

## CADMIUM AND CADMIUM COMPOUNDS

Cadmium and cadmium compounds were considered by previous working groups, in 1972, 1975 and 1987 (IARC, 1973, 1976, 1987a). New data have since become available, and these are included in the present monograph and have been taken into consideration in the evaluation. The agents considered are metallic cadmium, cadmium alloys and some cadmium compounds.

### 1. Exposure Data

#### 1.1 Chemical and physical data and analysis

##### 1.1.1 *Synonyms, trade names and molecular formulae*

Synonyms, trade names and molecular formulae for cadmium, cadmium-copper alloy and some cadmium compounds are presented in Table 1. The cadmium compounds shown are those for which data on carcinogenicity or mutagenicity were available or which are commercially important compounds. It is not an exhaustive list and does not necessarily include all of the most commercially important cadmium-containing substances.

**Table 1. Synonyms (Chemical Abstracts Service (CAS) names are in italics), trade names and atomic or molecular formulae of cadmium and cadmium compounds**

Chemical name	CAS Reg. No. <sup>a</sup>	Synonyms and trade names	Formula
<i>Cadmium</i>	7440-43-9	Cadmium metal; CI 77180	Cd
Cadmium acetate	543-90-8 (24558-49-4; 29398-76-3)	<i>Acetic acid, cadmium salt</i> ; bis(acetoxy)-cadmium; cadmium(II) acetate; cadmium diacetate; cadmium ethanoate; CI 77185	Cd(CH <sub>3</sub> COO) <sub>2</sub>
Cadmium carbonate	513-78-0 [93820-02-1]	<i>Carbonic acid, cadmium salt</i> ; cadmium carbonate (CdCO <sub>3</sub> ); cadmium mono-carbonate; chemcarb; kalcit; mikrokalcit; supermikrokalcit	CdCO <sub>3</sub>
<i>Cadmium chloride</i>	10108-64-2	Cadmium dichloride; dichlorocadmium	CdCl <sub>2</sub>
Cadmium hydroxide	21041-95-2 (1306-13-4; 13589-17-8)	<i>Cadmium hydroxide (Cd(OH)<sub>2</sub>)</i> ; cadmium dihydroxide	Cd(OH) <sub>2</sub>
Cadmium nitrate	10325-94-7 (14177-24-3)	<i>Nitric acid, cadmium salt</i> ; cadmium dinitrate; cadmium(II) nitrate; cadmium nitrate (Cd(NO <sub>3</sub> ) <sub>2</sub> )	Cd(NO <sub>3</sub> ) <sub>2</sub>
Cadmium stearate	2223-93-0	Alaixol II; cadmium distearate; cadmium octadecanoate; cadmium(II) stearate; octadecanoic acid; cadmium salt; SCD; stabilisator SCD; stabilizer SCD; stearic acid, cadmium salt	Cd(C <sub>36</sub> H <sub>72</sub> O <sub>4</sub> )

Table 1 (contd)

Chemical name	CAS Reg. No. <sup>a</sup>	Synonyms and trade names	Formula
Cadmium sulfate	10124-36-4 (62642-07-3) [31119-53-6]	Cadmium monosulfate; cadmium sulfate; <i>sulfuric acid, cadmium salt (1:1)</i>	CdSO <sub>4</sub>
<i>Cadmium sulfide</i>	1306-23-6 (106496-20-2)	Cadmium monosulfide; cadmium orange; cadmium yellow; CI 77199	CdS
<i>Cadmium oxide</i>	1306-19-0	Cadmium monoxide	CdO
Cadmium-copper alloy <sup>b</sup>	37364-06-0	<i>Copper base, Cu, Cd</i>	Cd.Cu
	12685-29-9 (52863-93-1)	<i>Cadmium nonbase, Cd, Cu</i>	Cd.Cu
	132295-56-8	<i>Copper alloy, base, Cu 99.75-100, Cd 0.05-0.15; IMI 143; UNS C14300</i>	Cd.Cu
	132295-57-9	<i>Copper alloy, base, Cu 99.60-100, Cd 0.1-0.3; UNS C14310</i>	Cd.Cu

<sup>a</sup>Replaced CAS Registry numbers are shown in parentheses; alternative CAS Registry numbers are shown in brackets.

<sup>b</sup>116 cadmium-copper alloys are registered with the Chemical Abstracts Service.

### 1.1.2 Chemical and physical properties of the pure substances

Selected chemical and physical properties of most of the cadmium and cadmium compounds covered in this monograph are presented in Table 2.

Cadmium (atomic number, 48; relative atomic mass, 112.41) is a metal, which belongs, together with zinc and mercury, to group IIB of the periodic table. The oxidation state of almost all cadmium compounds is +2, although a few compounds have been reported in which it is +1. There are eight naturally occurring isotopes (abundance is given in parentheses): 106 (1.22%), 108 (0.88%), 110 (12.39%), 111 (12.75%), 112 (24.07%), 113 (12.26%), 114 (28.86%) and 116 (7.58%). Although cadmium is slowly oxidized in moist air at ambient temperature, it forms a fume of brown-coloured cadmium oxide when heated in air. Other elements that react readily with cadmium metal upon heating include halogens, phosphorus, selenium, sulfur and tellurium (Hollander & Carapella, 1978; Schulte-Schrepping & Piscator, 1985).

There is no evidence that organocadmium compounds (in which the metal is bound covalently to carbon) occur in nature, although cadmium may bind to proteins and other organic molecules and form salts with organic acids (e.g. cadmium stearate) (WHO, 1992a).

Cadmium has a relatively high vapour pressure (0.001 mm Hg [0.133 Pa] at 218 °C; 1.0 mm Hg [133.3 Pa] at 392 °C; 100 mm Hg [13.3 kPa] at 611 °C). When reactive gases or vapours, such as oxygen, carbon dioxide, water vapour, sulfur dioxide, sulfur trioxide or hydrogen chloride, are present, cadmium vapour reacts to produce cadmium oxide, carbonate, hydroxide, sulfite, sulfate or chloride, respectively. These compounds may be formed in stacks and emitted into the environment (Schulte-Schrepping & Piscator, 1985; WHO, 1992a).

**Table 2. Physical and chemical properties of cadmium and cadmium compounds**

Chemical name	Relative atomic/molecular mass	Melting-point (°C)	Typical physical description	Density (g/cm <sup>3</sup> )	Solubility
Cadmium metal	112.41	320.9	Silver-white, blue-tinged malleable metal	8.642	Soluble in ammonium nitrate, dilute nitric acid, hot sulfuric acid; insoluble in water
Cadmium acetate	230.50	256	Colourless crystal with slight acetic acid odour	2.341	Soluble in water, ethanol, methanol
Cadmium carbonate	172.42	321 (dec.)	White trigonal solid	4.26 (4 °C)	Practically insoluble in water (28 µg/L) and ammonia; soluble in dilute acids; insoluble in organic solvents
Cadmium chloride	183.32	568	Colourless to white, hygroscopic, rhombohedral or hexagonal crystals	4.047	Soluble in water (1400 g/L) and acetone; slightly soluble in methanol, ethanol; insoluble in diethyl ether
Cadmium hydroxide	146.43	130 (dec.)	White trigonal crystal or amorphous solid	4.79 (15 °C)	Almost insoluble in water (2.6 mg/L); soluble in dilute acids and ammonium salts; insoluble in alkaline solutions
Cadmium nitrate	236.43	350	Colourless solid	NR	Soluble in water (1 kg/L at 0 °C, 3.3 kg/L at 60 °C); soluble in diethyl ether, ethyl acetate, acetone, ethanol; very soluble in dilute acids
Cadmium sulfate	208.47	1000	Colourless to white orthorhombic crystals	4.691	Soluble in water (755 g/L); insoluble in acetone, ammonia, ethanol
Cadmium sulfide	144.47	1750 (at 100 atm [101 × 10 <sup>2</sup> kPa])	Yellow-orange hexagonal (α) or cubic (β) dimorphic, semi-transparent crystals; yellow-brown powder	4.82 (α); 4.50 (β)	Soluble in concentrated or warm dilute mineral acids with evolution of hydrogen sulfide; very slightly soluble in ammonium hydroxide; almost insoluble in water (1.3 mg/L); forms a colloid in hot water
Cadmium oxide	128.41	> 1500	Dark-brown cubic crystals or amorphous powder	8.15 (crystal); 6.95 (amorphous)	Soluble in dilute acids and ammonium salts; almost insoluble in water (9.6 mg/L); insoluble in alkali

From Hollander & Carapella (1978); Parker (1978); Sax & Lewis (1987); Budavari (1989); Cadmium Association/Cadmium Council (1991); Lide (1991); WHO (1992a); Agency for Toxic Substances and Disease Registry (1989). NR, not reported; dec., decomposes

Some cadmium compounds, such as cadmium sulfide, carbonate and oxide, are practically insoluble in water. Few data are available, however, on the solubility of these compounds in biological fluids, e.g. in the gastrointestinal tract and lung. The water-insoluble compounds can be changed to water-soluble salts by acids or light and oxygen; e.g. aqueous suspensions of cadmium sulfide gradually photooxidize to soluble (ionic) cadmium. Cadmium sulfate, nitrate and halides are water-soluble (Ulicny, 1992; WHO, 1992a).

### 1.1.3 *Technical products and impurities*

**Cadmium metal**—produced in a wide range of forms and purities for various uses. Purities range from 99.0% (reagent grade) to 99.9999% (zone-refined), and forms include powder, foils, wires, ingots and others. Typical impurities (% , max.) include: Zn, 0.02–0.1; Cu, 0.0001–0.015; Pb, 0.0001–0.025; Fe, 0.0001–0.001; Bi, 0.0005; Sn, 0.01; Ag, 0.01; Sb, 0.001; and As, 0.003 (J.T. Baker, 1989; Alfa Products, 1990; Spectrum Chemical Mfg Corp., 1991; Aldrich Chemical Co., 1992; Strem Chemicals, 1992; Atomergic Chemetals Corp., undated; D.F. Goldsmith Chemical & Metal Corp., undated)

**Cadmium acetate**—reagent grade; 99.999% (Alfa Products, 1990)

**Cadmium chloride**—purities: 99.0– > 99.99%; American Chemical Society reagent grade, 95– > 99%; anhydrous, 99.99–99.999%; impurities (%): NO<sub>3</sub>, 0.003; SO<sub>4</sub>, 0.005–0.01; NH<sub>4</sub>, 0.002–0.01; Cu, 0.001; Fe, 0.001; Pb, 0.005; and Zn, 0.1 (J.T. Baker, 1989; Alfa Products, 1990; CERAC, Inc., 1991; Spectrum Chemical Mfg Corp., 1991; Aldrich Chemical Co., 1992; Strem Chemicals, 1992)

**Cadmium sulfate** (as 3CdSO<sub>4</sub>·8H<sub>2</sub>O)—purities: 98–99.999%; American Chemical Society reagent grade, 98–99.0%; impurities (%): Cl, 0.001; NO<sub>3</sub>, 0.003; Cu, 0.002; Fe, 0.001; Pb, 0.003; Zn, 0.1; and As, 1–2 ppm (J.T. Baker, 1989; Alfa Products, 1990; Aldrich Chemical Co., 1992)

**Cadmium sulfide**—purities: > 98–99.999%; phosphor (luminescent) grade, 99.99–99.999% (Alfa Products, 1990; CERAC, Inc., 1991; Aldrich Chemical Co., 1992; Strem Chemicals, 1992; D.F. Goldsmith Chemical & Metal Corp., undated). Some of the trade names associated with cadmium sulfide include: Cadmium Golden; Cadmium Golden 366; Cadmium Lemon Yellow; Cadmium Lemon Yellow 527; Cadmium Orange; Cadmium Primrose 819; Cadmium Sulfide Yellow; Cadmium Yellow; Cadmium Yellow 000; Cadmium Yellow 892; Cadmium Yellow Conc. Deep; Cadmium Yellow Conc. Golden; Cadmium Yellow Conc. Lemon; Cadmium Yellow Conc. Primrose; Cadmium Yellow 10G Conc.; Cadmium Yellow OZ Dark; Cadmium Yellow Primrose 47-4100; Cadmopur Golden Yellow N; Cadmopur Yellow; Capsebon; C.P. Golden Yellow 55; Ferro Lemon Yellow; Ferro Orange Yellow; Ferro Yellow; GSK; PC 108; Primrose 1466.

