Metais Tóxicos

Leitura Recomendada

- Spiro – Environmental Chemistry

Curvas de “Dose-Resposta”

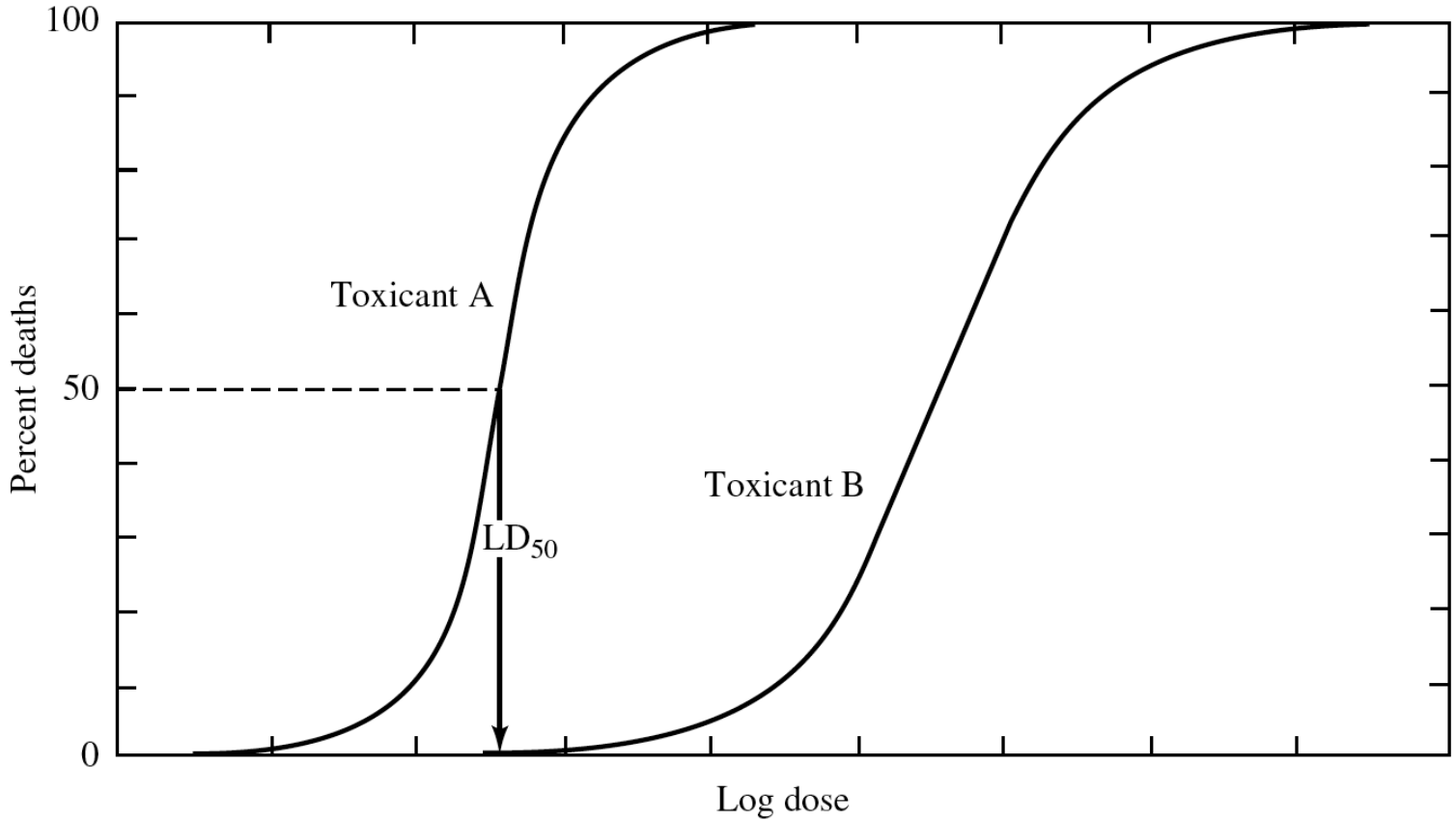


Figure 17.1 Illustration of a dose-response curve in which the response is the death of the organism; the cumulative percentage of deaths of organisms is plotted on the y-axis. *Source:* S. E. Manahan (1991). *Environmental Chemistry,* 5th Edition (Boca Raton, Florida: Lewis Publishers, an imprint of CRC Press). Copyright © 1991 by CRC Press. Reprinted with permission.

TABLE 17.1 LD_{50} VALUES OF SELECTED CHEMICALS

Chemical	LD_{50} (mg/kg)*
Sugar	29,700
Ethyl alcohol	14,000
Vinegar	3,310
Sodium chloride	3,000
Atrazine	1,870
Malathion (insecticide)	1,200
Aspirin	1,000
Caffeine	130
DDT (insecticide)	100
Arsenic	48
Parathion (insecticide)	3.6
Strychnine	2
Nicotine	1
Aflatoxin-B	0.009
Dioxin (TCDD)	0.001
Botulin toxin	0.00001

*For rats or mice

Source: P. Buell and J. Gerard (1994). *Chemistry in Environmental Perspective* (Upper Saddle River, New Jersey: Prentice Hall).

