ECOTOXICOLOGY

Lecture 6

Inorganic contamination

Fundamental Differences Organics vs. Inorganics

- For inorganics, what is essential at one dose may be toxic at another dose
- Natural abundance of inorganics can be high (soils, plants, air)
- Inorganics are not degraded
  - Change form (complexation with organics, new ligands, speciation)
  - Changes in form may affect ability to be absorbed by plants, stored in certain tissues, or affect toxicity

Composition (mg/kg) of Soil Reflects Composition (mg/kg) in Bedrock

Element (Symbol)	Average Content in Crustal Rocks	Typical Content in Basalt Rocks	Common Range for Soils
Essential			
Chromium (Cr)	100	16.3	1 - 1,000
Cobalt (Co)	25		1 - 40
Copper (Cu)	55	22.4	2 - 100
Iron (Fe)	60,000		7,000 - 550,000
Manganese (Mn)	950		20 - 3,000
Molybdenum (Mo)	2.3		0.2 - 5
Nickel (Ni)	75	15.0	5 - 500
Selenium (Se)	0.09		0.1 -2
Tin (Sn)	2		2 - 200
Vanadium (V)	135		20 -500
Zinc (Zn)	70	132	10 - 300

Lindsay 1979

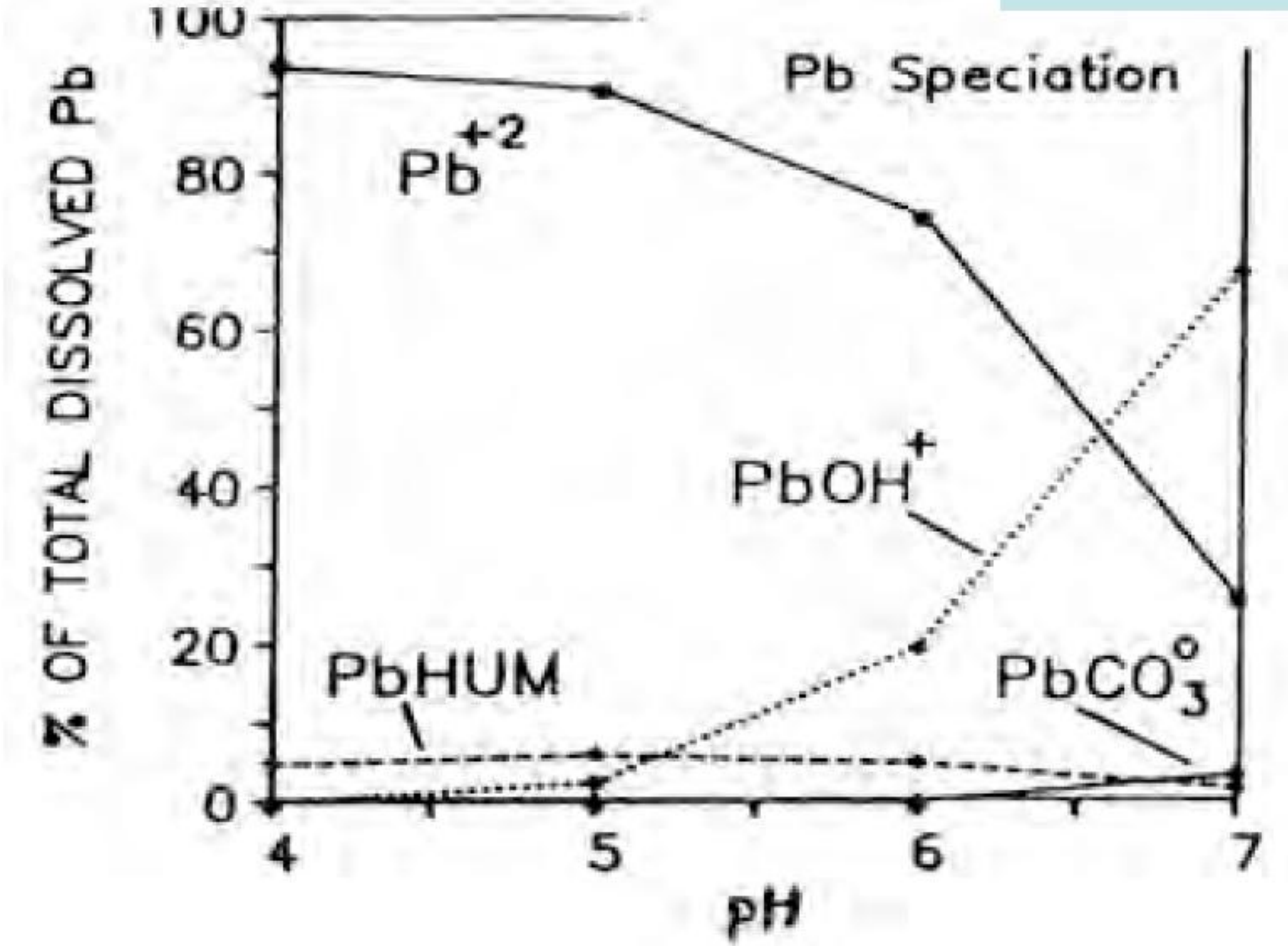
Composition (mg/kg) of Soil Reflects Composition (mg/kg) in Bedrock

Element (Symbol)	**Average Content in Crustal Rocks**	**Typical Content in Basalt Rocks**	**Common Range for Soils**
Nonessential			
Aluminum (Al)	81,000		10,000 - 300,000
Arsenic	**5**		**1 - 50**
Beryllium (Be)	2.8		0.1 - 40
Cadmium (Cd)	**0.2**	**0.07**	**0.01 - 0.70**
Lead (Pb)	**13**	**18.0**	**2 - 200**
Mercury (Hg)	0.1	0.01	0.01 - 0.3
Titanium (Ti)	6,000		1,000 - 10,000

Lindsay 1979

Speciation of Metals Influenced by pH

Brezonik et al. 1990



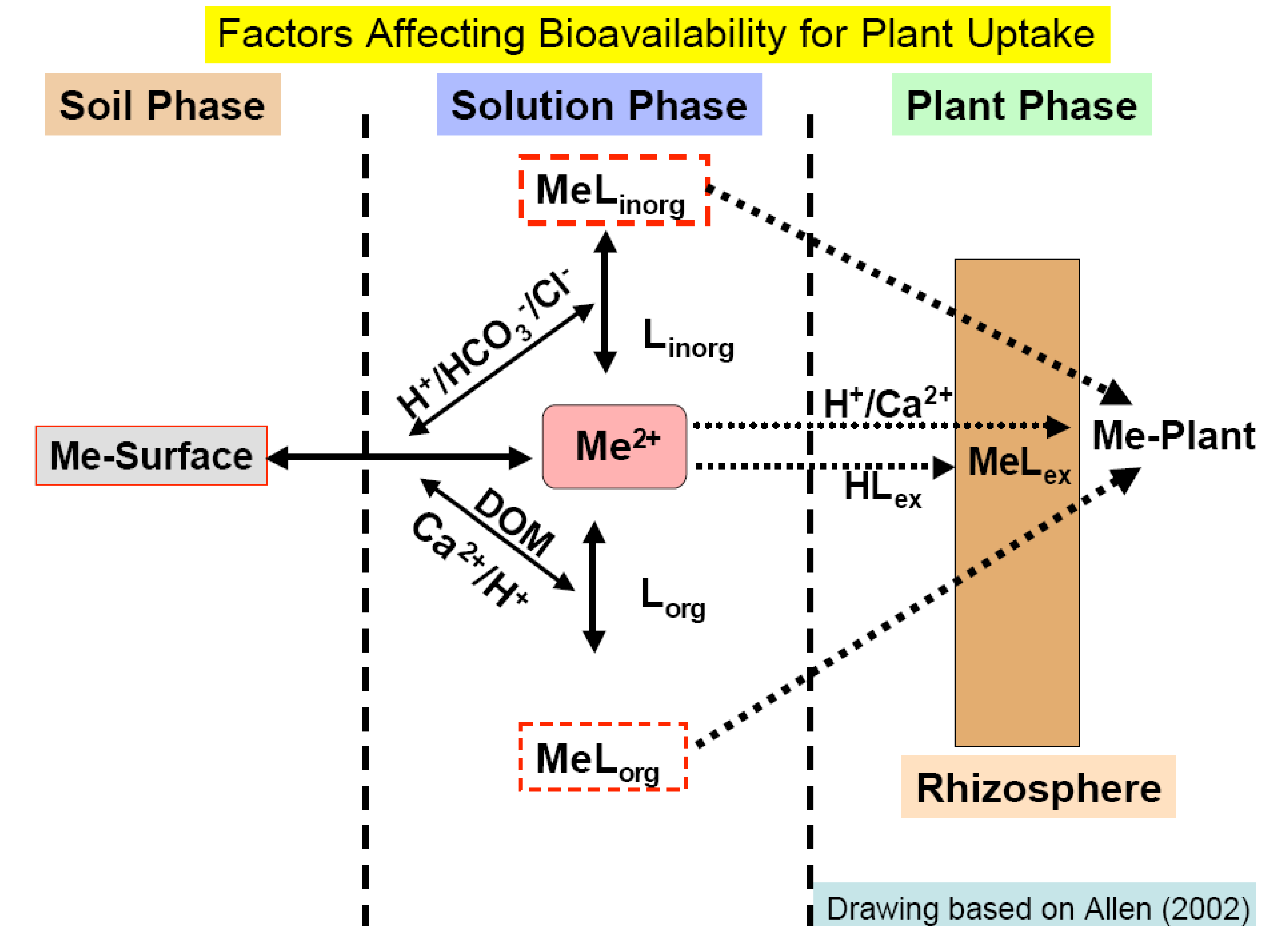
Variation in dissolved forms: lead

Global Discharge of Trace Metals (1000 metric tons/yr)

Nriagu & Pacyna (1988)

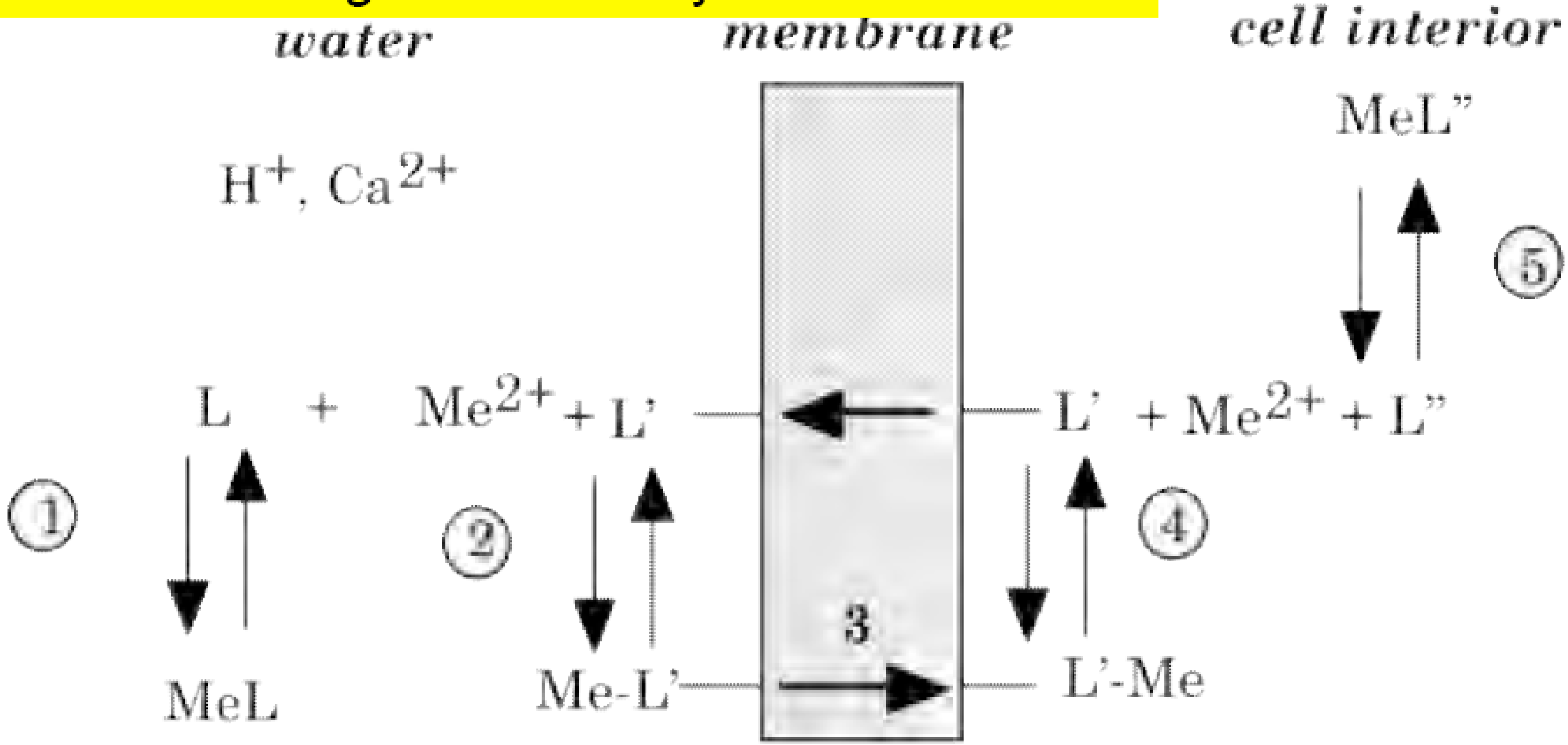
Metal	Water	Air	Soil
arsenic	41	19	82
cadmium	9.4	7.6	22
chromium	142	30	896
copper	112	35	954
lead	138	332	796
mercury	4.6	3.6	8.3
nickel	113	56	325
selenium	41	3.8	41
tin	no data	6.4	no data
zinc	226	132	1372

Largely industrial and municipal sources.
Note that fertilizer and sludge additions can also add metals to soil.