**Cadmium oxide**—purities: 99.0–99.9999%; reagent grade, 99.0%; commercial grade, 99.7%; impurities (%): Cl, 0.002; NO<sub>3</sub>, 0.01; SO<sub>4</sub>, 0.20; Cu, 0.005; Fe, 0.002; and Pb, 0.01 (J.T. Baker, 1989; Alfa Products, 1990; CERAC, Inc., 1991; Aldrich Chemical Co., 1992; Strem Chemicals, 1992; D.F. Goldsmith Chemical & Metal Corp., undated).

Impurities that occur in cadmium compounds that have been the subjects of previous monographs are lead (IARC, 1987b) and arsenic (IARC, 1987c).

## 1.1.4 Analysis

Selected methods for the determination of cadmium and cadmium compounds in various media are presented in Table 3.

**Table 3. Methods for the analysis of cadmium and cadmium compounds (as Cd)**

Sample matrix	Sample preparation	Assay procedure	Limit of detection	Reference
Air	Collect on membrane filter; dissolve with nitric acid	FLAA	0.03 $\mu\text{g}/\text{m}^3$ ; 0.002 $\mu\text{g}/\text{ml}$	Kleinman <i>et al.</i> (1989a)
	Collect on cellulose ester membrane filter; add nitric and hydrochloric acids; heat, then cool	FLAA	0.05 $\mu\text{g}/\text{sample}$	Eller (1987)
	Collect on cellulose ester membrane filter; ash with nitric:perchloric acid solution (4:1); heat; repeat; heat to dryness; dilute with nitric:perchloric acid solution (4:1)	ICP	1 $\mu\text{g}/\text{sample}$	Eller (1984a)
Water, ground- and surface	Acidify with nitric and hydrochloric acids (Method 3005)	FLAA; ICP at 226.5 nm	0.005 mg/L; 4 $\mu\text{g}/\text{L}$	US Environmental Protection Agency (1986a,b) (Methods 6010 & 7130)
Aqueous samples, extracts, wastes	Acidify with nitric acid; heat and evaporate to low volume; cool; add nitric acid; reheat and reflux with hydrochloric acid (Method 3010)			
Oils, greases, waxes	Dissolve in xylene or methyl isobutyl ketone (Method 3040)			
Sediments, sludges, soils	Digest with nitric acid and hydrogen peroxide; reflux with hydrochloric acid (Method 3050)			
Aqueous samples, extracts, wastes	Acidify with nitric acid; evaporate to low volume; cool; add nitric acid; heat to complete digestion (Method 3020)	GFAA	0.1 $\mu\text{g}/\text{L}$	US Environmental Protection Agency (1986c) (Method 7131)
Sediments, sludges, soils	Digest with nitric acid and hydrogen peroxide; reflux with nitric acid (Method 3050)	GFAA	0.1 $\mu\text{g}/\text{L}$	US Environmental Protection Agency (1986c) (Method 7131)
Tissue samples	Ash in hot concentrated nitric acid	AA	0.0006 $\mu\text{g}/\text{ml}$	Kleinman <i>et al.</i> (1989b)
Urine	Adjust pH to 2.0 and add polydithio-carbamate resin; filter through cellulose ester membrane filter; ash in low-temperature oxygen plasma or with nitric:perchloric acid solution (4:1)	ICP	0.1 $\mu\text{g}/\text{sample}$	Eller (1984b)

**Table 3 (contd)**

Sample matrix	Sample preparation	Assay procedure	Limit of detection	Reference
Urine (contd)	Complex with hexamethylene ammonium/hexamethylene dithiocarbamate; extract with diisopropyl ketone/xylene	GFAA	0.2 µg/L	Angerer & Schaller (1988)
Blood	Solubilize with Triton-X-100; deproteinate with 1 M nitric acid (Recommended reference method of the Commission of Toxicology of IUPAC)	GFAA	0.2 µg/L	Stoeppler & Brandt (1980); Angerer & Schaller (1985)

Abbreviations: FLAA, flame atomic absorption spectrometry; ICP, inductively coupled argon plasma atomic emission spectrometry; GFAA, graphite furnace atomic absorption spectrometry; AA, atomic absorption spectrometry

The cadmium concentrations in environmental and biological specimens vary widely: only a few nanograms of cadmium may be present in specimens of air, water and biological fluids, whereas hundreds of micrograms or more may be present in kidney, sewage sludge and plastics. Different techniques are therefore required for sample collection and preparation and for analysis. Atomic absorption spectrometry, electrochemical methods such as anodic stripping voltammetry and pulse polarography, neutron activation, X-ray microanalysis and spark source emission spectroscopy are used for the determination of cadmium in various media.

In general, the techniques available for measuring cadmium in the environment and in biological materials cannot differentiate between different compounds. With special separation techniques, cadmium-containing proteins can be isolated and identified. In most studies to date, the concentration or amount of cadmium in water, air, soil, plants and other environmental or biological material has been determined as the element.

The most commonly used methods, atomic absorption spectrometry and polarography, were discussed in detail in WHO (1992b). Atomic absorption spectrometry is the most reliable and practicable method, especially for the biological monitoring of exposure to cadmium. The sensitivity of flame atomic absorption spectrometry is about 10 µg/L; with graphite furnace atomic absorption spectroscopy, cadmium concentrations of about 0.1 µg/L can be determined in urine and blood. Standardized methods for the determination of cadmium in blood and urine have been published (Stoeppler & Brandt, 1980; Angerer & Schaller, 1985, 1988).

The precision and accuracy of the results are strongly influenced by the pre-analytical phase, so that special care must be taken to avoid contamination during sampling, transport and storage of specimens, particularly liquid samples. Contamination of biological samples by sampling devices, containers and sample preparations has been reported (WHO, 1992b). It is strongly recommended that analysis of cadmium be accompanied by an adequate internal and external quality assurance programme. Quality control materials are available for daily use in intralaboratory control and in national and international intercomparison

programmes for the determination of cadmium in blood and urine (Herber *et al.*, 1990a,b; Schaller *et al.*, 1991; Brown, 1992; WHO, 1992b).

A noninvasive technique for determination of cadmium in liver and kidney *in vivo* has been developed, which is based on the principle of neutron activation analysis and takes advantage of the very large cross-sectional area for capture of thermal neutrons of one of the naturally occurring stable isotopes of cadmium,  $^{113}\text{Cd}$  (Ellis *et al.*, 1981; Roels *et al.*, 1981). The lowest detection limits for 'field work' techniques currently in use are about 1.5 mg/kg in liver and 2.2 mg/kg in kidney (Ellis *et al.*, 1981). An alternative method for determination of cadmium concentrations in kidney cortex *in vivo* involves X-ray-generated atomic fluorescence (Ahlgren & Mattsson, 1981; Christoffersson & Mattsson, 1983). Skerfving *et al.* (1987) found the limit of detection of this method to be 17 mg/kg in kidney cortex. The analytical validity of these *in-vivo* techniques has not been studied sufficiently (WHO, 1992b; see also section 4.1).

## 1.2 Production and use

### 1.2.1 Production

#### (a) Cadmium metal

Cadmium is often considered to be a metal of the twentieth century: Unlike some other heavy metals, such as lead and mercury which have been used since ancient times, cadmium has been refined and used only relatively recently, and over 65% of the cumulative world production has taken place in the last few decades. After its discovery by Strohmeyer in 1817 as an impurity in zinc carbonate, more than a century elapsed before the metal or its compounds were used to any significant extent, and only in the last 40–50 years have production and consumption risen (Hollander & Carapella, 1978; Schulte-Schrepping & Piscator, 1985). Cadmium is a relatively rare element and is not found in the pure state in nature. Cadmium minerals do not occur in concentrations or quantities sufficient to justify mining them in their own right, and cadmium is almost invariably recovered as a by-product from the processing of sulfide ores of zinc, lead (see IARC, 1987b) and copper (Cadmium Association/Cadmium Council, 1991; WHO, 1992b).

Because cadmium is primarily a by-product of zinc processing, the level of cadmium output has closely followed the pattern of zinc production, little being produced prior to the early 1920s. The subsequent rapid increase corresponded to the commercial development of cadmium electroplating. Worldwide production reached a plateau in the 1970s, but appeared to be increasing again in the 1980s (Table 4). Canada is the largest source of cadmium concentrate; other major suppliers are Australia, Europe, Japan, Mexico, Peru and the USA. Outside of the former USSR (for which only estimates of production are available), Japan is the largest producer of primary refined cadmium, as it treats concentrates from South America and Australia as well as from its own mines. Australia, Belgium, Canada, China, Germany, Italy, Mexico and the USA are also major producers of refined cadmium. An important source of cadmium is the recycling of secondary raw materials, including cadmium-containing products which have become unusable, such as nickel-cadmium batteries (for the monograph on nickel, see IARC, 1990a); cadmium-containing by-products,

such as steel industry dust and electroplating sludges; and other types of materials the reprocessing of which has become economically feasible or required by law (Förstner, 1984; Cadmium Association/Cadmium Council, 1991; WHO, 1992b).