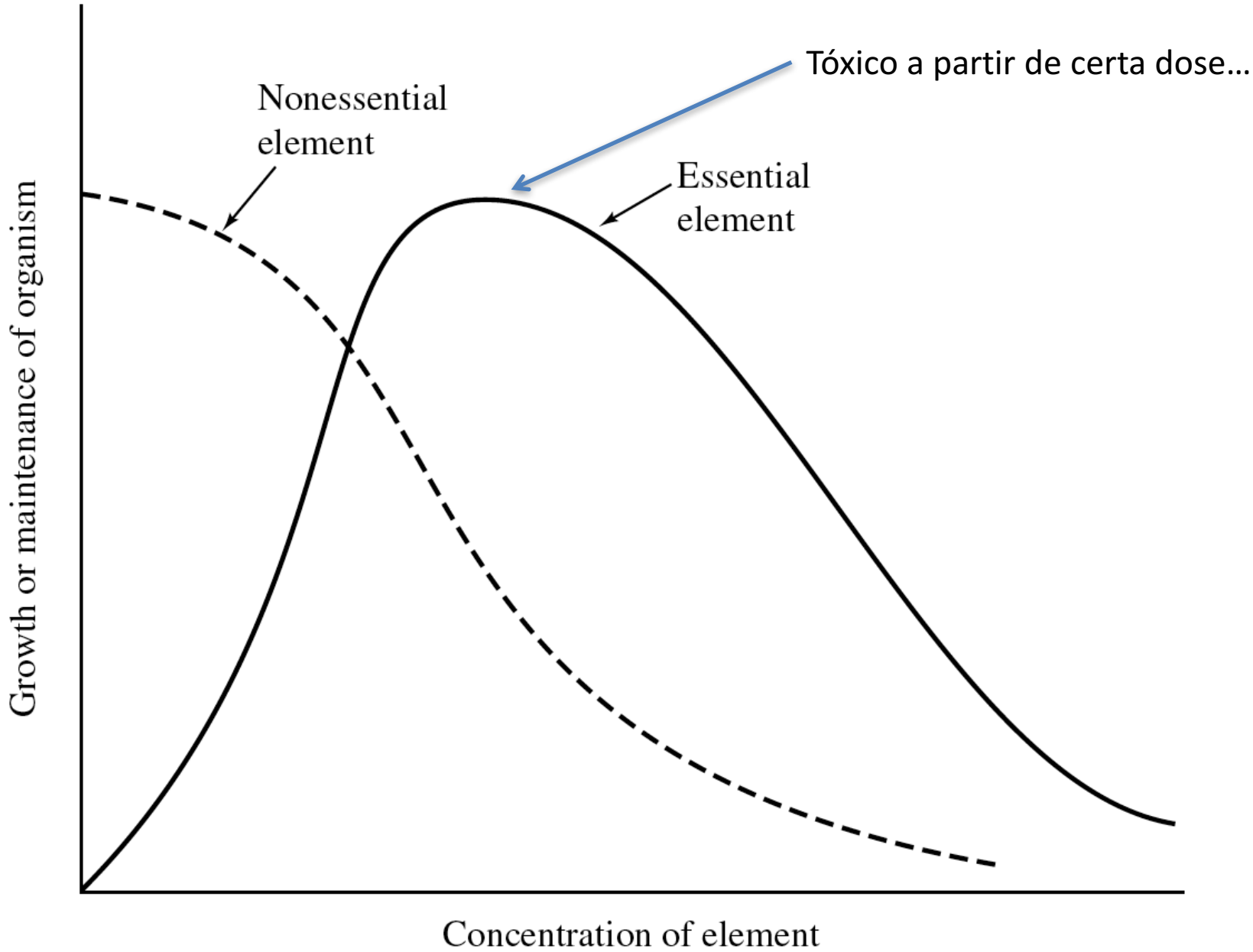


Figure 17.17 Dose-response curves for essential and nonessential elements in metabolic processes.

TABLE 17.7 RELATIVE MAMMALIAN TOXICITY OF ELEMENTS IN INJECTED DOSES AND DIETS

Element	Acute lethal doses (LD_{50}) injected into mammals* (mg/kg bodyweight)	Dose in human diet (mg/day)	
		Toxic	Lethal†
Ag	5–60	60	1.3k–6.2k
As	6	5–50	50–340
Au	10	—	—
Ba	13	200	3.7k
Be	4.4	—	—
Cd	1.3	3–330	1.5k–9k
Co	50	500	—
Cr	90	200	3k–8k
Cs	1,200	—	—
Cu	—	—	175–250
Ga	20	—	—
Ge	500	—	—
Hg	1.5	0.4	150–300
Mn	18	—	—
Mo	140	—	—
Nd	125	—	—
Ni	110–220	—	—
Pb	70	1	10k
Pt	23	—	—
(^{239}Pu)	1	—	—
Rh	100	—	—
Sb	25	100	—
Se	1.3	5	—
Sn	35	2,000	—
Te	25	—	2k
Th	18	—	—
Tl	15	600	—
U	1	—	—
V	—	18	—
Zn	—	150–600	6k

*Injected into the peritoneum to avoid absorption through the digestive tract; chemical form of the element will affect its toxicity

†k signifies thousands of milligrams/day

Source: H. J. M. Bowen (1979). *The Environmental Chemistry of the Elements* (London: Academic Press).

Metais Essenciais

- Ferro (5g) – não liga fortemente a proteínas;
- Cobre (0,08g) – liga fortemente a proteínas;
- Crômio (mas Cr(VI) é carcinogênico);
- Cádmio (liga a Metalotionina)

Metais Tóxicos

- Cádmio (liga a Metalotionina);
- Arsênio;
- Chumbo;
- Mercúrio.

Ácidos de Lewis moles – ligam a resíduos de cisteína..

Ciclos

- Todos os metais circulam naturalmente no ambiente;
- Liberados pela lixiviação de rochas, ação de microorganismos, etc.
- Fortemente modificados pela ação humana.