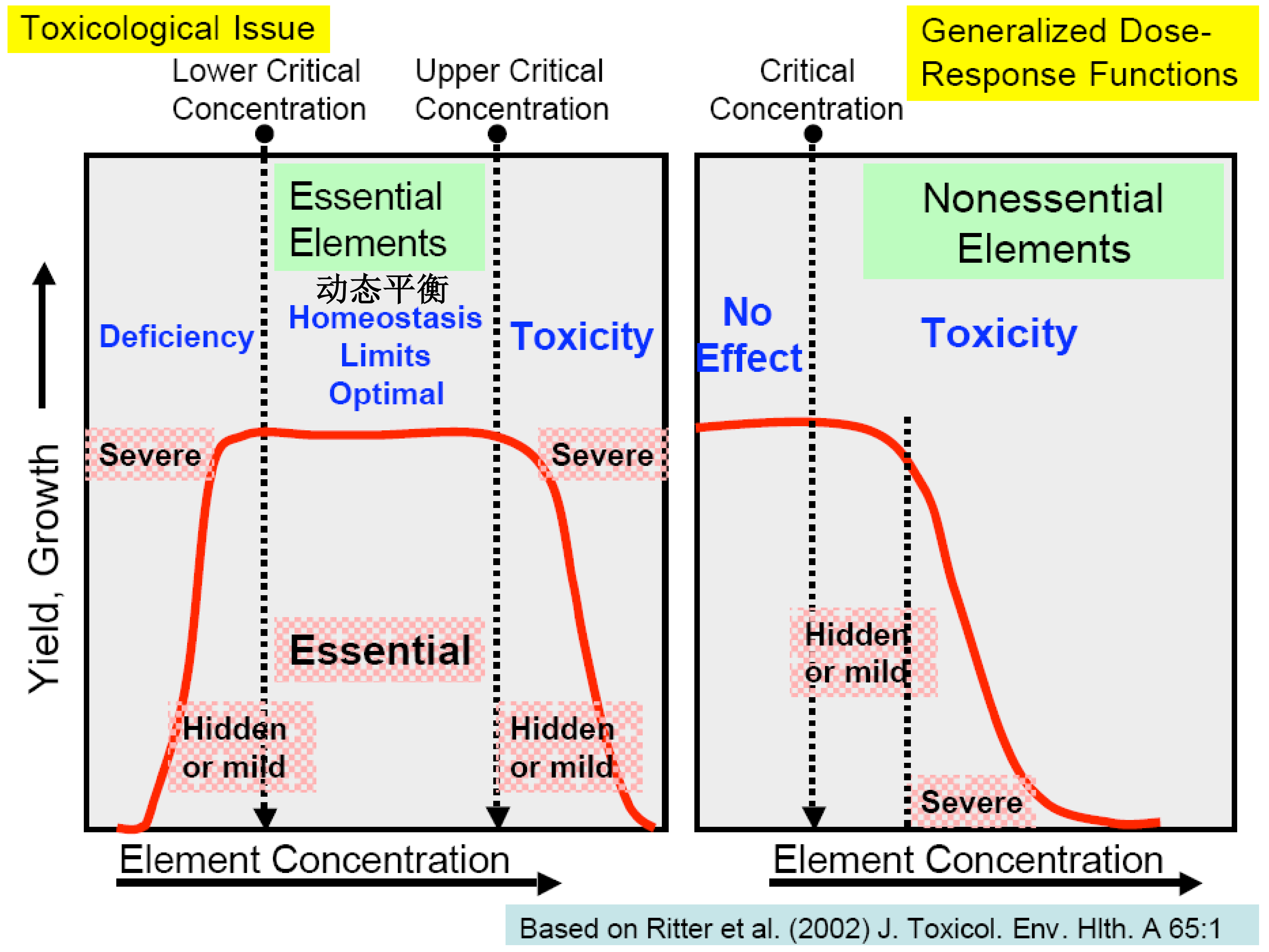


Factors Affecting Bioavailability for Plant Uptake
Soil Phase
Solution Phase
Plant Phase
MeL$_{inorg}$
H$^+$/HCO$_3^-$/Cl$^-$
L$_{inorg}$
H$^+$/Ca^{2+}
Me-Surface
Me^{2+}
MeL$_{ex}$
Me-Plant
HL$_{ex}$
DOM
Ca^{2+}/H$^+$
L$_{org}$
MeL$_{org}$
Rhizosphere
Drawing based on Allen (2002)

Factors Affecting Bioavailability to a Generic Cell



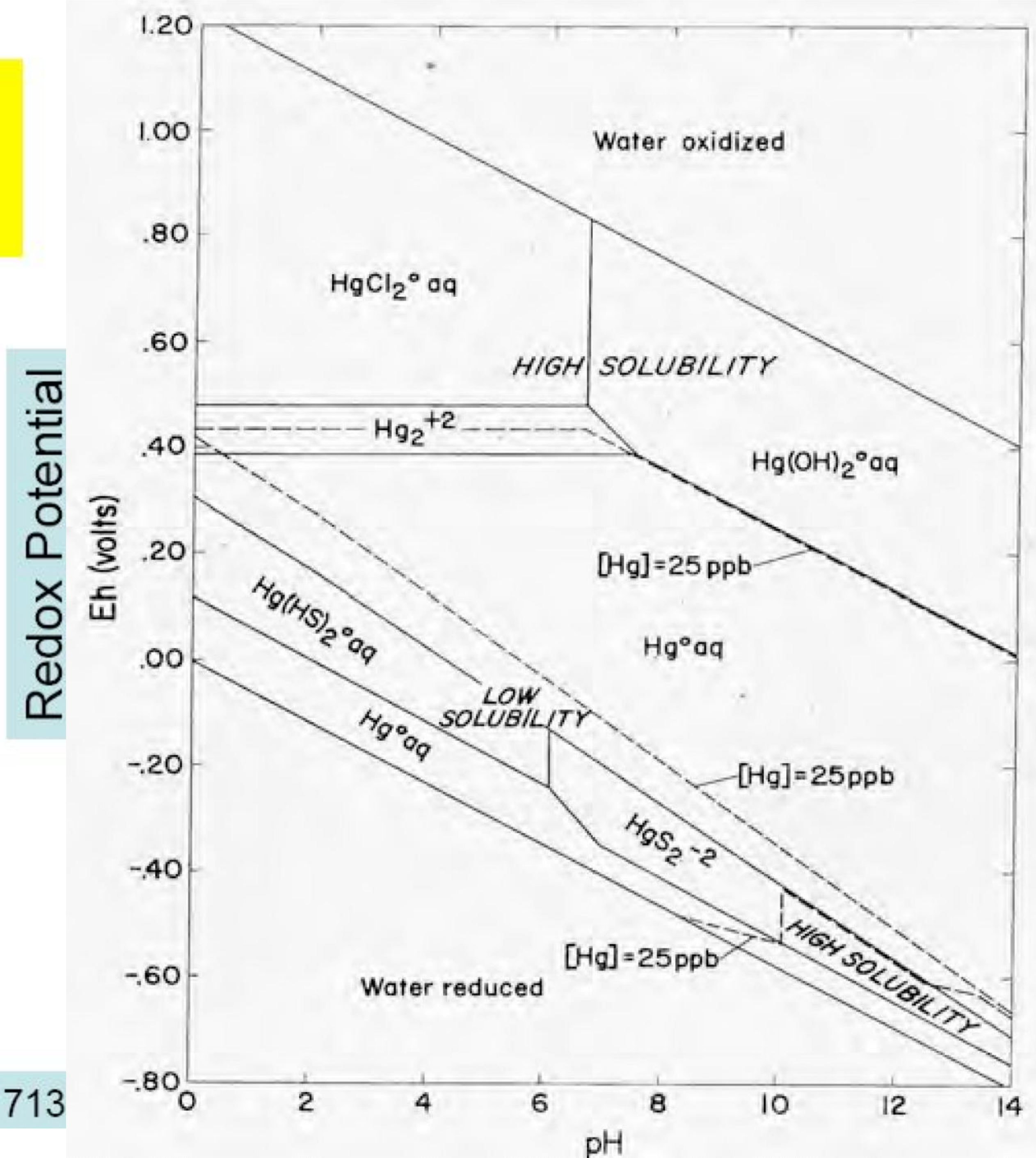
1. Metal & ligand associate in solution (MeL)
2. Metal ion binds to carrier protein (may be competition from H^+ and Ca^{2+})
3. Metal transported through cell membrane
4. Metal release in cell
5. Metal interacts with cellular protein


Toxicological Issue
Generalized Dose-Response Functions
Lower Critical Concentration
Upper Critical Concentration
Critical Concentration
Essential Elements
动态平衡
Homeostasis Limits Optimal
Deficiency
Toxicity
Severe
Severe
Essential
Hidden or mild
Hidden or mild
Nonessential Elements
No Effect
Toxicity
Hidden or mild
Severe
Yield, Growth
Element Concentration
Element Concentration
Based on Ritter et al. (2002) J. Toxicol. Env. Hlth. A 65:1

Mercury (Hg)

- Molecular wt. = 80
- Valence: +1 or +2
- Environmental forms
  - Metallic Hg (zero valence)
  - Inorganic (mercuric chloride, sulfides)
  - Organic (methyl mercury)
    - Considered the biologically active form regarding toxicity

Solubility of Hg relative to pH & redox potential



USGS Professional Paper 713

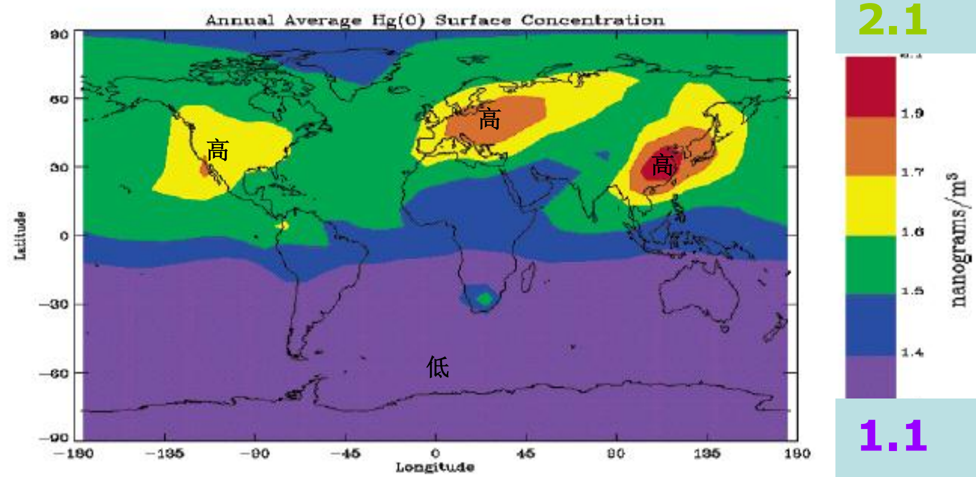
Worldwide Anthropogenic Input of Hg to Surface Waters

Source	Input (1000 metric tons/year)
Coal-burning power plants	0-3.6
Atmospheric fallout	0.22-1.8
Manufacturing processes	
Chemicals	0.02-1.5
Metals	0-0.75
Petroleum products	0-0.02
Domestic wastewater	
Central	0-0.18
Noncentral	0-0.42
Dumping of sewage sludge	0.01-0.31
Base metal mining and dressing	0-0.15
Smelting and refining, nonferrous metals	0-0.04

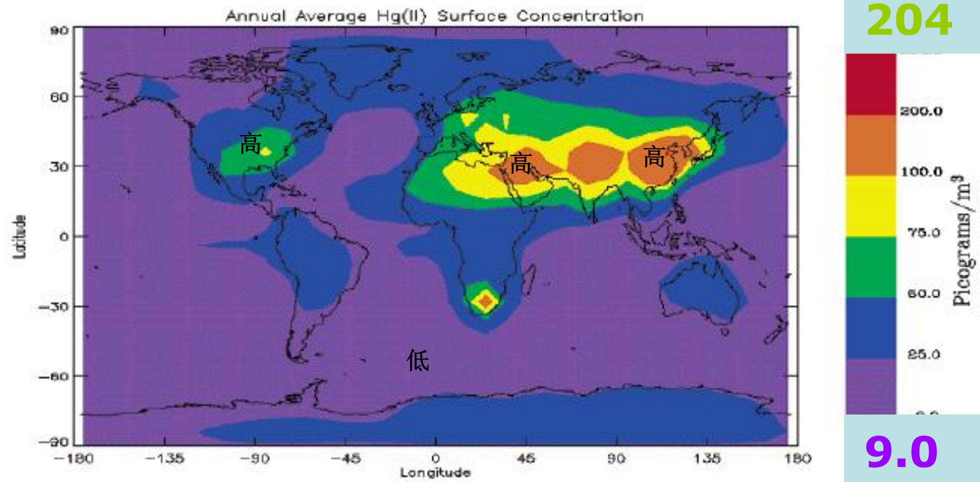
Moore 1991

- 全球地表Hg年均浓度分布图. Seigneur et al., 2004.

