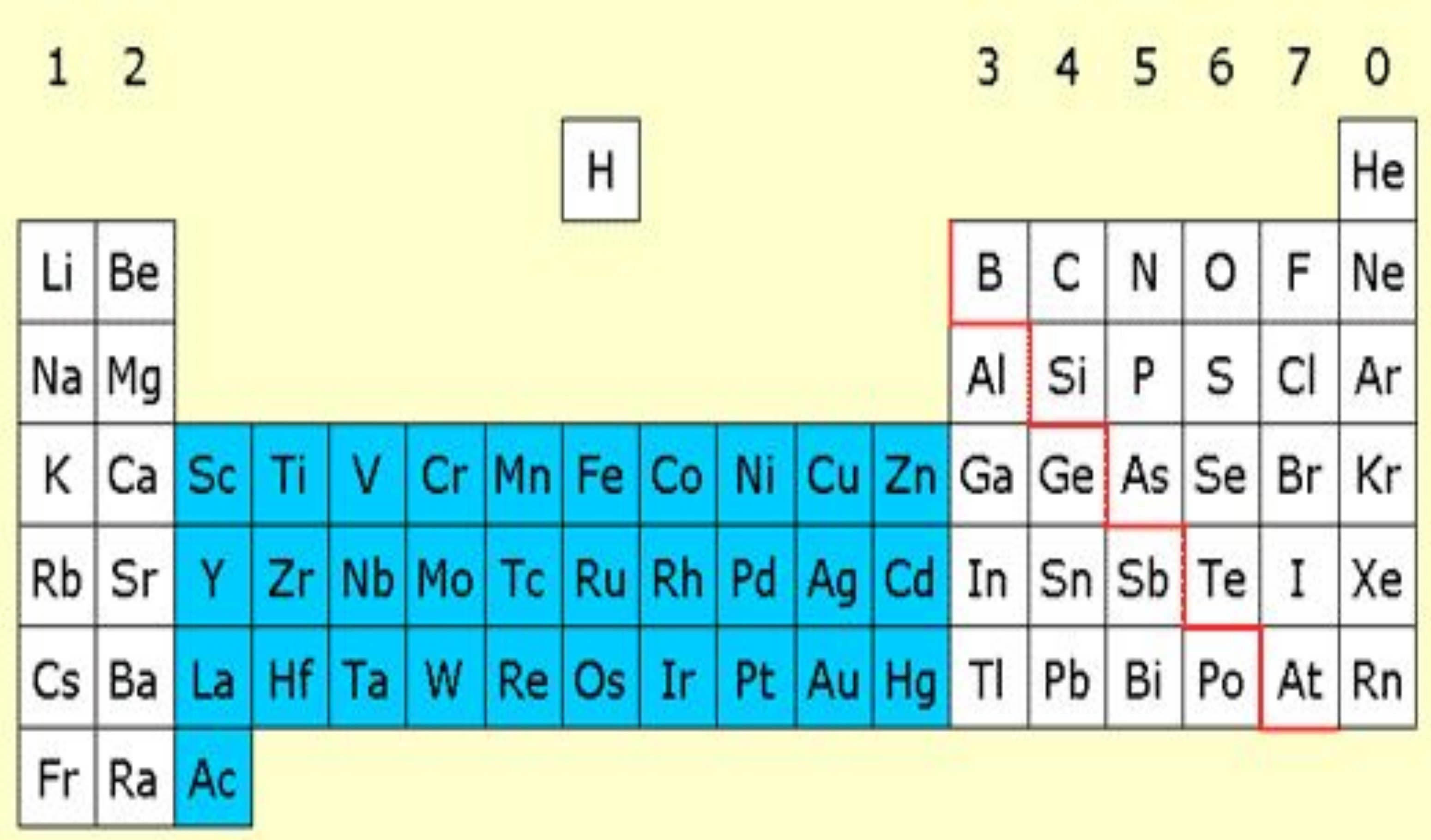
Lecture №2.
Heavy metals



1	2											3	4	5	6	7	0
						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															

Definition of Heavy Metal

1. "Heavy metals" are chemical elements with a <u>specific gravity at least 5 times that of water</u>.

The specific gravity of water is 1 at 4°C (39°F). Specific gravity is a measure of density of a given amount of a solid substance when it is compared to an equal amount of water.

Some well-known toxic metals with a specific gravity 5 or more times that of water are arsenic (5.7), cadmium (8.65), iron (7.9), lead (11.34), and mercury (13.546) (Linde 1992).

Definition of Heavy Metal

2. In the fundamental review paper written by Duffus (2002), 13 different works were cited that used lower limits on the density of a “heavy” metal ranging from 3.5 to 7 g / cm^{-3}. The author stated that the threshold varied depending on the author, and that “it is impossible to come up with a consensus”. Moreover, he concluded that “any idea of defining “heavy metals” on the basis of density must be abandoned as yielding nothing but confusion”.

However, this is beside the point; although half of the works cited suggested similar lower limits of 4.5 or 5 g cm^{-3}, plants do not have the ability to detect the density of a metal.

Definition of Heavy Metal

Thus, “heavy metal” remains an obscure term in the life sciences. It should also be noted that the review paper of Duffus (2002) was commissioned by the International Union of Pure and Applied Chemistry (IUPAC http://www.iupac.org), and certainly represents a chemical point of view that is often neglected by biologists.

Definition of Heavy Metal

- Some define a **heavy metal** as a metal with an atomic mass greater than that of sodium (iron), whereas others define it as a metal with a density above 3.5–6 g cm^{-3}.
- The term is also applied to **semi-metals** (elements that have the physical appearance and properties of a metal but behave chemically like a non-metal), such as arsenic, presumably because of the hidden assumption that ‘heaviness’ and ‘toxicity’ are in some way identical.

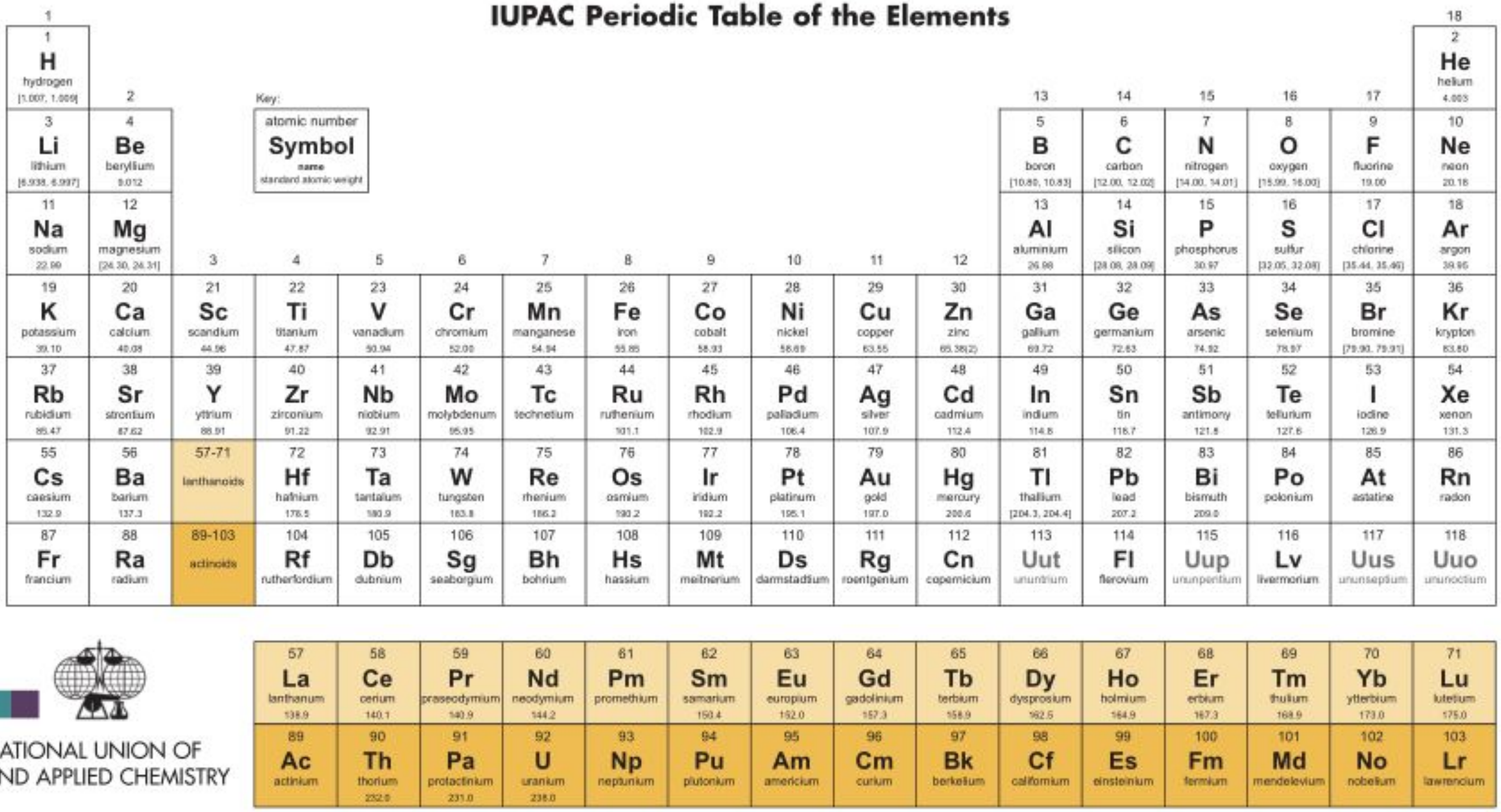
Definition of Heavy Metal

- The term **heavy metals** (or trace metals) is applied to the group of metals and semimetals (metalloids) that have been associated with contamination and potential toxicity or however, the term is only loosely defined and there is no single authoritative definition.

Definition of Heavy Metal

- Despite the fact that the term **heavy metals** has no sound terminological or scientific basis, it is used here in the way it has been used in much of the scientific environmental literature, namely to refer to metals or semi-metals which meet the definitions given above. Common heavy metals include zinc (Zn), copper (Cu), lead (Pb), cadmium (Cd), mercury (Hg), chromium (Cr), nickel (Ni), tin (Sn), arsenic (As), and silver (Ag).

IUPAC 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, 1.009]																	2 **He** helium 4.003
3 **Li** lithium [6.938, 6.997]	4 **Be** beryllium 9.012											5 **B** boron [10.80, 10.83]	6 **C** carbon [12.00, 12.02]	7 **N** nitrogen [14.00, 14.01]	8 **O** oxygen [15.99, 16.00]	9 **F** fluorine 19.00	10 **Ne** neon 20.18
11 **Na** sodium 22.99	12 **Mg** magnesium [24.30, 24.31]											13 **Al** aluminium 26.98	14 **Si** silicon [28.08, 28.09]	15 **P** phosphorus 30.97	16 **S** sulfur [32.05, 32.08]	17 **Cl** chlorine [35.44, 35.46]	18 **Ar** argon 39.95
19 **K** potassium 39.10	20 **Ca** calcium 40.08	21 **Sc** scandium 44.96	22 **Ti** titanium 47.87	23 **V** vanadium 50.94	24 **Cr** chromium 52.00	25 **Mn** manganese 54.94	26 **Fe** iron 55.85	27 **Co** cobalt 58.93	28 **Ni** nickel 58.69	29 **Cu** copper 63.55	30 **Zn** zinc 65.38(2)	31 **Ga** gallium 69.72	32 **Ge** germanium 72.63	33 **As** arsenic 74.92	34 **Se** selenium 78.97	35 **Br** bromine [79.90, 79.91]	36 **Kr** krypton 83.80
37 **Rb** rubidium 85.47	38 **Sr** strontium 87.62	39 **Y** yttrium 88.91	40 **Zr** zirconium 91.22	41 **Nb** niobium 92.91	42 **Mo** molybdenum 95.95	43 **Tc** technetium	44 **Ru** ruthenium 101.1	45 **Rh** rhodium 102.9	46 **Pd** palladium 106.4	47 **Ag** silver 107.9	48 **Cd** cadmium 112.4	49 **In** indium 114.8	50 **Sn** tin 118.7	51 **Sb** antimony 121.8	52 **Te** tellurium 127.6	53 **I** iodine 126.9	54 **Xe** xenon 131.3
55 **Cs** caesium 132.9	56 **Ba** barium 137.3	57-71 lanthanoids	72 **Hf** hafnium 178.5	73 **Ta** tantalum 180.9	74 **W** tungsten 183.8	75 **Re** rhenium 186.2	76 **Os** osmium 190.2	77 **Ir** iridium 192.2	78 **Pt** platinum 195.1	79 **Au** gold 197.0	80 **Hg** mercury 200.6	81 **Tl** thallium [204.3, 204.4]	82 **Pb** lead 207.2	83 **Bi** bismuth 209.0	84 **Po** polonium	85 **At** astatine	86 **Rn** radon
87 **Fr** francium	88 **Ra** radium	89-103 actinoids	104 **Rf** rutherfordium	105 **Db** dubnium	106 **Sg** seaborgium	107 **Bh** bohrium	108 **Hs** hassium	109 **Mt** meitnerium	110 **Ds** darmstadtium	111 **Rg** roentgenium	112 **Cn** copernicium	113 **Uut** ununtrium	114 **Fl** flerovium	115 **Uup** ununpentium	116 **Lv** livermorium	117 **Uus** ununseptium	118 **Uuo** ununoctium

57 **La** lanthanum 138.9	58 **Ce** cerium 140.1	59 **Pr** praseodymium 140.9	60 **Nd** neodymium 144.2	61 **Pm** promethium	62 **Sm** samarium 150.4	63 **Eu** europium 152.0	64 **Gd** gadolinium 157.3	65 **Tb** terbium 158.9	66 **Dy** dysprosium 162.5	67 **Ho** holmium 164.9	68 **Er** erbium 167.3	69 **Tm** thulium 168.9	70 **Yb** ytterbium 173.0	71 **Lu** lutetium 175.0
89 **Ac** actinium	90 **Th** thorium 232.0	91 **Pa** protactinium 231.0	92 **U** uranium 238.0	93 **Np** neptunium	94 **Pu** plutonium	95 **Am** americium	96 **Cm** curium	97 **Bk** berkelium	98 **Cf** californium	99 **Es** einsteinium	100 **Fm** fermium	101 **Md** mendelevium	102 **No** nobelium	103 **Lr** lawrencium

INTERNATIONAL UNION OF
PURE AND APPLIED CHEMISTRY

For notes and updates to this table, see www.iupac.org. This version is dated 8 January 2016.

Role in biochemical processes and

- At their natural concentrations, many metals play an **essential role** in biochemical processes and are thus required in small amounts by most organisms for normally healthy growth (e.g. Zn , Cu , Se, Cr).
- Other metals, however, **are not essential** and do not cause deficiency disorders if absent (e.g. Cd, Pb, Hg, Sn, and the semi-metal As).

