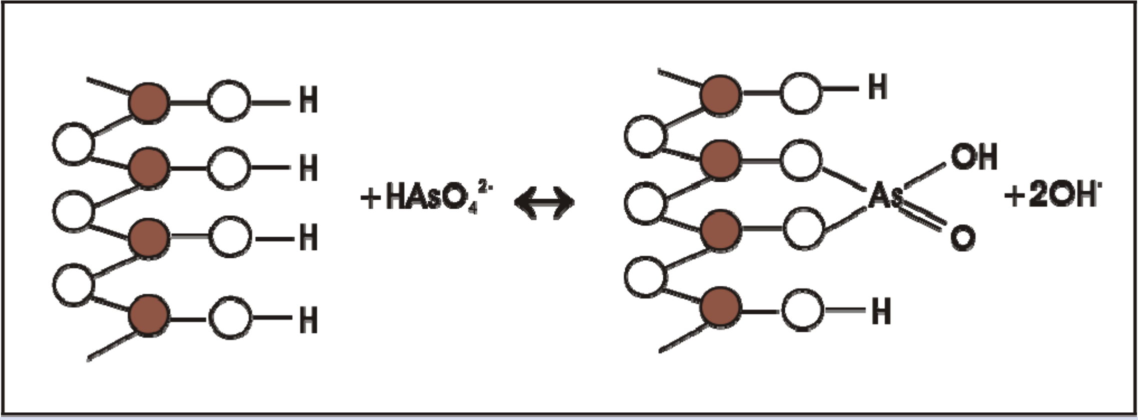
- Oxidation of pyrite *(Rarely used anymore)*
  - Requires oxic water
- Competitive exchange with phosphorus
  - Phosphate (PO_4^{3-})
  - Dissolved As and P exchange for one another
- Dissolution of iron oxy-hydroxides (FeOOH)
  - FeOOH strongly adsorb As
  - Correlation between Fe and As
  - Anaerobic microbes

Are microbes involved?

- As-CH_4 and As-NH_4 correlations
  - As microbes are oxidizing organic matter, they are breaking down FeOOH
  - Microbes converting As(V) to As(III)
  - Microbes
    - *Shewanella alga* BrY
    - MIT-13
    - *Geospirillum barnesii SES-3*

Arsenic Geochemistry

- Species
  - As(V), Arsenate, AsO_4^{3-}
  - As(III), Arsenite, $As_2O_4^{2-}$
    - 30-60X toxic and 5-10X mobile
- As strongly adsorbs onto iron oxy-hydroxides (FeOOH)