**Table 4. World production of refined cadmium (tonnes)**

Country or region	1980	1981	1982	1983	1984	1987	1988	1989	1990	1991
Algeria	60	65	65	50	50	102	55	46	65	65
Argentina	18	NR	21	19	20	46	46	54	48	50
Australia	1 012	1 031	1 010	1 100	1 200	944	855	696	638	800
Austria	36	55	48	46	45	26	26	49	44	22
Belgium	1 524	1 176	996	800	850	1 308	1 836	1 761	1 956	1 800
Brazil	41	45	73	189	180	214	161	197	200	200
Bulgaria	210	210	200	200	200	250	300	350	309	300
Canada	1 303	1 298	809	1 107	1 200	1 571	1 694	1 620	1 437	1 400
China	250	270	300	300	300	680	750	800	1 000	1 200
Democratic People's Republic of Korea	140	140	100	100	100	100	100	100	100	100
Finland	581	621	566	616	600	690	703	612	568	593
France	789	663	793	540	500	457	558	790	780	700
Germany	1 210	1 208	1 046	1 111	1 116	1 143	1 189	1 234	990	1 105
India	89	113	131	131	120	214	237	275	277	280
Italy	568	489	475	450	400	320	705	770	665	734
Japan	2 173	1 977	2 034	2 214	2 400	2 450	2 614	2 694	2 451	2 889
Mexico	778	590	607	642	650	935	1 117	976	882	900
Namibia	69	NR	110	25	25	51	106	88	75	75
Netherlands	455	518	497	521	525	517	563	505	590	549
Norway	130	117	104	117	110	147	169	206	286	236
Peru	172	307	421	451	460	351	303	352	265	350
Poland	698	580	570	570	570	620	642	485	373	350
Republic of Korea	365	300	320	320	300	NR	490	500	500	450
Romania	85	85	80	80	80	75	75	70	62	60
Spain	309	303	286	278	250	297	438	361	355	350
United Kingdom	375	278	354	340	340	498	399	395	438	449
USA	1 578	1 603	1 007	1 052	1 686	1 515	1 885	1 550	1 678	1 676
Former USSR	2 850	2 900	2 900	3 000	3 000	3 000	3 000	3 000	2 800	2 500
Former Yugoslavia	201	208	174	48	100	305	405	471	362	280
Zaire	168	230	281	308	310	299	281	224	213	120
Total <sup>a</sup>	18 238	17 381	16 378	16 725	17 687	19 169	21 761	21 325	20 493	20 673

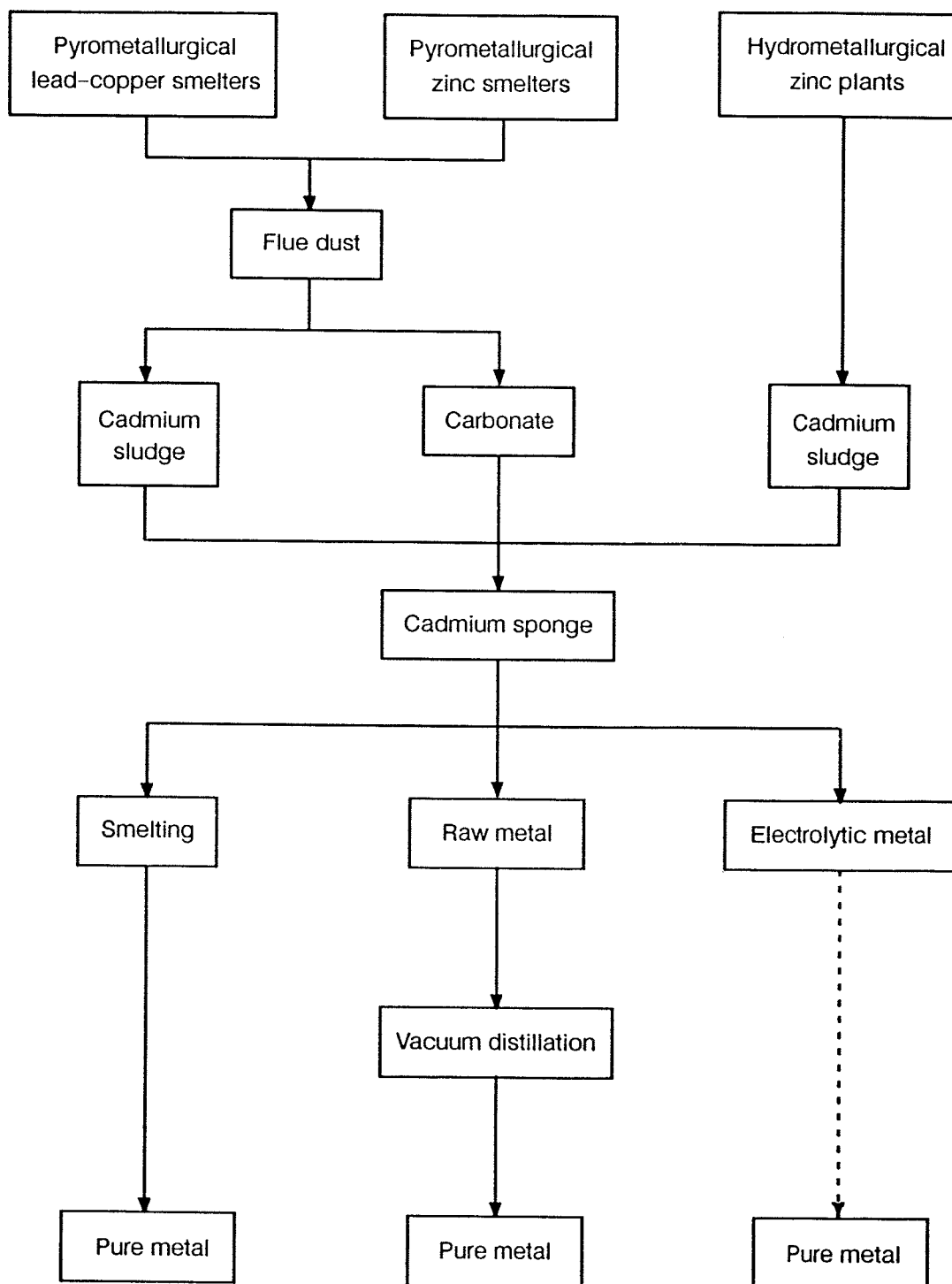
From Plunkert (1985) for 1980–84; Llewellyn (1992) for 1987–91; some figures are estimates. NR, not reported  
<sup>a</sup>Totals do not add up because they have been revised.

Figure 1 summarizes the individual steps in the process and their combination for the production of cadmium metal. The flue dust on which volatile cadmium collects when zinc, copper and lead ores are heated in air is the primary starting material for cadmium recovery and refining. This dust must usually be recirculated in order to obtain high concentrations of cadmium. If the primary flue dust is reduced in a rotary oven, lead and zinc remain, while the



cadmium is volatilized and enriched in the secondary flue dust (Schulte-Schrepping & Piscator, 1985).

**Fig. 1. Processes for the production of cadmium metal**



From Schulte-Schrepping & Piscator (1985)

Zinc metal can be produced by either pyrometallurgical or electrolytic processes, and cadmium is recovered and refined at a number of stages. In one type of pyrometallurgical process, complex lead-zinc ores are refined by the Imperial smelting process. When the concentrate is roasted at 700–1200 °C in sintering furnaces, cadmium-containing flue dust and fume are produced. This is leached in a sulfuric acid solution, and the cadmium is subsequently precipitated as cadmium carbonate, which is dried and refined by distillation to cadmium metal. The cadmium in secondary raw materials, after enrichment in a special furnace, can be added to the concentrate and processed at the same time (Schulte-Schrepping & Piscator, 1985; Cadmium Association/Cadmium Council, 1991).

In hydrometallurgical zinc refining, cadmium-containing zinc concentrate is leached with sulfuric acid, and cadmium is removed from the solution together with copper by reduction with zinc dust, to give a metallic sludge. These cadmium sludges are the most important starting materials for cadmium refining today (Schulte-Schrepping & Piscator, 1985).

In electrolytic processes, the zinc concentrate is also roasted under oxidizing conditions to remove the sulfur, usually in fluidized bed roasters which produce a fine calcine suitable for acid leaching. The calcine is dissolved in sulfuric acid in a leaching plant, then neutralized to precipitate any iron. The bulk of the cadmium is precipitated from the sulfate solution during the second zinc dust stage and the remainder in the third stage. The cadmium precipitate is filtered and forms a cake containing about 25% cadmium, 50% zinc and small amounts of copper and lead; the cake is redissolved in sulfuric acid. A reasonably pure cadmium sponge is produced after two additional acid solution/zinc dust precipitation stages. The sponge is again dissolved in sulfuric acid, and the solution is passed into electrolytic cells where the cadmium is deposited on cathodes. The cathodes are then removed and stripped, and the cadmium is melted and cast into required shapes; it is typically 99.99% pure (Cadmium Association/Cadmium Council, 1991).

#### (b) *Cadmium alloys*

Cadmium can be combined with a number of other nonferrous metals to form alloys with useful commercial properties. Typically, metallic cadmium is added to the molten metal(s) with which it is to be alloyed and, after thorough mixing, the resultant alloy is cast into the desired form (ingot, wire, rod). Depending on the alloy and its application, the cadmium content ranges from < 0.1 to 15%. To facilitate mixing, a master alloy containing much higher levels of cadmium may be prepared first and added to the molten alloying metal (Hollander & Carapella, 1978; Holden, 1982).

#### (c) *Cadmium acetate*

Cadmium acetate is produced by the reaction of acetic acid with cadmium metal or oxide, or by treating cadmium nitrate with acetic anhydride. The dihydrate is obtained by dissolving cadmium metal or oxide in acetic acid, followed by crystallization. Calcination of the dihydrate can be controlled to yield cadmium acetate monohydrate and the anhydrous acetate (Parker, 1978; Budavari, 1989).

(d) *Cadmium chloride*

Cadmium chloride is produced by reacting molten cadmium with chlorine gas at 600 °C or by dissolving cadmium metal or the oxide, carbonate, sulfide or hydroxide in hydrochloric acid (see IARC, 1992), and subsequently vaporizing the solution to produce a hydrated crystal. In order to prepare the anhydrous salt, the hydrate is refluxed with thionyl chloride or calcined in a hydrogen chloride atmosphere. It may also be obtained by the addition of dry cadmium acetate to a mixture of glacial acetic acid and acetyl chloride or by distillation from a mixture of cadmium nitrate tetrahydrate in hot concentrated hydrochloric acid (Parker, 1978; Schulte-Schrepping & Piscator, 1985; Sax & Lewis, 1987).

(e) *Cadmium hydroxide*

Cadmium hydroxide has been prepared by the addition of a solution of cadmium nitrate to boiling sodium or potassium hydroxide (Parker, 1978). It has also been produced by the action of sodium hydroxide on a cadmium salt solution (Sax & Lewis, 1987).

(f) *Cadmium nitrate*

Cadmium nitrate has been produced by the action of nitric acid on cadmium metal or cadmium oxide, hydroxide or carbonate (Parker, 1978; Schulte-Schrepping & Piscator, 1985; Sax & Lewis, 1987).