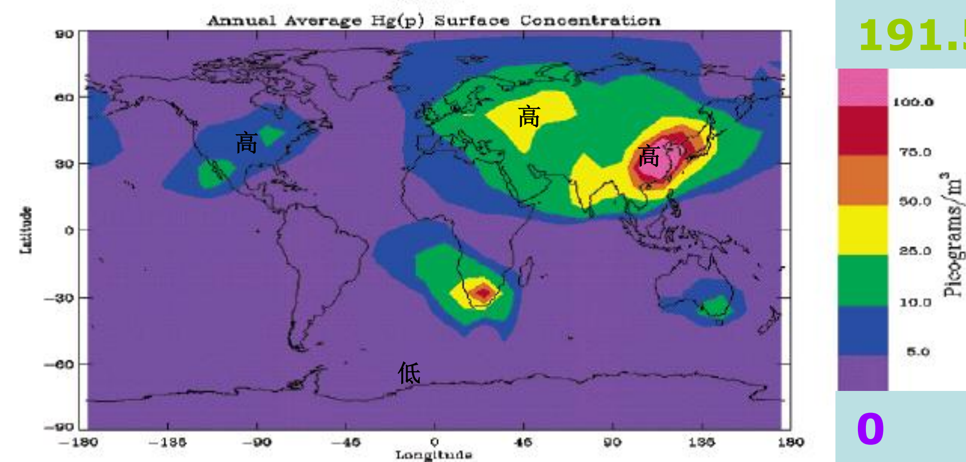
Hg(0) →



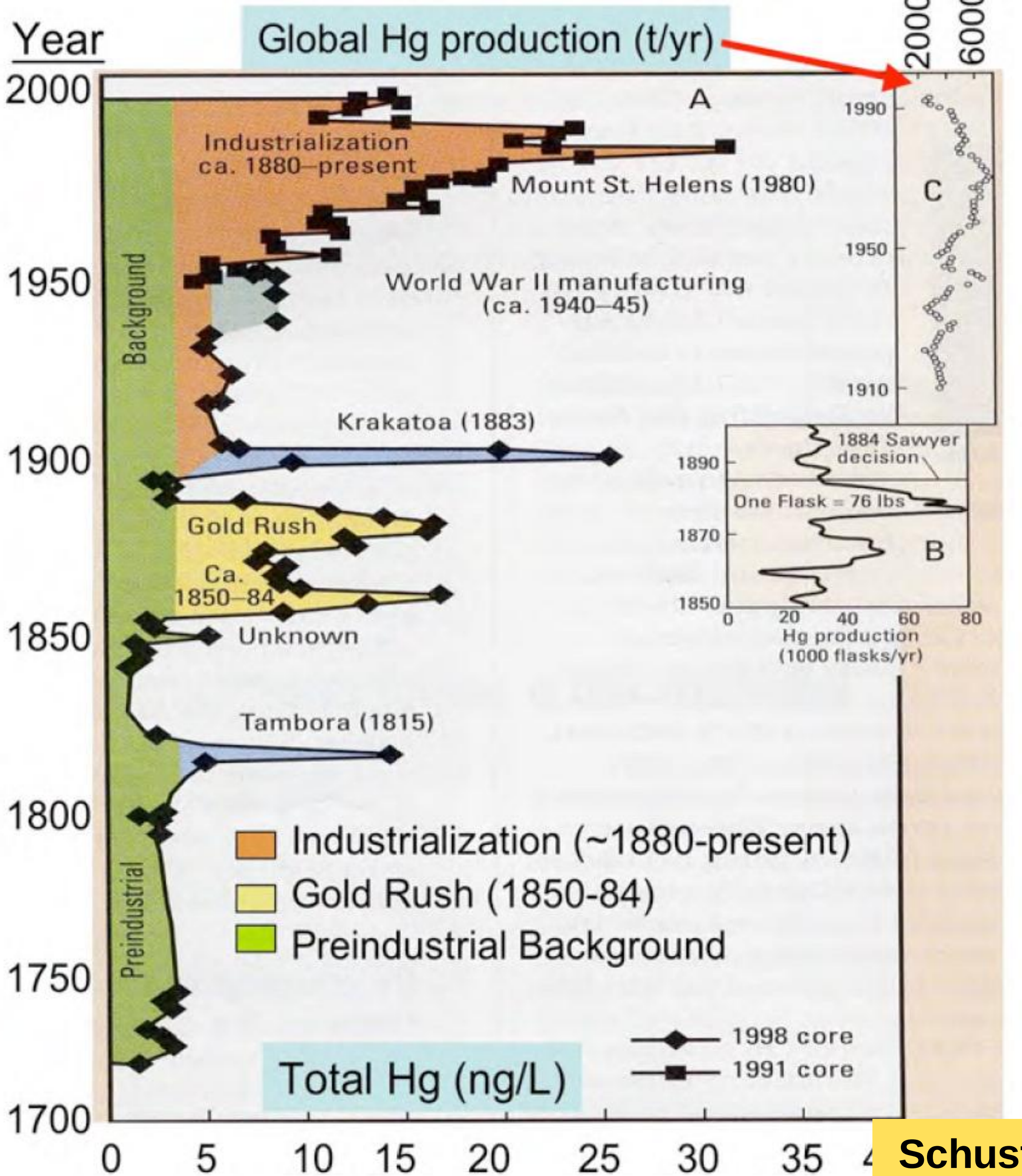
Hg(II) →



Hg(颗粒态) →



Historical Deposition



- Ice cores from Wyoming glacier
  - 1720-1993
  - Total Hg analysis
- Sources:
  - Anthropogenic: 52%
  - Volcanoes: 6%
  - Background: 42%
- Over last 100 years, anthropogenic sources contributed 70% of deposition
- Current record suggest a decline in atmospheric Hg deposition

Schuster et al. 2002 ES& T 36:2303

Toxicology

- Methyl mercury is the form of most concern
- Neurotoxicity, especially to developing fetus, but post natal exposure is also of concern
- Reference Dose protective of brain development in fetus is 0.1 μg/kg/day

Environmental Chemistry of Lead (Pb)

- Inorganic lead ubiquitous in soil environment (avg. ~15-25 mg/kg)
- Group IV element (includes C and Si) but does not bind with itself
- Stable +2 and +4 oxidation states
- In freshwater forms low solubility complexes with anions: hydroxide, carbonate, sulfides, sulfates
- Chelates with humic and fulvic acids
- Solubility increases as pH is lowered
- ~75% of lead in rivers is in suspension, 25% in solution

Anthropogenic Sources

- Banned pesticide “lead arsenate”
- Refuse incineration
  废物
- Coal combustion
- Production of chemicals, including caulking 堵塞材料 compounds, paint pigments, solder, cable 焊料 covering, ammunition, storage batteries
  弹药 蓄电池
- Manufacture of glass & ceramics
- **Combustion of fuels containing lead additives**
  - **Organoleads (a.k.a. alkylleads, esp. tetraethyl Pb) added to gasoline starting ~1923** 四乙基铅

Fuel Emissions

- Alkyl leads added as anti-knock compound to achieve better fuel combustion
- 20-55% of lead consumed by an engine is exhausted
- Emitted as lead halides, chiefly as PbBrCl or as $PbCl_2$ 卤化物
  - The Cl comes from the exhaust system scavengers, ethylene dichloride and ethylene dibromide

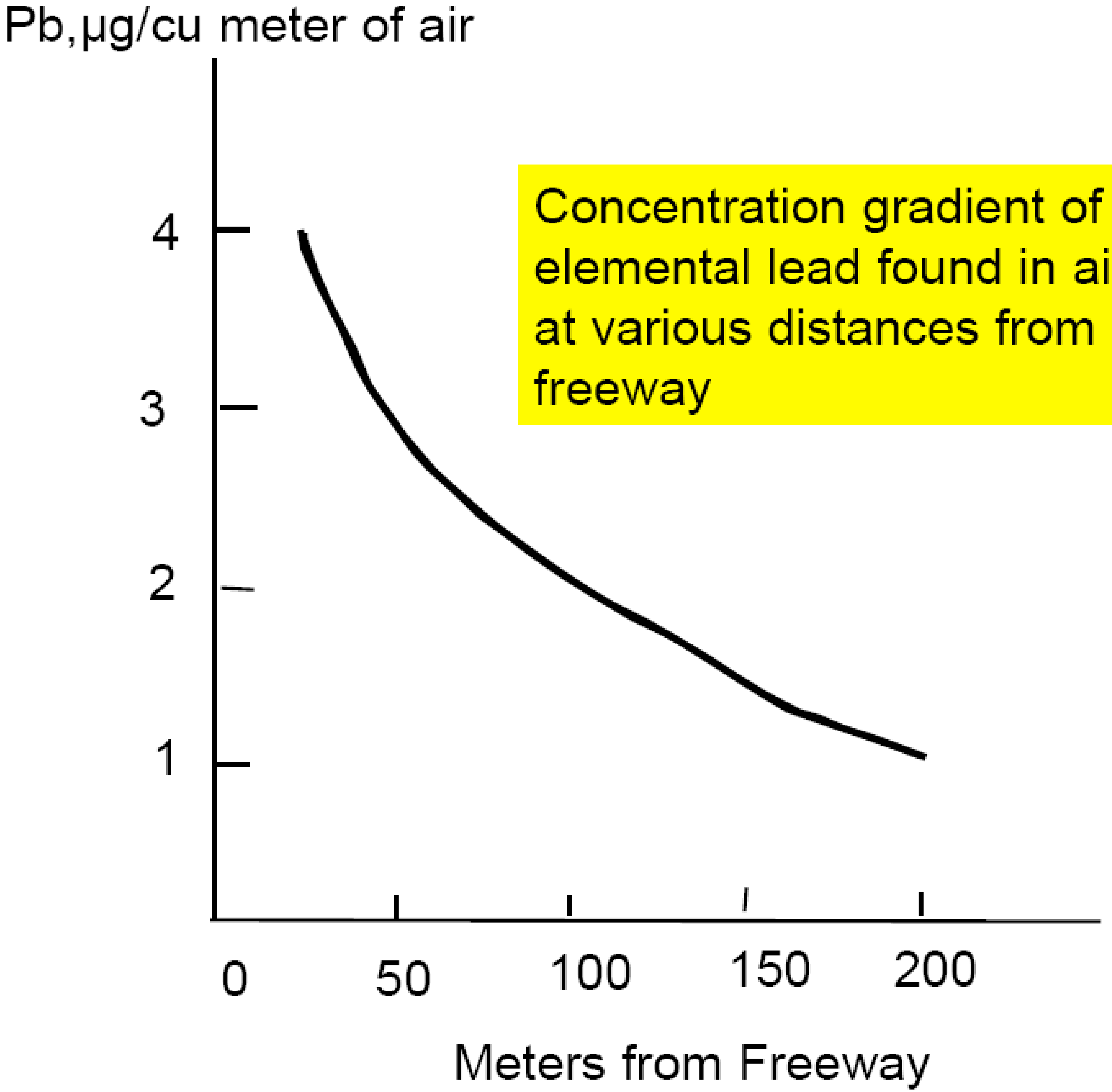
净化剂 二氯乙烯 二溴乙烯

- ~18 h after emission, 30-40% of chlorides and 75% of bromides transformed into carbonates and oxides
- Aerosol-bound lead precipitated by rainfall
  - 50-90% of lead particles are less than 1 μm diam.