Classification of naturally occuring metals by toxicity and hydrologic availability

[Metals that normally do not exist as dissolved species in natural waters or are very rare in crustal rocks are in italics]

Nontoxic		Low toxicity		Moderate to high toxicity			
Aluminum	Magnesium	Barium	*Praseodymium*	*Actinium*	Indium	Polonium	Uranium
Bismuth	Manganese	*Cerium*	*Promethium*	Antimony	*Iridium*	*Radium*	Vanadium
Calcium	Molybdenum	*Dysprosium*	*Rhenium*	Beryllium	Lead	*Ruthenium*	Zinc
Cesium	Potassium	*Erbium*	*Rhodium*	Boron	Mercury	Silver	*Zirconium*
Iron	Strontium	*Europium*	*Samarium*	Cadmium	Nickel	*Tantalum*	
Lithium	Rubidium	*Gadolinium*	Scandium	Chromium	*Niobium*	Thallium	
	Sodium	*Gallium*	*Terbium*	Cobalt	*Osmium*	Thorium	
		Germanium	Thulium	Copper	Palladium	*Titanium*	
		Gold	*Tin*	*Hafnium*	Platinum	*Tungsten*	
		Holmium	*Ytterbium*				
		Neodymium	Yttrium				

U.S. GEOLOGICAL SURVEY CIRCULAR 1133, 1995

Toxic Elements

Element	Reference Range	Reference Range in µg/g
Aluminum	2.8	<= 17.3
Antimony	0.028	<= 0.016
Arsenic	0.065	<= 0.080
Barium	0.54	<= 1.70
Bismuth	0.170	<= 0.178
Cadmium	0.024	<= 0.022
Gadolinium	0.0059	<= 0.0005
Lead	0.407	<= 0.700
Mercury	3.10	<= 1.32
Nickel	0.12	<= 0.55
Rhodium	<dl	<= 0.0005
Rubidium	0.002	<= 0.040
Thallium	<dl	<= 0.0004
Tin	0.128	<= 0.149
Uranium	0.0020	<= 0.0057

Ratios

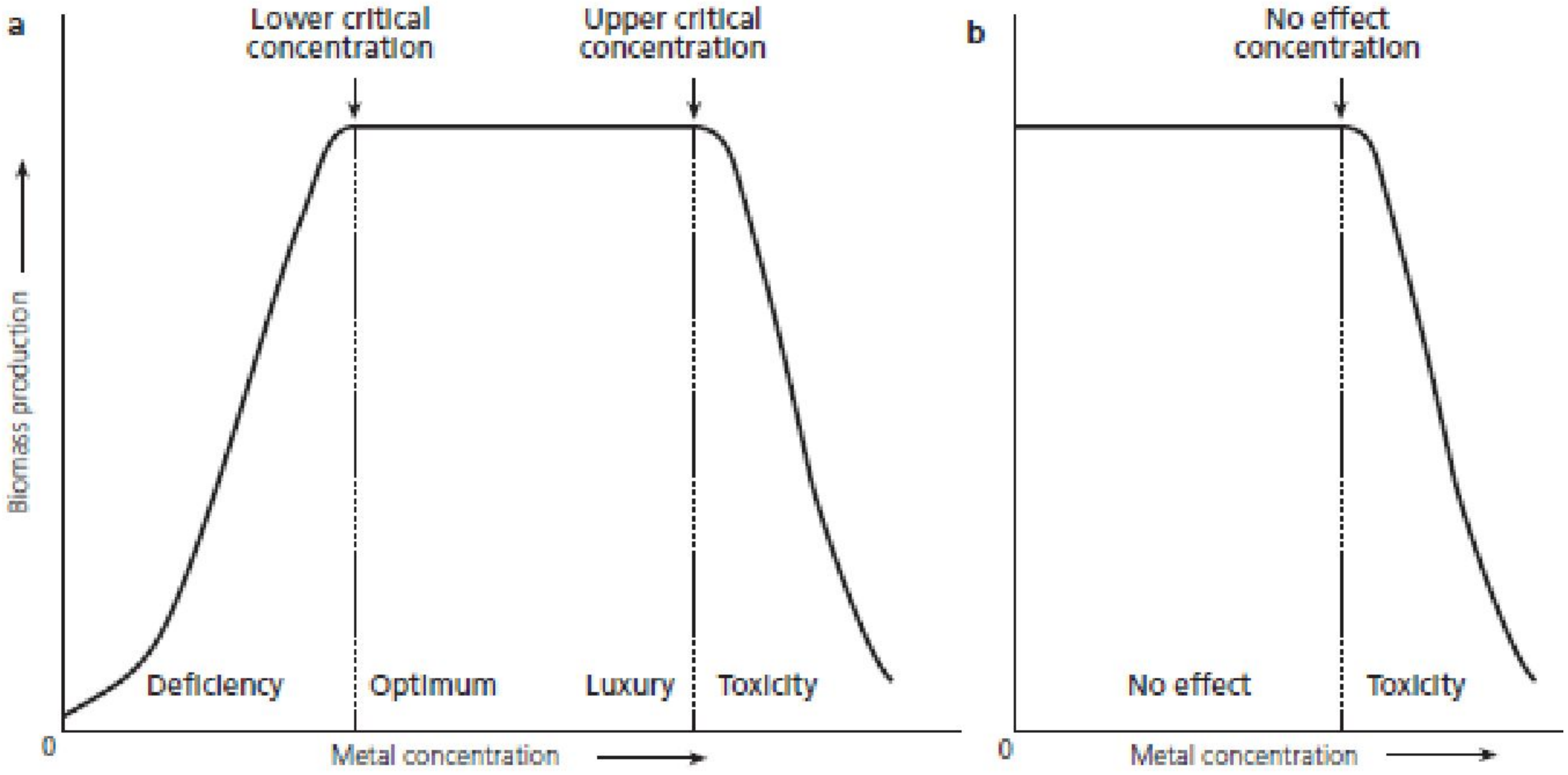
	Inside Range	Outside Range	Reference Range
Ca/Mg	17		5-29
Ca/P	3		1-9

Nutrient Elements

Element	Reference Range	Reference Range in µg/g
Calcium	327	192-1,588
Chromium	0.09	0.01-1.58
Cobalt	0.003	0.001-0.129
Copper	10	8-136
Iron	5.8	5.2-24.4
Magnesium	19	11-122
Manganese	0.12	0.04-1.93
Molybdenum	0.04	0.01-1.24
Phosphorous	96	104-206
Selenium	1.07	0.58-1.13
Sodium	3	14-426
Strontium	0.63	0.01-4.40
Sulfur	46,757	41,781-60,894
Vanadium	0.027	0.003-0.108
Zinc	146	119-245

	Reference Range	
Lithium	<dl	<= 0.302
Potassium	1	<= 174

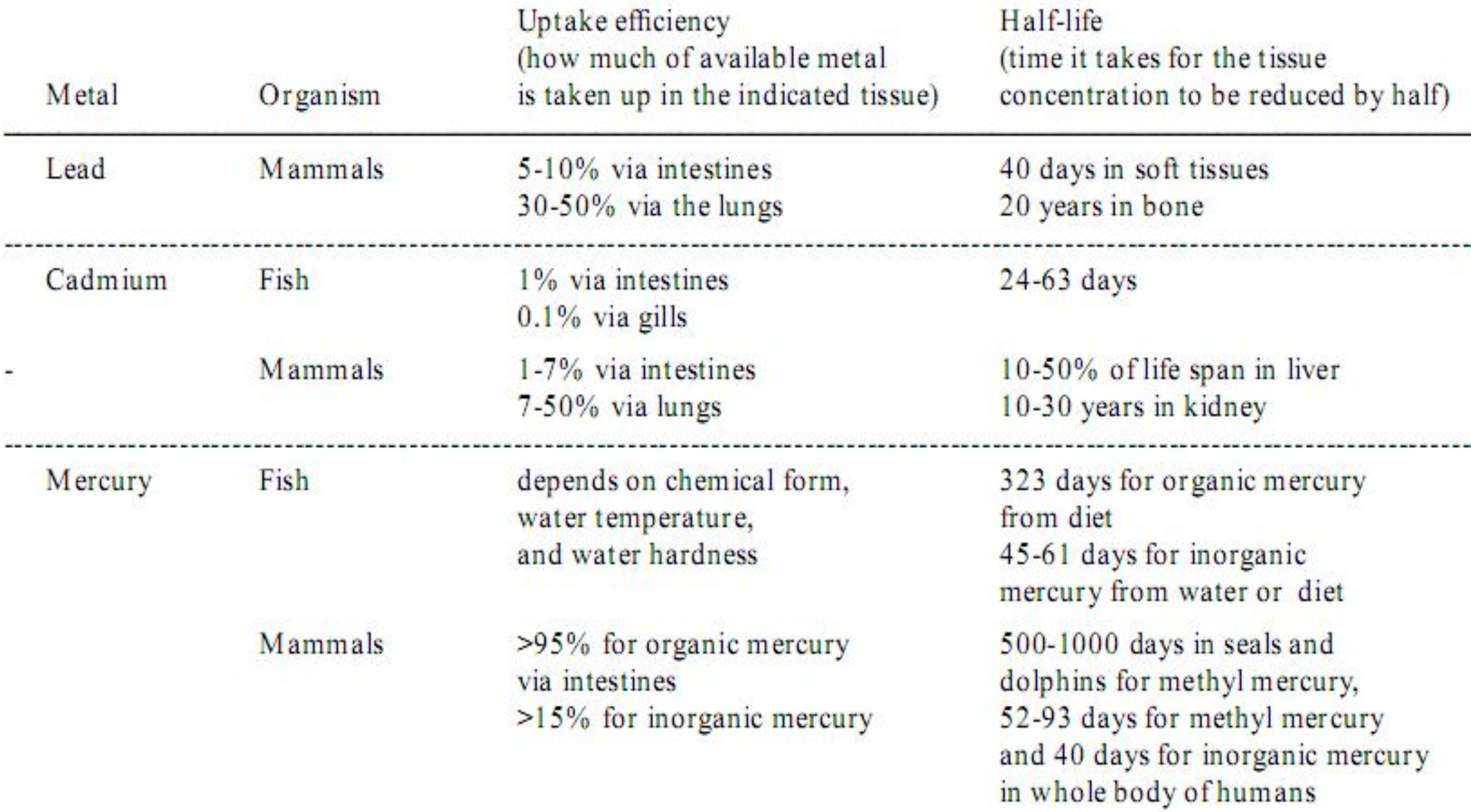
Figure. Typical dose–response curves for a) essential trace metals, and b) non-essential trace metals (modified from Alloway and Ayres, 1997).



Bioaccumulation and biomagnification

- virtually all heavy metals **are toxic** – especially to animals and humans – although organisms are also able to adapt themselves, at least partly, to increased levels of metals.
- Most heavy metals accumulate in organism tissues **(bioaccumulation)** and as they are transferred through the food chain **(biomagnification).**

Metals can transform and accumulate in the body (AMAP)



Metal	Organism	Uptake efficiency (how much of available metal is taken up in the indicated tissue)	Half-life (time it takes for the tissue concentration to be reduced by half)
Lead	Mammals	5-10% via intestines 30-50% via the lungs	40 days in soft tissues 20 years in bone
Cadmium	Fish	1% via intestines 0.1% via gills	24-63 days
-	Mammals	1-7% via intestines 7-50% via lungs	10-50% of life span in liver 10-30 years in kidney
Mercury	Fish	depends on chemical form, water temperature, and water hardness	323 days for organic mercury from diet 45-61 days for inorganic mercury from water or diet
	Mammals	>95% for organic mercury via intestines >15% for inorganic mercury	500-1000 days in seals and dolphins for methyl mercury, 52-93 days for methyl mercury and 40 days for inorganic mercury in whole body of humans

Toxicity of metals

- Metals generally produce their toxicity **by forming complexes with organic compounds** (ligands).
- The modified molecules lose their ability to function properly, causing the affected cells to malfunction or die.
- Metals commonly bind to biological compounds containing oxygen, sulphur, and nitrogen , which may **inactivate** certain **enzyme systems**.

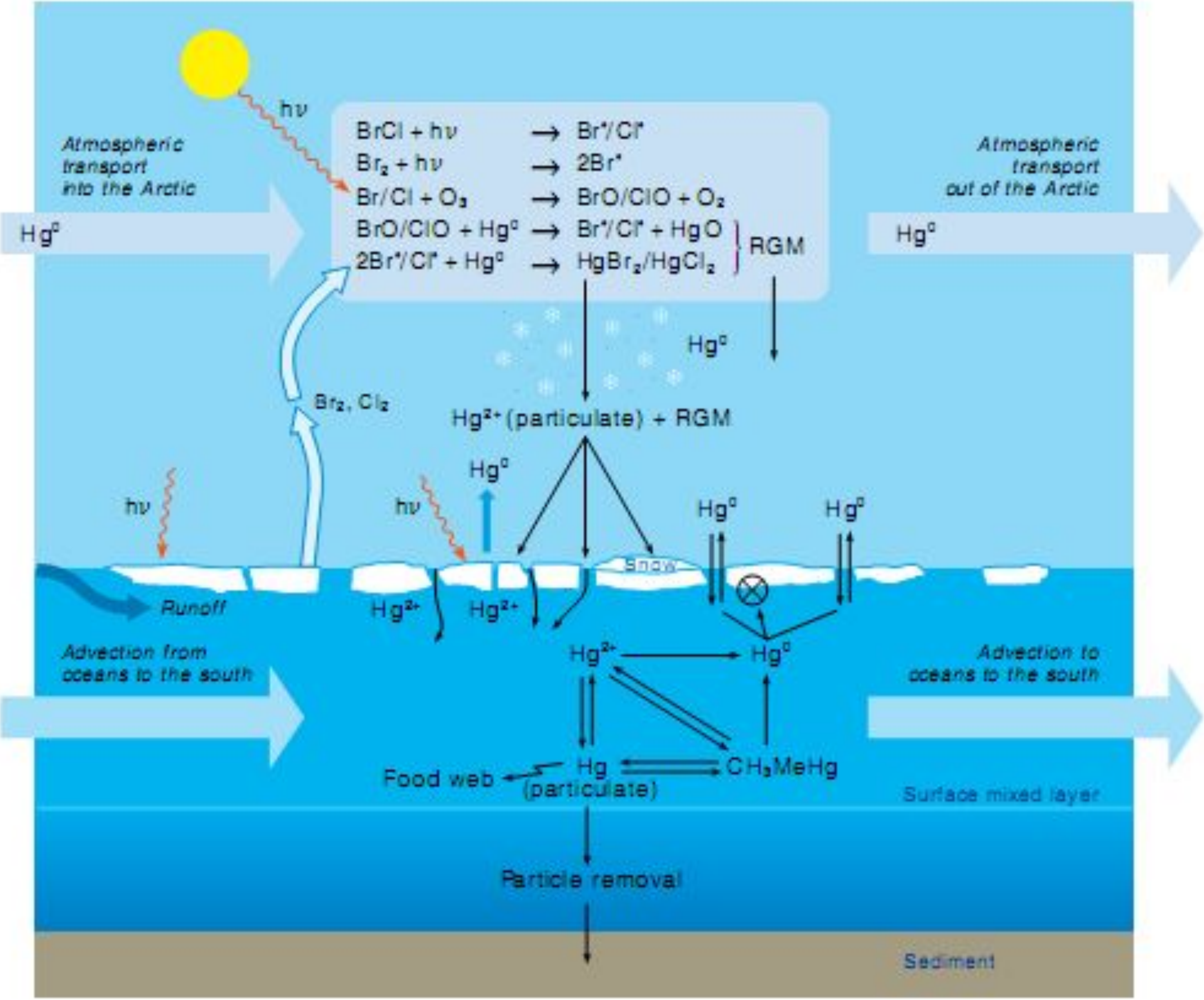
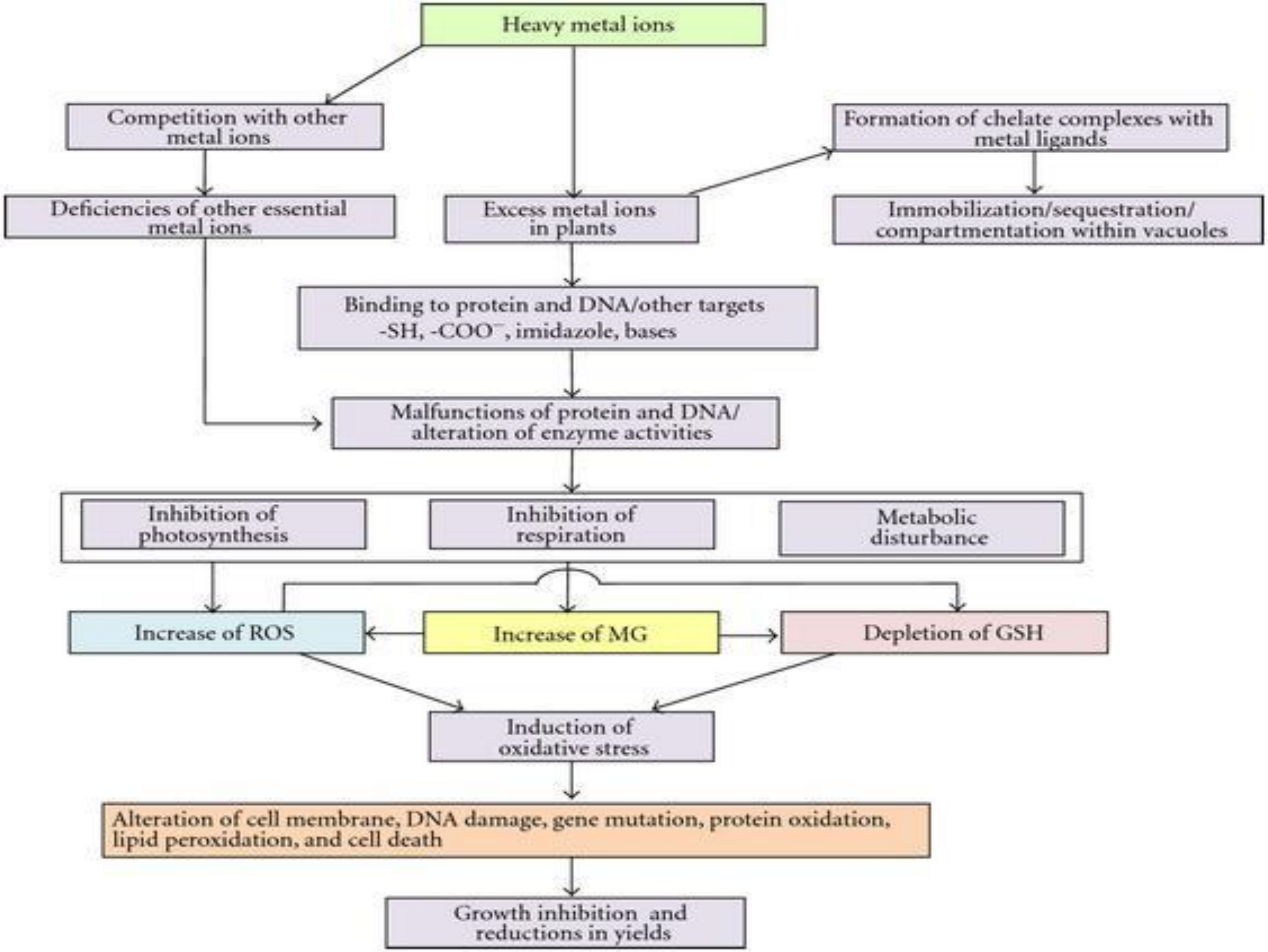