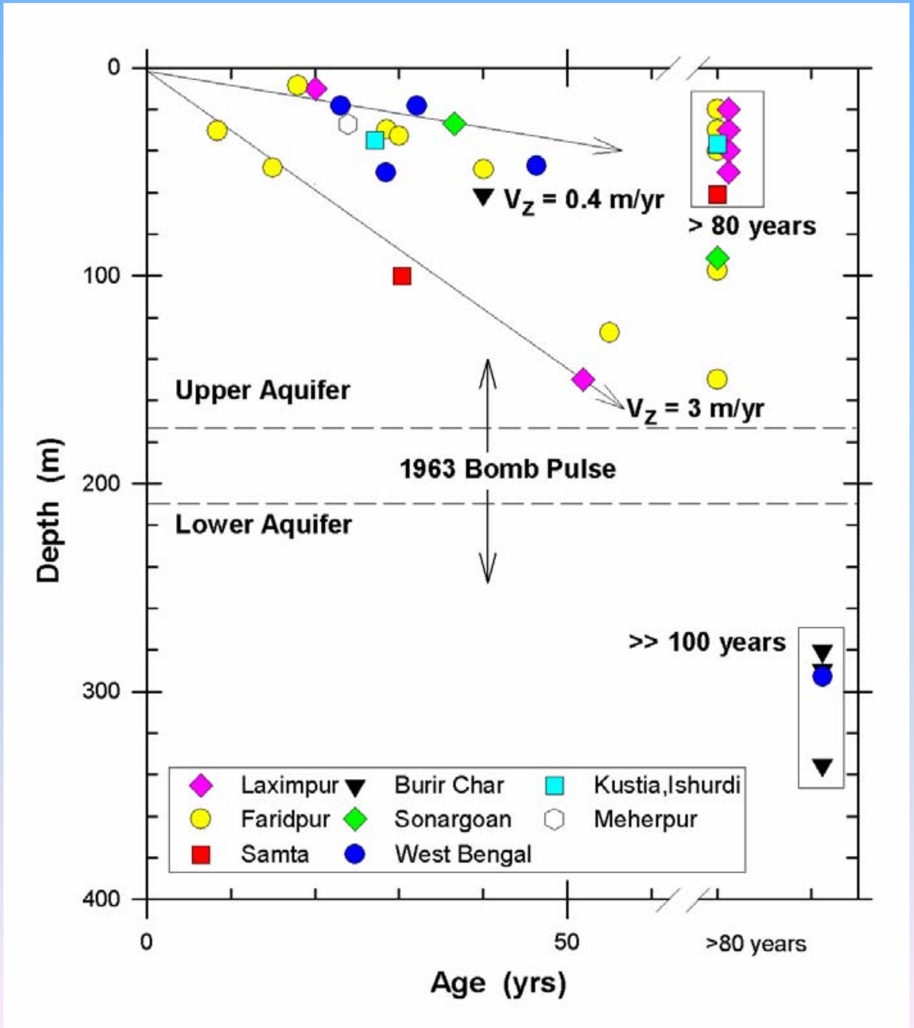
- As-laden FeOOH are deposited in estuaries and wetlands

Groundwater Age Dating

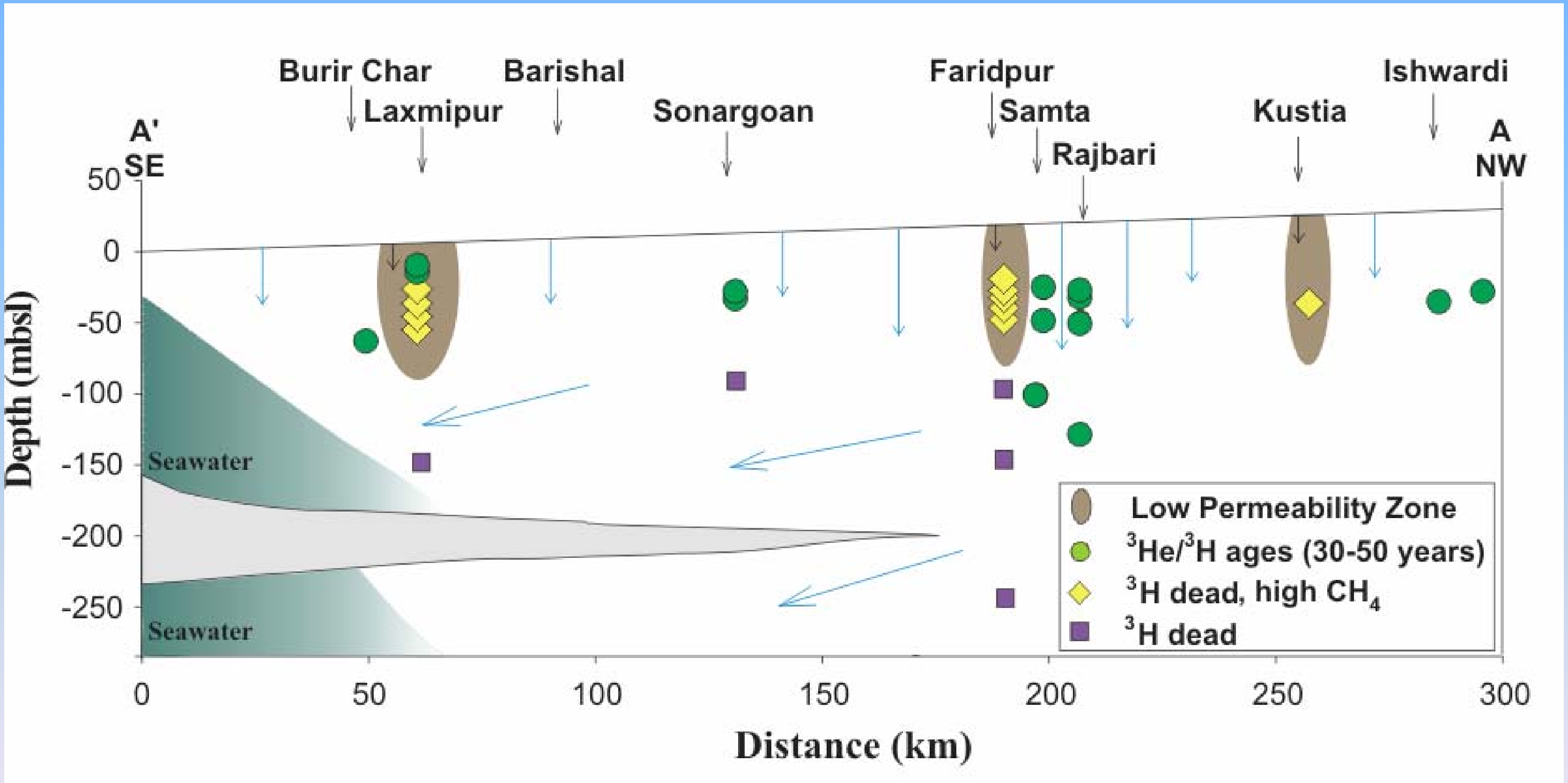
- $^3H/^3He$ Age Dating Technique
- Tritium (^3H) is formed
  - Above ground nuclear testing
  - Cosmogenic reactions ($^{14}N + n = {}^3H + {}^{12}C$)
- Component of water molecule (^3H_2O)
- ^3H decays to ^3He
  - $t_{1/2}=12.4$ yrs
- Groundwater residence time:
  - $t=(1/\lambda)\ln\{1+({}^3He^*/{}^3H)\}$