Nano-particles

Deposition

- Sedimentation and rainfall are responsible for widespread lead distribution
  - In late 1960's, average concentrations in precipitation were ~35-40 μg/L
  - Roadside concentrations (measured as elemental Pb) were much higher than concentrations measured at a distance



Concentration gradient of elemental lead found in air at various distances from a freeway

Lead species in rainwater runoff, soils, and dust in an urban environment; note the amount of organic bound lead

Sample	Total Pb mg/kg	Organic Bound mg/kg	Extractable mg/kg	Triethyl Pb µg/kg	Diethyl Pb µg/kg
First rainwater runoff; 5 m from gas station, residential area	-	1.45	1.39	0.16	1.8
First runoff, 45 m from gas station, urban area	2.6	0.37	-	0.40	0.47
First runoff; busy street intersection, urban area	17.9	17	8.5	0.28	0.36
Soil from a park; 5 m from bust street, urban area	568	248	132	1.2	10
Soil from a potted tree; 1 m from busy street, urban area	50	14	13	0.7	4
Street dust; busy street; urban	1669	1313	305	8	42
Street dust; 5 m from a gas station; urban area	1062	377	447	29	166

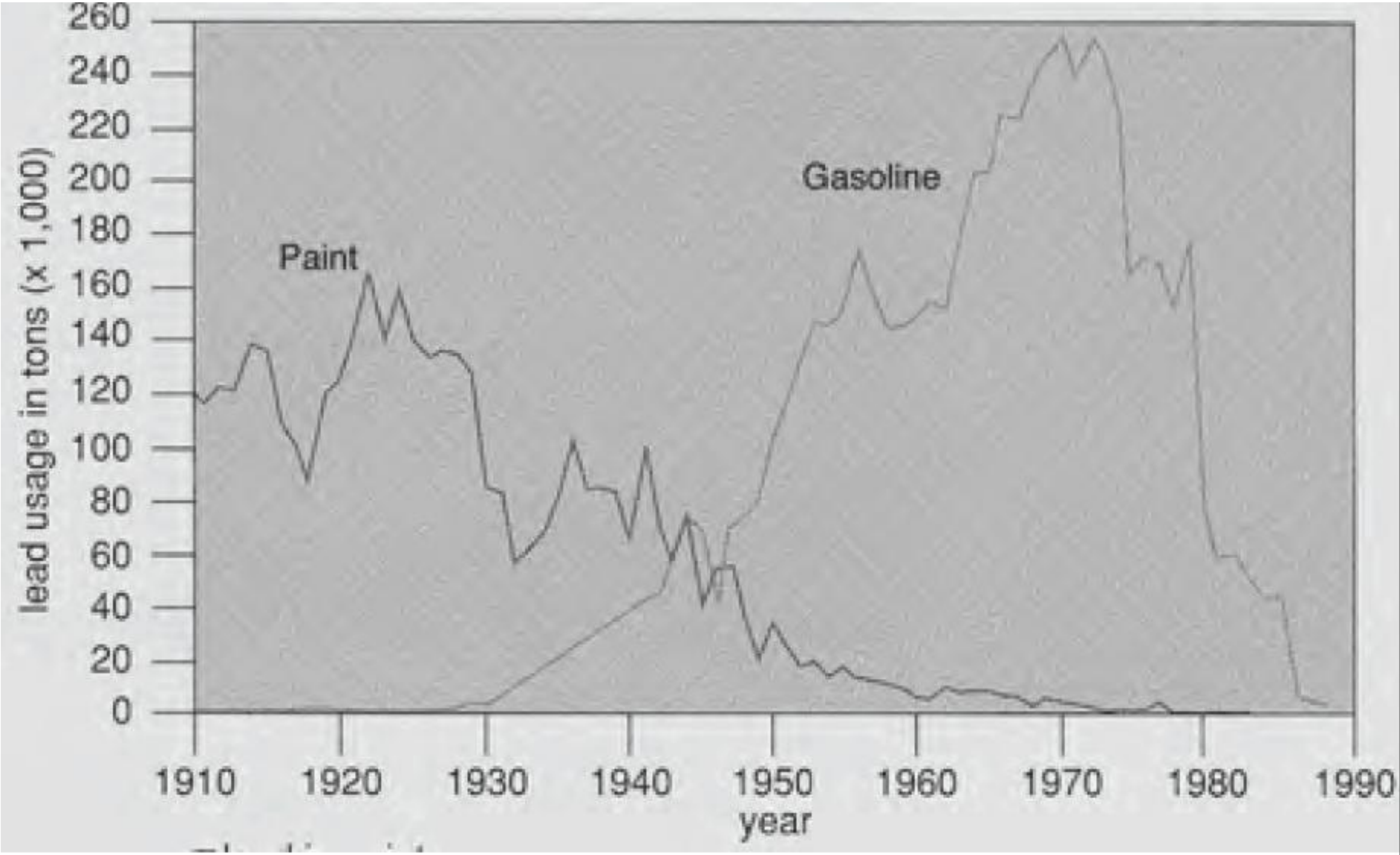
Blais & Marshall (1986) JEQ v. 15

Disposition of Organolead in Soils Spiked with Triethyl- and Diethyl Lead; note that DDTA extracts represent organolead; phosphate buffer represents non-lead organics

Soil Depth (cm)	^{14}CO	Hexane-NaDDTA	Phosphate Buffer	Nonextract ^{14}C	Recovery (% of adde
14C-triethyl lead					
0-15	15.4	22.1	9.4	27.8	74.7
15-30	16.0	20.7	6.0	23.8	66.5
30-45	16.2	20.7	3.0	28.5	68.4
14C-diethyl lead					
0-15	18.3	23.5	11.2	37.0	90.0
15-30	19.4	7.6	10.3	32.7	70.0
30-45	19.2	8.3	6.0	21.2	54.7

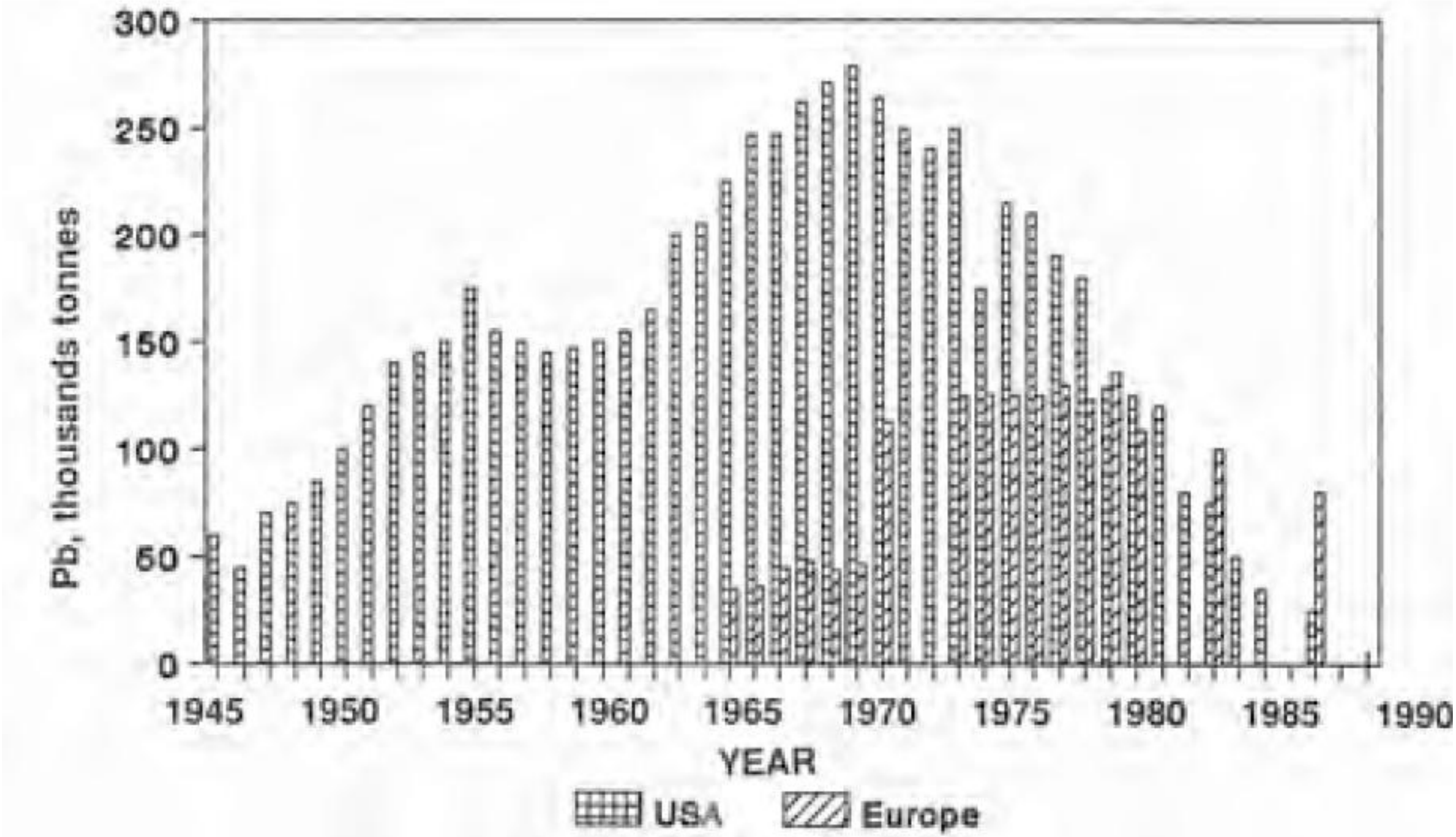
Sterilization of the soil resulted in significant decrease in mineralization (production of $^{14}CO_2$)

Ou et al. (1995) ETAC 14:545



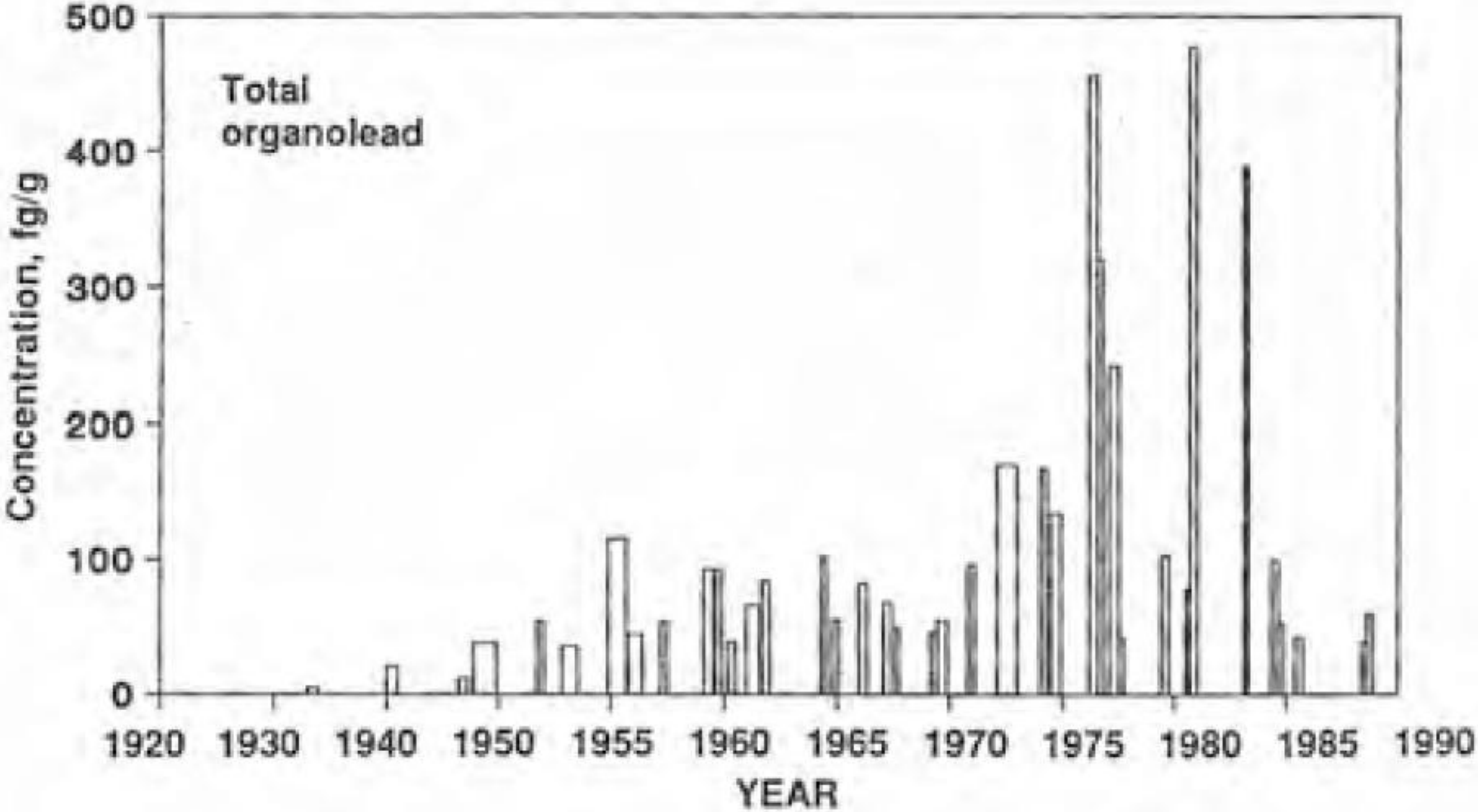
Historical use of lead in gasoline in comparison to use in paint

Mielke (199) Am. Sci.