hν
$BrCl + h\nu \rightarrow Br^*/Cl^*$
$Br_2 + h\nu \rightarrow 2Br^*$
$Br/Cl + O_3 \rightarrow BrO/ClO + O_2$
$BrO/ClO + Hg^0 \rightarrow Br^*/Cl^* + HgO$
$2Br^*/Cl^* + Hg^0 \rightarrow HgBr_2/HgCl_2$
RGM
Atmospheric transport into the Arctic
Hg^0
Atmospheric transport out of the Arctic
Hg^0
Hg^0
Br_2, Cl_2
Hg^{2+} (particulate) + RGM
Hg^0
hν
hν
Hg^0
Hg^0
Snow
Runoff
Hg^{2+}
Hg^{2+}
Hg^{2+}
Hg^0
Advection from oceans to the south
Advection to oceans to the south
Food web
Hg (particulate)
CH_3MeHg
Surface mixed layer
Particle removal
Sediment

Figure: Possible biochemical and molecular mechanisms of heavy metal-mediated ROS induction and damage to the development of higher plants.



HM in the Environment

- most heavy metals are present as cations, though some semi-metals may occur as oxyanions (e.g. arsenate AsO_4^{3-}). Heavy metals occur naturally in the Earth's crust as impurities isomorphously substituted for various macroelement constituents in the lattices of many primary and secondary minerals. The heavy metal content varies greatly both within and between different types of rocks. The maximum concentrations of trace elements are commonly found in areas near ore deposits, which are often associated with past or present volcanic activity. This may give rise ecotoxicity; it usually refers to common metals such as copper, lead, or zinc.

- Heavy metals (Ag, As, Cd, Cu, Cr, Hg, Ni, Pb, and Zn) can be present in the aquatic system in both dissolved forms (which can cause toxic effects on a wide diversity of organisms, including vertebrates) and particulated ones (including adsorbed on sediments, suspended particulate matter or colloids, in transitional complexes, and Fe/Mn hydroxides nets, linked to organic matter and carbonates, etc.). The dynamics which regulates the transference of heavy metals between the dissolved and the particulated phases (in both senses) depends on the pH and oxidereduction potential of the system. Also these parameters regulate the chemical speciation of heavy metals within the system.

- The principal geochemical processes controlling the retention of heavy metals in soil and water are adsorption and precipitation. For these processes the redox potential and pH are the key variables governing the distribution of metals between the solid and dissolved phases and, consequently, their dispersal in the environment and their bioavailability. In general, many solids control the fixation of heavy metals, namely clay minerals, organic matter, iron, manganese, and aluminium oxides and hydroxides for adsorption, and poorly soluble sulphide , carbonate , and phosphate minerals for precipitation

- Under oxidised conditions, the major process controlling the speciation of heavy metals is adsorption to the negatively charged exchange sites of clay minerals and organic matter. In general, adsorption causes the heavy metals to be relatively immobile in soils. Many metals show specific adsorption and compete actively with protons for surface sites. They may even be adsorbed on mineral and organic matter surfaces that are positively charged.

- Nevertheless, the amount of adsorbed metals decreases with decreasing pH . Another reason why the pH is often found to be the most important factor determining the distribution coefficient of heavy metals in soil and sediment is the specificity of heavy metals for surfaces that can deprotonate. At a given pH, the concentration in the dissolved phase is approximately proportional to the concentration adsorbed to the solid phase

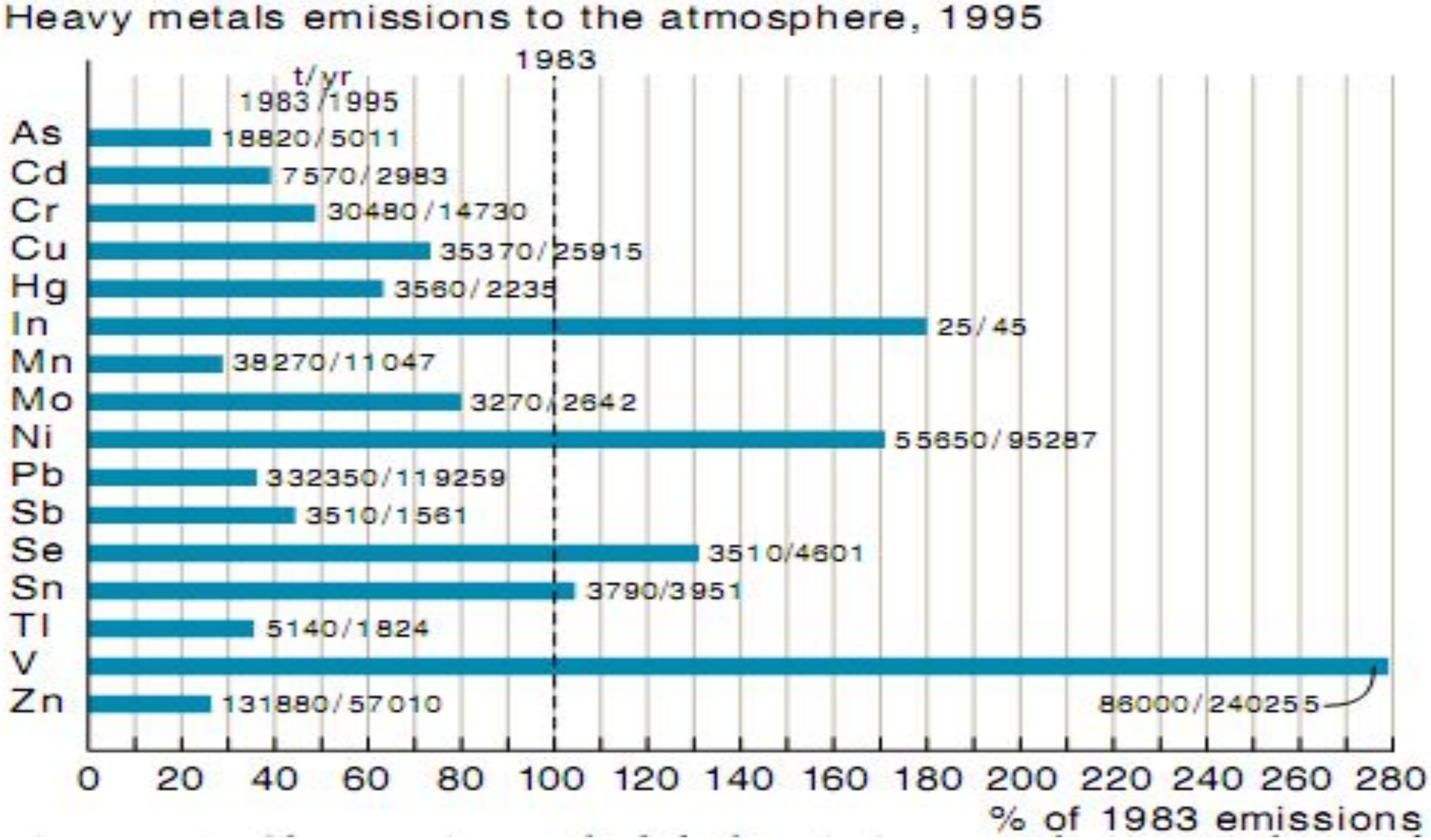
- Some metals (e.g. copper and lead) also tend to form complexes with dissolved and sediment organic matter, some of which are mobile. This process of ligand formation increases with decreasing pH. At high pH values, heavy metals may also precipitate as carbonates or hydroxides. Furthermore, heavy metals may be removed from an aqueous solution due to ***coprecipitation*** (i.e. the inclusion of additional species within or on the surface of a precipitate as it is formed) with calcite or iron , aluminium , and manganese oxyhydroxides . It should be clear from the above that the pH is the master variable determining the mobility of heavy metals under oxidising conditions, as it controls adsorption, complexation , and precipitation. All these processes bring about a decrease in the mobility of heavy metals with increasing pH.

- Under reduced conditions, the mobility of most metals is further decreased due to the formation of barely soluble sulphide minerals. In this case, the concentration of heavy metals in the dissolved phase is controlled by the solubility product of the sulphide minerals, which means that the total concentration of heavy metals barely influences the concentration of dissolved heavy metals

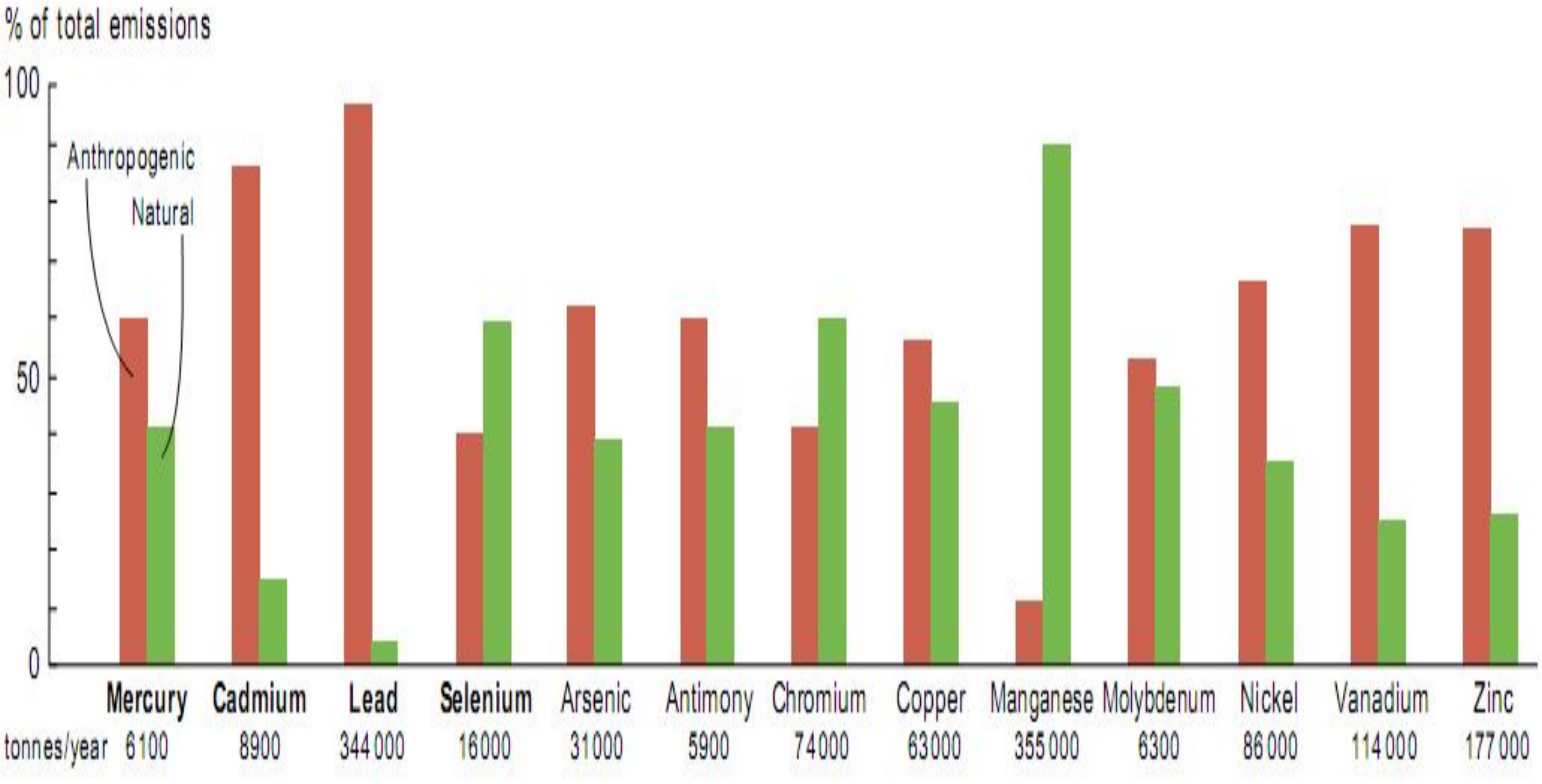
Sources of pollution

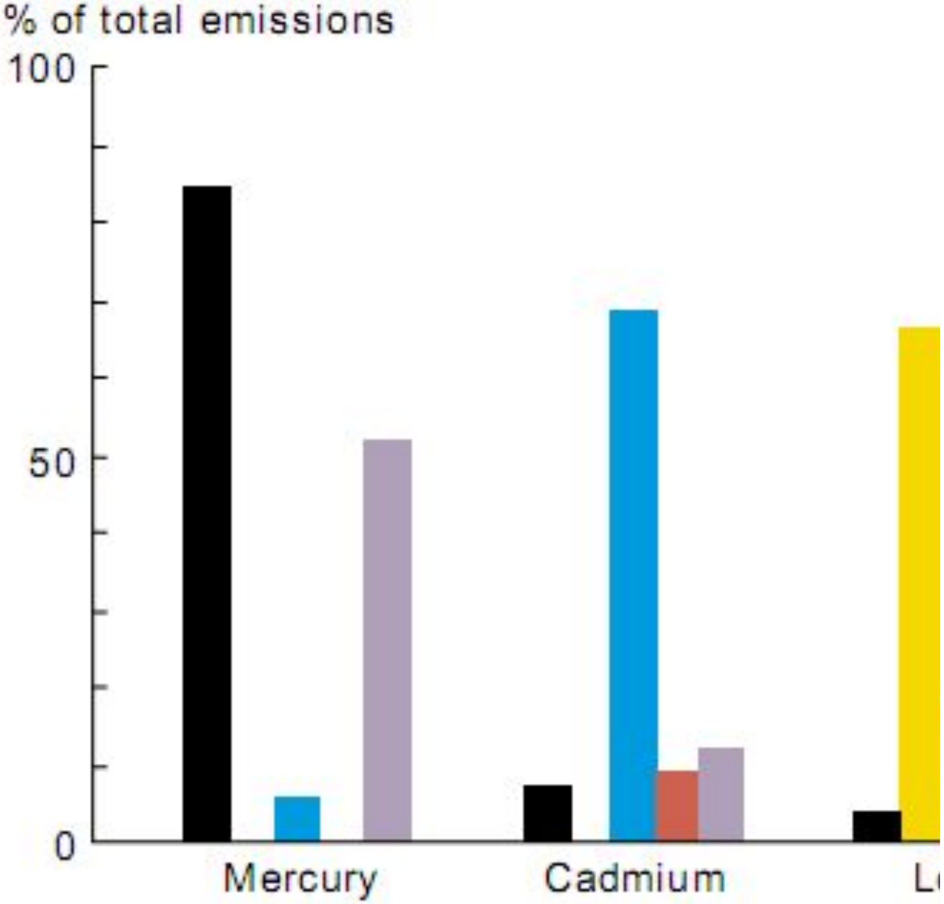
- Heavy metals are emitted to the atmosphere from both natural and anthropogenic sources. Very few of the sources that directly result in the contamination of the Arctic environment are located in the Arctic. Metals released to the environment outside the Arctic are transported to the Arctic via air currents, rivers, and ocean currents.