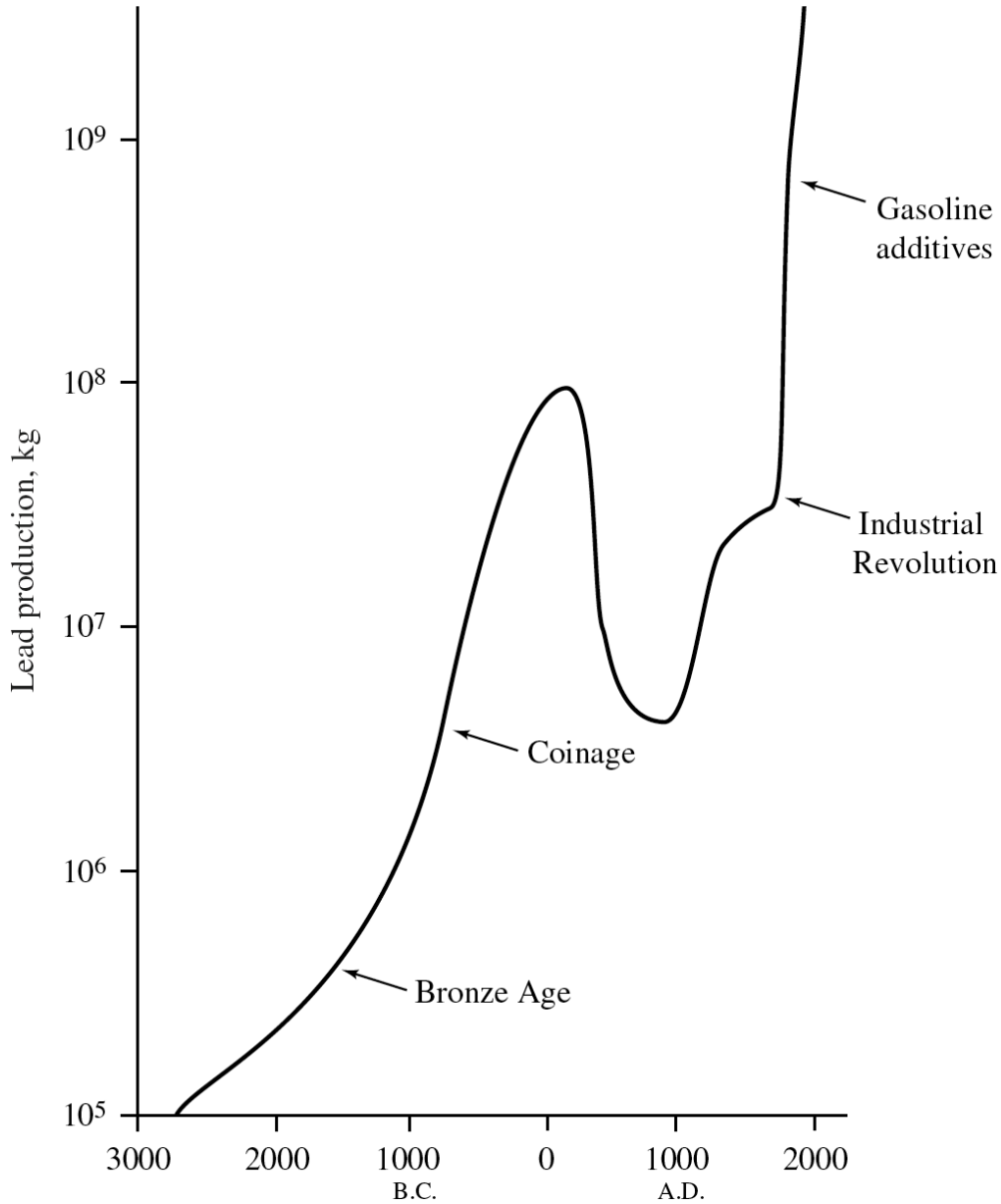


Figure 17.18 Historical production and consumption of lead. *Source:* Adapted from J. Nriagu (1978). *Biogeochemistry of Lead* (Amsterdam: Elsevier); and P. M. Stokes (1986). *Pathways, Cycling, and Transport of Lead in the Environment* (Ottawa: Royal Society of Canada).