Historical Use of Lead in Gasoline

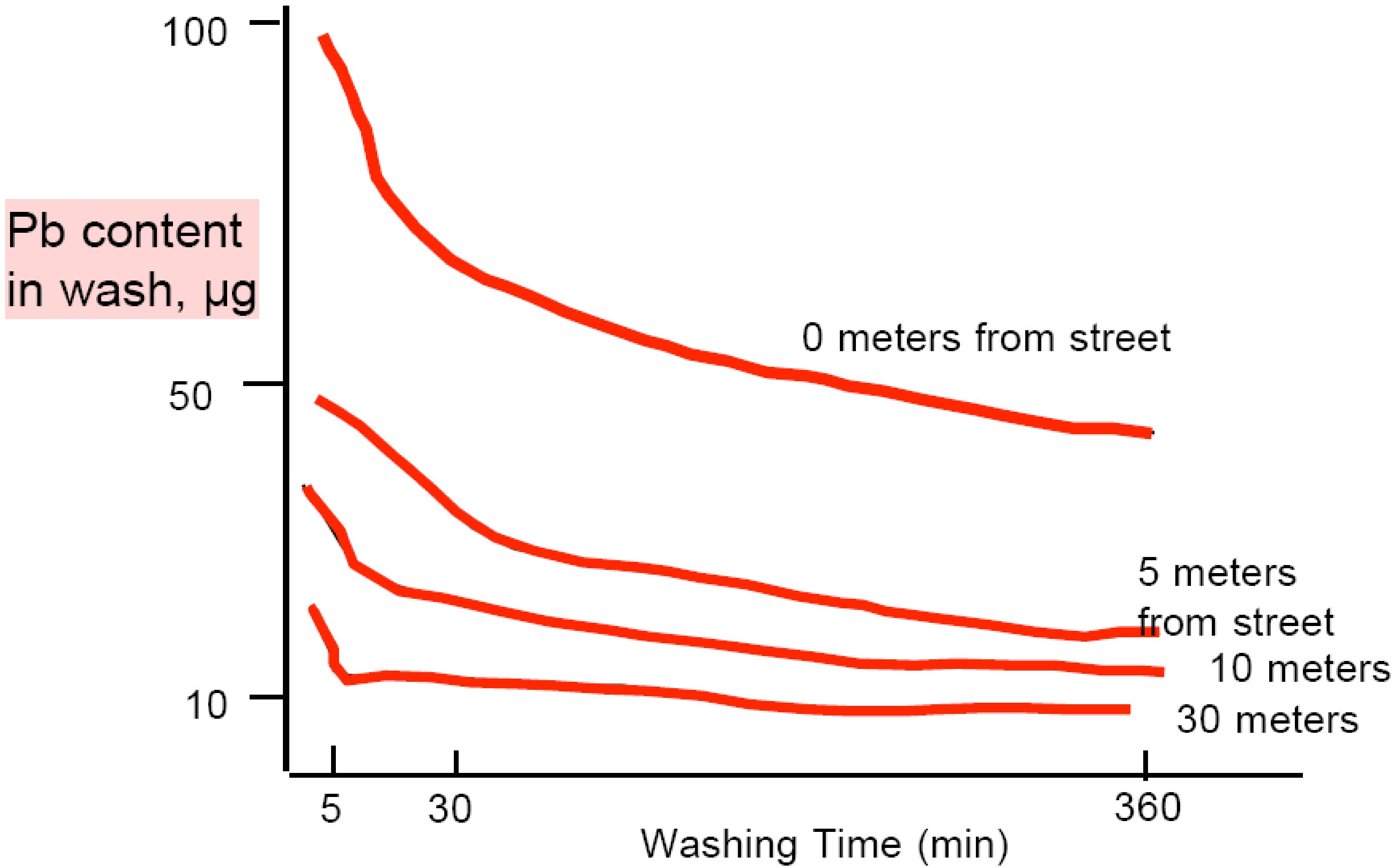
Lobinski et al. (1994) ES&T 28:1459



Historical deposition of organolead as evidenced by snow cores from Greenland

Lobinski et al. 1994

Lead content is highest on leaf surfaces of a plant compared to roots, stems, fruit, etc. Probably due to deposition from air. This portion of lead can be washed off the leaf. Shown in the graph are dislodgeable lead levels relative to placement of plant from a street. 移离



Toxicological Issues

- Excessive lead exposure has been associated with hematological disease, kidney disease, and neurological disorders including impaired intellectual and behavioral development in children 智力的
  - Adults absorb about 5-10% of ingested lead, but children absorb significantly more
  - 150-day old monkeys (infants) retained ~70% of an oral lead nitrate dose compared with 3.2% retained by adult monkeys
  - Organoleads are stored in adipose tissue 脂肪的
  - Under steady state intake, ~40-70% of ingested dose is excreted in the urine
  - No “biomagnification”

Toxicokinetics

- Human volunteers were given 156-215 μg/day of a lead salt for 108-210 days
- Three compartments of bioconcentration:
  - Blood lead (mostly red blood cell associated (1900 μg average; turnover every 36 days
  - Soft tissue (for ex., liver, kidneys); ~600 μg average; turnover every 40 days
  - Bone; contained 200 mg average; turned over every 104 days

Diagnostic Blood Levels

- Prior to 1970, benchmark blood concentrations considered without effect were 80 µg Pb/100 mL (dL) for adults and 50-60 µg/dL for children
- After 1970, adult and children benchmark levels considered to be 40 µg/dL (based on disruption of heme synthesis)
亚铁血红素
- After 1985, Centers for Disease Control recommended intervention level be revised downward to 10 µg Pb/dL
  - Based on literature that suggested pre-school children were at risk for long-lasting adverse neurobehavioral effects when blood levels >10 µg/dL

Environment

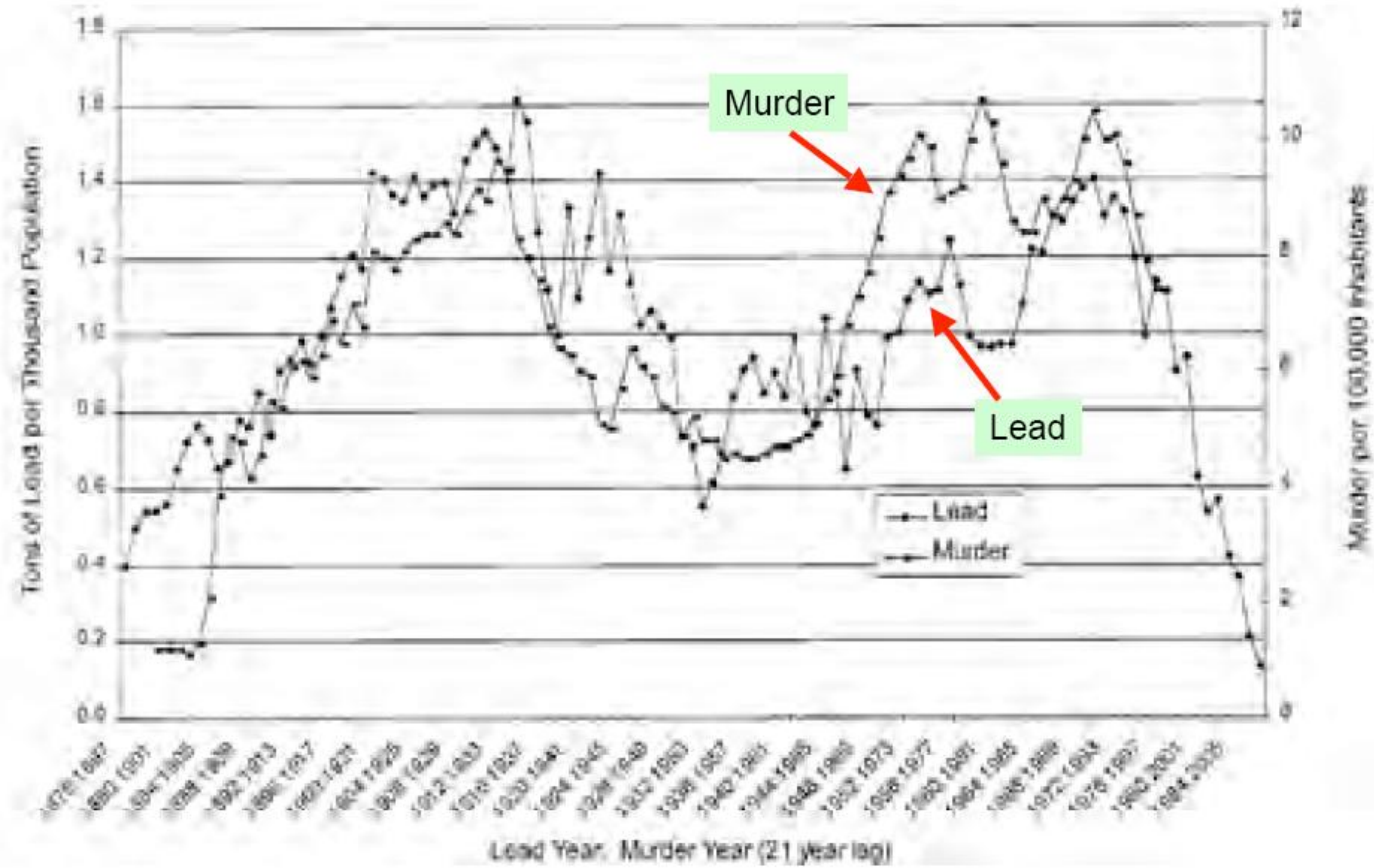
ENVIRONMENT NEWS SERVICE

Lead Exposure Linked to Antisocial Behavior

CINCINNATI, Ohio, March 1, 2002 (ENS) - Exposure to lead in childhood could lead to antisocial or even criminal behavior in adults, a new study suggests. The first comprehensive lead study to track children over a period of time found that both prenatal and postnatal exposure to lead were associated with antisocial behavior in children and adolescents.

Trend in Tons of Lead Used Per 1000 Persons and Murder Rate per 100,000 Inhabitants

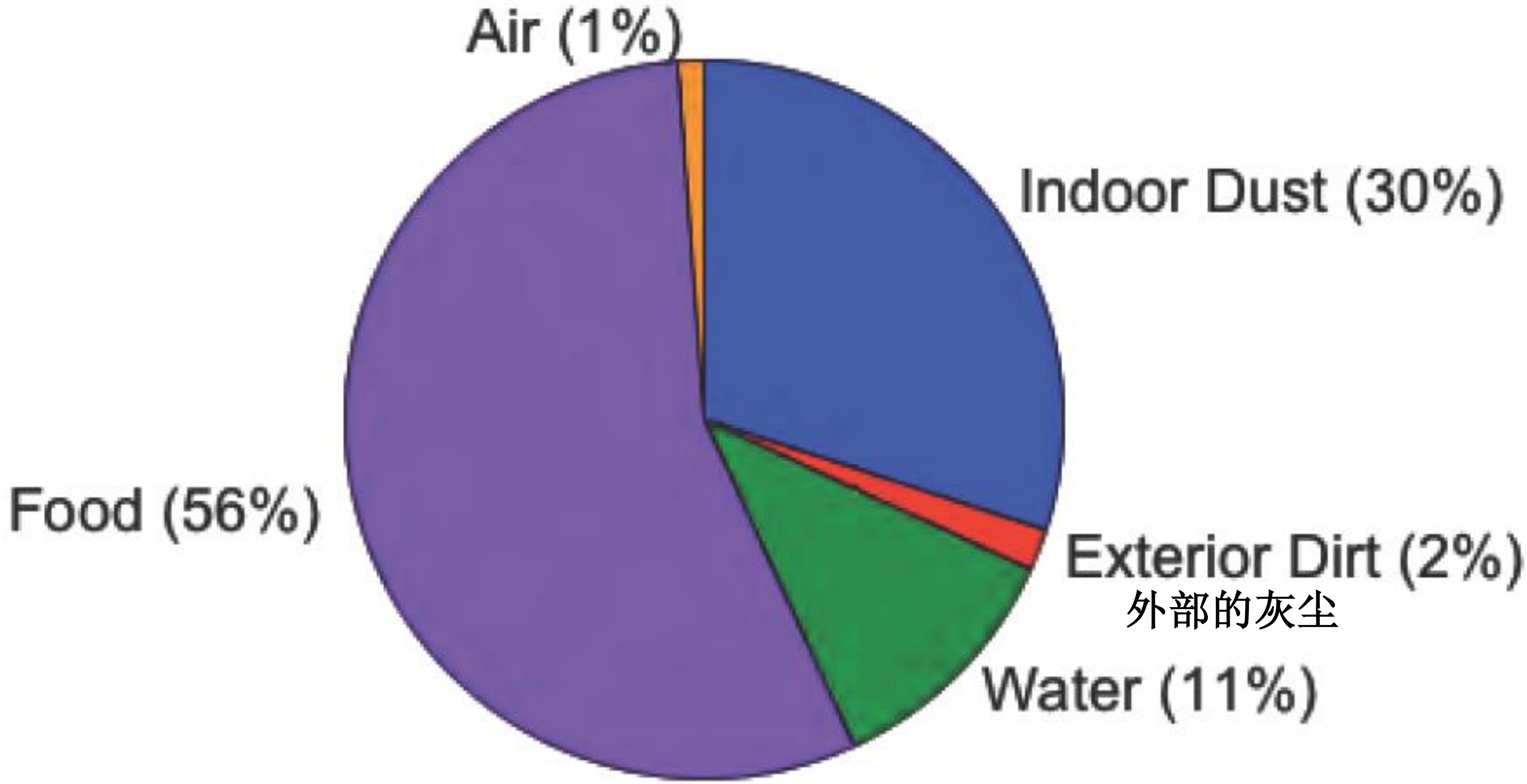
Nevin (2000) Environ. Res. A83:1-22



How Are Children Exposed?