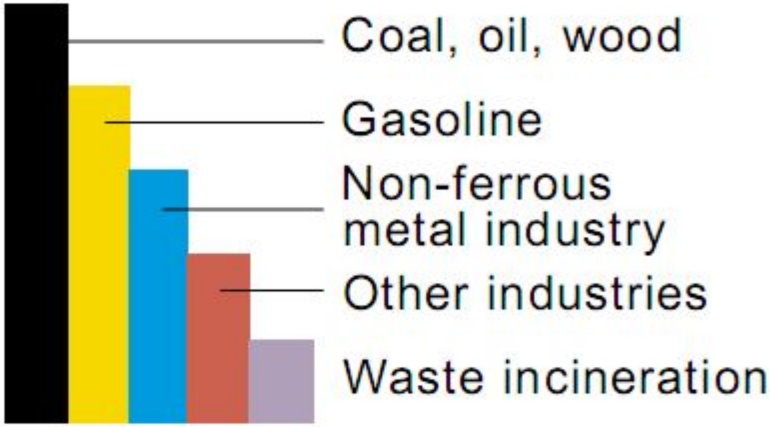
Changes in total global emissions to the atmosphere of heavy metals from major anthropogenic sources based on 1983 and 1995 data (Pacyna and Pacyna, 2001).



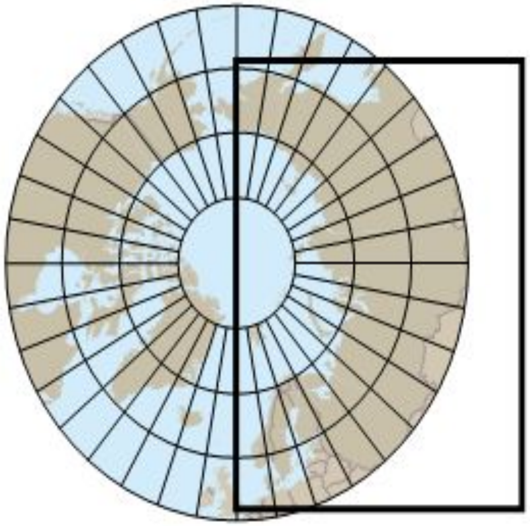
Sources


% of total emissions
100
50
0
Anthropogenic
Natural
Mercury
Cadmium
Lead
Selenium
Arsenic
Antimony
Chromium
Copper
Manganese
Molybdenum
Nickel
Vanadium
Zinc
tonnes/year
6100
8900
344 000
16000
31000
5900
74000
63000
355 000
6300
86 000
114 000
177 000



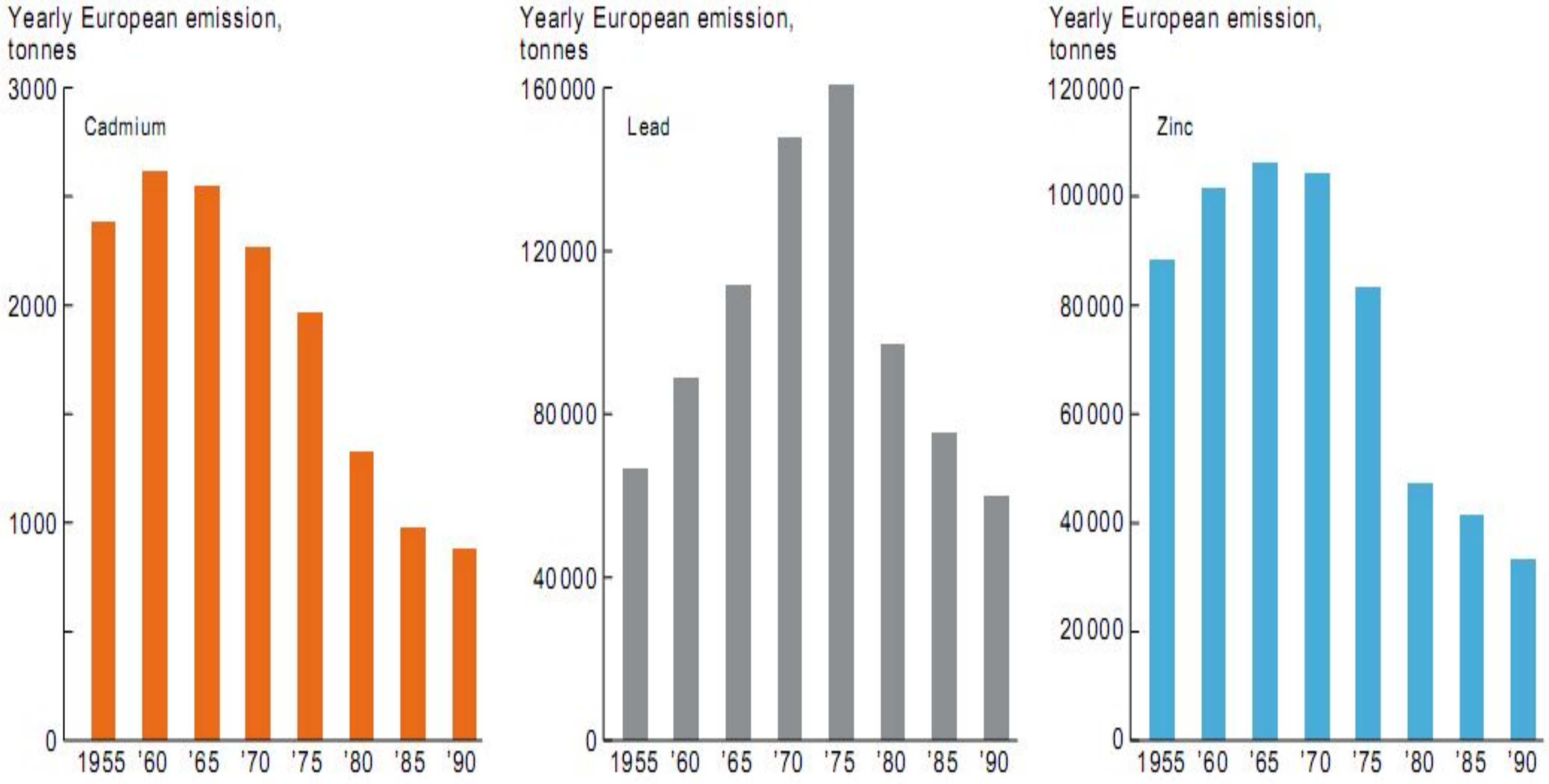


The relative importance of anthropogenic sources of metals world-wide. The percentages shown in the bars are based on range values and therefore do not sum to 100 percent.

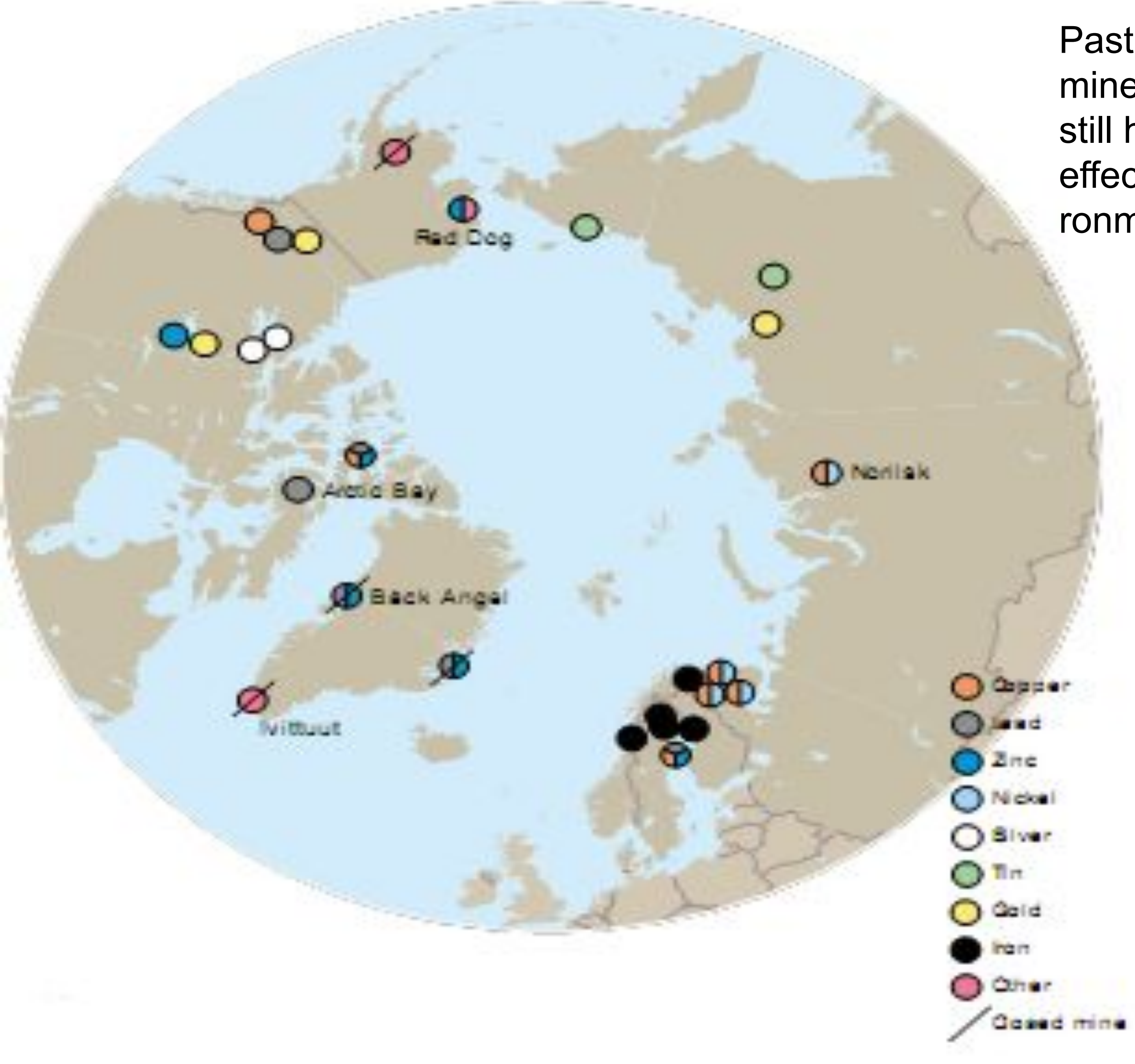


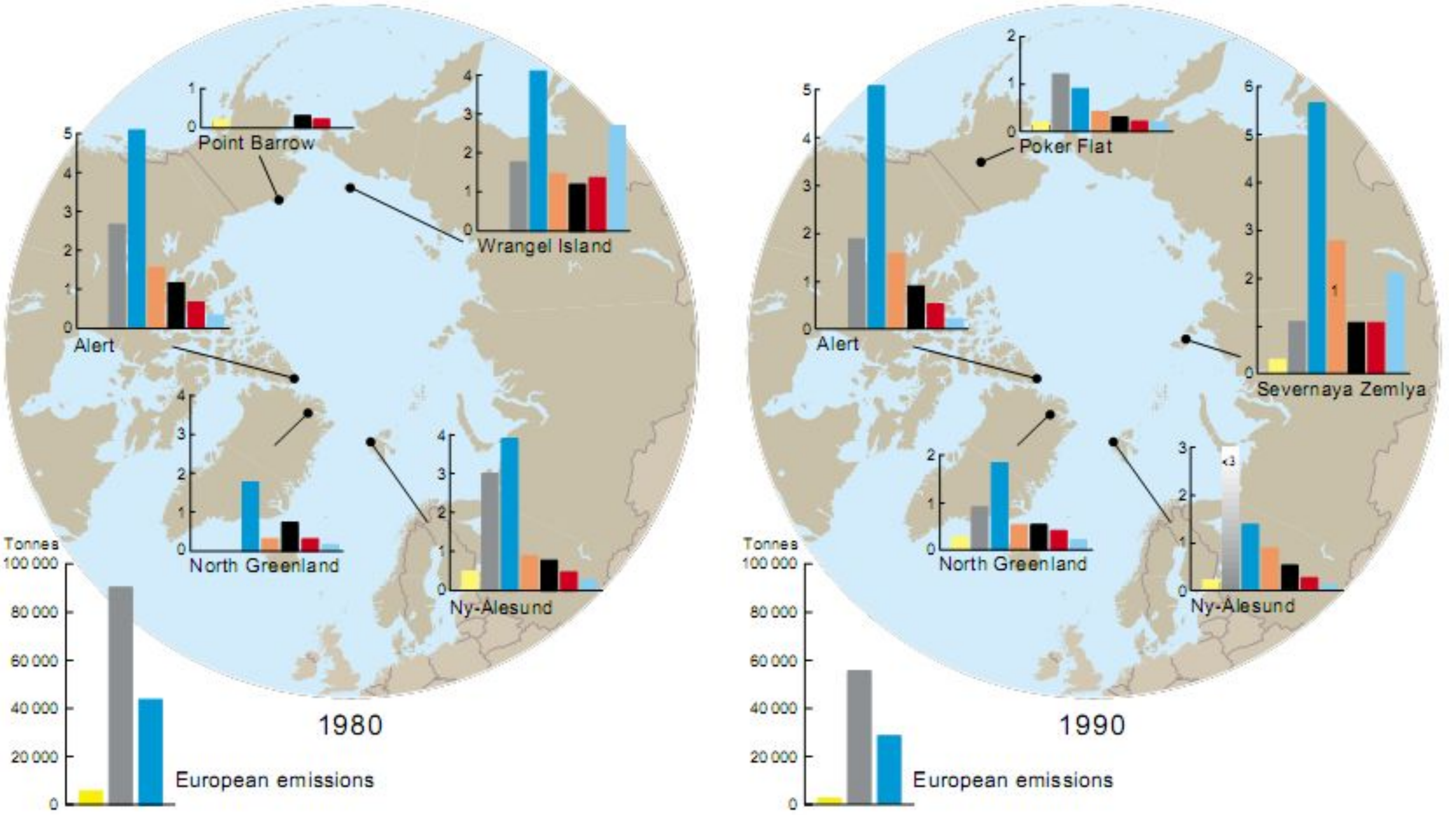
Major point sources in the former Soviet Union of heavy metals to the air.

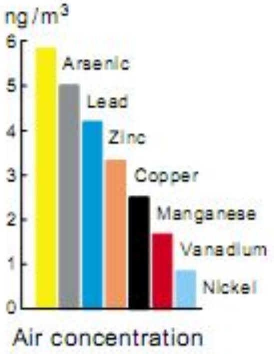
Time trend in European atmospheric emissions of cadmium, lead, and zinc



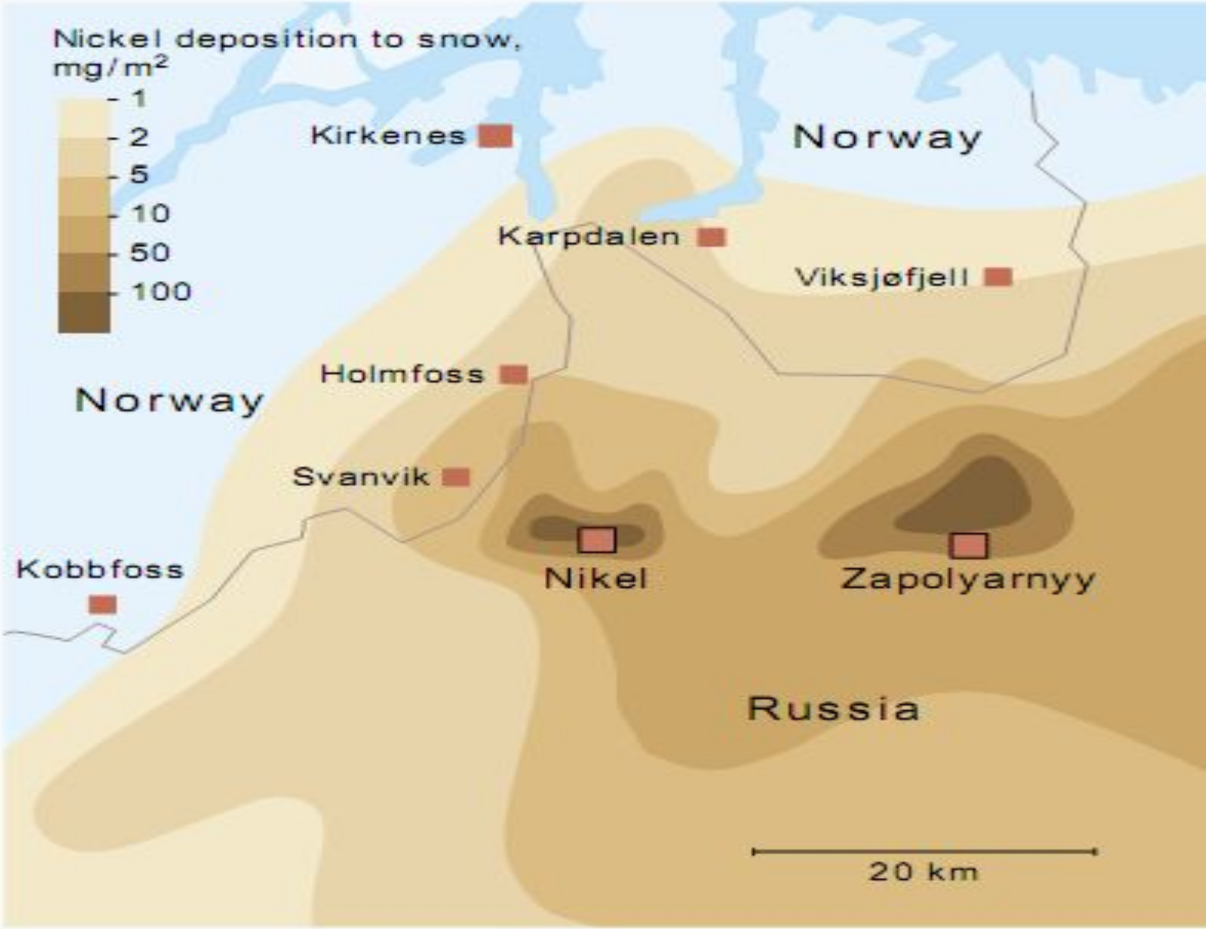
Past and present metal mines in the Arctic that still have a significant effect on the local environment.