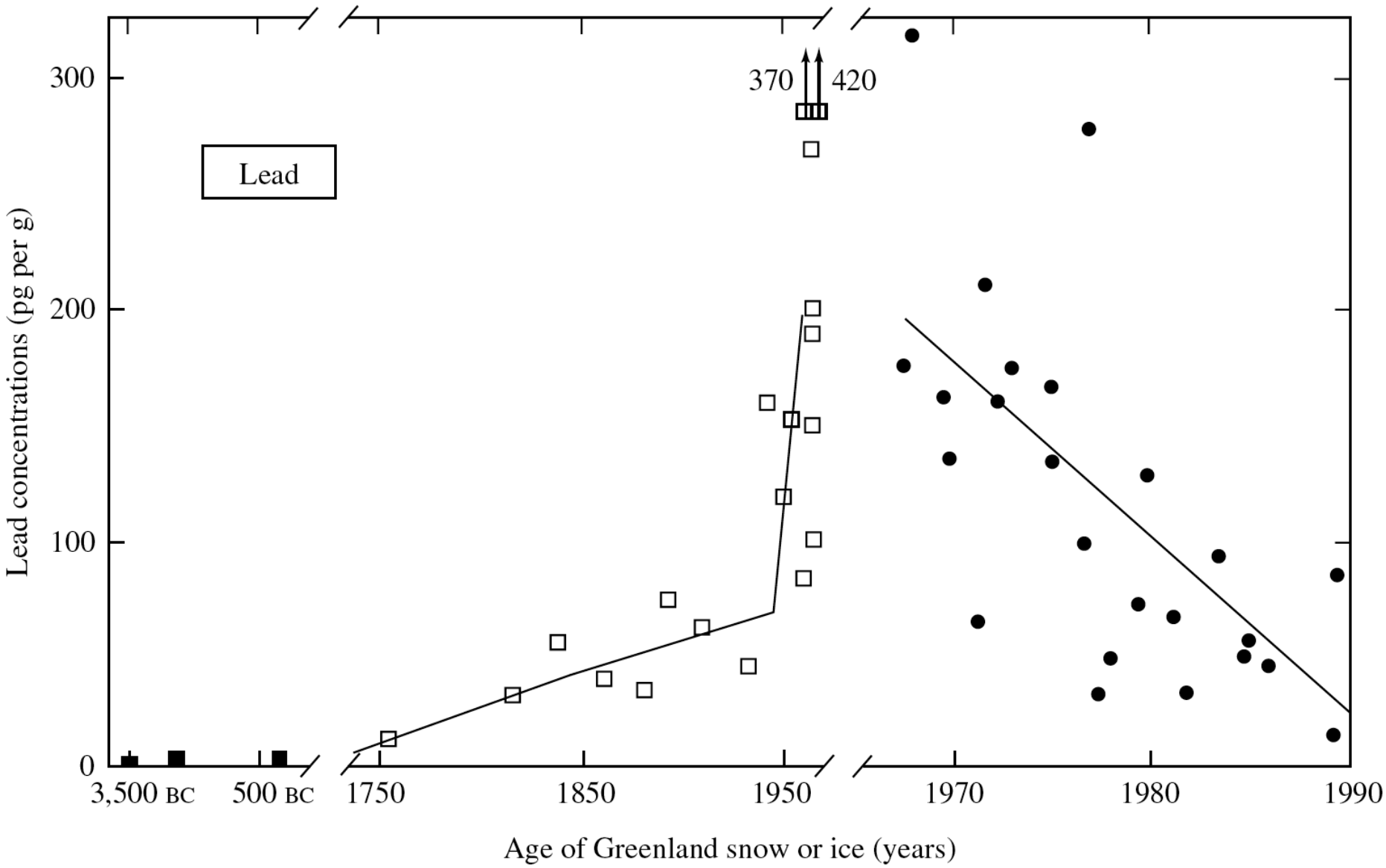

Lead
370
420
300
200
100
0
Lead concentrations (pg per g)
3,500 BC
500 BC
1750
1850
1950
1970
1980
1990
Age of Greenland snow or ice (years)

TABLE 17.8 PRIMARY PRODUCTION OF METALS AND GLOBAL EMISSIONS TO SOIL (10^3 t/yr)

Metal	Production in 1930	Production in 1985	Global emissions to soil in 1980s
Cd	1.3	19	22
Cr	560	9,940	896
Cu	1,611	8,114	954
Hg	3.8	6.8	8.3
Ni	22	778	325
Pb	1,696	3,077	796
Zn	1,394	6,024	1,372

Source: J. O. Nriagu (1988). A silent epidemic of environmental poisoning? *Environmental Pollution* 50:139–161.

Cádmio

- Química similar à do Zinco;
- Plantas absorvem ativamente (zinco é metal essencial) – maior parte da nossa absorção vem da alimentação (fumantes têm níveis elevados);
- Aparece associado ao Zinco (por exemplo no aço galvanizado);
- Outras fontes: baterias, eletrodeposição, pigmentos, estabilizantes de polímeros;