Groundwater Age Dating

- Variations in groundwater velocities
  - ~0.4 m/yr
  - ~3 m/yr
- Complicated stratigraphy
- Complex distribution of As

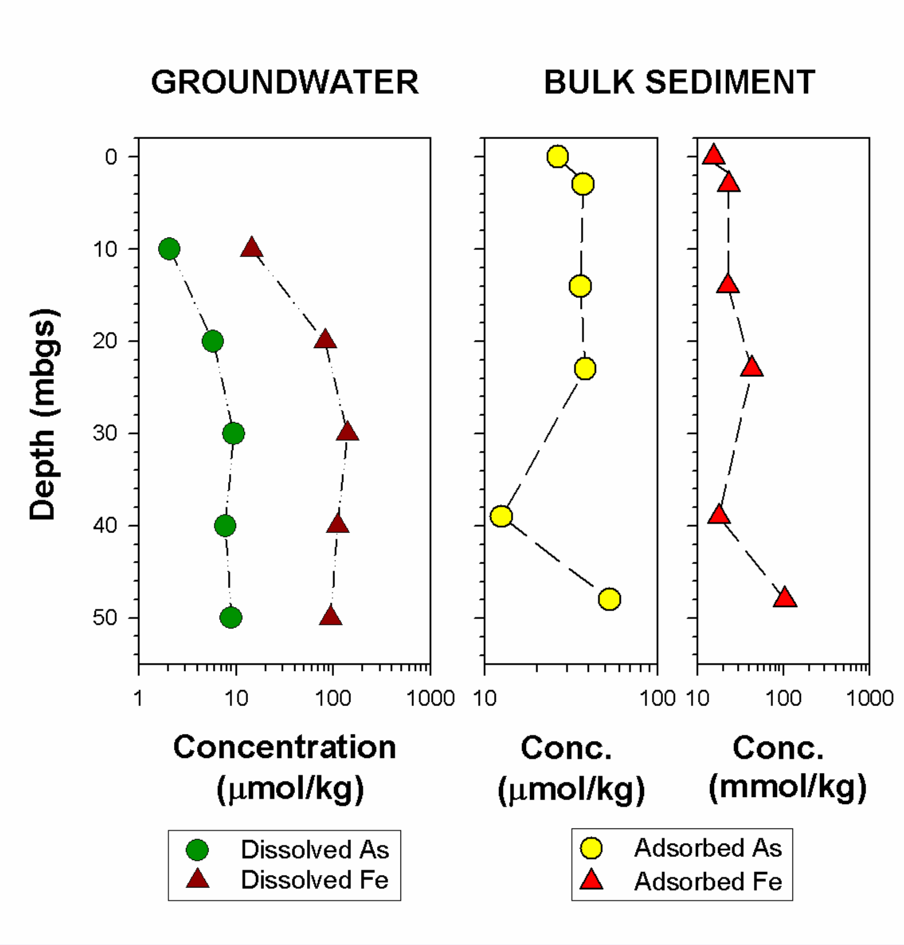


Watershed Hydrology



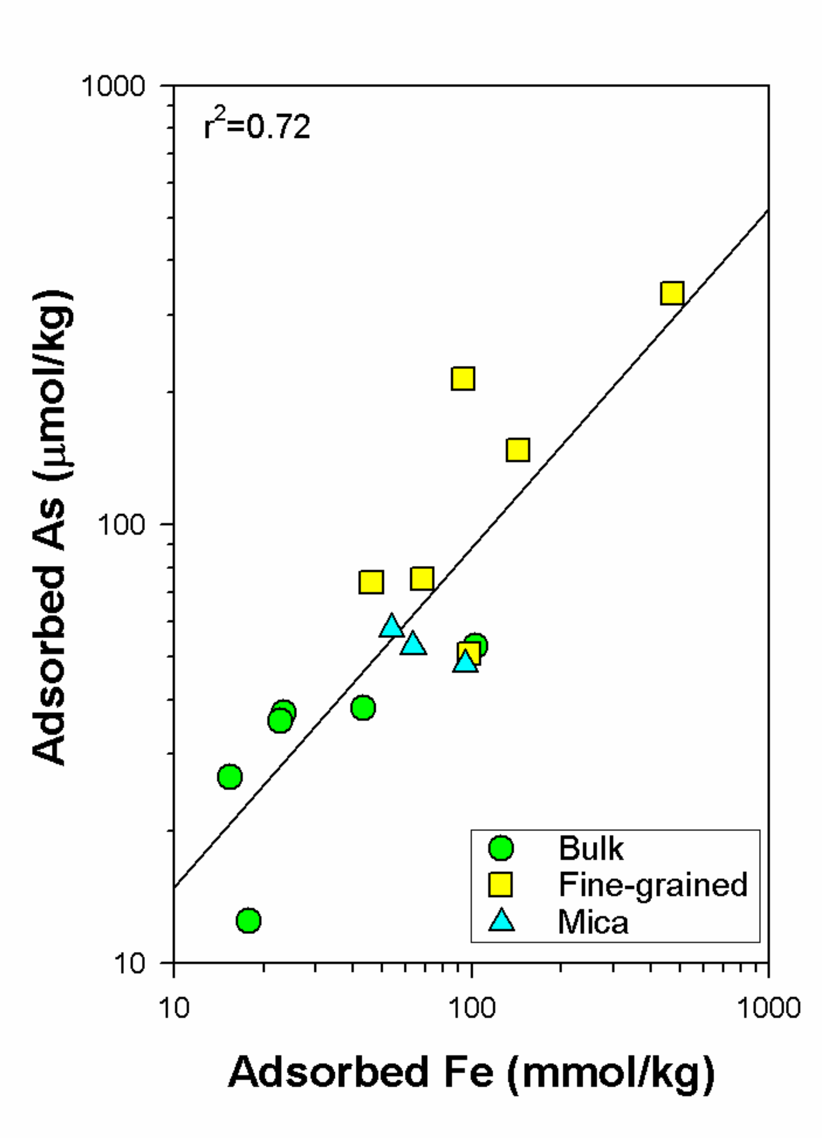
What is the source of As?