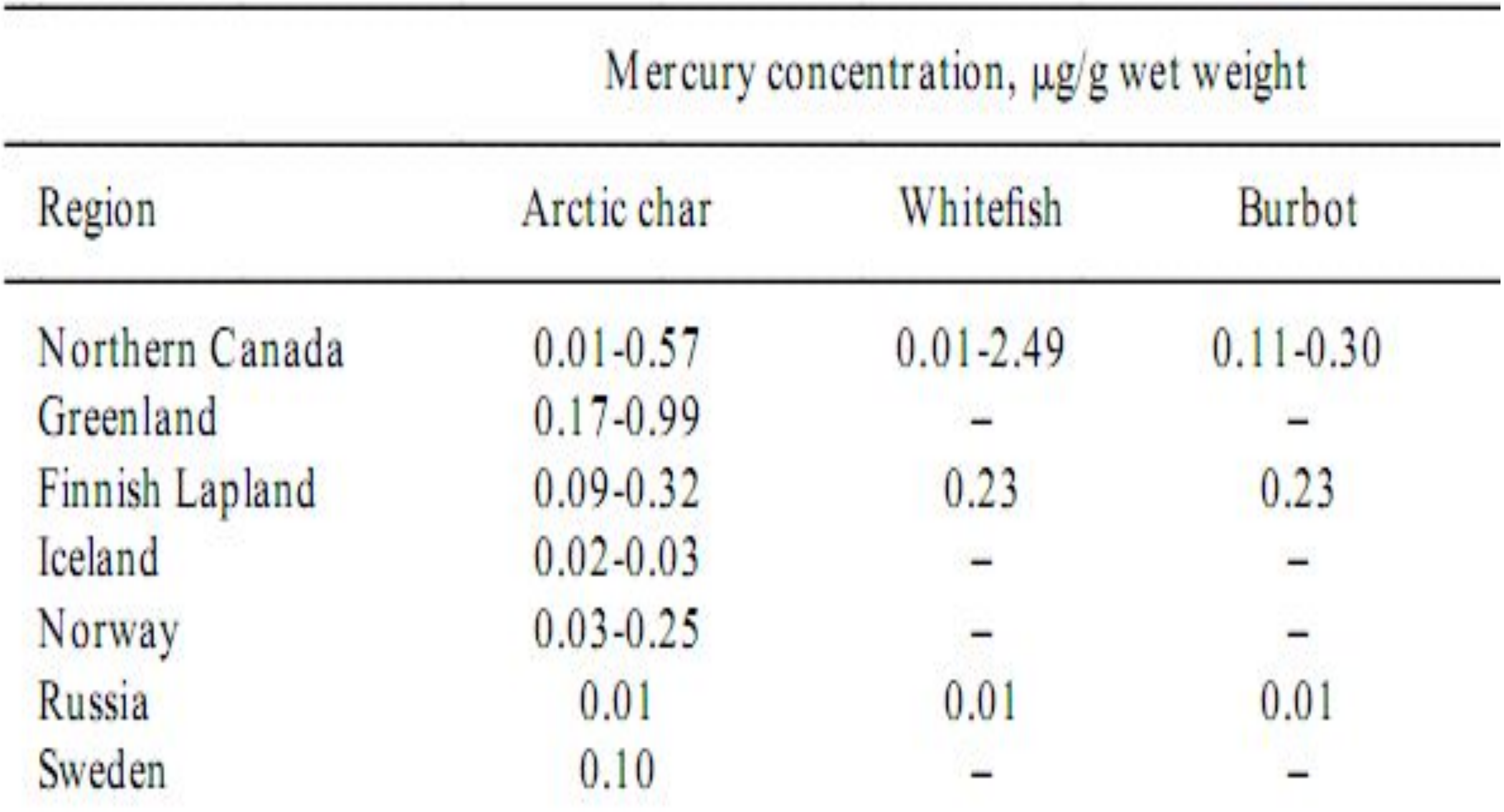




Winter air concentrations of heavy metals at remote Arctic sites and European emissions of arsenic, lead, and zinc in 1980 and 1990.


Nickel deposition to snow, mg/m²
1
2
5
10
50
100
Kirkenes
Norway
Karpdalen
Viksjøfjell
Holmfoss
Norway
Svanvik
Kobbfoss
Nikel
Zapolyarnyy
Russia
20 km

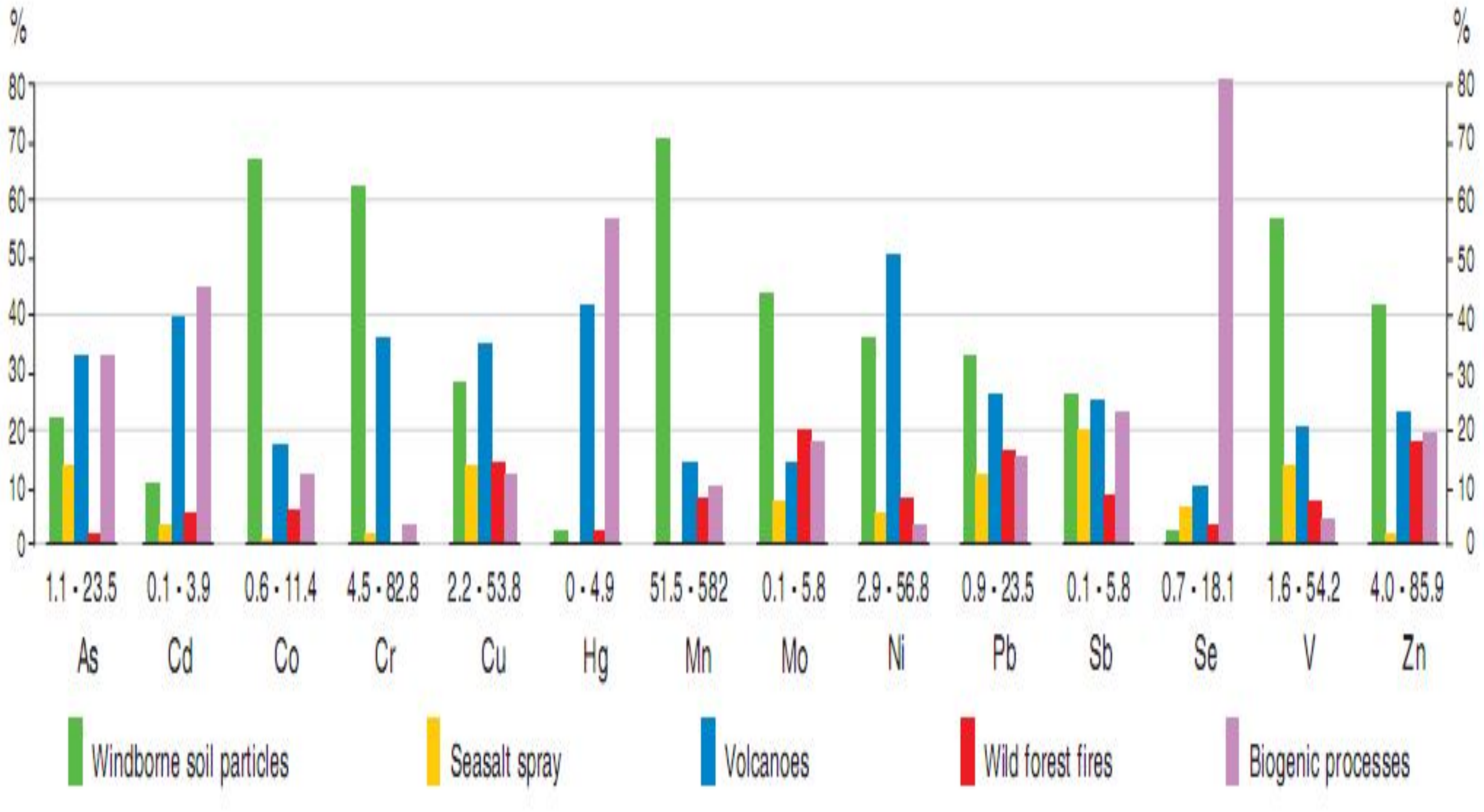
Mercury concentrations in Arctic freshwater fish.



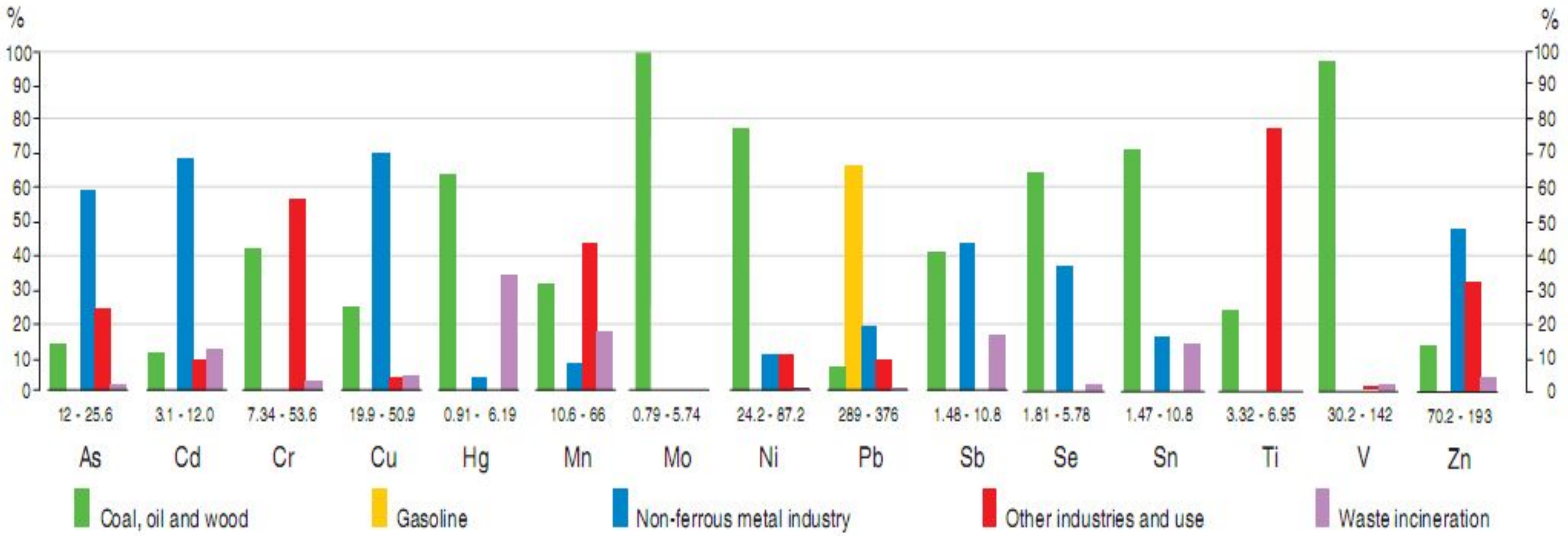
	Mercury concentration, µg/g wet weight		
Region	Arctic char	Whitefish	Burbot
Northern Canada	0.01-0.57	0.01-2.49	0.11-0.30
Greenland	0.17-0.99	–	–
Finnish Lapland	0.09-0.32	0.23	0.23
Iceland	0.02-0.03	–	–
Norway	0.03-0.25	–	–
Russia	0.01	0.01	0.01
Sweden	0.10	–	–

Natural sources

- The principal natural source of heavy metals in the environment is from crustal material that is either weathered on (dissolved) and eroded from (particulate) the Earth’s surface or injected into the Earth’s atmosphere by volcanic activity. These two sources account for 80% of all the natural sources; forest fires and biogenic sources, account for 10% each. Particles released by erosion appear in the atmosphere as windblown dust. In addition, some particles are released by vegetation. The natural emissions of the six heavy metals are 12,000 (Pb); 45,000 (Zn); 1,400 (Cd); 43,000 (Cr); 28,000 (Cu); and 29,000 (Ni) metric tons per year, respectively. Abundant quantity of metals are emitted into the atmosphere from natural sources.



Numbers under columns : range of estimates (103 t/y).
Figure 7·1. Global emissions of trace metals to the atmosphere from natural sources (after Nriagu 1989). Numbers under the columns are the range of estimates of the emissions in thousands of tonnes per year. The percentages shown by the bars are calculated using the maximum value of the range of the total and individual source category estimates.



Numbers under columns : range of estimates (10 t/y).

Figure 7·2. Global emissions of trace metals to the atmosphere at the beginning of the 1980s from anthropogenic sources (after Nriagu and Pacyna 1988). Numbers under the columns are the range of estimates of the emissions in thousands of tonnes per year. The percentages shown by the bars are calculated using the maximum value of the range of the total and individual source category estimates.

Figure 7·3. Comparison of global emissions of trace metals to the atmosphere from natural and anthropogenic sources in 1983. Numbers under the columns are the median values of estimates of total emissions in thousands of tonnes per year. The percentages shown by the bars are calculated from the median values of the ranges of the estimates for natural and anthropogenic sources.