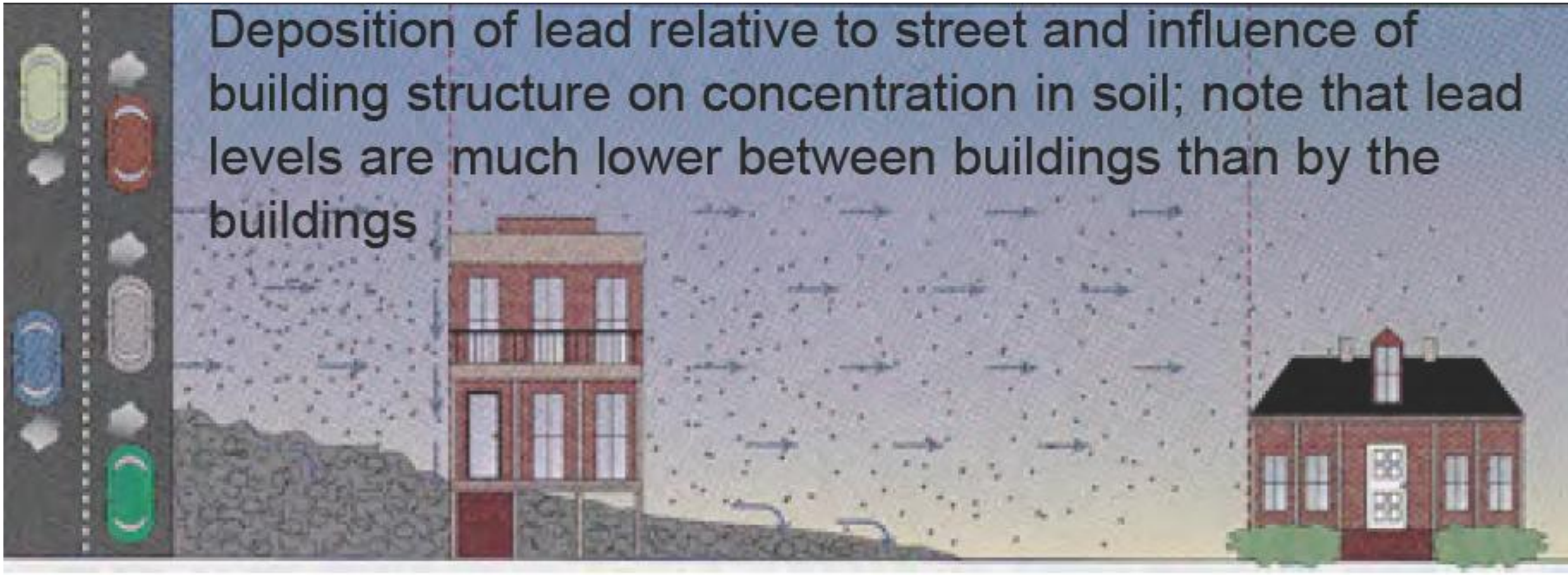
- Original hypothesis for excessive exposure of children involved lead paint chipping and associated dust in households
  - This pathway would predominate in houses built prior to the 1950's when lead-based paint was predominantly used
- More recent hypothesis suggest the lead originated from outdoor soil and surface deposition owing to combustion of leaded gasoline
  - Hand-to-mouth behavior of children would raise exposure potential

Contribution of Source to Children's Exposure (Based on Geometric Means of Measurements)

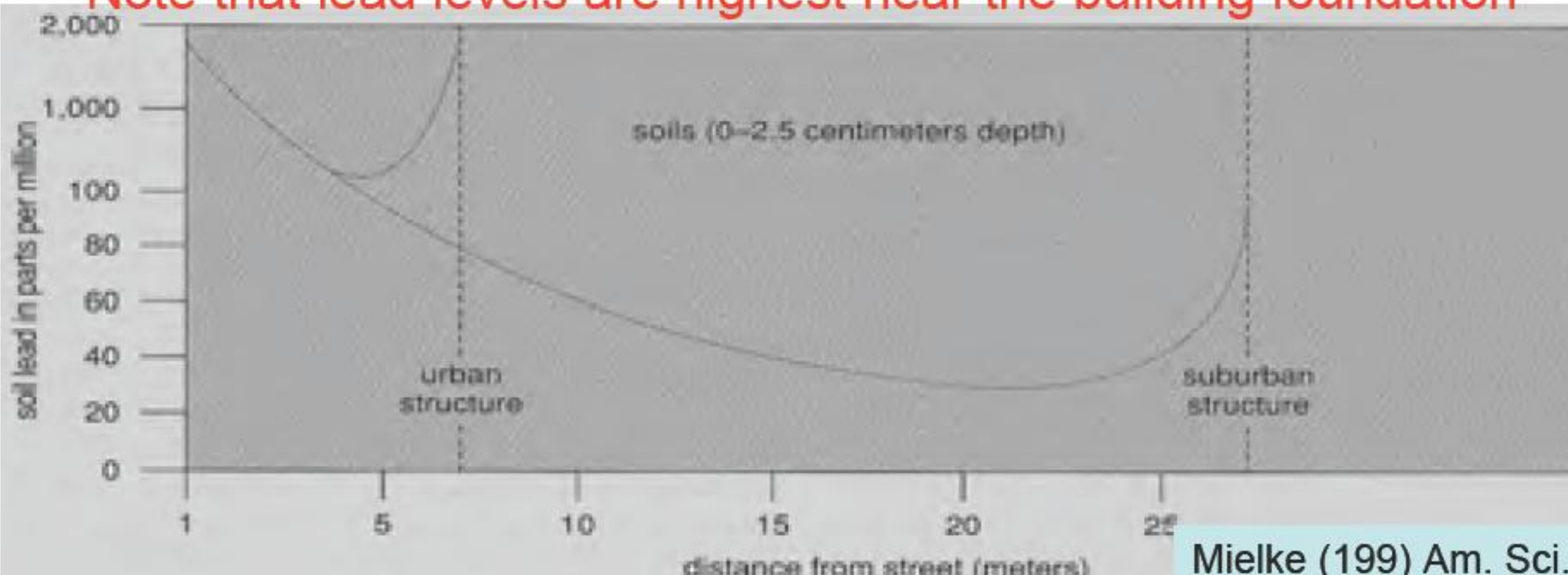


Rasmussen et al. (2001) Sci. Total Environ. 267:125

Deposition of lead relative to street and influence of building structure on concentration in soil; note that lead levels are much lower between buildings than by the buildings

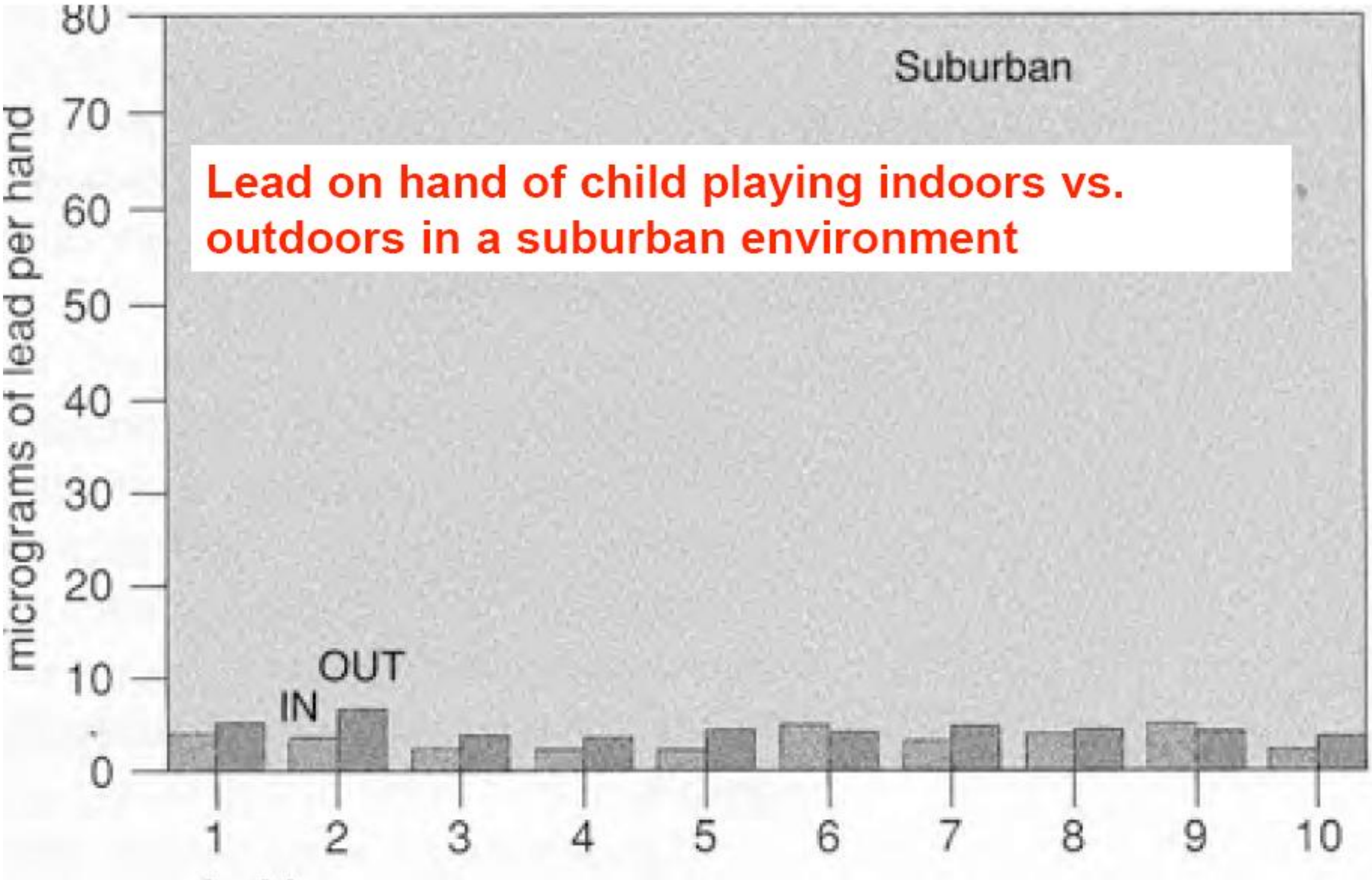


Note that lead levels are highest near the building foundation



Mielke (199) Am. Sci.

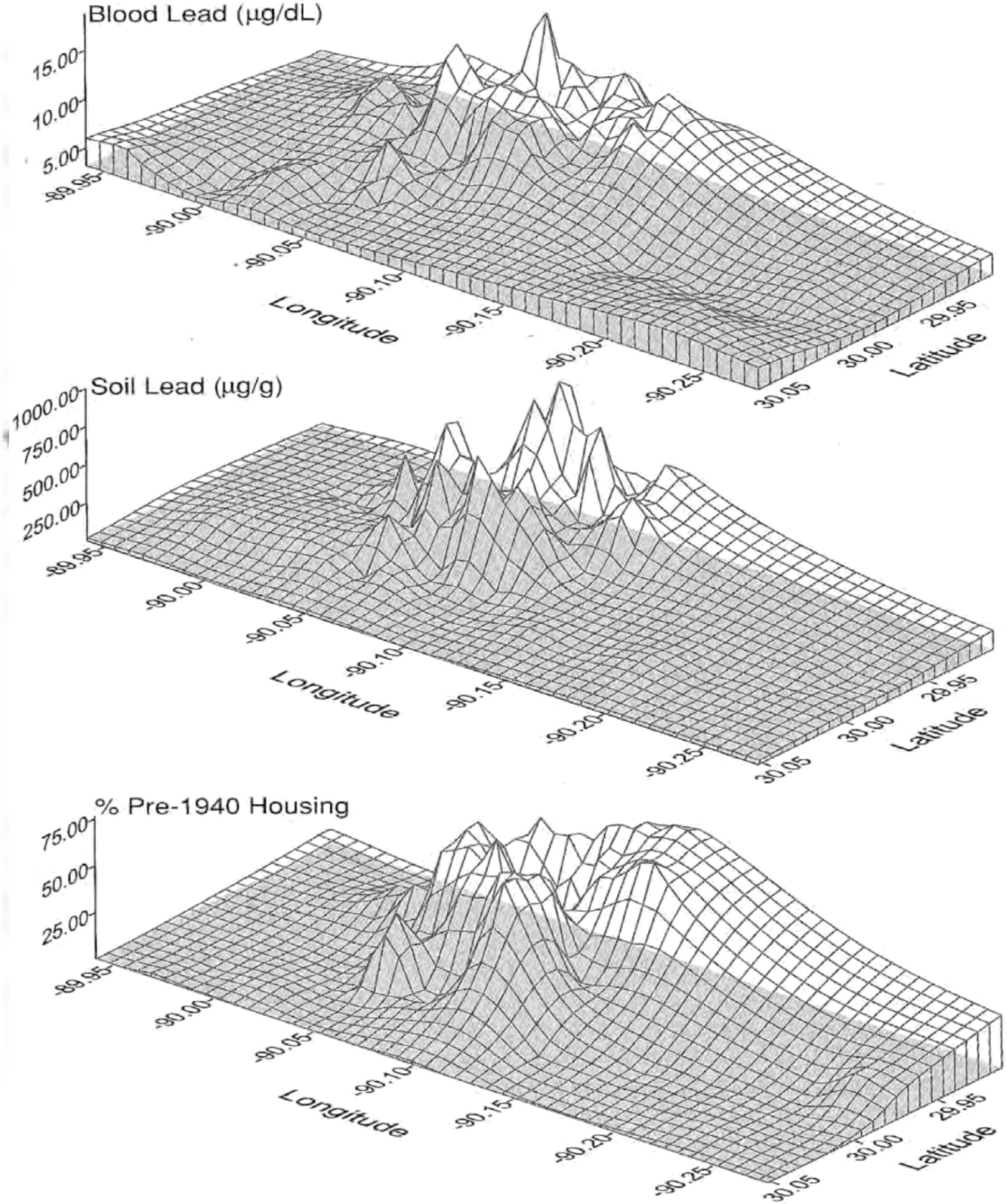
Mielke (199) Am. Sci.