(g) *Cadmium oxide*

Cadmium oxide is produced by the reaction of cadmium metal vapour with air. Pure cadmium metal is melted in a cast-iron or steel kettle and pumped to a heated chamber, where it is vaporized. The vapour is conducted to a reactor, and air is blown through, oxidizing the cadmium and carrying the reaction product into a 'baghouse'. Finer or coarser particles are produced, depending on the ratio of air to cadmium vapour. Cadmium oxide can also be obtained by thermal decomposition of cadmium nitrate or carbonate or by oxidation of molten cadmium by an oxidizing agent (Parker, 1978; Schulte-Schrepping & Piscator, 1985). Cadmium oxide is generated as either a dust or fume, depending on how it is produced.

(h) *Cadmium stearate*

Cadmium stearate, one of the cadmium alkanoate salts used as polyvinyl chloride stabilizers, is prepared by the addition of sodium stearate to a solution of cadmium chloride. The cadmium salt precipitates from solution and is filtered, washed and dried. Other salts (laurate, myristate, palmitate) are prepared in analogous reactions (Parker, 1978).

(i) *Cadmium sulfate*

The principal cadmium sulfates are  $\text{CdSO}_4$ ,  $\text{CdSO}_4 \cdot \text{H}_2\text{O}$  [13477-20-8] and  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$  [7790-84-3]. They are crystallized from cadmium sulfate solutions or can be precipitated by addition of ethanol. Anhydrous cadmium sulfate is prepared by oxidation of the sulfide or sulfite at elevated temperatures, or by the action of dimethyl sulfate on finely powdered cadmium nitrate, halides, oxide or carbonate. Solutions are prepared by dissolving cadmium metal, oxide, sulfide, hydroxide or carbonate in sulfuric acid. Anhydrous cadmium

sulfate is also produced by melting cadmium with ammonium or sodium peroxodisulfate. Cadmium sulfate monohydrate, which is the form usually marketed, is produced by evaporating a cadmium sulfate solution above 41.5 °C (Parker, 1978; Schulte-Schrepping & Piscator, 1985).

(j) *Cadmium sulfide*

Cadmium sulfide can be prepared by the reaction between hydrogen sulfide and cadmium vapour at 800 °C, or by heating a mixture of cadmium or cadmium oxide with sulfur. Usually, the sulfides are precipitated from aqueous solutions of cadmium salts by adding hydrogen sulfide or a soluble sulfide such as sodium sulfide. Cadmium sulfide can also be prepared by passing hydrogen sulfide gas into a solution of a cadmium salt acidified with hydrochloric acid; the precipitate is filtered and dried. It also occurs naturally as the mineral greenockite. The dimorphic sulfide, CdS, is the most widely used cadmium compound. The  $\beta$  form can be transformed to the  $\alpha$  form by heating at 750 °C in a sulfur atmosphere. Both forms can be prepared in colours ranging from lemon-yellow through orange and red, depending on the method of preparation and particle size (Parker, 1978; Sax & Lewis, 1987).

1.2.2 *Use*

Typical use patterns for cadmium and its compounds and alloys in several industrialized countries are presented in Table 5.

**Table 5. Patterns of use of cadmium in several industrialized countries (%)**

Use category	1970 <sup>a</sup>	1973 <sup>a</sup>	1976 <sup>a</sup>	1979 <sup>a</sup>	1982 <sup>a</sup>	1990 <sup>b</sup>
Coating and plating	37	30	36.5	34	29	8
Batteries	8	15	21.5	23	28.5	55
Pigments	24	30	25	27	24	20
Stabilizers for PVC	23	17	12	12	12	10
Alloys and other uses	8	8	5	4	6.5	7

<sup>a</sup>From Schulte-Schrepping & Piscator (1985); figures are based on totals of published statistics for Germany, Japan, the United Kingdom and the USA.

<sup>b</sup>From Cadmium Association/Cadmium Council (1991); figures are for Belgium, France, Germany, Japan, the United Kingdom and the USA.

(a) *Cadmium*

Cadmium has a limited number of principal applications, but within the range the metal, its alloys and compounds are used in a large variety of consumer and industrial materials. The principal applications of cadmium fall into five categories: active electrode material in nickel-cadmium batteries; pigments used mainly in plastics, ceramics and glasses; to stabilize polyvinyl chloride (PVC) against heat and light; engineering coatings on steel and some nonferrous metals; and as a component of various specialized alloys. Detailed statistics on use are available for only a limited number of countries, but these indicate that the pattern of

use varies considerably from country to country (Cadmium Association/Cadmium Council, 1991; WHO, 1992a).

Japan is by far the largest user of cadmium, followed by the USA, Belgium, the United Kingdom, France and Germany. Worldwide consumption of cadmium for all uses in 1990 was estimated to have been 18 500 tonnes. The cadmium compounds of greatest commercial importance are cadmium oxide and cadmium sulfide; other important compounds are the hydroxide, chloride, nitrate, sulfate and stearate (adapted from Cadmium Association/Cadmium Council, 1991).

Examination of the reported trends in cadmium consumption over the last 25 years reveals considerable change in the relative importance of the major applications. The use of cadmium for engineering coatings and electroplating represents the most striking decrease; in 1960, this sector accounted for over half the cadmium consumed worldwide, but in 1985 its share was less than 25%. The decline is usually linked to the widespread introduction of progressively more stringent limits on effluents from plating works and, more recently, to the introduction of restrictions on certain cadmium products in some European countries. In contrast, the use of cadmium in batteries has shown considerable growth in recent years, from only 8% of the total market in 1970 to 37% by 1985. The use of cadmium in batteries is particularly important in Japan, where it represented over 75% of total consumption in 1985 (WHO, 1992b).

Of the remaining applications of cadmium, pigments and stabilizers are the most important, accounting for 22 and 12%, respectively, of total world consumption in 1985. The share of the market represented by cadmium pigments remained relatively stable between 1970 and 1985, but use of the metal in stabilizers during the period showed a considerable decline, largely as a result of economic factors. The use of cadmium as a constituent of alloys is relatively small and has also declined in importance in recent years: it accounted for about 4% of total cadmium use in 1985 (WHO, 1992b).

(b) *Cadmium alloys* (from Cadmium Association/Cadmium Council, 1991, unless otherwise specified)

Cadmium forms many binary and more complex alloys, which have useful properties for many commercial applications. Most commercial alloys containing cadmium fall into two major groups, where:

- (i) the presence of cadmium improves some feature of the alloy. Small amounts of cadmium can improve hardness and wear resistance, mechanical strength, fatigue strength, castability and electrochemical properties. Cadmium is added principally to alloys based on copper, tin, lead and zinc, although several others benefit from its presence.
- (ii) lower melting-points are obtained. Such alloys range from low-melting-point eutectic ('fusible') alloys to high-melting-point non-eutectic alloys used in metal joining.

*Cadmium-copper alloys*, which have almost twice the mechanical strength and wear resistance of pure copper yet still retain 90% of its conductivity, contain 0.8–1.2% cadmium. The major uses of such alloys are in telephone wires, wiring for railway overhead electrification, conductors for flexible telephone cords, special cables for military and aerospace

uses and electrical components such as contact strips and electric blanket and heating-pad elements (Ricksecker, 1979).

*Zinc alloys* containing 0.1% cadmium improve the mechanical properties of rolled, drawn or extruded zinc. Zinc alloys containing cadmium in the range of 0.025 to 0.15% are used in anodes to protect structural steelwork immersed in seawater against corrosion.

*Lead alloys* with up to 0.075% cadmium are sometimes used as sheaths for cables subject to cyclic stress.

*Tin-based white metal-bearing alloys* with up to 1% cadmium have adequate tensile and fatigue strength for use in marine engines and gearboxes.

*Precious metal alloys* for jewellery incorporate cadmium for improved hardness and strength. Levels of up to 5% cadmium in gold-silver-copper alloys make Greek gold, a greenish-tinged gold.

*Silver electric contacts* incorporating 10–15% cadmium or cadmium oxide are useful in many heavy duty electrical applications, such as relays, switches and thermostats.

A *tin-lead-bismuth-cadmium alloy*, which melts at 70 °C, is more commonly known as Woods metal and is used in the bonding of metallized ceramic and glass components to metal frames and chassis, where higher soldering temperatures are not possible. The presence of Woods metal in water sprinkler valves automatically activates the water supply when the local temperature exceeds 70 °C, when it melts.

*Cadmium alloyed with silver, zinc or tin* makes excellent solders, with tensile strengths two to three times greater than most common solders in the same temperature range. Cadmium is an important component in quaternary alloys with silver, copper and zinc in the lower temperature range of brazing alloys.

The low melting-points and rapid fusing or solidifying characteristics of *low-temperature fusible alloys* containing cadmium lead to a variety of uses. Heat-sensitive fusible links in fire safety devices or kilns and ovens can activate control mechanisms when they melt at specific temperatures. The alloys are used to mount glass lenses firmly during grinding operations.

(c) *Cadmium acetate*

Cadmium acetate is the starting material for cadmium halides and is a colourant in glass, ceramics (iridescent glazes) and textiles. It is also used in electroplating baths, as a laboratory reagent and in the separation of mercaptans from crude oils and gasolines (Greene, 1974; Parker, 1978; Sax & Lewis, 1987).

(d) *Cadmium chloride*

Cadmium chloride is used in electroplating. The significance of cadmium chloride as a commercial product is declining; however, it occurs as an intermediate in the production of cadmium-containing stabilizers and pigments, which are often obtained from cadmium chloride solutions, themselves obtained from cadmium metal, oxide, hydroxide or carbonate. It is also used in the preparation of cadmium sulfide, in analytical chemistry, in photography, in dyeing and calico printing, in the manufacture of special mirrors and of cadmium yellow, in the vacuum tube industry and as a lubricant (Schulte-Schrepping & Piscator, 1985; Sax & Lewis, 1987; Budavari, 1989).

(e) *Cadmium hydroxide*

Cadmium hydroxide is a component of cadmium–nickel and silver–cadmium batteries. It often replaces the oxide as the starting material for other cadmium compounds (Parker, 1978; Schulte-Schrepping & Piscator, 1985; Cadmium Association/Cadmium Council, 1991).

(f) *Cadmium nitrate*

Cadmium nitrate is the preferred starting material for cadmium hydroxide; it is also used in photographic emulsions (Budavari, 1989; Parker, 1978) and in colouring glass and porcelain (Schulte-Schrepping & Piscator, 1985; Sax & Lewis, 1987).

(g) *Cadmium stearate*

Cadmium stearate is commonly used in combination with other salts to retard the degradation processes which occur in PVC and related polymers on exposure to heat and ultraviolet light (sunlight). The stabilizers consist of mixtures of barium, lead and organic cadmium salts, usually cadmium stearate or cadmium laurate, which are incorporated into the PVC before processing and which arrest any degradation reactions as soon as they occur. They ensure that PVC develops good initial colour and clarity and allow high processing temperatures to be employed; they also ensure longer service life.