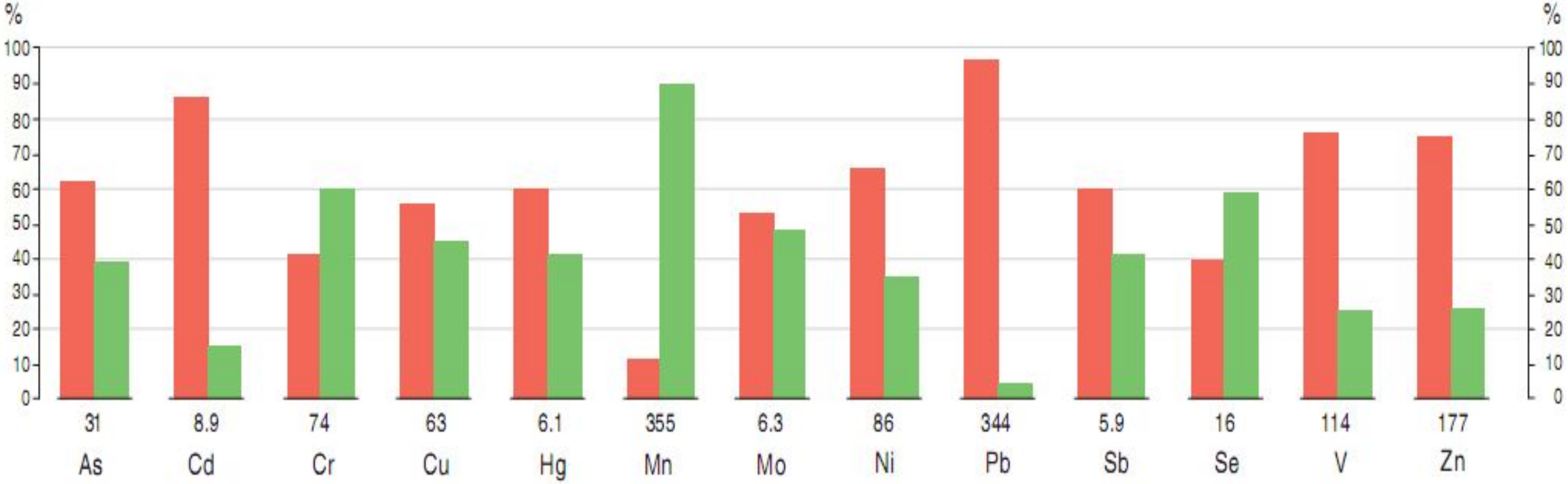
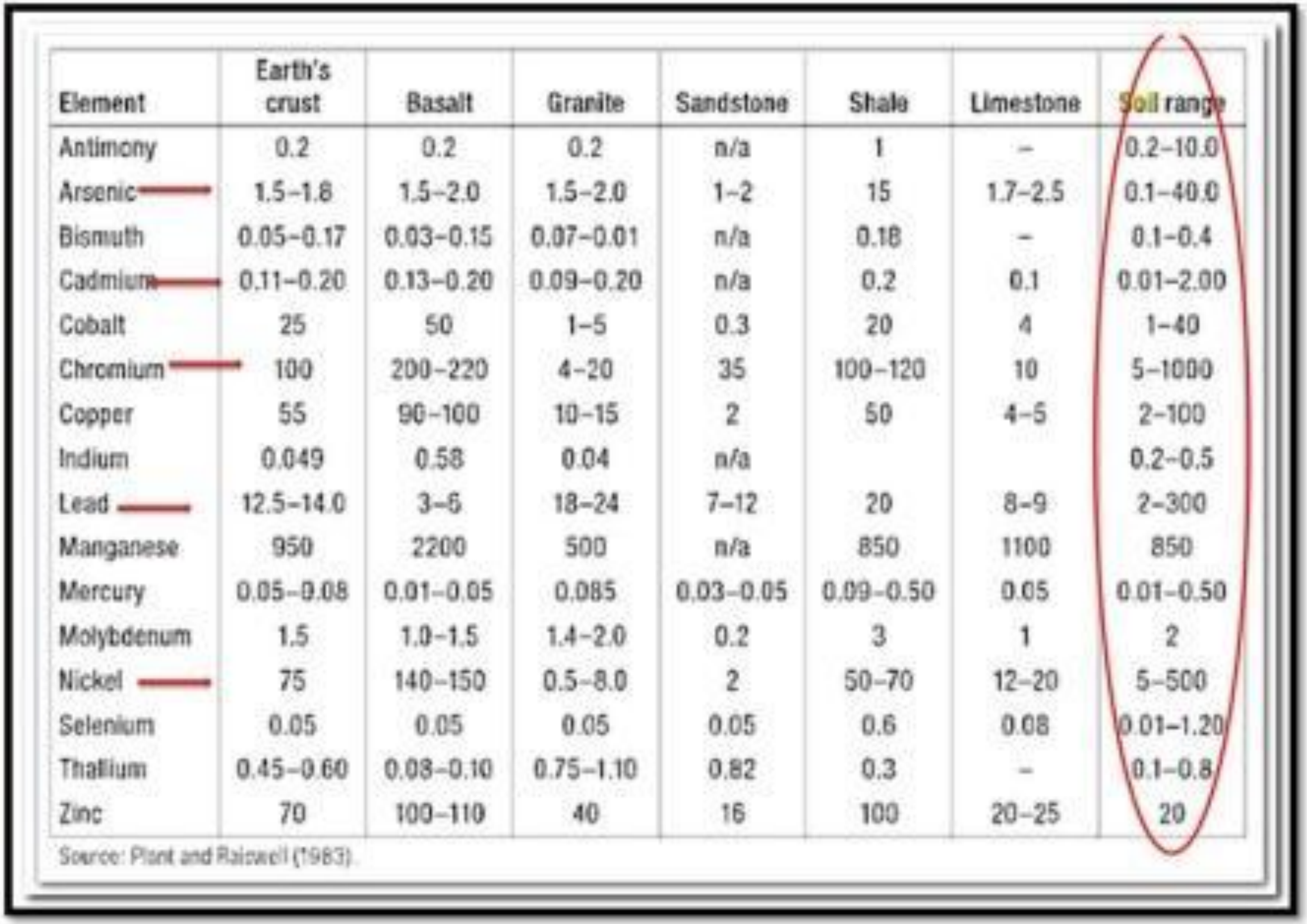


Figure 7·3. Comparison of global emissions of trace metals to the atmosphere from natural and anthropogenic sources in 1983. Numbers under the columns are the median values of estimates of total emissions in thousands of tonnes per year. The percentages shown by the bars are calculated from the median values of the ranges of the estimates for natural and anthropogenic sources.



Element	Earth's crust	Basalt	Granite	Sandstone	Shale	Limestone	Soil range
Antimony	0.2	0.2	0.2	n/a	1	–	0.2–10.0
Arsenic	1.5–1.8	1.5–2.0	1.5–2.0	1–2	15	1.7–2.5	0.1–40.0
Bismuth	0.05–0.17	0.03–0.15	0.07–0.01	n/a	0.18	–	0.1–0.4
Cadmium	0.11–0.20	0.13–0.20	0.09–0.20	n/a	0.2	0.1	0.01–2.00
Cobalt	25	50	1–5	0.3	20	4	1–40
Chromium	100	200–220	4–20	35	100–120	10	5–1000
Copper	55	90–100	10–15	2	50	4–5	2–100
Indium	0.049	0.58	0.04	n/a			0.2–0.5
Lead	12.5–14.0	3–6	18–24	7–12	20	8–9	2–300
Manganese	950	2200	500	n/a	850	1100	850
Mercury	0.05–0.08	0.01–0.05	0.085	0.03–0.05	0.09–0.50	0.05	0.01–0.50
Molybdenum	1.5	1.0–1.5	1.4–2.0	0.2	3	1	2
Nickel	75	140–150	0.5–8.0	2	50–70	12–20	5–500
Selenium	0.05	0.05	0.05	0.05	0.6	0.08	0.01–1.20
Thallium	0.45–0.60	0.08–0.10	0.75–1.10	0.82	0.3	–	0.1–0.8
Zinc	70	100–110	40	16	100	20–25	20

Source: Plant and Raiswell (1983).

Natural sources in the Arctic

- An accurate inventory of heavy metal sources and emissions to the atmosphere from natural processes is needed to make a complete assessment of the extent of regional and global pollution by heavy metals in the Arctic. It is generally presumed that the principal natural sources of heavy metals include wind-borne soil particles, volcanoes, seasalt spray, and wild forest fires. Recent studies have shown, however, that particulate organic matter is the dominant component of atmospheric aerosols in non-urban areas and that over 60% of the airborne heavy metals in forested regions can be attributed to aerosols of biogenic origin.

- Biogenic sources can account, on average, for over 50% of the Se, Hg, and Mo, and from 30 to 50% of the As, Cd, Cu, Mn, Pb, and Zn, released annually to the atmosphere from natural sources. Volcanic emissions can account for 40-50% of the Cd and Hg and 20-40% of the As, Cr, Cu, Ni, Pb, and Sb released annually from natural sources. Seasalt aerosols seem to account for <10% of atmospheric heavy metals from natural sources. Finally, soil-derived dusts can account for over 50% of the total Cr, Mn, and V emissions, as well as for 20-30% of the Cu, Mo, Ni, Pb, Sb, and Zn released annually to the atmosphere. As the accuracy of emission estimates for natural sources is low, these percentage contributions should be considered as approximations only.

- The natural sources of heavy metals which influence the freshwater, terrestrial, and marine environment are even more difficult to assess than the atmospheric sources. In general, soils and sediments tend to reflect the composition of their parent material. Soils and sediments in mineralized areas, therefore, usually have the highest concentrations of the corresponding metals. For example, rocks with high Hg content usually occur in areas of crustal instability where volcanic and geothermal activity are high. It is also very difficult to assess the extent to which emissions from natural processes affect the contamination of the Arctic environment. In general, fluxes from these processes within the Arctic are regarded as less significant than anthropogenic releases, both within and outside the Arctic.

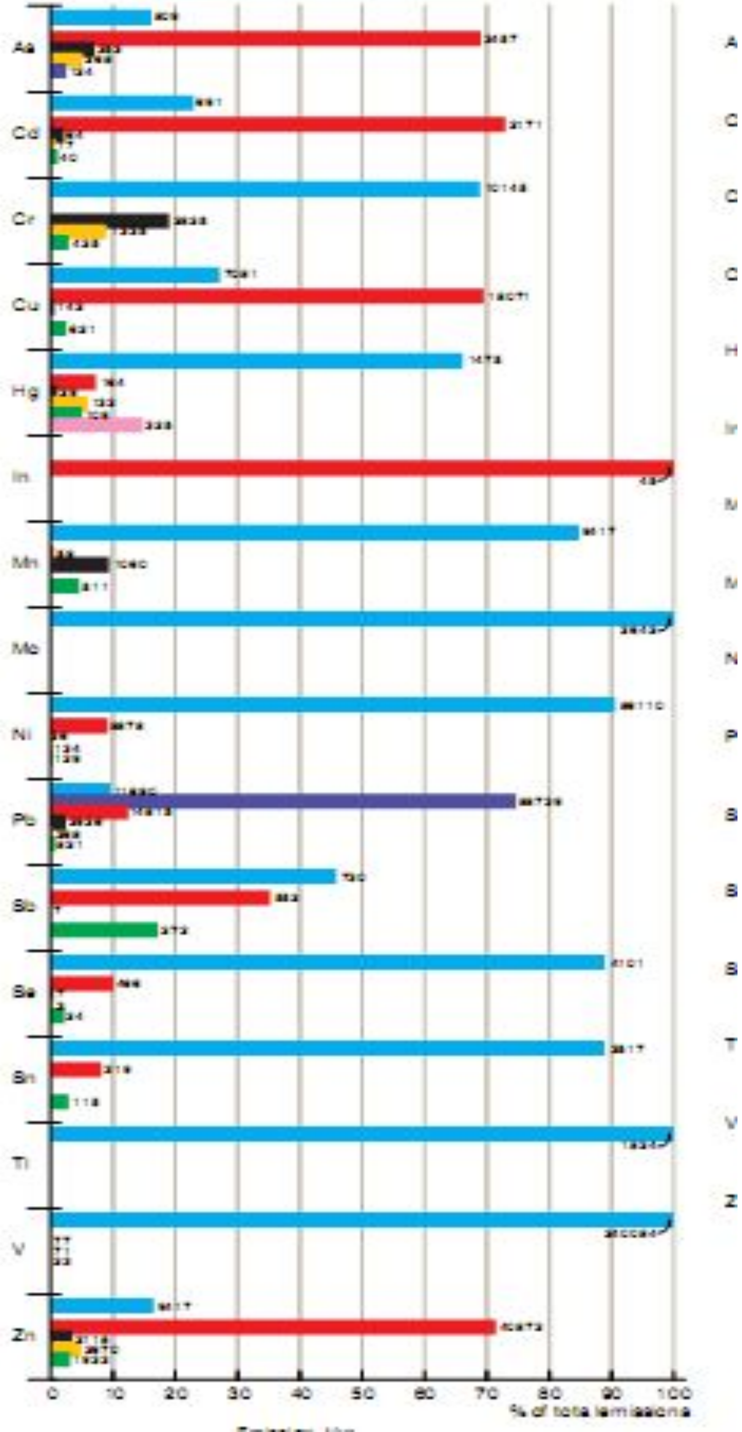
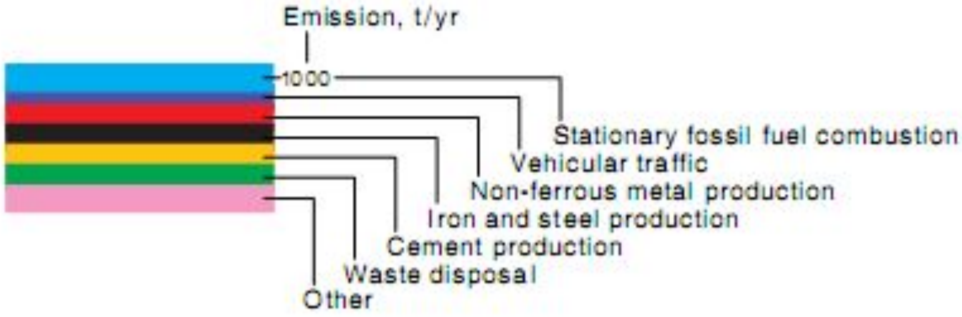


Figure. Metals emitted from anthropogenic sources based on
1995 inventories (Pacyna and Pacyna, 2001).



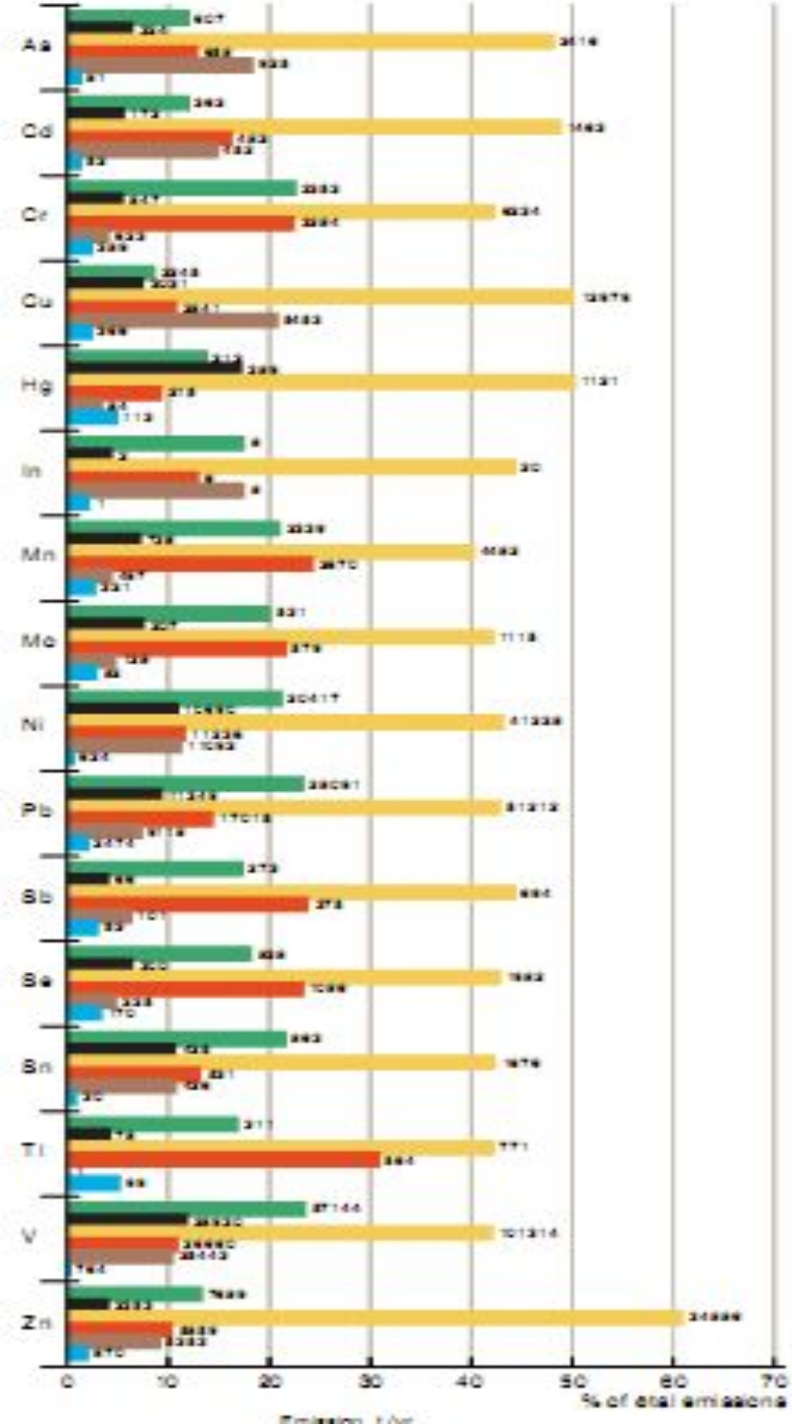
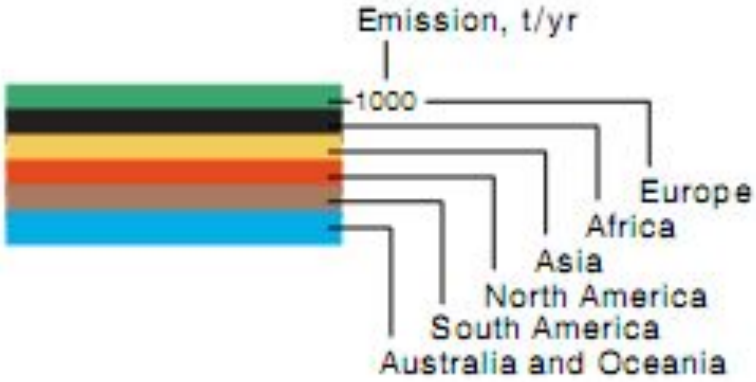


Figure Worldwide emission estimates of anthropogenic heavy metals by continent (Pacyna and Pacyna, 2001).



