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Emission Factors of Atmospheric Cd, Pb and Zn for Major Source Categories in Europe in 1950 through 1985

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SUMMARY

Emission factors of Cd, Pb and Zn for various source categories have been reviewed with major aim to assess their changes during the period from the 1950's up to 1985. A progress made in developing industrial technologies and emission control techniques has been considered when calculating emission factors applicable for the 1950's, 1960's, 1970's and 1989 and 1985. It was concluded that the atmospheric emissions of Cd, Pb and Zn in Europe peaked in the mid 1970's. Emission factors of Cd, Pb and Zn before the mid 1970's were ca. three times higher than the factors estimated for the 1980's for major source categories such as non-ferrous metal production and combustion of fuels.

**EMISSION FACTORS OF ATMOSPHERIC
Cd, Pb AND Zn FOR MAJOR SOURCE CATEGORIES IN EUROPE
IN 1950 THROUGH 1985**

1 INTRODUCTION

Studies on source-receptor relationships for pollutants provide information which is needed for politicians to formulate environmental strategies, often related to reduction of emissions. The International Institute for Applied Systems Analysis (IIASA) has been contracted to study input of toxic pollutants to the Rhine river waters. A part of the pollutants enter the Rhine river waters via atmospheric deposition.

Major goals of this work is to assess emission factors of atmospheric Cd, Pb and Zn for major source categories in order to evaluate atmospheric emissions of the metals and their contribution to the contamination of the Rhine river waters. Both, current and historical emission factors are presented in a view to trace changes of atmospheric emissions of Cd, Pb, and Zn in Europe, beginning from the 1950's.

The following tasks have been performed to achieve the above goal:

- review of progress made in developing industrial technologies between 1950 and 1985,
- review of advancement in emission control techniques, and particularly dust control techniques, and
- review of current emission factors of Cd, Pb and Zn with a view of their changes from the 1950's through 1985 due to the development of industrial technologies and control devices.

Major emphasis was placed on countries in the Rhine river region, such as Switzerland, Germany, France, the Netherlands and Belgium.

2 EMISSION FACTORS FOR ELECTRIC POWER PLANTS

2.1 COAL COMBUSTION

Emission factors of Cd, Pb and Zn emitted from coal-fired power plants can be estimated using the following equation:

$$E = P x e_f x (1 - C_c x C_t) x S \quad (1)$$

where:

E = the trace metal emissions, mg of metal/day

e_f = the emission factors (uncontrolled), kg of dust/1 tonne of coal

P = daily coal requirements, tonnes of coal/day

C_c = the average operating efficiency of control equipment for each metal

C_t = the fraction of the production capacity on which control equipment has been installed, and

S = concentrations of trace metals in stack dust emitted during coal combustion, mg of metal/kg of dust.

2.1.1 Daily coal requirements

The daily coal requirement (P) of a coal-fired electric power plant is given by:

$$\text{DCR(tonnes/day)} = \frac{(N)}{100} \times C(\text{MWe}) \times 10^3 \frac{\text{kW}}{\text{MW}} \times 24 \frac{\text{h}}{\text{day}} \times 3412 \frac{\text{Btu}}{\text{kWh}} \times \frac{100}{E} \times \frac{1 \text{ lb coal}}{B_c \text{ (Btu)}} \times \frac{1 \text{ ton}}{2000 \text{ lb}} \times \frac{1 \text{ tonne}}{1.1 \text{ sh tn}} \quad (2)$$

where:

C = the noted capacity of the plant, in megawatts (MWe)

N = the capacity or plant factor, i.e., the percentage of capacity at which the plant operates, averaged over one year. A typical value of N is 70 per cent.

E = the efficiency of the plant, in per cent.

E = kWh of electrical energy output from the plant per kWh of 100 coal energy input into the plant. Typically E ranges from 36-40 per cent.

B_c = the heat content, in Btu per pound of coal.

The daily coal requirements of the four model plants considered in this work are given in Table 1 for the three standard coal types.

Table 1: Daily coal requirements of the four model power plants burning three standard coal types.

Plant size (MWe)	Daily coal requirement, tonnes/day		
	Bituminous	Subbituminous	Lignite
100	495	600	834
350	1730	2100	2920
700	3460	4200	5830
2100	10400	12600	17500

It was assumed in Table 1 that the plants use pulverized coal furnaces, have a thermal efficiency of 38 per cent and operate at 70 per cent capacity. It was also assumed, that the heat values are the following: for bituminous coal 13 850 Btu/lb, subbituminous 11 430 Btu/lb and lignite 8220 Btu/lb. Daily coal requirements of power plants using cyclone firing are similar to daily coal requirements of plants using pulverized coal furnaces.