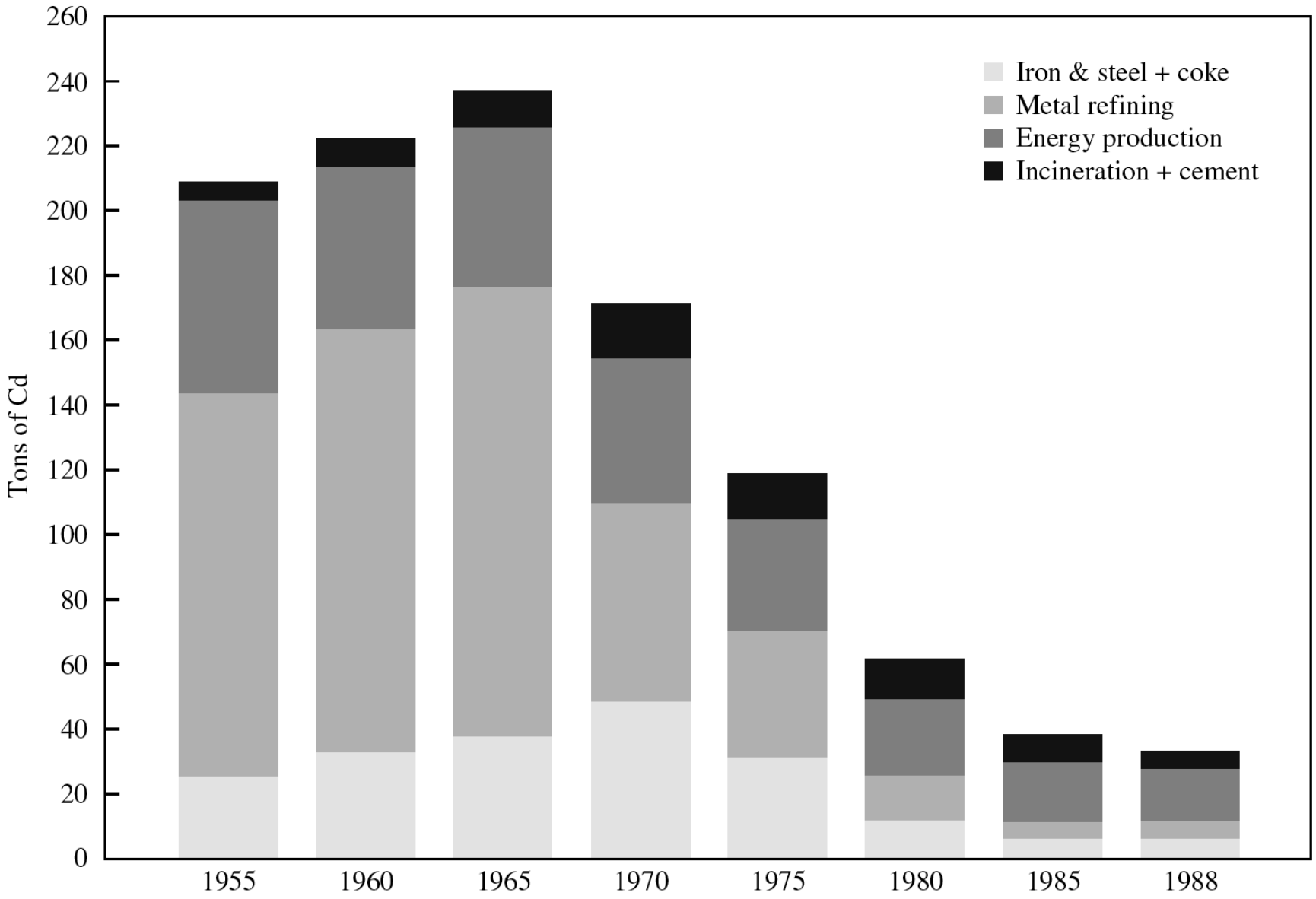


Figure 17.23 Trends in atmospheric emissions of cadmium in the Rhine River Basin by industrial sector (1955–1988). *Source:* S. Anderberg and W. M. Stigliani (1995). Private communication (Laxenburg, Austria: International Institute for Applied Systems Analysis).

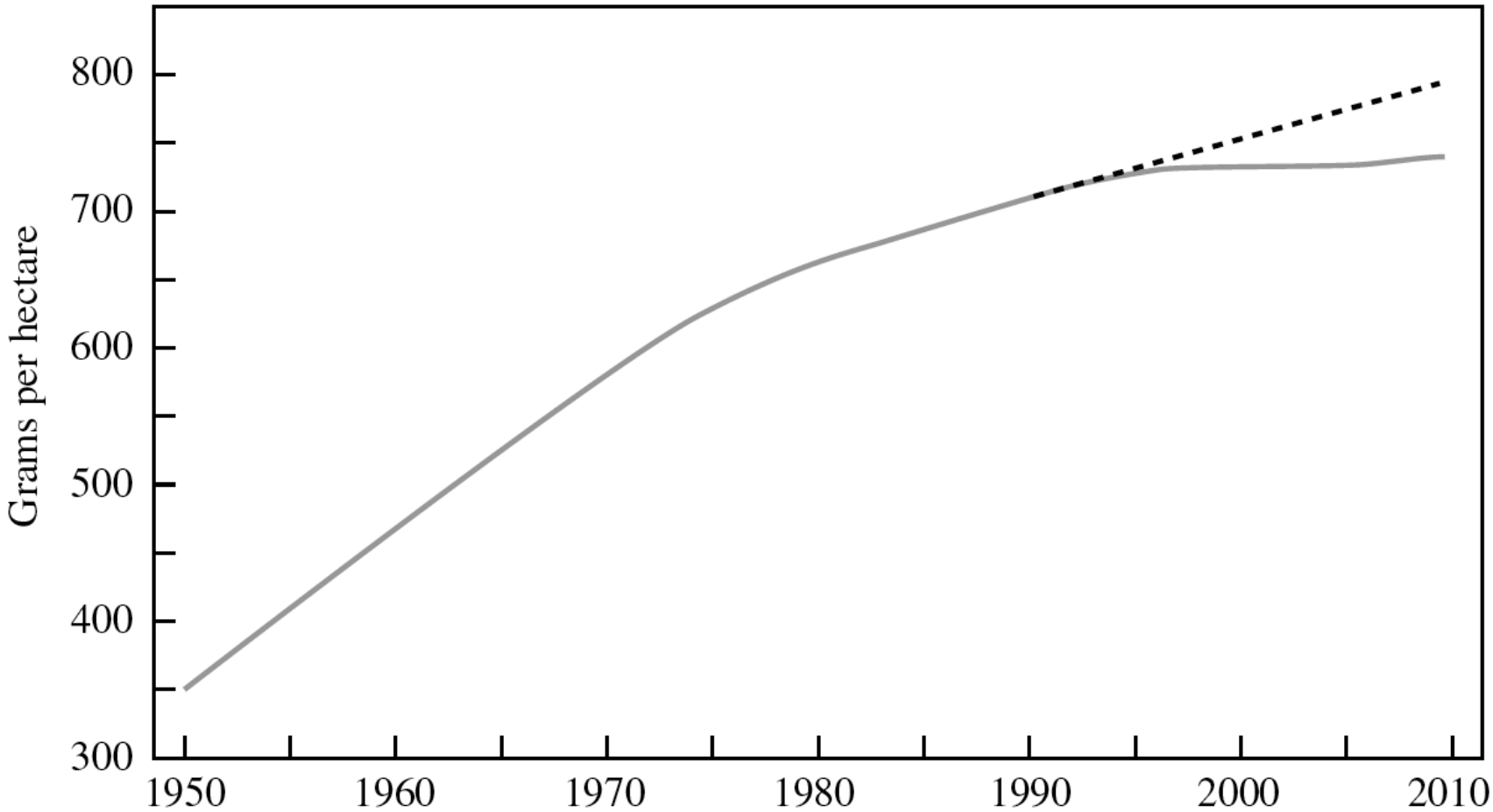


Figure 17.24 Time trend in soil concentration of cadmium in top 20 cm of typical agricultural soil in the Rhine Basin. In projections to the year 2010, solid line assumes cadmium in phosphate fertilizer is eliminated by the year 2000; the dashed line assumes no reduction of cadmium in fertilizer. *Source:* W. M. Stigliani et al. (1993). Heavy metal pollution in the Rhine Basin. *Environmental Science and Technology* 27(5):786–793. Copyright © 1993 by American Chemical Society. Reprinted with permission from ES&T.