Barium–cadmium stabilizers typically contain 1–15% cadmium and usually constitute about 0.5–2.5% of the final PVC compound. They are incorporated into PVC used, for example, in rigid profiles for window and door frames, water and drain pipes, hoses and electrical insulation (Parker, 1978; Cadmium Association/Cadmium Council, 1991).

(h) *Cadmium sulfate*

Cadmium sulfate is used in electroplating and as a starting material for pigments, stabilizers and other cadmium compounds that can be precipitated from aqueous solution. It is also used to produce fluorescent materials, in analytical chemistry and as a nematocide. Cadmium sulfate solution is a component of Weston cells (portable standards for electromagnetic frequency) (Schulte-Schrepping & Piscator, 1985; Sax & Lewis, 1987; Budavari, 1989).

(i) *Cadmium sulfide*

The main use of cadmium sulfide is for pigments. Pure yellow cadmium sulfides are formulated with red cadmium selenides in varying proportions to make chemically pure toners ranging from yellows and oranges with a low selenium content to reds and maroons with a high selenium content. Cadmium colourants are used in special paints (especially artists' colours, such as cadmium yellow), for colouring textiles, paper, rubber, plastics, glasses and ceramic glazes and in fireworks. Red and yellow cadmium sulfide–zinc sulfide fluorescent and phosphorescent pigments are also produced. Cadmium sulfide is used in the conversion of solar energy to electrical power. Its photoconductive and electroluminescent properties have been applied not only in photocells but also in a wide variety of phosphors, light amplifiers, radiation detectors, thin film transistors and diodes, electron beam-pumped lasers and household smoke detectors (Parker, 1978; Sax & Lewis, 1987; Budavari, 1989).

(j) *Cadmium oxide*

The main use of cadmium oxide is in the manufacture of nickel-cadmium batteries. In the first step in the preparation of negative electrodes (paste preparation), cadmium oxide is hydrated to form a paste of cadmium hydroxide. The dried paste is then mixed with graphite, iron oxide and paraffin, milled and finally compacted between rollers (Malcolm, 1983; Adams, 1992).

Cadmium oxide is used as a starting material for PVC heat stabilizers and for other inorganic cadmium compounds. It is also used as a catalyst in oxidation-reduction reactions, dehydrogenation, cleavage, polymerization, the production of saturated alcohols, hydrogenation of unsaturated fatty acids and as a mixed catalyst component to produce methanol from carbon monoxide and water. Further uses are in resistant enamels, metal coatings for plastics, heat-resistant plastics and selenium ruby glass. Cadmium oxide combined with an alkali-metal cyanide is the salt mixture used in baths for cadmium electroplating. High-purity cadmium oxide is used as a second depolarizer (in addition to silver oxide) in silver-zinc storage batteries. It is temperature resistant and, together with silver, useful in heavy-duty electrical contacts. In veterinary medicine, it has been used as a nematocide, vermicide and ascaricide in swine (Parker, 1978; Schulte-Schrepping & Piscator, 1985; Sax & Lewis, 1987; Budavari, 1989; Cadmium Association/Cadmium Council, 1991).

Other cadmium compounds used industrially include: cadmium cyanide (electroplating), cadmium carbonate (starting material for pigments), cadmium arsenides (electronic devices), cadmium selenide (photocells, luminous paints, colourant in glass), cadmium telluride (photocells, infra-red optics) and cadmium tungstate (X-ray screens, phosphors) (Parker, 1978; Schulte-Schrepping & Piscator, 1985).

### 1.3 Occurrence

#### 1.3.1 *Natural occurrence*

Cadmium is widely but sparsely distributed over the Earth's surface; it is found most commonly as the mineral greenockite (cadmium sulfide) and in weathered ores such as otavite (cadmium carbonate). Other minerals that contain cadmium are hawleyite (cadmium sulfide), xanthocroite (cadmium sulfide hydrate), cadmoselite (cadmium selenide) and monteponite (cadmium oxide). It occurs in nature associated mainly with zinc but also with lead or copper; in minerals and ores, cadmium and zinc are present typically in a ratio of 1:100 to 1:1000 (Fairbridge, 1974; Alessio *et al.*, 1983; Förstner, 1984).

Cadmium is a relatively rare element, comprising about 0.1–0.5 mg/kg of the Earth's crust; however, higher concentrations (15 mg/kg) are present in some sedimentary rocks. Trace quantities of cadmium can also be found in fossil fuels and oils (Bowen, 1966; WHO, 1992a,b).

#### 1.3.2 *Occupational exposure*

Workers may be exposed to cadmium and cadmium compounds in a variety of occupational settings (Table 6). The major sources of such exposure are smelting and refining of zinc, lead and copper ores, electroplating, manufacture of cadmium alloys and of pigments and plastic stabilizers, production of nickel-cadmium batteries and welding.



**Table 6. Occupations in which there is potential exposure to cadmium and cadmium compounds**

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Alloy production <sup>a</sup>
Battery production <sup>a</sup>
Brazing
Coating
Diamond cutting
Dry colour formulation
Electroplating
Electrical contacts production
Enamelling
Engraving
Glasswork
Laser cutting
Metallizing
Paint production and use
Pesticide production and use
Phosphorus production
Pigment production and use <sup>a</sup>
Plastics production <sup>a</sup>
Plating
Printing
Semiconductor and superconductor production
Sensors production
Smelting and refining <sup>a</sup>
Solar cells production
Soldering
Stabilizer production
Textile printing
Thin film production
Transistors production
Welding <sup>a</sup>

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<sup>a</sup>Activities in which risk is highest because atmospheric concentrations of cadmium can be high and because the number of workers employed is relevant (modified from Odone *et al.*, 1983)

It has been estimated that about 510 000 workers in the USA are exposed to cadmium (Thun *et al.*, 1991). In 1987, an estimated 210 000 workers were exposed to concentrations equal to or greater than 1  $\mu\text{g}/\text{m}^3$ ; 65% were exposed to concentrations of 1–39  $\mu\text{g}/\text{m}^3$ , 21% to 40–99  $\mu\text{g}/\text{m}^3$  and 14% to concentrations greater than 100  $\mu\text{g}/\text{m}^3$  (US National Toxicology Program, 1991). Airborne concentrations of cadmium found in occupational settings vary considerably according to the type of industry and to specific working conditions. Cadmium oxide fumes are generated at high temperatures (US Occupational Safety and Health Administration, 1992) and can be absorbed very efficiently through the lung, while deposition and absorption of dust of different cadmium compounds depends on particle size (Alessio *et al.*, 1983; Thun *et al.*, 1991). Improvements in occupational hygiene have led to a

progressive reduction in the concentrations of cadmium in occupational environments, and 5–20  $\mu\text{g}/\text{m}^3$  can now be achieved (Hassler *et al.*, 1983; Friberg *et al.*, 1986a; US Occupational Safety and Health Administration, 1992).

Data on exposure to cadmium and cadmium compounds and the results of biological monitoring in different occupational situations are summarized below. Occupational exposure to cadmium can be assessed both by ambient air monitoring ('external dose') and by biological monitoring ('internal dose'). Individual external doses can be measured only by personal sampling of ambient air; individual uptake is estimated by biological monitoring of cadmium in blood and urine (Alessio *et al.*, 1983; Ghezzi *et al.*, 1985; see also section 4.1).

(a) *Cadmium production and refining*

Smith *et al.* (1980) made a detailed assessment of exposures to cadmium in a production facility in the USA where cadmium metal had been refined and cadmium compounds, such as cadmium oxide and yellow cadmium pigment, had been produced since 1925. An epidemiological study carried out at the plant (Thun *et al.*, 1985) is described on pp. 152–153. Exposure to cadmium oxide dusts occurred during sampling, loading and transport of dust between the roasting, mixing and calcining operations and during loading of purified oxide. Exposure to cadmium oxide fume occurred in roaster, calcining, retort and foundry operations. Exposure to cadmium sulfate mist occurred during solution and tankhouse operations. The concentrations of cadmium differed substantially between the departments and with time. The highest exposures ( $1500 \mu\text{g}/\text{m}^3$ ) were estimated to have occurred in the mixing and retort areas prior to 1950 and in the calcining area prior to 1960. Estimates of exposures by inhalation, based on historical data derived from area monitoring and adjusted to reflect actual exposures of workers wearing respirators, were 200–1500  $\mu\text{g}/\text{m}^3$  before 1950 and 40–600  $\mu\text{g}/\text{m}^3$  during 1965–76. In 1946, an average concentration of 18 900  $\mu\text{g}/\text{m}^3$  was reported during grinding of cadmium sulfide and 31 300  $\mu\text{g}/\text{m}^3$  in the cadmium sulfide packaging room (Princi, 1947); cadmium concentrations in the solution room were approximately 3000  $\mu\text{g}/\text{m}^3$  before 1955, 1500  $\mu\text{g}/\text{m}^3$  in 1955–64 and 150  $\mu\text{g}/\text{m}^3$  subsequently (Thun *et al.*, 1985; Commission of the European Communities, 1991a,b).

At a zinc–lead–cadmium smelter in the United Kingdom, mean airborne cadmium concentrations were 80  $\mu\text{g}/\text{m}^3$  in the cadmium plant and 200  $\mu\text{g}/\text{m}^3$  in the sintering plant before 1970, whereas a mean level of 15  $\mu\text{g}/\text{m}^3$  was measured in each department in 1977. These assessments were considered to be accurate within a factor of 2–5. Urinary cadmium concentrations ranged from a geometric mean of 2.5 nmol/mmol creatinine [2.5  $\mu\text{g}/\text{g}$  creatinine] for workers in the sinter area to 6.3 nmol/mmol creatinine (6.3  $\mu\text{g}/\text{g}$  creatinine) for workers in the cadmium plant. [Some of the workers were exposed to cadmium sulfate and cadmium sulfide, but cadmium oxide is the compound to which they were most likely to have been exposed predominantly.] Copper and, from time to time, arsenic had also been refined in the plant (Kazantzis & Armstrong, 1983; Ades & Kazantzis, 1988). Epidemiological studies at the smelter are described on pp. 154–156.

Concentrations of cadmium were measured in the blood and urine of workers employed at two cadmium-producing factories and at a nickel–cadmium battery plant in Belgium. The cadmium content of the airborne respirable dust was usually below 90  $\mu\text{g}/\text{m}^3$ . In 96 workers without kidney damage, the mean urinary concentration of cadmium was  $16.3 \pm 1.7$

(SE)  $\mu\text{g/g}$  creatinine and that in blood was  $21.4 \pm 1.9 \mu\text{g/L}$ . In 25 workers with kidney lesions, the levels were  $48.2 \pm 8.5 \mu\text{g/g}$  creatinine and  $38.8 \pm 7.7 \mu\text{g/L}$ , respectively (Lauwerys *et al.*, 1976).