For the purpose of this work, it was assumed that the three parameters: thermal efficiency of power plants, capacity factor and heat content of coals have been changed between the 1950 and 1985 only to the extent which can be covered by the overall inaccuracy of the emission estimates for the studied elements.

2.1.2 Uncontrolled emission factors and efficiency coefficients C_c and C_t .

Table 2 lists data on e_f , C_t and C_c for different boilers, assuming ESP installations with control efficiency of 99 per cent.

Table 2: Values of e_f , C_c and C_t for different boilers ESP equipped (for the reference years 1980 and 1985).

	e_f^{*1} kg of dust/ 1 tonne of coal	C_c	C_t	$C_c \times C_t$
Cyclone	13.64	0.99	0.71	0.70
Stoker	59.09	0.99	0.87	0.86
Pulverized	72.73	0.99	0.97	0.96

*1 Assuming 10% of ash in coal. For another ash contents factor e_f can be calculated using equations:

$$e_f = 1.364 \times A \text{ for cyclone}$$

$$e_f = 5.909 \times A \text{ for stoker}$$

$$e_f = 7.273 \times A \text{ for pulverized}$$

where:

A is content of ash, %.

The above data reflect the technological advancement in the beginning of the 1980's. They can be representative for both reference years 1980 and 1985. On the basis of literature review, and particularly on extended work at the Midwest Research Institute in USA (MRI, 1971) the factors for the reference years 1960 and 1970 can be assumed as in Table 3.

Table 3: Values of e_f , C_c and C_t for different utility boilers (in the reference years 1960 and 1970).

	e_f kg of dust/ 1 tonne of coal	C_c	C_t	$C_c \times C_t$
Cyclone	13.64	0.91	0.71	0.64
Stoker	59.09	0.80	0.87	0.70
Pulverized	72.73	0.92	0.97	0.89

The above literature source suggests that the efficiency of dust collection at the beginning of the 1950's was ca. 15 per cent lower than at the beginning of the 1960's. Thus, for the reference year 1950 the following factors ($C_c \times C_t$) can be suggested: 0.54 for cyclone, 0.60 for stokers and 0.76 for pulverized furnaces.

2.1.3 Concentrations of Cd, Pb and Zn in stack dust.

Concentrations of Cd, Pb and Zn in the stack dust depend on their concentrations in coal and technological parameters of combustion. The concentrations of Cd, Pb and Zn that can be suggested for most of the European coals are presented in Table 4.

Table 4: The Cd, Pb and Zn concentrations in the European coals.

Trace element	Bituminous coal µg/g		Subbituminous coal µg/g		Lignite µg/g	
	Range	Average	Range	Average	Range	Average
Cd	0.3-1.8	0.47	0.4-0.6	0.46	0.5-2.1	0.61
Pb	3.7-6.1	4.9	2.1-10.1	4.8	1.5-9.6	4.7
Zn	30.5-37.6	35.0	15.5-32.5	27.0	19.0-33.5	28.0

During combustion the volatile species in the coal evaporate in the firebox and recondense as submicron aerosol particles, or on the surface of ash particles as the flue gas cools in the convective sections. The concentrations of Pb, Cd and Zn increase markedly with decreasing particle size.

The knowledge of the enrichment mechanism of elements analysed during coal combustion permits establishing the concentrations of these constituents in the fine dust particles. Table 5 shows concentrations of trace metals under study in different size particles.

Table 5: Mean concentrations of Cd, Pb and Zn in different size particles emitted during coal combustion.

Element	Concentration in µg/g of dust fraction				
	>10 µm	3-10 µm	1-3 µm	0.5-1.0 µm	<0.5 µm
Cd	9.0	11.5	26.0	100.0	178.0
Pb	160.0	320.0	500.0	580.0	650.0
Zn	240.0	500.0	630.0	830.0	990.0

The theoretical (calculated) percentage distribution of particles in different size of stack dust is presented in Table 6.

Table 6: Assumed percentage distribution of different size particles in stack dust.

Boilers	Assumed percentage distribution of particles			
	<1 μm	1-3 μm	3-10 μm	>10 μm
Cyclone	9	37	21	33
Stoker	4	10	36	50
Pulverized	10	22	28	40

The data from Tables 5 and 6 can be used to calculate concentrations of Cd, Pb and Zn in stack dust. The results are shown in Table 7.

Table 7: Concentrations of Cd, Pb and Zn in stack dust, emitted during coal combustion in different boilers.

Element	Concentration in $\mu\text{g/g}$		
	Cyclone	Stoker	Pulverized
Cd	31.0	18.4	30.3
Pb	363	271	329
Zn	506	403	474

2.1.4 Emission factors for Cd, Pb and Zn emitted from coal-fired power plants

Information in Tables 1, 2, 3 and 7 can be used to estimate emission factors for Cd, Pb and Zn emitted from coal-fired power plants in the years 1950, 1960, 1970, 1980 and 1985. The results are shown in Table 8.