- Sediments influence groundwater
  - Mineralogy
  - Grain size
  - Adsorption/desorption
- Dissolved As and Fe have similar patterns
- Adsorbed As and Fe have comparable patterns
- Bulk capable of supplying As to groundwater



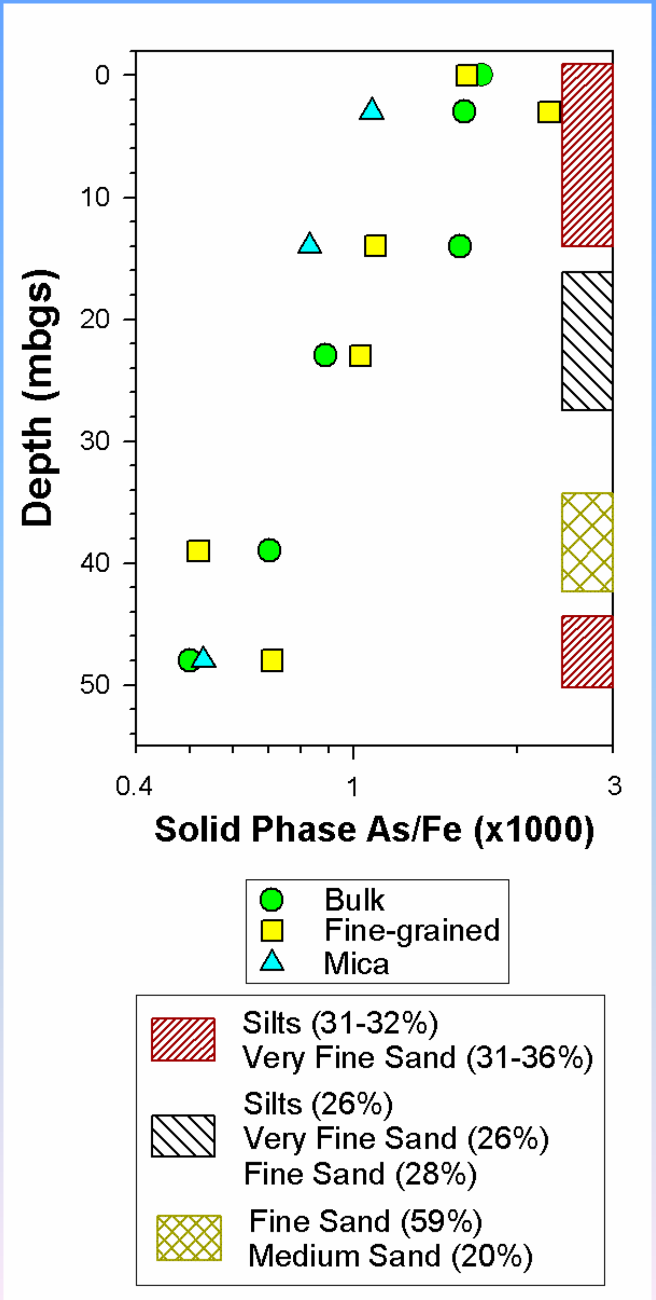
Sediment As Fe

- Modest correlation at any depth
  - r^2=0.7
- Sources of As and Fe in all solid phases may be the same
  - Microbial dissolution of FeOOH
- Grain size plays an important role