Airborne cadmium concentrations of 2500–6500  $\mu\text{g/m}^3$  in the crushing and roasting area, 10 800–23 300  $\mu\text{g/m}^3$  in the dry smelting area, 10–160  $\mu\text{g/m}^3$  in the cadmium melting area and 2800–4700  $\mu\text{g/m}^3$  in the ingot making area were measured in 1988 at a Chinese plant which employed about 10 000 workers; 358 were employed in those areas (Nomiyama *et al.*, 1992).

As part of an epidemiological study of Chinese smelter workers (see p. 156), Ding *et al.* (1987) reported a mean air concentration of 186  $\mu\text{g/m}^3$  in the cadmium shop, where workers were exposed to cadmium oxide, and 14  $\mu\text{g/m}^3$  in the sintering shop. The concentrations in the cadmium shop were reported to have been much higher (535  $\mu\text{g/m}^3$ ) prior to 1980.

(b) *Cadmium–copper and silver–cadmium alloy production*

In two plants for the production of cadmium–copper alloys in the United Kingdom, mean exposure concentrations of cadmium oxide as cadmium were 38–106  $\mu\text{g/m}^3$  in 1953 in one factory (Bonnell *et al.*, 1959) and 13–89  $\mu\text{g/m}^3$  in the rocker furnace area in the other factory (King, 1955). Concentrations of cadmium oxide were reported to have been at least 1000  $\mu\text{g/m}^3$  prior to 1953, up to 150  $\mu\text{g/m}^3$  between 1953 and 1957 and approximately 50  $\mu\text{g/m}^3$  subsequently (Holden, 1980a,b). Similar levels (mean, 130  $\mu\text{g/m}^3$ ) were reported in the 1960s at a Japanese silver–cadmium alloy factory (Tsuchiya, 1967).

In an Italian cadmium alloy plant in 1982, mean concentrations of 67  $\mu\text{g/m}^3$  and 28  $\mu\text{g/m}^3$  were detected using personal samplers in two foundries in the same factory; during alloy processing, 3  $\mu\text{g/m}^3$  were measured. Atmospheric concentrations of cadmium of up to 1500  $\mu\text{g/m}^3$  were measured with area samplers in 1975 (Ghezzi *et al.*, 1985).

As part of an epidemiological study of copper–cadmium alloy workers in Sweden (see pp. 151–152), the concentration of cadmium in cadmium oxide fumes was reported to be 100–400  $\mu\text{g/m}^3$  during the 1960s and 50  $\mu\text{g/m}^3$  during the 1970s (Kjellström *et al.*, 1979).

(c) *Battery manufacture*

Although the oxide is the form of cadmium used as the raw material in the manufacture of nickel–cadmium batteries, it is converted to cadmium hydroxide during the process. No information was available in the studies described below about which species of cadmium workers were actually exposed to. Exposures to nickel during the manufacture of nickel–cadmium batteries were described in a previous monograph (IARC, 1990a).

In a nickel–cadmium battery factory in Singapore, atmospheric, urinary and blood concentrations of cadmium were measured. The highest geometric mean atmospheric concentration (870  $\mu\text{g/m}^3$ ) was detected during spot welding; measurements during the period 1973–80 showed levels of 31–2900  $\mu\text{g/m}^3$ . The geometric mean concentration of cadmium in blood was 75.2  $\mu\text{g/L}$  for 41 women and 40.4  $\mu\text{g/L}$  for six men; the geometric means in urine were 66.0 and 22.9  $\mu\text{g/g}$  creatinine, respectively. The highest concentrations were detected in the subgroup of spot welders (Chan *et al.*, 1982).

The average concentrations of cadmium in a battery factory in the United Kingdom in 1957 were 500  $\mu\text{g/m}^3$  in the plate-making department and 100  $\mu\text{g/m}^3$  in the assembly

department (Adams *et al.*, 1969). In a nickel-cadmium battery factory in the United Kingdom, in which an epidemiological study was conducted (see pp. 149–150), the air concentration of cadmium in plate-making and assembly shops was 600–2800  $\mu\text{g}/\text{m}^3$  in 1949. After installation of local exhaust ventilation in 1950, concentrations were reduced to less than 500  $\mu\text{g}/\text{m}^3$  in most parts of the factory. After further improvements in the ventilation systems and the building of new departments in 1975, the levels were below 50  $\mu\text{g}/\text{m}^3$  (Sorahan & Waterhouse, 1983).

In a Swedish nickel-cadmium battery factory, where a series of epidemiological studies were carried out (see pp. 150–151), the concentration of cadmium was about 1000  $\mu\text{g}/\text{m}^3$  before 1947 but decreased gradually thereafter, to about 300  $\mu\text{g}/\text{m}^3$  in 1947–62 and 50  $\mu\text{g}/\text{m}^3$  in 1962–74. After 1975, 20  $\mu\text{g}/\text{m}^3$  was seldom exceeded (Adamsson, 1979; Elinder *et al.*, 1985). In 1977 in the same factory, the arithmetic mean concentration of cadmium in workroom air, based on 181 observations, was 7.6  $\mu\text{g}/\text{m}^3$ ; the arithmetic mean concentration in samples from 18 workers was 14.1  $\mu\text{g}/\text{L}$  in blood and 4.9  $\mu\text{g}/\text{g}$  creatinine in urine (Hassler *et al.*, 1983).

(d) *Polyvinyl chloride compounding*

A study was carried out in eight PVC production factories in Singapore where cadmium compounds were used as thermal stabilizers in liquid form or as cadmium stearate powder. A geometric mean concentration of 100  $\mu\text{g}/\text{m}^3$  cadmium was measured in the mixing area of one plant, where maintenance and work practices were poor; and < 10  $\mu\text{g}/\text{m}^3$  in the other seven plants. Geometric mean concentrations in samples from 53 male workers were 0.78  $\pm$  2.9  $\mu\text{g}/\text{g}$  creatinine in urine and 2.25  $\pm$  2.51  $\mu\text{g}/\text{L}$  in blood (Chan *et al.*, 1982).

(e) *Pigment manufacture*

Concentrations of cadmium in respirable dust were measured in 1976 and 1977 in a small Australian plant producing cadmium selenosulfide and cadmium sulfide pigments; exposure to cadmium carbonate also occurred. All time-weighted average exposures in the furnace, crushing-cleaning and general duties areas were greater than 1000  $\mu\text{g}/\text{m}^3$  in 1977; about 50% of the dust particles were in the respirable range. Biological monitoring of nine workers was begun in 1976: concentrations of < 0.5–32  $\mu\text{g}/\text{L}$  were found for urinary cadmium and 6–54  $\mu\text{g}/\text{L}$  for blood cadmium (De Silva & Donnan, 1981).

In a Japanese factory for the manufacture of cadmium pigments, cadmium sulfide and cadmium selenide, the arithmetic mean atmospheric concentrations of cadmium in seven areas of the plant in 1986 ranged from 3 to 350  $\mu\text{g}/\text{m}^3$ ; the highest values were found in the canning area. The geometric mean urinary cadmium concentrations in nine subjects who worked in the canning area were 1.7 (0.5–5.8)  $\mu\text{g}/\text{g}$  creatinine in April 1986 and 2.3 (1.3–4.1)  $\mu\text{g}/\text{g}$  creatinine in September 1986 (Kawada *et al.*, 1989).

(f) *Soldering*

One limited investigation in the United Kingdom indicated air concentrations of cadmium in excess of 50  $\mu\text{g}/\text{m}^3$  in five firms involved in the small specialized trade for both the manufacture and repair of metal frames (jigs), which entails soldering with cadmium-containing electrodes in small workrooms without exhaust ventilation. All 32

workers with more than five years of exposure and 11 of 21 with fewer than five years of exposure had 'raised' blood and urinary concentrations of cadmium; 30 had urinary cadmium concentrations in excess of 10 nmol/mmol ( $\mu\text{g/g}$ ) creatinine (Smith *et al.*, 1986).

(g) *Other*

A biological monitoring programme was conducted between 1980 and 1989, involving 919 workers employed in 16 different cadmium-processing industries in The Netherlands. The main industrial processes included in the survey were metal recycling, alloy production, enamelling, printing, production of coloured plastics, stabilizers, paints and pigments, electroplating and manufacture of cathode-ray tubes. The cadmium compounds to which workers were exposed included the oxide, chloride, carbonate, laurate, cyanide, sulfate and phosphate. Urinary cadmium concentrations ranged from 0 to 60.4  $\mu\text{g/g}$  creatinine and those in blood from 0 to 48.4  $\mu\text{g/L}$ . The highest concentrations were measured in workers using silver-cadmium solder (Zwennis & Franssen, 1992).

### 1.3.3 *Air*

Most of the cadmium that occurs in air is associated with particulate matter in the respirable range. Cadmium oxide is presumed to constitute a large proportion of airborne cadmium, but, in principle, other cadmium salts, such as cadmium chloride, used as stabilizers and pigments in plastics, could enter the environment, especially during incineration. Atmospheric emissions of cadmium from man-made sources exceed those of natural origin by one order of magnitude (UNEP, 1984, 1992). Traditional municipal solid-waste incinerators may make a significant contribution to the concentration of cadmium in ambient air and to its deposition rates. The rates of emission of cadmium from incinerators in Europe, Canada and the USA ranged from 20 to 2000  $\mu\text{g/m}^3$  from the stacks of traditional incinerators and from 10 to 40  $\mu\text{g/m}^3$  from advanced incinerators. Such emissions could result in deposition rates of 1–40 and 0.02–0.8  $\mu\text{g/m}^2$  per day, respectively (WHO, 1988). Cadmium sulfate also occurs in atmospheric emissions from thermal processes involving cadmium (IARC, 1976; Friberg *et al.*, 1985, 1986b).

Estimated emissions of cadmium to the atmosphere from natural and human sources are shown in Table 7. In both the European Economic Community and worldwide, 10–15% of total airborne emissions arise from natural processes, volcanic action being one of the major sources (WHO, 1992a,b). Mean global emission rates were estimated in 1983 to be 1000 tonnes cadmium per year from natural sources and 7570 tonnes from human sources (Nriagu & Pacyna, 1988).

In many countries, cadmium concentrations in the atmosphere are monitored regularly. In European countries, average values were 0.001–0.005  $\mu\text{g/m}^3$  in rural areas, 0.005–0.015 in urban areas and up to 0.05  $\mu\text{g/m}^3$  in industrialized areas. Concentrations of 0.003–0.023  $\mu\text{g/m}^3$  were found in urban areas of the USA, and 0.003–0.0063  $\mu\text{g/m}^3$  cadmium have been measured in urban areas in Japan (Friberg *et al.*, 1974, 1985, 1986b; WHO, 1992b). Higher concentrations of cadmium have been detected in areas close to atmospheric sources of the metal, such as cadmium-related industries. The nonferrous metal industry accounts for the largest fraction of cadmium emitted (Nriagu & Pacyna, 1988). Fluctuations in the data occur as a result of changing emission characteristics and weather conditions (WHO, 1992b).