Lead on hand of child playing indoors vs. outdoors in a suburban environment

Mielke (199) Am. Sci.

Correspondence of blood lead levels and soil lead concentrations are better than correspondence of blood lead and pre-1940 housing, which would be expected to have a lot of lead-based paint.



Mielke (199) Am. Sci.

Arsenic

Worldwide anthropogenic input of arsenic to freshwater

Moore 1991

Source	Input 1000 metric tons/yr
Domestic Wastewater	3.0-15.3
Sewage sludge	0.4-6.7
Manufacturing Processes	
Metals	0.3-1.5
Chemicals	0.6-7.0
Pulp & Paper 纸浆	0.4-4.2
Petroleum Products	0-0.1
Smelting & refining	1.0-13
Base metal mining	0-0.75
Steam electrical production	2.4-14
Atmospheric production (combustion processes)	3.6-7.7
Total Input	12-70

Figure 2.1. Documented cases of arsenic problems in groundwater related to natural contamination. Cases include some of the major mining and geothermal occurrences reported in the literature.

BGS and DPHE (2001)

Table 1.Maximum permissible limits for arsenic in drinking water in different countries

Country	Guidelines (µg/L)	References
Argentina	50	Firentin et al.,1998
Bangladesh	50	Chakraborti et al.,2004
Chile	50	Caceres et al.,2005
China	50	Gu et al.,2001
India	10	BIS 10500 :1991,Amendment II,2003
Mexico	50	Ongley et al.,2001
Nepal	50	Shrestha et al.,2003
Newzeland	10	R bins n et al.,2003
Taiwan	10	Tseng,1989;Tseng et al.,2005
USA	10	USEPA,2001
Vietnam	10	Berg et al.(2001)

Health effects of drinking water arsenic

- Arsenic-related diseases

short term: skin lesions, respiratory illnesses, and eye problems. Commonly called "black foot disease."

long term: cancer, heart disease and neurological disorders.

- Toxicity: As(III) (arsenite) > As(V) (arsenate) >> Organic As (MMA, DMA, and arseno-sugar, etc.)

- Dissolved As is highly bioavailable. Adsorbed in stomach and intestine肠and methylated in liver to MMA then DMA. New study found ability of methylation is key – varies among population.

Fundamentals of Arsenic Geochemistry

❑ Arsenate and arsenite dominate

At circum-neutral pH conditions of groundwater, Main dissolved species are: H_3AsO_3, $H_2AsO_4^-$, $HAsO_4^{2-}$.

❑ Redox control

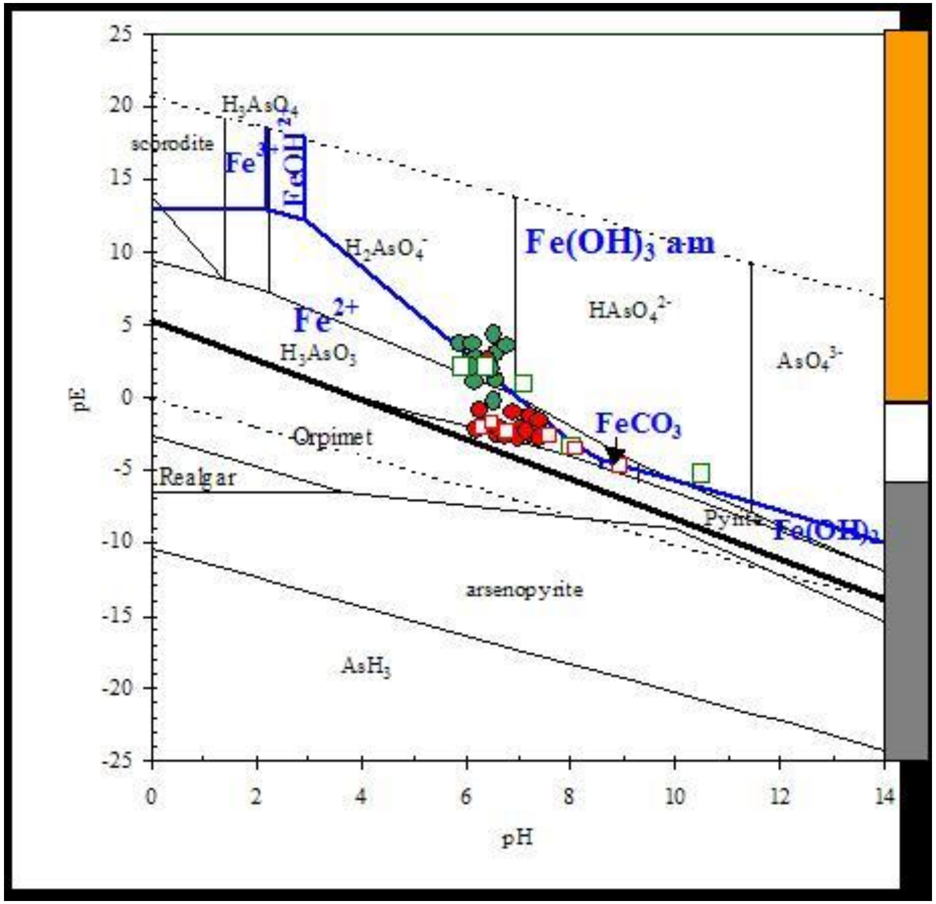
Arsenate is the main form in oxidized environment (e.g., surface and near surface), while arsenite in control in slightly reducing condition. Under very reducing redox state, As will form Fe/S minerals that sequester As.

❑ Fe-oxides play key role

Main pathways that controls the mobilization and fixation of As in natural and remediation systems are through various forms of Fe-oxides and hydroxides.

❑ Arsenate similar to PO_4^{3-}

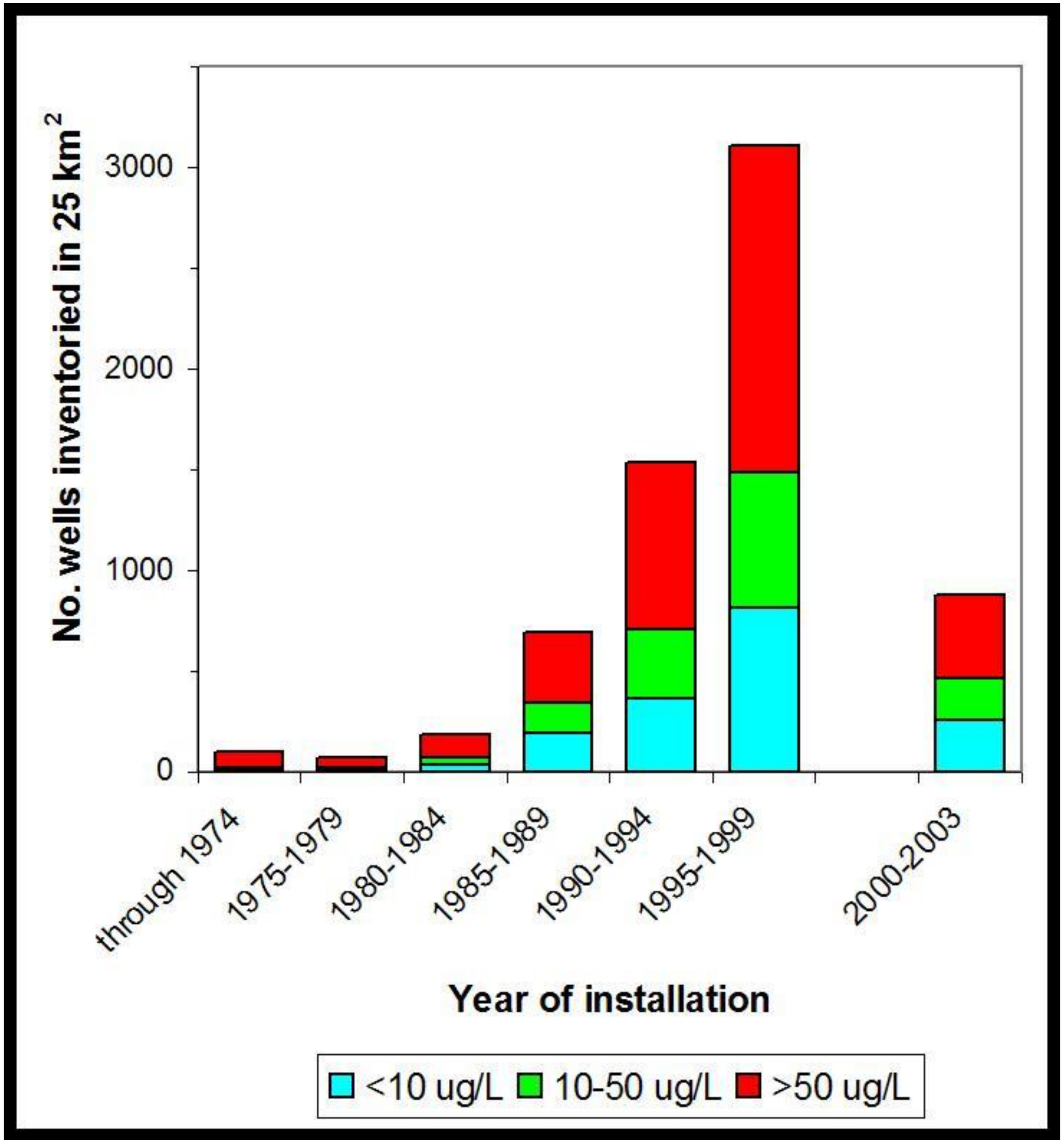
Strong competition in adsorption

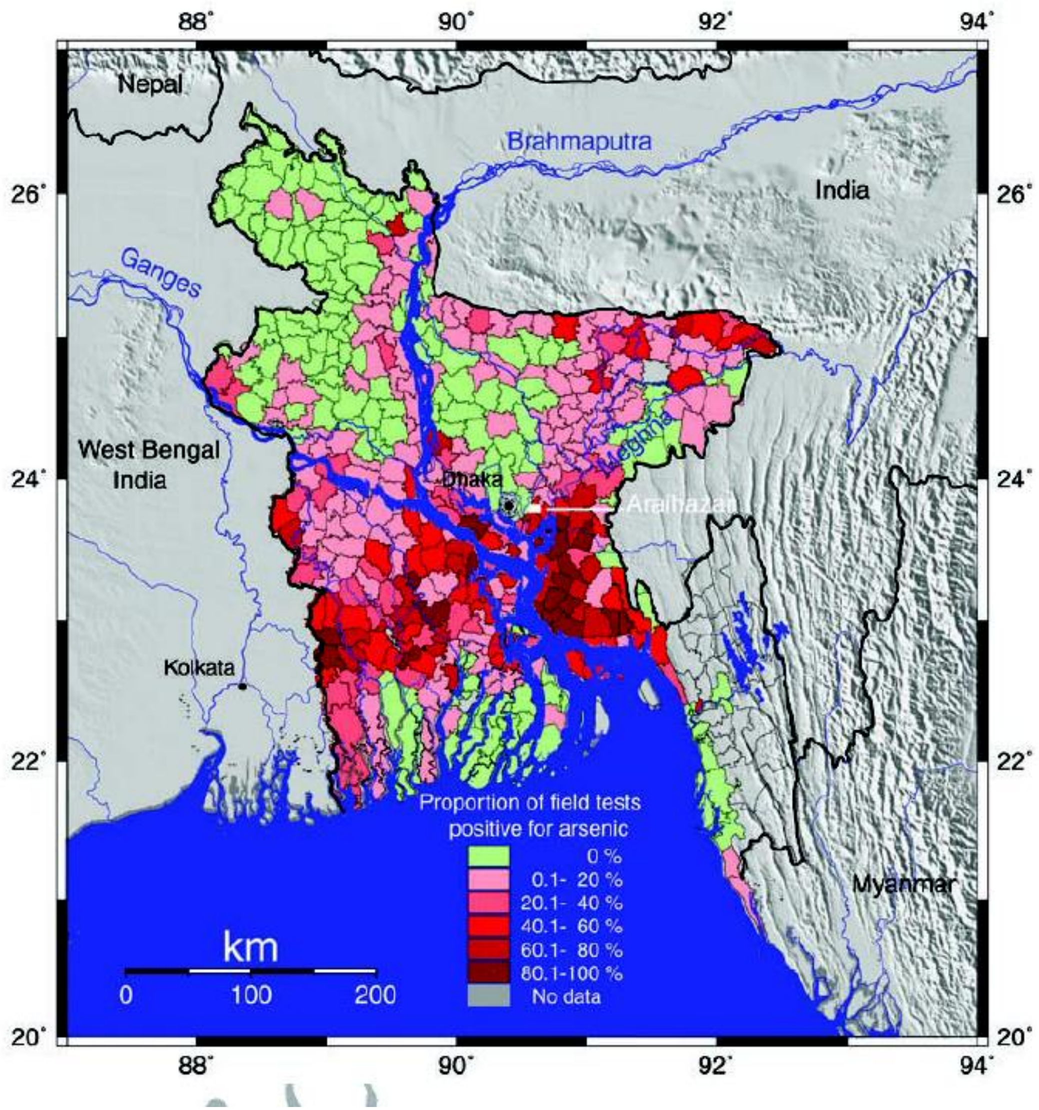


modified from [Ferguson and Gavis, 1972]