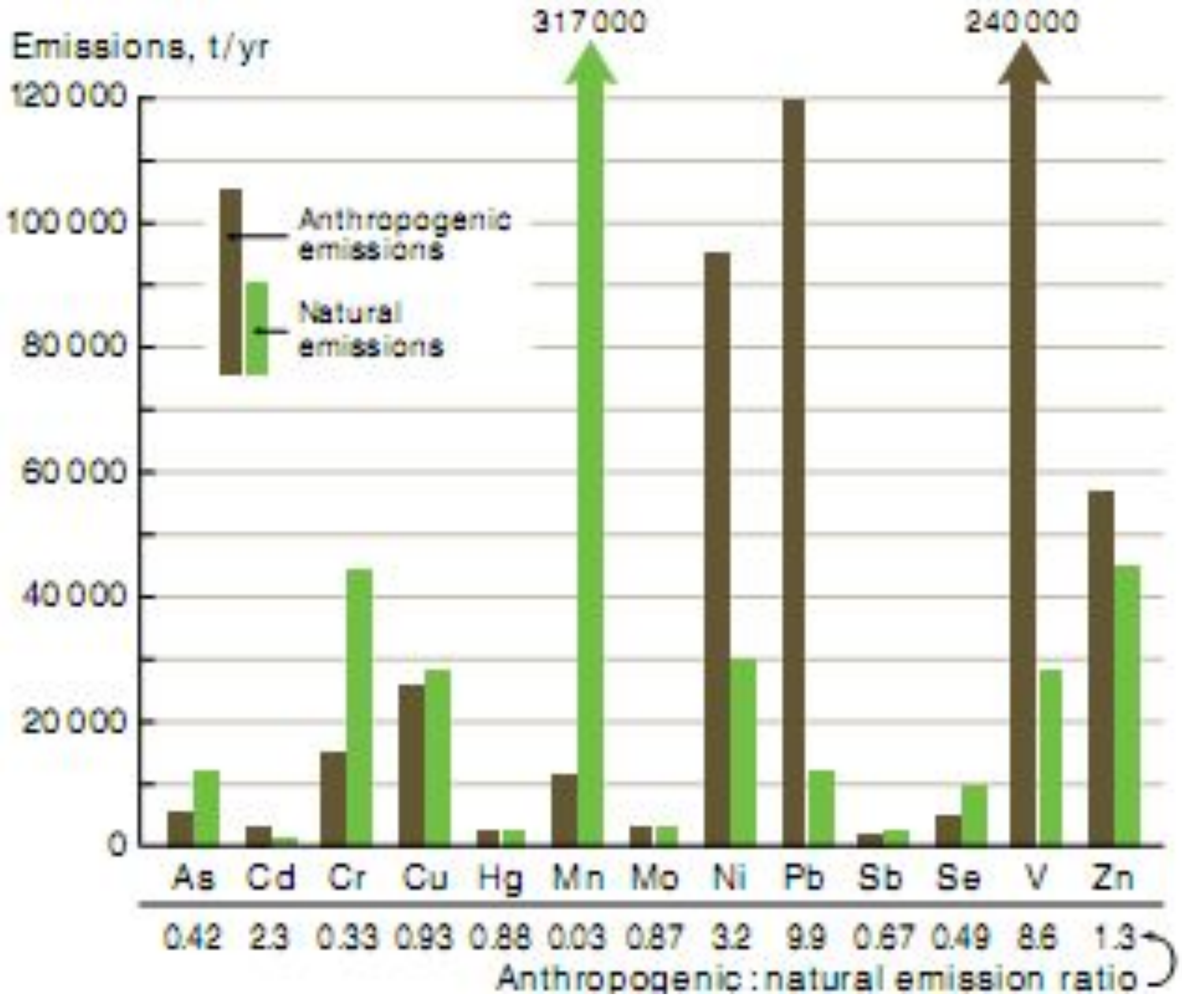


Figure. Estimated global anthropogenic emissions of heavy metals in the mid-1990s (Pacyna and Pacyna, 2001) compared to estimates from natural sources (Nriagu, 1989).

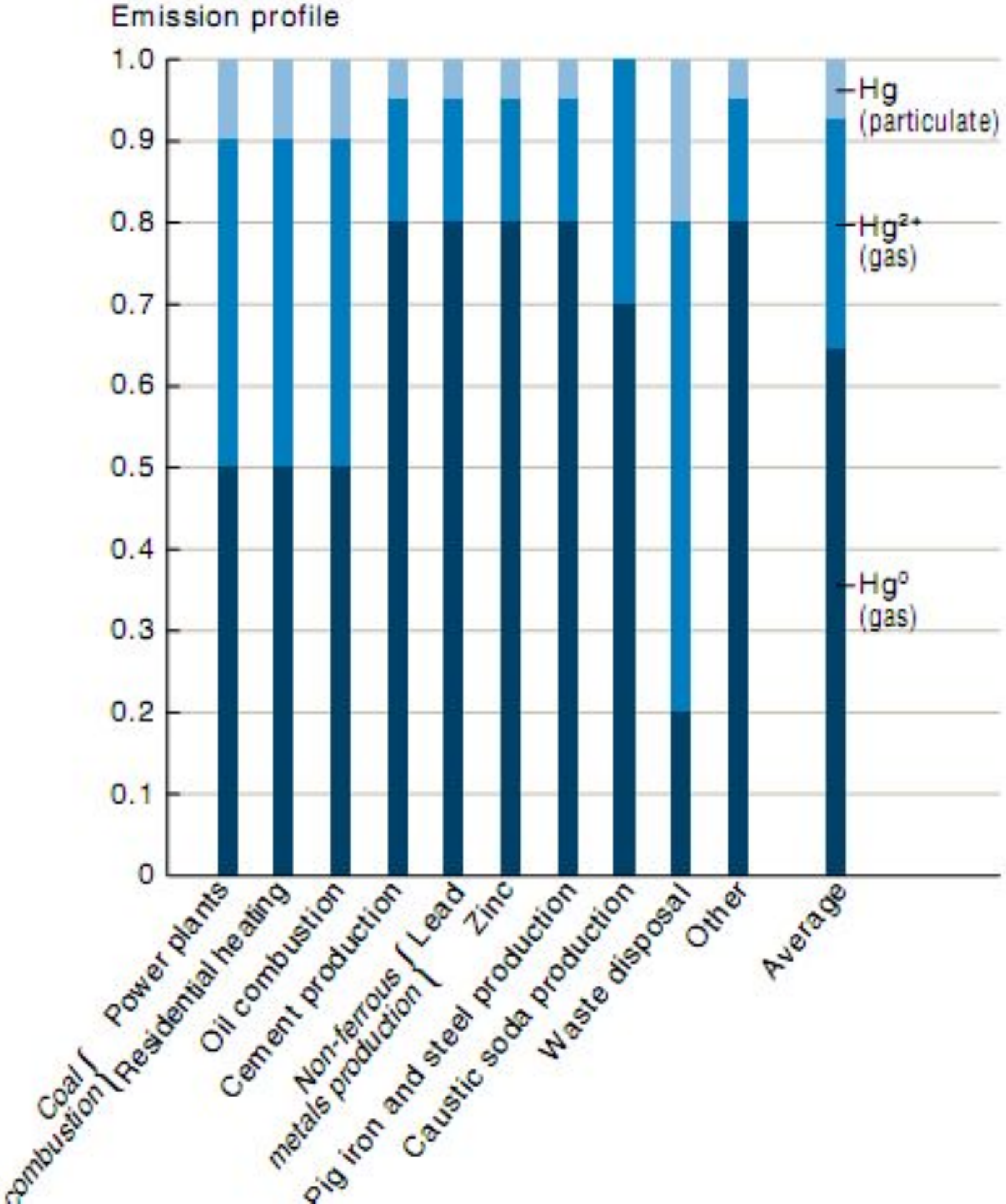


Figure. Atmospheric emission profiles for the three most important forms of mercury emitted from anthropogenic sources in 1995 (Pacyna and Pacyna, 2002).

- There is very long range transport within air masses of soil particles from deserts in Asia and Africa to the High Arctic. A series of haze bands over Barrow, Alaska in April and May 1976 were found to consists of dust. The bulk elemental composition of the particles was crustal or nearcrustal and their mass-median radius of about 2 m indicated that they could have originated more than 5000 km from Alaska. Trajectory analysis showed that these particles could have passed over the arid and semi-arid regions of eastern Asia during intense dust storms which had occurred there. This hypothesis has been confirmed by measurements in the Norwegian Arctic and in the Canadian Arctic. The origin and evolution of dust clouds in central Asia has recently received consideration. The existence of natural constituents in the Arctic aerosol in central Asia was explained by long-range transport of eroded dust from the deserts in Asia and Africa during dust storms. However, no quantitative assessment has been made of how much of the eroded dust and attached heavy metals is transported from the Asian and African deserts to the Arctic.

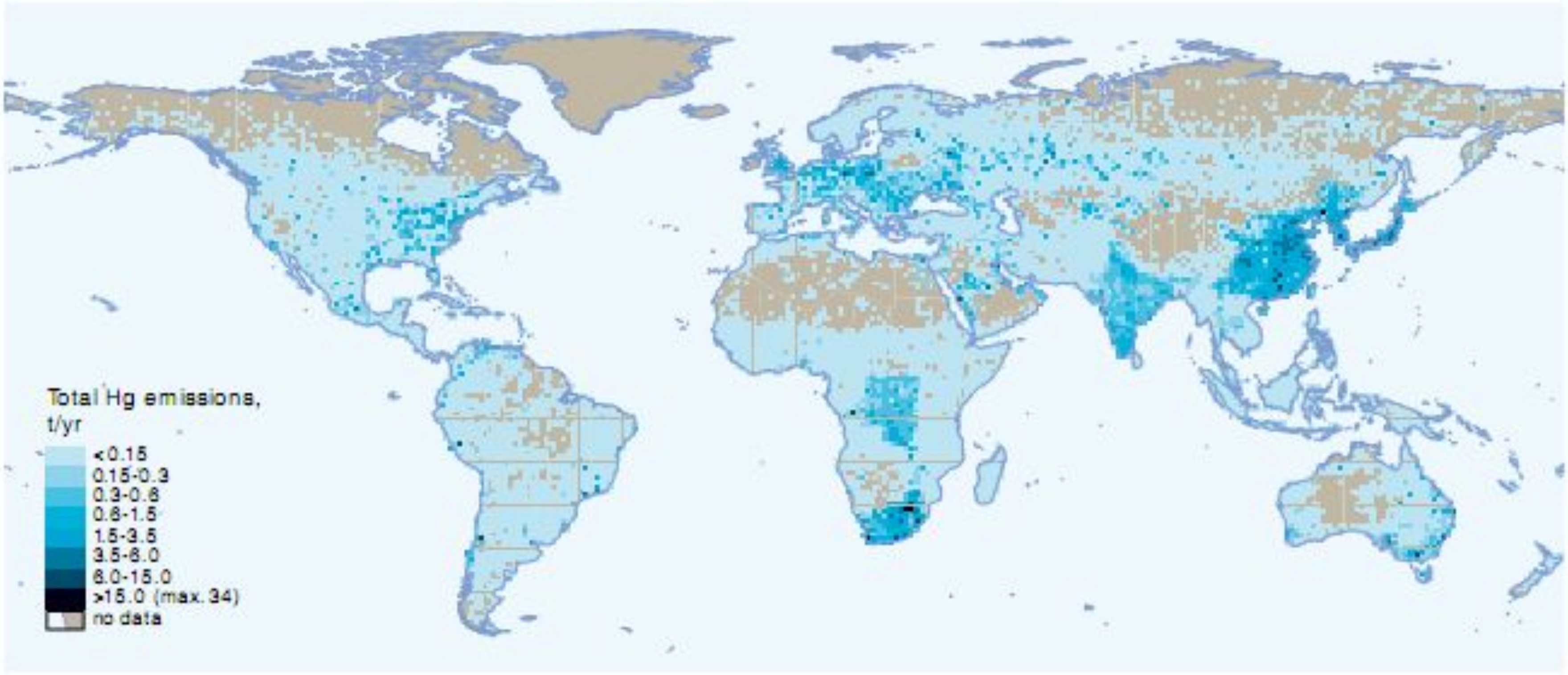


Figure. Global emissions in 1995 from anthropogenic sources of total mercury (Pacyna and Pacyna, 2002).

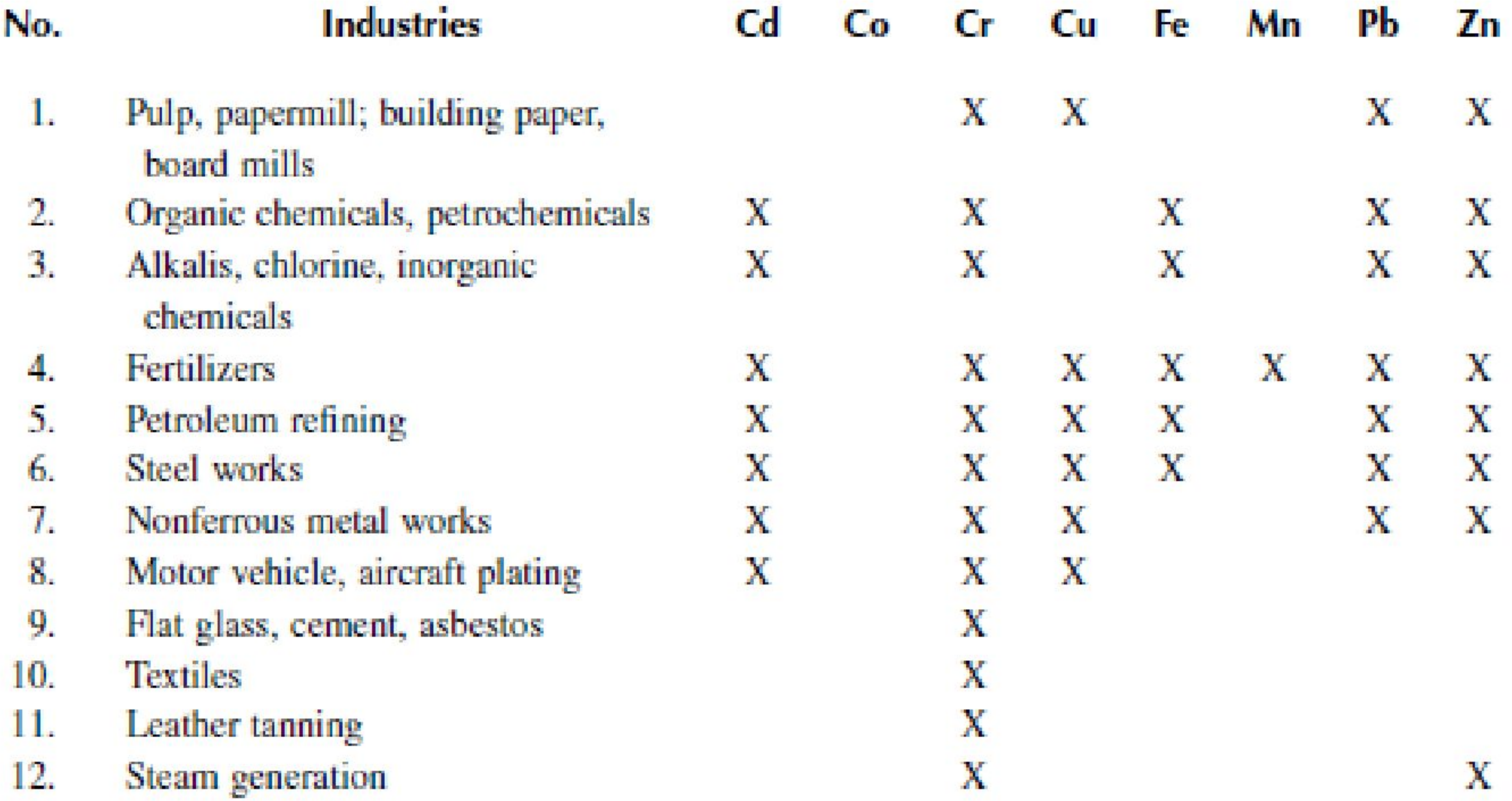
Anthropogenic sources

- There are a multitude of anthropogenic emissions in the environment. The major source of these metals is from mining and smelting. Mining releases metals to the fluvial environment as tailings and to the atmosphere as metal-enriched dust whereas smelting releases metals to the atmosphere as a result of high-temperature refining processes.