**Table 7. Estimated atmospheric emissions of cadmium (tonnes/year) from natural and human sources**

Source	European Economic Community	Worldwide
Natural source	20	800
Nonferrous metal production		
Mining	NR	0.6-3
Zinc and cadmium	20	920-4600
Copper	6	1700-3400
Lead	7	39-195
Secondary production	NR	2.3-3.6
Iron and steel production	34	28-284
Fossil fuel combustion		
Coal	6	176-882
Oil	0.5	41-246
Refuse incineration	31	56-1400
Sewage sludge incineration	2	3-36
Phosphate fertilizer manufacture	NR	68-274
Cement manufacture	NR	8.9-534
Wood combustion	NR	60-180
Total	130	3900-12 800

Modified from WHO (1992a,b). NR, not reported

In Sweden, weekly mean levels of  $0.3 \mu\text{g}/\text{m}^3$  were recorded 500 m from a factory where cadmium-copper alloys were used. In Japan, a mean level of  $0.2 \mu\text{g}/\text{m}^3$  was recorded 400 m from a zinc smelter (Friberg *et al.*, 1971). In Colorado (USA), the mean annual airborne concentration of cadmium in an area about 1 km from a zinc smelter was  $0.023 \mu\text{g}/\text{m}^3$  (Wysowski *et al.*, 1978).

#### 1.3.4 Water

Cadmium enters the aquatic environment from numerous diffuse and point sources and by different routes. At the global level, the smelting of nonferrous metal ores has been estimated to be the largest human source of cadmium released into the aquatic environment (Nriagu & Pacyna, 1988). The cadmium content of ore bodies, mine management policies and climatic and geographical conditions all influence the quantities of cadmium released from individual sites. Contamination can arise from entry into aquifers of mine drainage water, wastewater, overflow from tailing ponds and rainwater run-off from mine areas (WHO, 1992a).

Other human sources are spent solutions from plating operations and phosphate fertilizers, which are known to contain cadmium: cadmium constitutes up to 255 mg/kg of phosphorus pentoxide in West Africa and up to 35 mg/kg in the USA (WHO, 1992a,b). Atmospheric fall-out of cadmium to water courses and marine waters represents the major worldwide source of cadmium in the environment (Nriagu & Pacyna, 1988). Acidification of

soils and lakes may result in mobilization of the metal from soils and sediments toward surface and groundwaters (Impens *et al.*, 1989; WHO, 1992b). Other point sources are mining residue dumps, solid-waste deposits and wastewater of both municipal and industrial origin (Muntau & Baudo, 1992). Cadmium salts such as cadmium carbonate, cadmium chloride and cadmium sulfate may also contaminate surface waters as a result of run-off from industrial processes (IARC, 1976). In polluted rivers, high concentrations can be found in bottom sediments (Muntau & Baudo, 1992).

The concentration of cadmium dissolved in surface waters of the open ocean is less than 0.005 µg/L (WHO, 1992b). Ice samples from the Arctic contained an average of 5 ng/kg, while those from the Antarctic contained 0.3 ng/kg (Wolff & Peel, 1985).

The concentration of cadmium in drinking-water is generally less than 1 µg/L, but it may increase up to 10 µg/L as a result of industrial discharge and leaching from metal or plastic pipes (Friberg *et al.*, 1971).

### 1.3.5 *Soil and plants*

The sources of cadmium in soil are nonferrous metal mines and smelters, agricultural application of phosphate fertilizers, use of batteries, PVC stabilizers, pigments and alloys, sewage-sludge landfill, sewage-sludge and solid-waste incineration, and application of municipal sewage sludge to agricultural soil (UNEP, 1984, 1992; WHO, 1992a,b). The concentration of cadmium in soil can vary widely. In non-polluted areas, concentrations are usually below 1 mg/kg (Friberg *et al.*, 1971, 1974), whereas in polluted areas levels of up to 800 mg/kg have been detected (Friberg *et al.*, 1985; 1986b; WHO, 1992b). With increasing acidification of soils due to acid rain and the use of fertilizers (and sewage sludge), increased uptake of cadmium from soil may occur (UNEP, 1984; 1992; WHO, 1992b).

Plants may be contaminated with cadmium *via* two routes: (i) soil-plant transfer, due to absorption of mobile forms of cadmium by the roots: increased soil content of cadmium results in increased plant uptake of the metal; the long-term availability of cadmium to plants is uncertain; (ii) air-plant transfer, due to deposition of cadmium particles and to precipitation of soluble forms on the epigeal parts of plants (Impens *et al.*, 1989). Cadmium residues in plants are normally less than 1 mg/kg (Friberg *et al.*, 1986a); however, plants growing in soil contaminated with cadmium may contain significantly higher levels (UNEP, 1984, 1992; WHO, 1992b).

### 1.3.6 *Cigarette smoke*

Tobacco plants naturally accumulate relatively high concentrations of cadmium in the leaves. The cadmium content of cigarette tobacco is generally 1–2 µg per cigarette, although the concentrations differ among regions. A smoker who smokes 20 cigarettes per day has an estimated daily uptake of 2–4 µg and accumulates 0.5 mg cadmium in one year (Lewis *et al.*, 1972; UNEP, 1984; Friberg *et al.*, 1985; IARC, 1986a; UNEP, 1992; WHO, 1992b).

### 1.3.7 *Food*

Food is the main source of cadmium for non-occupationally exposed people, although uptake (gastrointestinal absorption) from food is generally much less efficient than from water or air, as cadmium binds to food constituents. Cadmium is present in most foods, and

an extremely wide range of concentrations in foodstuffs has been reported from different countries (Friberg *et al.*, 1986a,b; WHO, 1992b). While average dietary concentrations are usually below the provisional tolerable weekly intake of 7 µg/kg bw proposed by FAO/WHO (1989), they are exceeded in some population groups (UNEP, 1984, 1992).

Meat, eggs, fish and milk products generally contain little cadmium—less than 0.01 µg/g wet weight—whereas internal organs, especially liver and kidney, may contain much more: concentrations of up to 1 µg/g wet weight have been reported in animal organs. Even higher concentrations have been detected in oysters (up to 8 µg/g) and salmon flesh (3 µg/g) (Friberg *et al.*, 1974); internal organs of fish and shellfish may also contain high amounts of the metal (Banat *et al.*, 1972; WHO, 1992b).

In general, vegetable products contain more cadmium than animal products. Two important dietary staples, rice and wheat, accumulate high amounts of the metal, depending on the season (Nordberg & Nordberg, 1988). In unpolluted areas, concentrations of 0.01–0.1 µg/g have been reported in rice and wheat, whereas in Japan and some other Asian countries the cadmium content may be higher (Friberg *et al.*, 1985; Watanabe *et al.*, 1989; Rivai *et al.*, 1990). An analysis of the cadmium content of 207 samples of common rice and glutinous rice collected in various areas of Asia showed no difference; the geometric mean cadmium concentration was about 20 ng/g dry wt (range, 0.8–259.3) (Watanabe *et al.*, 1989).

The average daily intake of cadmium varies among countries, and large individual variations occur. In unpolluted areas, intake is estimated to be 10–60 µg/day; values tend to be lower in Europe and North America than in Japan. In areas of Japan that are considered to be unpolluted, average daily intakes are generally 15–50 µg, whereas in polluted areas values as high as 500 µg have been reported (Friberg *et al.*, 1974; Kowal *et al.*, 1979; Friberg *et al.*, 1985; Watanabe *et al.*, 1985; Louekari *et al.*, 1991; Watanabe *et al.*, 1992; WHO, 1992b).

#### 1.3.8 *Animal tissues* (some of which may be used as food)

High levels of cadmium have been found particularly in seabirds and sea mammals; much of the cadmium occurs in the kidney and liver. Typical concentrations are in the range 0.1–2 mg/kg wet weight in liver and 1–10 mg/kg wet weight in kidney (Elinder, 1992; WHO, 1992b).

Long-lived terrestrial mammals, such as horses and moose, can also have remarkable burdens of cadmium in liver and kidney; concentrations of up to 200 mg/kg have been reported in kidney cortex samples of old horses (Elinder, 1992; WHO, 1992a). In small mammals living in polluted areas, cadmium also accumulates in the liver and kidney: concentrations ranged from 1.5 to 280 mg/kg dry weight in liver and from 7.4 to 193 mg/kg in kidney. In animals from unpolluted sites, concentrations in liver ranged from 0.5 to 25 mg/kg and those in kidney from 1.5 to 26 mg/kg (WHO, 1992a).

#### 1.3.9 *Human tissues and secretions*

Cadmium accumulates in the body. The total body burden of non-occupationally exposed adult subjects has been estimated to range from 9.5 to 40 mg in the USA and Europe. The International Register of Potentially Toxic Chemicals (UNEP, 1984, 1992) considered that the body burden of a proportion of the population is already approaching the



critical value of 10–15  $\mu\text{g}$ , which is the amount that must be retained daily to result in impaired kidney function after 50 years. Cadmium deposition increases with age and is greater in smokers than nonsmokers (Alessio *et al.*, 1983). Concentrations of 1–3 mg/kg wet weight have been detected in liver and 15–50 mg/kg in kidney cortex. Concentrations are usually higher in the Japanese; average concentrations in kidney cortex ranging from about 50 to 100 mg/kg were detected in people 50 years of age (Friberg *et al.*, 1985).

After long-term exposure to low levels, 40–80% of the retained cadmium (mainly bound to metallothionein) was found in liver and kidneys and about one-third in kidneys alone. Concentrations of 100–450 mg/kg wet weight were measured in kidney cortex of cadmium-exposed subjects who showed no renal changes or only slight changes in tubular function. The lungs of non-occupationally exposed subjects contained about 2% of the cadmium body burden (Alessio *et al.*, 1983; WHO, 1992b). In unselected autopsies in Germany, the mean concentrations of cadmium in lungs were found to be  $1.48 \pm 1.22 \mu\text{g/g}$  dry weight in the age group 20–45,  $1.73 \pm 1.42 \mu\text{g/g}$  in the age group 45–65 and  $1.18 \pm 1.27 \mu\text{g/g}$  for people aged > 65 (Kollmeier *et al.*, 1990). Placentas from nonsmokers contained  $13.7 \pm 6.4 \text{ ng/g}$  cadmium, and those from smokers contained  $18.1 \pm 7.3 \text{ ng/g}$  (Kuhnert *et al.*, 1982).