Table 8: Emission factors of trace metals*¹ ($\mu\text{g}/\text{MJ}$).

Element	Bituminous			Subbtuminous			Lignite		
	Cyclone	Stoker	Pulverized	Cyclone	Stoker	Pulverized	Cyclone	Stoker	Pulverized
1950									
Cd	11.0	25.0	31.0	13.2	30.0	36.6	18.5	42.0	51.0
Pb	128	366	329	155	446	398	216	620	554
Zn	178	570	474	216	660	576	300	918	798
1960 and 1970									
Cd	8.0	18.6	14.0	9.7	22.5	16.8	13.5	31.5	23.4
Pb	93.7	274	151	113	334	183	158	464	254
Zn	131	409	217	158	494	264	220	687	366
1980 and 1985									
Cd	7.3	8.7	5.1	8.8	10.5	6.1	12.3	14.7	8.5
Pb	85.2	128	54.8	103	156	66.4	144	217	92.3
Zn	119	191	79	144	231	96	200	321	133

*¹ 10% of ash in coal was assumed.

2.2 OIL COMBUSTION

The emission factors for Cd, Pb and Zn from combustion of oil in electric power plants can be calculated using the following equation:

$$E = E_p \cdot C \quad (3)$$

E = the trace element emission factor, mg metal/ 10^3 liters

E_p = the particulate emission factor, kg dust/ 10^3 liters

C = the trace element content in the emitted dust, mg metal/kg dust

The E_p factor was calculated from:

$$E_p = 1.25 \times S + 0.38 \quad (4)$$

where:

S = the percentage by weight of sulfur in the crude oil.

The trace metal content in dust emitted from oil-fired power plants varies from one plant to another. Table 9 presents mean concentrations of trace metals in dust emitted from European oil-fired power plants in 1982 ("C" in equation 3).

Table 9: Trace elements in dust from European oil-fired power plants.

Element	Concentration range, $\mu\text{g/g}$	Average concentration, $\mu\text{g/g}$
Cd	75-190	158
Pb	700-1800	1700
Zn	350-2000	1200

The average concentrations of trace metals in dust listed in Table 9 were calculated on the basis of measurements of trace elements in dust emitted from oil power plants in some European countries and figures of crude oil import from different areas to Europe together with distillate yields and trace element concentrations in crude oils.

The E_p factor was calculated assuming $S = 1\%$. The daily oil requirements are shown in Table 10.

Table 10: Daily oil requirements in electric power plants.

Plant size (MWe)	Fuel oil consumption 10^3 liters/day
100	392
350	1 372
700	2 744
2 100	8 232

Using the information from Table 9 in Equations 3 and 4 and the information from Table 10, the following emission factors were obtained (Table 11).

Table 11: Emission factors of trace metals*¹ ($\mu\text{g}/\text{MJ}$).

Element	Emission factor
Cd	11.6
Pb	125.7
Zn	88.7

*¹ Assuming 1% of sulphur

Taking into account the assumption that emissions of Cd, Pb and Zn from oil-fired power plants are not dependent on the efficiency of control abatement (the whole amount is emitted), their emission factors will not change within the years. Of course, the sulphur content of oil may change in the countries as this depends on export-import relationships for crude oil, so the emission factors for individual countries can vary from year to year.

3 EMISSION FACTORS FOR TRACE ELEMENTS FROM INDUSTRIAL, COMMERCIAL AND RESIDENTIAL COMBUSTION OF COAL AND OIL

3.1 COMBUSTION OF COAL

Pacyna (1986) has elaborated a set of emission factors for several trace elements during combustion of coal and oil in industrial, commercial and residential boilers. These factors have been estimated for boilers with dust removal installations of 82 to 85 per cent efficiency and application of control equipment covering from 91 to 95 per cent of sources within the combustion process. Such conditions can be described for the reference years 1980 and 1985. Average collection efficiency in the 1950s was ca. 16 per cent lower than in the 1980s. The corresponding values for the 1960s were 11 per cent, and the 1970s 4 per cent. Therefore the values of C_c and C_t from equation (1) are for the industrial, commercial and residential boilers as in Table 12.

Table 12: Values of C_c and C_t for different boilers applied for industrial, commercial and residential purposes.