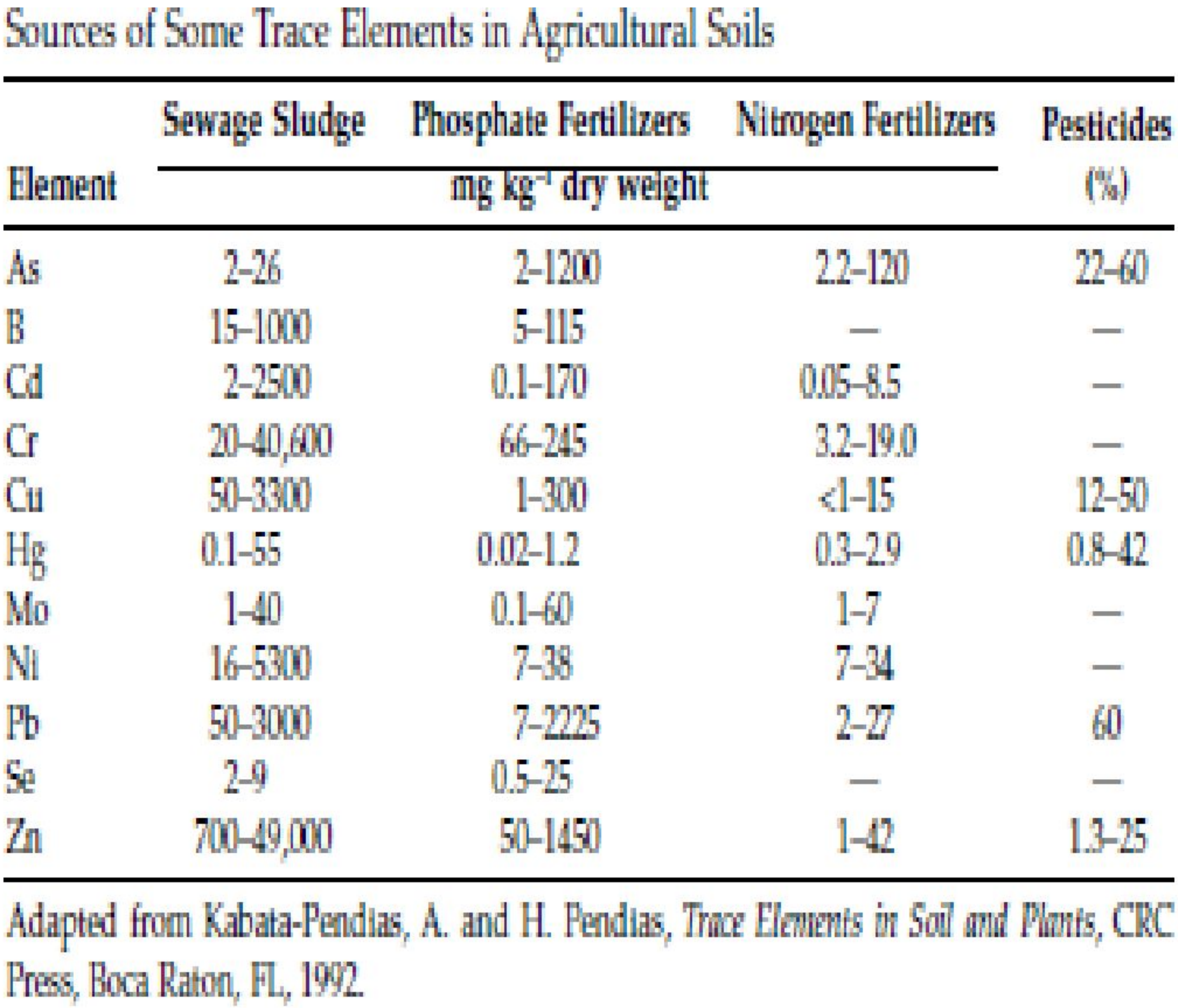
- Enhanced environmental concentrations of heavy metals are often associated with mining and smelting. These activities cause air pollution and associated atmospheric deposition of contaminated dust. Most mine tailing ponds and heaps are potentially hazardous, because pyrite contained in the ores oxidises to form sulphuric acid . Other important potential anthropogenic sources of heavy metals include sewage sludge (when spread on the land), phosphate fertilisers , manure , and atmospheric fallout (from smelting, or from burning coal and gasoline), leaching from building materials (roofs, gutters, pipes, lead slabs), deposition of contaminatedriver sediments, and direct domestic or industrial discharges and disposals.

- Computers, televisions, and other electronic equipment contain an array of trace materials, including lead, mercury , cadmium , and arsenic . In the past twenty years, the releases of heavy metals to the environment has been considerably reduced as a result of improved waste air and water purification techniques, waste recycling, and the implementation of more stringent environmental regulations.

Major Industries Employing and Releasing Heavy Metals



No.	Industries	Cd	Co	Cr	Cu	Fe	Mn	Pb	Zn
1.	Pulp, papermill; building paper, board mills			X	X			X	X
2.	Organic chemicals, petrochemicals	X		X		X		X	X
3.	Alkalis, chlorine, inorganic chemicals	X		X		X		X	X
4.	Fertilizers	X		X	X	X	X	X	X
5.	Petroleum refining	X		X	X	X		X	X
6.	Steel works	X		X	X	X		X	X
7.	Nonferrous metal works	X		X	X			X	X
8.	Motor vehicle, aircraft plating	X		X	X				
9.	Flat glass, cement, asbestos			X					
10.	Textiles			X					
11.	Leather tanning			X					
12.	Steam generation			X					X



Sources of Some Trace Elements in Agricultural Soils

Element	Sewage Sludge	Phosphate Fertilizers	Nitrogen Fertilizers	Pesticides
	mg kg^{-1} dry weight			(%)
As	2–26	2–1200	2.2–120	22–60
B	15–1000	5–115	—	—
Cd	2–2500	0.1–170	0.05–8.5	—
Cr	20–40,600	66–245	3.2–19.0	—
Cu	50–3300	1–300	<1–15	12–50
Hg	0.1–55	0.02–1.2	0.3–2.9	0.8–42
Mo	1–40	0.1–60	1–7	—
Ni	16–5300	7–38	7–34	—
Pb	50–3000	7–2225	2–27	60
Se	2–9	0.5–25	—	—
Zn	700–49,000	50–1450	1–42	1.3–25

Adapted from Kabata-Pendias, A. and H. Pendias, *Trace Elements in Soil and Plants*, CRC Press, Boca Raton, FL, 1992.

- In the lead industry, Pb–Cu–Zn–Cd are released in substantial quantities; during Cu and Ni smelting, Co–Zn–Pb–Mn as well as Cu–Ni are released; and in the Zn industry, sizeable releases of Zn–Cd–Cu–Pb occur (Adriano, 1986). Table 1 shows that the world metal production during the 1970s and the 1980s has remained relatively constant except for Cr production that substantially increased during the 1980s due to the technological advances and increased importance.

- Much of the demand for Cr was due to steel and iron manufacturing and the use of Cr in pressure treated lumber. Anthropogenic atmospheric emissions decreased substantially from the 1970s to the 1980s for Pb, Zn, and Cu. On the other hand, Cd and Cr have remained the same and Ni emissions have increased in the 1980s. In addition, anthropogenic emissions of Cr are only about one-half of those from the natural sources. The major contributor of Cr to natural atmospheric emissions is windblown dust.

- Other important sources of metals to the atmosphere include fossil-fuel combustion (primarily coal), municipal waste incineration, cement production, and phosphate mining. Important sources of metals to the terrestrial and aquatic environment include discharge of sewage sludges, use of commercial fertilizers and pesticides, animal waste and wastewater discharge. Metal emissions to soil are several times those to air, suggesting that land disposal of mining wastes, chemical wastes, combustion slags, municipal wastes, and sewage sludges are the major contributors of these emissions.

Source and Pathways

- The two main pathways for heavy metals to become incorporated into air–soil–sediment–water are transport by air (atmospheric) and water (fluvial). In the previous section it was shown that heavy-metal emissions to air and water are a significant percentage of theamounts of metals that are extracted from the Earth’s crust by mining. Ores are refined by smelting thus releasing large amounts of metal waste to the environment (primary source).

- Relatively pure metals are incorporated into a multitude of technological products which, when discarded, produce a secondary, but important, source of metals to the environment. Metals are also incorporated naturally and technologically into foodstuffs which, when consumed and discarded by man, result in an important metal source to the aquatic environment (sewage wastewater), soils, and sediments (sewage sludge).

Except for Pb in the terrestrial environment and Cd in the marine environment, metal transport to the lakes and to the oceans via water (fluvial) is many times greater (2–10) than that by air (atmospheric). This undoubtedly reflects the prevalence of wastewater discharges from sewage–municipal– industrial inputs that are so common in our industrialized society. The prevalence of Pb atmospheric emissions is probably due to the burning of leaded gasoline which was phased out in North America and Western Europe by the early 1990s but is still occurring in the Third World countries. Natural atmospheric emissions of Cd (volcanoes) are most likely the cause of substantial atmospheric Cd fluxes to the marine environment.

- Background levels in soil, lakes, rivers, and oceans generally fall within the global ranges.
- Cadmium levels in some terrestrial birds and mammals are high compared with global background, as are Hg levels in some freshwater fish. Cd levels in marine organisms from large parts of the Arctic exceed global background. Mercury and Se levels in marine mammals are high, but do not exceed the highest global levels. Lead levels in large parts of the Arctic are at the lower end of global background.

Emission inventories for sources within and outside the Arctic

- During winter, about two-thirds of the heavy metals in air in the High Arctic are transported from Eurasia, particularly from the Kola Peninsula, the Norilsk region, the Urals, and the Pechora Basin. Five to ten percent of these emissions are deposited in the High Arctic. The remaining one third of the heavy metals in High Arctic air in winter is transported from industrial regions in Europe and North America. In summer, local sources dominate the contamination of the High Arctic.

- The highest concentrations of atmospheric heavy metals in Arctic air occur in the vicinity of smelter complexes on the Kola Peninsula and at Norilsk and result from emissions from these smelters.
- Near point sources such as mine sites and some Russian estuaries, heavy metals exceed background levels up to 30 km from the source.
- Riverine transport of heavy metals toward the Arctic Basin is approximately half the atmospheric contribution for metals like Cd and Pb, while for others such as Zn the rivers are more important, carrying five times the atmospheric load. Such mass balance calculations will change considerably with the distance from the sources and the time of year, since the source contributions are strongly seasonal.

- Heavy metal concentrations in air in the High Arctic are one order of magnitude lower than concentrations in other remote locations and about two orders of magnitude lower than the concentrations around major point sources in the Kola Peninsula. Air concentrations mea- sured on the Kola Peninsula are comparable with the concentrations in the most polluted regions of Europe and North America.

MECHANISMS OF METAL IONS CONTAMINATION

- The mechanisms of the distribution and contamination of the environment by metal ions are simple to describe. Basically, the origin of metal ions is in the earth’s crust, and they are in direct contact with groundwater. Metal ions are leached into groundwater from their ores in the earth’s crust. The excessive withdrawal of groundwater creates spaces in aquifers that are filled by atmospheric air. The air present in these spaces oxidizes some metal ions in the oresthat then contaminates groundwater. Sometimes, chemical reduction and bacteriological action are also responsible for the leaching of metal ions into groundwater, for example, arsenic is released through the reduction process and bacteriological action.

- Geological weathering is also responsible for groundwater contamination. The exposure of pyrite (FeS2) and of other sulfide minerals to atmospheric oxygen results in one of the most acidic of all known weathering reactions. The contamination of soil occurs due to irrigation using contaminated ground, surface, and wastewater. The contamination of soil also occurs during rainy seasons. Major contributions to metal pollution of surface waters and soil are due to effluent discharges by many metal industries. The use of leaded gasoline and other man-made activities also lead to contamination of the environment. Briefly, beginning at the earth’s crust, metal ions contaminate our environment by undergoing several reactions, processes, and cycles

Table 3. Multi-step selective sequential extraction scheme for fractionation of solid metal phases (Krishnamurti and Naidu, 2000)

	Target species	Reagent	Shaking time and temperature
Step 1	Exchangeable	10 mL of M NH_4NO_3 (pH 7)	4 h at 25°C
Step 2	Specifically adsorbed	25 mL of M CH_3COONa (pH 5)	6 h at 25°C
Step 3	Metal-organic complex -bound	30 mL of 0.1 M $Na_4P_2O_7$ (pH 10)	20 h at 25°C
Step 4	Easily reducible Metal oxide-bound	20 mL of 0.1 M $NH_2OH.HCl$ in 0.01 M HNO_3	30 min at 25°C
Step 5	Organic-bound	5 mL of 30% H_2O_2 (pH 2), 3 mL of 0.02 M HNO_3	2 h at 85°C
		3 mL of 30% H_2O_2 (pH 2), 1 mL of 0.02 M HNO_3	2 h at 85°C
		cool, add 10 mL 2 M NH_4NO_3 in 20% HNO_3	30 min at 25°C
Step 6	Amorphous mineral colloid-bound	10 mL of 0.2 M $(NH_4)_2C_2O_4$/0.2 M $H_2C_2O_4$ (pH 3)	4 h at 25°C (dark)
Step 7	Crystalline Fe oxide-bound	25 mL of 0.2 M $(NH_4)_2C_2O_4$/0.2 M $H_2C_2O_4$ (pH 3) in 0.1 M ascorbic acid	30 min at 95°C
Step 8	Residual	Digestion with HF-$HClO_4$	

30 mL of 0.1 M $Na_4P_2O_7$ extract was brought to 1.0 pH with the addition of 6 M HCl and the suspension was left overnight for humic acid. The suspension was centrifuged at 12000g for 10 min. Metal-fulvate complexes were determined in the supernatant. The residue was solubilised with 0.1 M $Na_4P_2O_7$ and the metal-humate complexes were determined in the solution.

Table 2. Operationally defined fraction and corresponding extracted components (by Fedotov and Miró, 2008).

Defined fraction	**Extracted components** (Possible forms of binding TEs)	**Physicochemical mobility**	**Potential bioavailability**	**Common extractants**
Water soluble	Free ions	Mobile	Easily available	Deionized water
Exchangeable (A)	Exchangeable ions (metals retained by weak electrostatic interactions)	Mobile	Easily available	$Ca(NO_3)_2$, $Mg(NO_3)_2$, $CaCl_2$, $MgCl_2$, CH_3COONH_4
Acid soluble (B)	Carbonates (for noncalcareous soils: other specifically adsorbed forms of TEs)	Easily mobilizable	Easily available	CH_3COOH, CH_3COONa ($pH < 6.0$)
Easily reducible (C)	Mn oxyhydroxides	Readily mobilizable	Readily available	$NH_2OH \cdot HCl$
Easily oxidizable (D)	Metal-organic complexes	Readily mobilizable	Readily available	$K_4P_2O_7$, $Na_4P_2O_7$, $NaOH$
Moderately reducible (E)	Amorphous Fe (and Al) oxyhydroxides	Poorly mobilizable	Poorly available	Oxalate buffer, $NH_2OH \cdot HCl$
Moderately and poorly oxidizable (F)	Refractory organic compounds and sulfides	Poorly mobilizable	Poorly available	H_2O_2/CH_3COONH_4
Poorly reducible (G)	Crystalline Fe and Al oxyhydroxides	Poorly mobilizable	Poorly available	$(NH_4)_2C_2O_4$/ascorbic acid
Residual	Mineral lattice (metals retained within the crystal structure)	Immobile	Unavailable	HF, HNO_3, $HClO_4$