Tempo de residência

- Elevado em solos (especialmente acima de pH 6);
- Muito menor na atmosfera e em água;

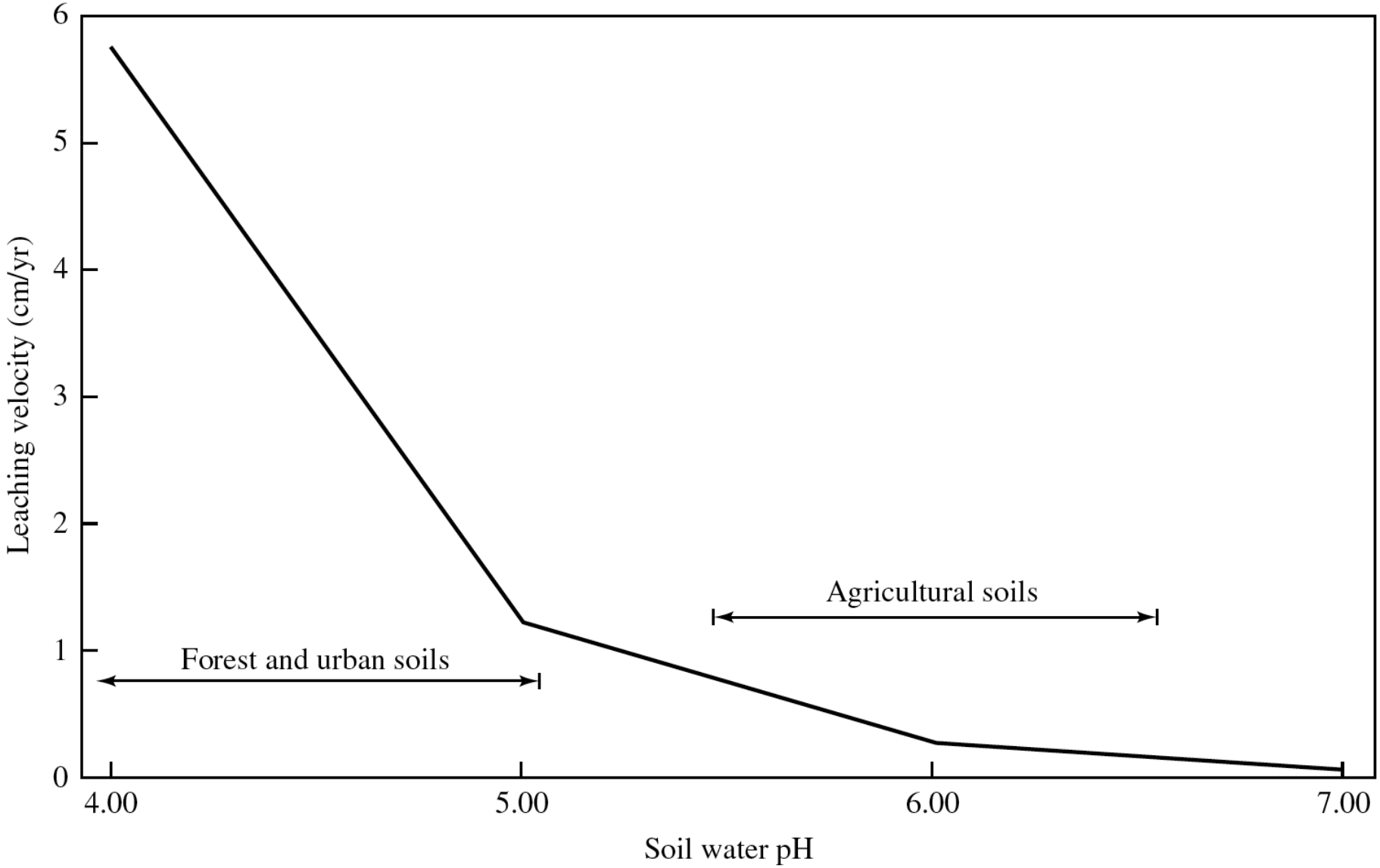


Figure 12.13 Leaching velocity of cadmium in soil as a function of soil water pH. *Source:* W. M. Stigliani and P. R. Jaffe (1992), private communication (Laxenburg, Austria: International Institute for Applied Systems Analysis).

Efeitos

- Altera absorção de Ca^{+2} – doença do “Ai, ai”;
- Doença cardíaca/pulmonar;
- Supressão do sistema imunológico;
- Doença dos rins (metalotionina) e fígado

Arsênio

- Química similar à do fósforo (mas é mais facilmente reduzido de estado de oxidação V a III);
- As(III) (AsO_3^{-3}, arsenito) é mais tóxico que As(V) (AsO_4^{-3}, arsenato), provavelmente pela melhor ligação com grupos sulfidrila em proteínas;
- As(III) pode sofrer metilação

Arsênio no Meio Ambiente

- Encontrado associado a minerais do tipo sulfeto (especialmente pirita);
- Bangladesh e Bengala Oeste na Índia – altíssimos níveis na água subterrânea – 200.000 pessoas diagnosticadas com arsenicose em Bengala Oeste;
- Níveis acima de 500ppb;