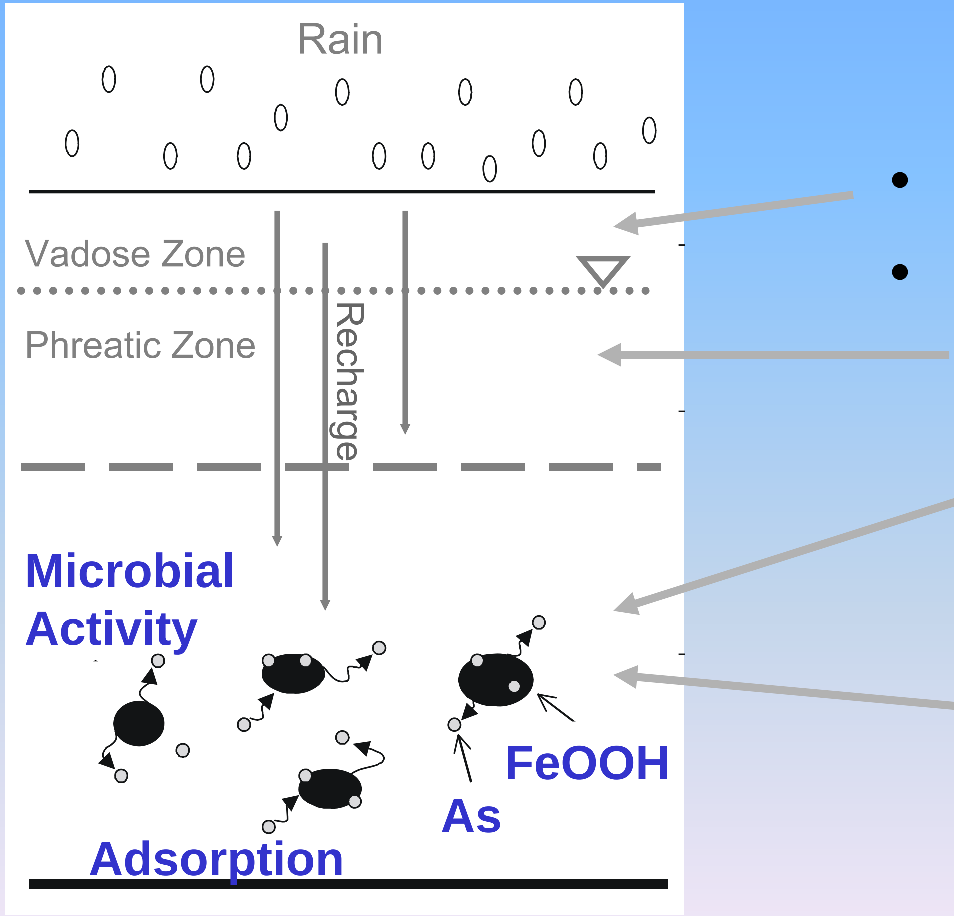


As/Fe Ratios with Depth

- As-Fe ratios decrease with depth
- More groundwater has flowed through the deeper sediments
- Removed As from deeper aquifer system



Overview of As Release



- Vadose Zone (unsaturated)
- Phreatic Zone (saturated)
  - Aerobic organisms consume O_2
  - Anaerobic microbes reduce FeOOH
    - Releases Fe and As
  - Dissolved As levels
    - Biological activity
    - Adsorption reactions

Summary

- As in groundwater
  - 30-60% population is affected
  - 60% of the samples above WHO MCL (0.13 μM)
  - Depth less than 60 m
  - Anoxic groundwater greater than 60 yrs
- Complicated distribution of As in groundwater

Summary

- Source of As
  - The As-laden sediments
  - Released from the sediments through microbes
  - Bulk sediments are capable of supplying all of the arsenic to the groundwater

Present

- The Bad News
  - Groundwater will have high arsenic levels for a very long period of time.
- The Good News
  - The drinking supply wells can be drilled to deeper depths.

(Modified from http://www.central.k12.ca.us)

- Universal Problem??
  - Rapid accumulation of sediments from Himalayas
    - Yangtze River
    - Irrawaddy River
    - Mekong River
  - Sea level changes and river migration
  - Mekong Delta, Vietnam