History and Timeline

- **Early 1970's, because sewage bacteria tainted pond and river water in rural Bangladesh. UNICEF spent millions of dollars for tube wells to provide "clean" drinking water. Some local people called it "devil water."**
- **Cases of arsenic contamination began surface in 1993 (some claim to as early as 1985). Well water never tested for As before 1993.**
- **The international community finally appeared to accept some responsibility to solve this mass poisoning of Bangladesh in 1998.**
- **Columbia University's Superfund Basic Research Program was first funded in 2001 with focus on the Bangladesh groundwater arsenic problem.**


No. wells inventoried in 25 km^2
0
1000
2000
3000
through 1974
1975-1979
1980-1984
1985-1989
1990-1994
1995-1999
2000-2003
Year of installation
<10 ug/L
10-50 ug/L
>50 ug/L



Map prepared by J. W. Rozenboom (UNICEF-Dhaka)

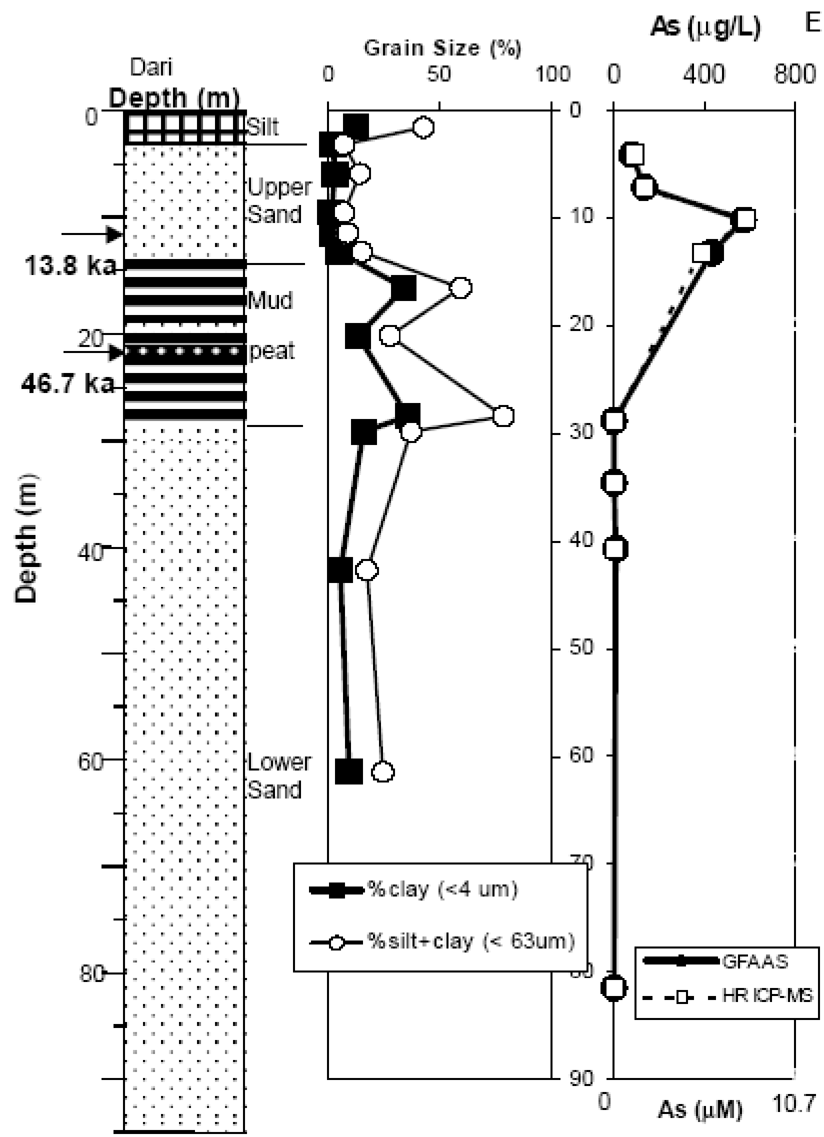
Early survey suggest about 1/3 wells have As above 50 ug/L (Bangladesh limit), and 2/3 above 10 ug/L (WHO limit)

At least 25 million people drink tube well water containing As > 50 ug/L

The biggest fear is that because the effect of drinking water As is chronic, people (especially kids) have been drinking As-laiden water for 10-15 years, we may see a dramatic increase of patients: "the worst is yet to come"

Parameters Studied:

- Lithology – color quantified by spectro-reflectance
- Dissolved As profile



Site A, Zheng et al., 2003

First Order Findings

- Shallow wells (<30 m) dominant, and higher % As contaminated wells. These usually tap Holocene grey sediments. Those usually have more "mobilizable" As.
- Deeper wells that tap orange Pleistocene sandy aquifer are usually safe. 更新世
- Often very old groundwater – a few years to thousands of years.

Starting point: As-Fe interactions …

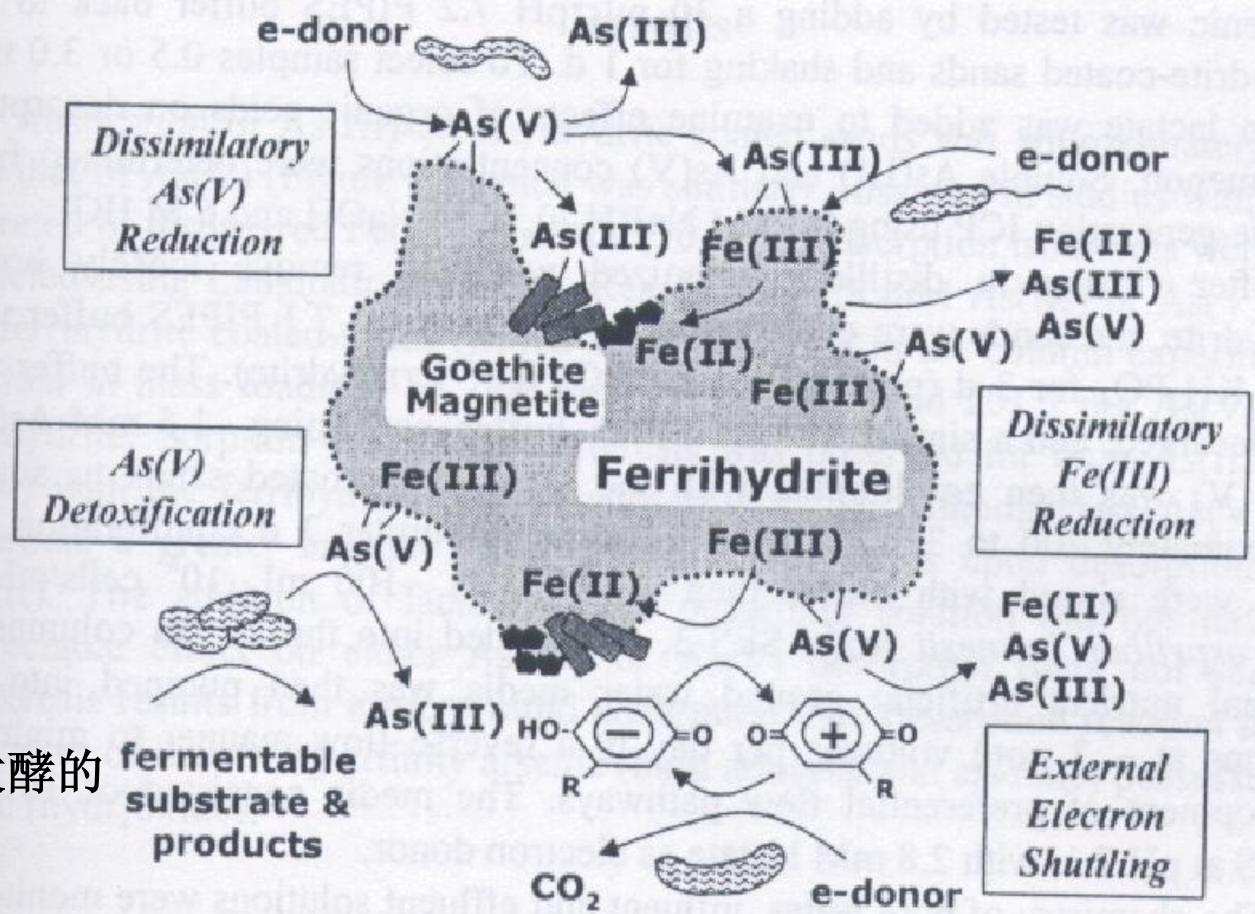


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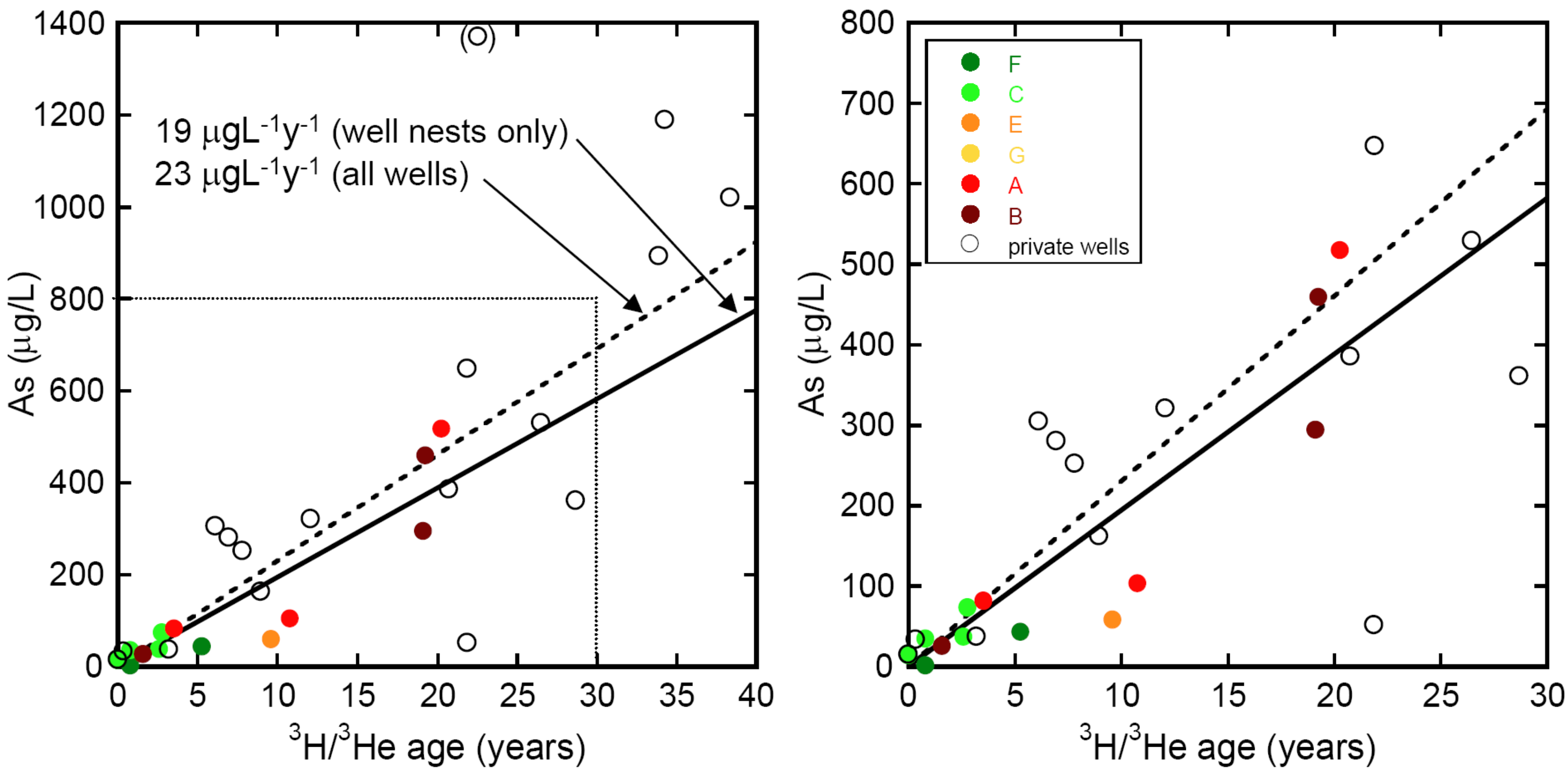
Figure 1. Bacterial mobilization processes for iron oxide-complexed arsenic.

Abiotic mobilization?



Stute et al, revised & submitted, WRR

Thank you for your attentions!