Efeitos

- Doenças de pele;
- Câncer;
- Deterioração de funções renais e hepáticas

Chumbo

- Mais problemático;
- Abundante na poeira (0,1g pode conter 10microgramas de Pb);
- Pigmentos; $PbCrO_4$, $Pb_3(OH)_2(CO_3)_2$,
- Água (canos); $2Pb + O_2 + 4H^+ = 2Pb^{2+} + 2H_2O$
- Gasolina com “chumbo tetraetila”

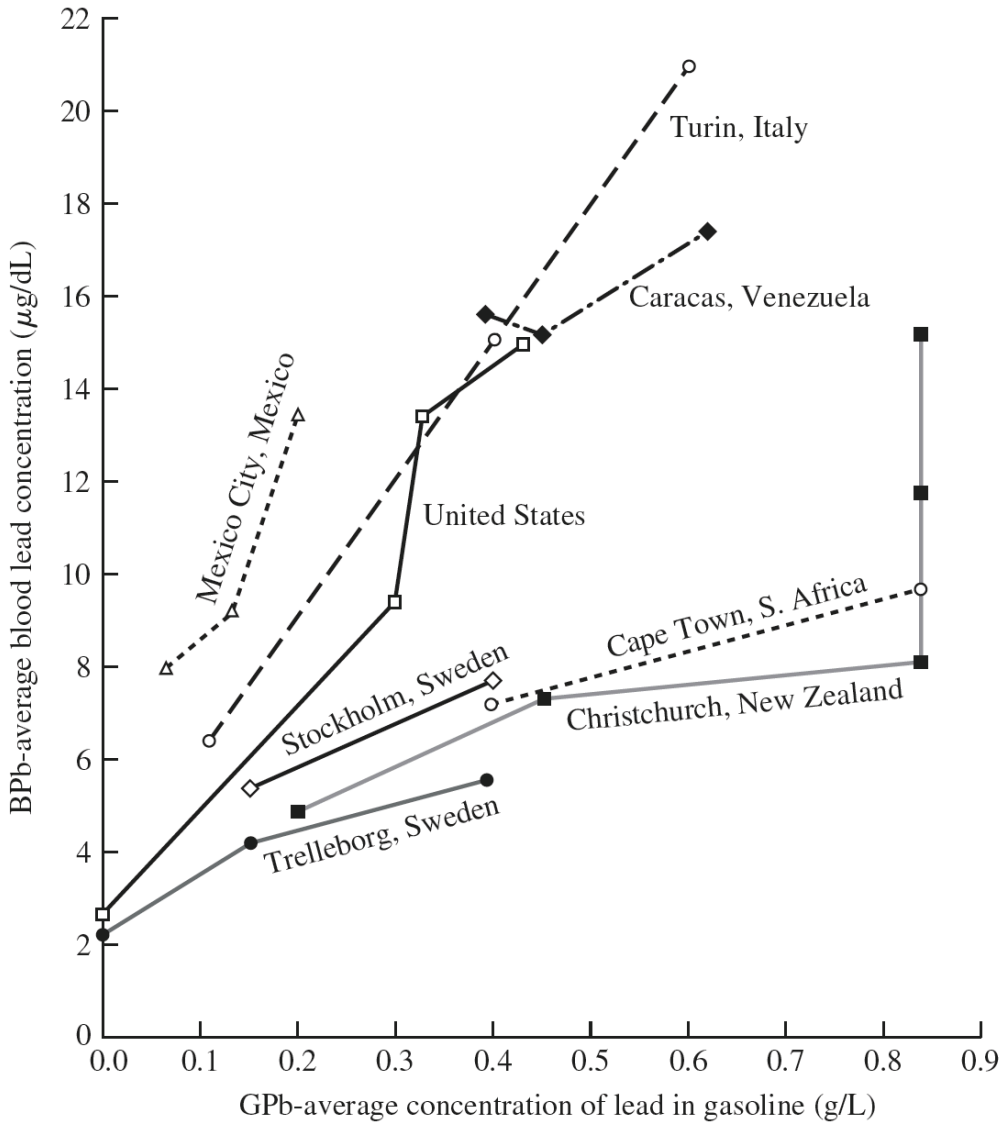


Figure 17.25 Eight studies of changes in population blood lead concentrations with changes in concentration of lead in gasoline. Adapted from V. M. Thomas et al. (1999). Effects of reducing lead in gasoline: An analysis of the international experience. *Environmental Science and Technology* 33:3942–3948. Copyright © 1999 by American Chemical Society. Reprinted with permission from ES&T.

Biodisponibilidade do Chumbo

- 7-15% adultos, 30-40% em crianças são absorvidos;

Efeitos Tóxicos

- Saturnismo;
- Anemia (deficiência de porfirina de ferro);