Concentrations of cadmium in urine and blood of subjects non-occupationally exposed to the metal have been reported in only a few studies, most of which were not designed for the definition of reference values but involved control groups for toxicological and epidemiological investigations (Alessio *et al.*, 1992). Mean urinary cadmium concentrations measured in several countries in Europe, Japan and the USA ranged from about 0.4 to 4  $\mu\text{g/L}$ . Urinary cadmium concentrations are significantly higher in smokers than in nonsmokers; on a group basis, they increase with age in nonsmokers. Mean blood concentrations ranged from about 0.2 to 4  $\mu\text{g/L}$ ; they were significantly higher in smokers and were influenced by age (Kowal *et al.*, 1979; Bruaux *et al.*, 1983; Elinder *et al.*, 1983; Friberg *et al.*, 1985; Watanabe *et al.*, 1985; Abe *et al.*, 1986; Pocock *et al.*, 1988; Alessio *et al.*, 1990; Buchet *et al.*, 1990; Alessio *et al.*, 1992; Kawada *et al.*, 1992).

#### 1.4 Regulations and guidelines

Occupational exposure limits and guidelines, whether legally binding or not, established in different parts of the world are given in Table 8. Separate engineering control air limits for cadmium in selected industries in the USA are shown in Table 9. WHO (1980, 1987, 1988) estimated the hazards to human health of lifetime exposure to different levels of cadmium in air and concluded that the concentration of cadmium in respirable dust should be well below 20  $\mu\text{g/m}^3$ , and short-term exposures to cadmium oxide fumes and respirable dust should not exceed 250  $\mu\text{g/m}^3$ .

In Sweden, an 8-h time-weighted average concentration of 0.01 mg/m<sup>3</sup> became applicable for respirable dust of cadmium and cadmium compounds in new and renovated plants as of 1 July 1991 (UNEP, 1993).

The American Conference of Governmental Industrial Hygienists (1992) adopted a biological exposure index of 10  $\mu\text{g/g}$  creatinine for cadmium in urine and 10  $\mu\text{g/L}$  for cadmium in blood. They have also proposed a reduction in these values to 5  $\mu\text{g/g}$  creatinine in urine and 5  $\mu\text{g/L}$  in blood, in agreement with the health-based biological limits recommended by WHO (1980).

**Table 8. Occupational exposure limits and guidelines for cadmium and cadmium compounds**

Country or region	Year valid	Concentration (mg/m <sup>3</sup> )	Substances affected	Interpretation <sup>a</sup>
Argentina	1991	0.05	Cadmium and cadmium salts (as Cd)	TWA, potential carcinogen
Australia	1990	0.05	Cadmium, cadmium compounds (as Cd), cadmium oxide, fumes	TWA, probable human carcinogen
Austria	1982	0.05	Cadmium dusts and salts (as Cd)	TWA
Belgium	1990	0.05	Cadmium, cadmium compounds (as Cd), cadmium oxide	TWA
		0.05	Cadmium oxide, fumes	Ceiling
Bulgaria	1984	0.1	Cadmium oxide, fumes (as Cd)	TWA
China	1979	0.1	Cadmium oxide, fumes (as Cd)	TWA
Denmark	1990	0.01	Cadmium, cadmium oxide, fumes	TWA
		0.01	Inorganic cadmium compounds (as Cd)	TWA, suspected carcinogen
Finland	1990	0.02	Cadmium, cadmium compounds (as Cd)	TWA, suspected of having carcinogenic potential
		0.01	Cadmium oxide, fumes	TWA, suspected of having carcinogenic potential
		0	Cadmium (respirable dust), cadmium chloride, inorganic cadmium compounds (as Cd), inorganic cadmium compounds (respirable dust) (as Cd)	Suspected of having carcinogenic potential
France	1990	0.05	Cadmium oxide	TWA
		0.05	Cadmium oxide, fumes	STEL
		0	Cadmium chloride	Suspected carcinogen
Germany	1992	0	Cadmium, cadmium compounds (as Cd), cadmium oxide, cadmium chloride, cadmium sulfate, cadmium sulfide	A2
Hungary	1983	0.05	Cadmium oxide, fumes (as Cd)	TWA
		0.1	Cadmium oxide, fumes (as Cd)	STEL (twice during one work shift)
Indonesia	1978	0.2	Cadmium dusts and salts (as Cd)	TWA
		0.2	Cadmium oxide, fumes (as Cd)	Ceiling
Italy	1978	0.05	Cadmium dusts and salts (as Cd)	TWA
		0.01	Cadmium oxide, fumes (as Cd)	TWA
Japan	1990	0.05	Cadmium, cadmium compounds (as Cd)	TWA

**Table 8 (contd)**

Country or region	Year valid	Concentration (mg/m <sup>3</sup> )	Substances affected	Interpretation <sup>a</sup>
Mexico	1984	0.05	Cadmium dusts and salts (as Cd); cadmium oxide, fumes (as Cd); cadmium oxide, production (as Cd)	TWA
		0.2	Cadmium dusts and salts (as Cd); cadmium oxide, fumes (as Cd); cadmium oxide, production (as Cd)	STEL (15 min four times a day)
Netherlands	1986	0.02	Cadmium and cadmium compounds (as Cd)	TWA, suspected carcinogen
		0.05	Cadmium oxide, fumes (as Cd)	TWA
Poland	1984	0.1	Cadmium oxide, fumes (as Cd)	TWA
Romania	1975	0.2	Cadmium oxide, fumes (as Cd)	STEL
Sweden	1991	0.05	Cadmium (total dust), inorganic cadmium compounds (as Cd) (total dust)	TWA, suspected of having carcinogenic potential
		0.02	Cadmium (respirable dust), inorganic cadmium compounds (respirable dust)	TWA, suspected of having carcinogenic potential
Switzerland	1984	0.05	Cadmium dusts and salts (as Cd), cadmium choride	TWA
		0.05	Cadmium oxide, fumes (as Cd)	Ceiling
Taiwan	1981	0.1	Cadmium dusts and salts (as Cd)	TWA
United Kingdom <sup>b</sup>	1992	0.05	Cadmium and cadmium compounds (dusts and fumes) (as Cd) (except cadmium oxide fumes and cadmium sulfide pigments), cadmium oxide fumes (as Cd)	TWA, MEL
		0.05	Cadmium oxide fumes (as Cd)	STEL, MEL (10 min)
		0.04	Cadmium sulfide pigments (respirable dust) (as Cd)	TWA
USA	1992	0.005	Cadmium	TWA, PEL
		0.015–0.050	Cadmium	SECAL (see Table 9)
ACGIH <sup>c</sup>	1992	0.05	Cadmium dusts and salts (as Cd), cadmium oxide production	TWA, TLV
		0.05	Cadmium oxide fumes (as Cd)	Ceiling

**Table 8 (contd)**

Country or region	Year valid	Concentration (mg/m <sup>3</sup> )	Substances affected	Interpretation <sup>a</sup>
Venezuela	1978	0.05	Cadmium dusts and salts (as Cd)	TWA
		0.15	Cadmium dusts and salts (as Cd), cadmium compounds (as Cd)	Ceiling
		0.05	Cadmium oxide, fumes (as Cd)	Ceiling

From Arbeidsinspectie (1986); Cook (1987); International Labour Office (1991); American Conference of Governmental Industrial Hygienists (ACGIH) (1992); Deutsche Forschungsgemeinschaft (1992); Health and Safety Executive (1992); US Occupational Safety and Health Administration (OSHA) (1992); UNEP (1993)

<sup>a</sup>The concentrations given may or may not have regulatory or legal status in the various countries; for interpretation of the values, the original references or other authoritative sources should be consulted. TWA, time-weighted average; STEL, short-term exposure limit; MEL, maximal exposure limit; PEL, permissible exposure limit; SECAL, separate engineering control air limit; TLV, threshold limit value; A2, compounds which in the Commission's opinion have proven so far to be unmistakably carcinogenic in animal experimentation only; namely under conditions which are comparable to those for possible exposure of a human being at the work place, or from which such comparability can be deduced.

<sup>b</sup>New maximal exposure limits have been proposed, to take effect from 1 January 1994: 0.04 mg/m<sup>3</sup> for cadmium sulfide and its pigments, and 0.025 mg/m<sup>3</sup> for cadmium and other cadmium compounds (Anon., 1992).

<sup>c</sup>A change has been proposed in the 'adopted' values: to 0.01 mg/m<sup>3</sup> for total dust or particulates of cadmium and cadmium compounds, and 0.002 mg/m<sup>3</sup> for the respirable fraction of dust (respirable particulate mass), considered to be suspected human carcinogens.

**Table 9. Separate engineering control air limits (SECALs) for cadmium processes in selected US industries**

Industry	Process	SECAL (mg/m <sup>3</sup> )
Nickel-cadmium battery	Plate-making, plate preparation	0.050
	All other processes	0.015
Zinc and cadmium refining <sup>a</sup>	Cadmium refining, casting, melting, oxide production, sinter plant	0.050
Pigment manufacture	Calcining, crushing, milling, blending	0.050
	All other processes	0.015
Stabilizer manufacture <sup>a</sup>	Cadmium oxide charging, crushing, drying, blending	0.050
Lead smelting <sup>a</sup>	Sinter plant, blast furnace, baghouse, yard area	0.050
Plating <sup>a</sup>	Mechanical plating	0.015

From US Occupational Safety and Health Administration (1992)

<sup>a</sup>Processes used in these industries that are not specified in the table must achieve the permissible exposure limit by using engineering controls and changing work practices. Industries that are not listed must meet the permissible exposure limit of 0.005 mg/m<sup>3</sup> (see Table 8).

In Sweden, cadmium workers are required to undergo a medical examination twice a year. Workers who have blood cadmium concentrations exceeding 150 nmol/L (16.5 µg/L) are removed from exposure and are not allowed to return until the concentration is below 100 nmol (11 µg/L) (Arbetarskyddsstyrelsens, 1989).

The guideline for all forms of cadmium in drinking-water recommended by WHO (1984, 1992c) is 3 µg/L. The maximal level of cadmium in drinking-water and the permissible level in bottled water in the USA is 10 µg/L (US Environmental Protection Agency, 1991; US Food and Drug Administration, 1992).

The Joint FAO/WHO Expert Committee of Food Additives (WHO, 1989) proposed a provisional tolerable weekly intake for cadmium of 7 µg/kg body weight. The provisional guidelines set by the Japanese Ministry of Health and Welfare are 0.4 mg/kg in rice and up to 10 µg/L in drinking-water (Förstner, 1984).

Cadmium and cadmium compounds are not permitted in cosmetic products in the countries of the European Economic Community (Commission of the European Communities, 1990, 1991c). A Directive has been adopted aimed at restricting the manufacture and use of certain cadmium-bearing pigments, stabilizers and plating and the discharge of cadmium into the environment (Commission of the European Communities, 1983, 1991d,e; Shagarofsky-Tummers, 1992). In Sweden, cadmium is not allowed for use as a pigment, for surface coatings or as a stabilizer (Svensk Författningssamling, 1979, 1980).

The International Register of Potentially Toxic Chemicals of UNEP included cadmium together with lead and mercury in its listing of environmentally dangerous chemical substances and processes of global significance (UNEP, 1984, 1992).