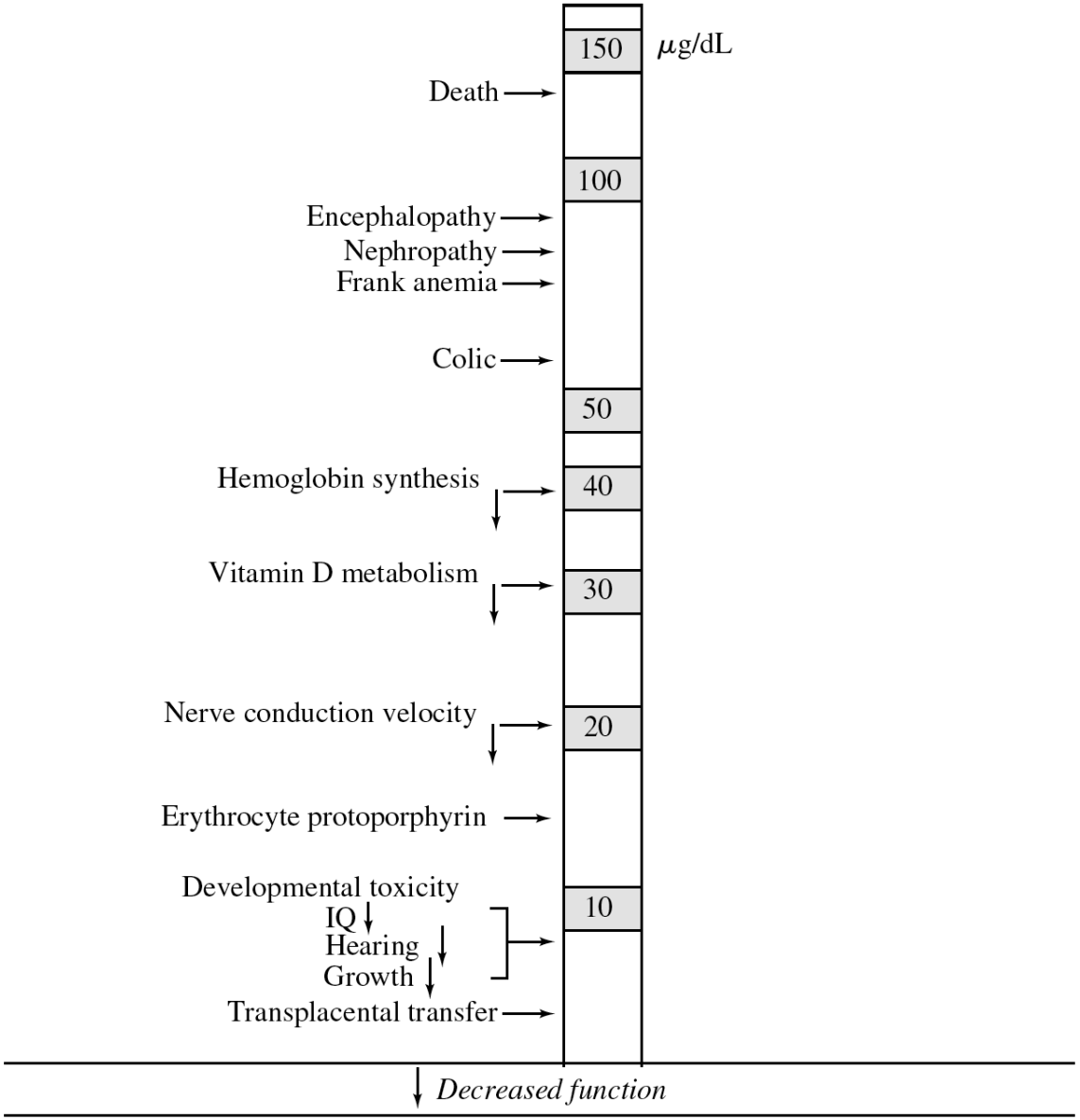
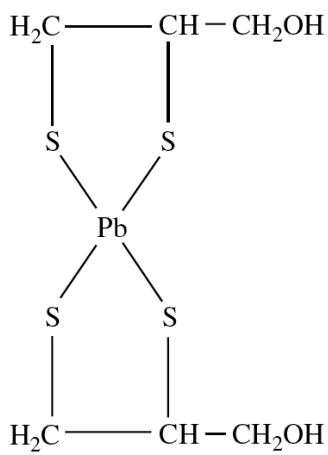
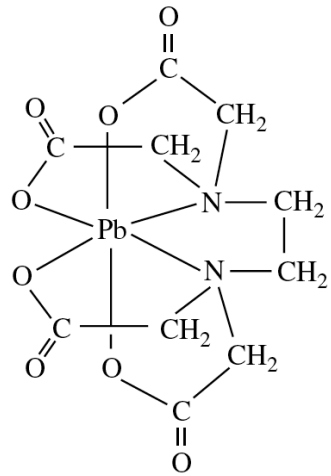


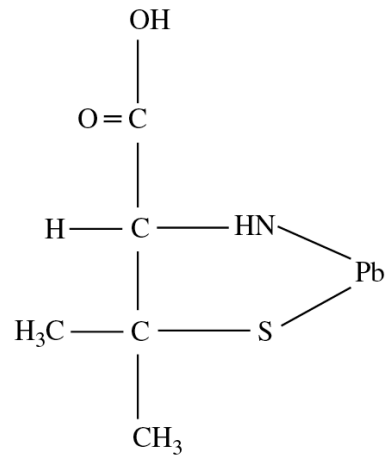
Figure 17.26 Lowest observed effect levels of inorganic lead in children (μg/dL). *Source:* Agency for Toxic Substances Disease Registry (1988). *The Nature and Extent of Lead Poisoning in Children in the United States: A Report to Congress* (Atlanta, Georgia: ATSDR).



Pb bound to BAL



Pb bound to EDTA



Pb bound to d-penicillamine

Lead removal from body

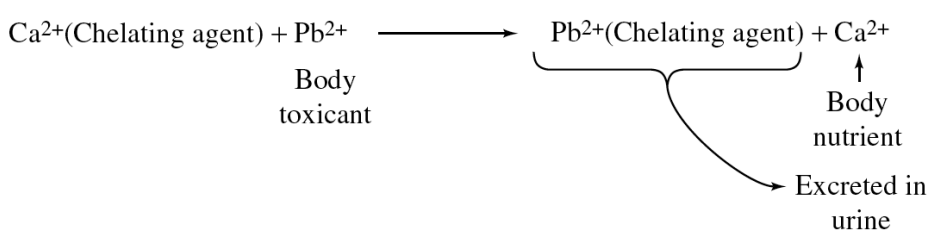


Figure 17.27 Chelating agents for removing lead from the body.