Boiler	C_c	C_t	$C_c \times C_t$	$1 - (C_c \times C_t)$
1950				
Cyclone	0.69	0.91	0.63	0.37
Stoker	0.71	0.91	0.65	0.35
Pulverized	0.71	0.95	0.67	0.33
1960				
Cyclone	0.73	0.91	0.66	0.34
Stoker	0.76	0.91	0.69	0.31
Pulverized	0.76	0.95	0.72	0.28
1970				
Cyclone	0.79	0.91	0.72	0.28
Stoker	0.82	0.91	0.75	0.25
Pulverized	0.82	0.95	0.78	0.22
1980 and 1985				
Cyclone	0.82	0.91	0.75	0.25
Stoker	0.85	0.91	0.77	0.23
Pulverized	0.85	0.95	0.81	0.19

Most of the boilers employed in industry are of stoker type. Therefore, it was assumed that the emission factors Cd, Pb, Zn for stokers are relevant for all industrial, commercial and residential boilers. These factors are given in Table 13 after using data from Table 12 and a set of factors elaborated by Pacyna (1986).

Table 12: Emission factors of trace elements from coal-fired industrial, commercial and residential units (g of trace element/tonne of coal burned).

Reference year	Cd	Pb	Zn
1950	0.80	11.70	17.30
1960	0.70	10.40	15.40
1970	0.57	8.40	12.40
1980	0.52	7.70	11.40
1985	0.52	7.70	11.40

3.2 COMBUSTION OF OIL

The following emission factors are suggested after Pacyna (1986):

Cd	-	0.65	g/10 ³	liters	of	oil
Pb	-	6.4	"	"	"	"
Zn	-	4.5	"	"	"	"

Again, these factors are not dependent on the efficiency of control equipment, thus, are equal for the whole study period.

3.3 COMBUSTION OF GASOLINE

Information on the use of lead additives in gasoline in various European countries is available for the period from the late 1970's until today. Important regulations concerning the reduction of lead additives have been introduced in many countries at the end of the 1970's. Lead content of gasoline was limited to 0.4 g Pb/l in the Federal Republic of Germany (FRG) from 1 January 1972. Low-leaded gasoline with 0.15 g Pb/l has been introduced in FRG already in 1976 (the Federal Republic of Germany). In the Scandinavian countries, low-leaded gasoline was introduced in Norway and Denmark in 1982 and in Sweden in 1983. Other countries, such as Belgium, Finland, Luxembourg, The Netherlands and the United Kingdom followed the suit in 1986.

Unleaded gasoline (no lead additives but some lead content due to the contamination of crude oil) was introduced in Europe in the mid 1980's. However, amounts of unleaded gasoline were very low at that time compared with leaded and low-leaded gasoline. For example, the contribution of unleaded gasoline to the total consumption of gasoline in the Federal Republic of Germany was 1 per cent in 1985, 11 per cent in 1986 and 25 per cent in

1987. In Scandinavia, unleaded gasoline was introduced in 1986, but in 1987 its contribution to the total consumption of gasoline was at a level of 10 per cent.

The most recent data from the European Fuel Oxygenates Association shows that the market share of unleaded gasoline in Europe in the spring of 1989 was as in Table 13.

Table 13: Market share of unleaded gasoline (in per cent) in the Spring of 1989.

Country	Market share
Fed. Rep. of Germany	58
Switzerland	50
Austria	38
Sweden	35
The Netherlands	31.5
Norway	26
the United Kingdom	20
Belgium	9.3
Finland	2
France	<1
Italy	<1
Spain	<1

While the above countries introduced low-leaded and unleaded gasoline in the mid 1980's, other countries, particularly in Eastern and Southern Europe were passing regulation on required content of 0.4 g Pb/l. A list of these countries includes Czechoslovakia, Poland, Hungary, Portugal, Spain, Greece and partly the Soviet Union.

Much less information is available on the use of lead additives in gasoline in Europe in the 1950's, 1960's and 1970's. On the basis of information available from the UK Petroleum Industry Association and the UK Department of Energy the amount of lead in gasoline between the 1950's and 1970's was varying from 0.5 to 0.65 g/liter. Various data from the German Umweltbundesamt seem to suggest similar values for the content of lead in gasoline in the Federal Republic of Germany.

Information collected by the author on the use of lead in gasoline additives in other countries in Europe in the period between the 1950's and 1970's seems to suggest that lead content of gasoline was ca. 1.0 g Pb/l.

The author was reviewing various national documents as well as information from the lead additive producers, mainly the Associated Octel Company Limited. The Octel company provided the author with statistics on gasoline lead compound usage in Western Europe in 1950-1990. This data are presented in Table 14.

Table 14: Gasoline lead compound usage in Western Europe in 1950-1990 (in 10^3 t).

Year	Usage	Year	Usage
1950	17	1970	129
1955	21	1975	144
1960	44	1980	139
1965	85	1985	101
		1990	57

The following shall be noted:

- for Western Europe Octel means the 12 Member States of the European Economic Communities and the EFTA countries;
- one tonne of lead compound contains 39.39% lead; and
- vehicle lead emissions are generally 75-80% of lead consumed in the gasoline.

The above information on the usage of lead compounds in Western Europe was then considered together with the information from some individual European countries to calculate the amount of lead in one liter of gasoline during the period from 1950

through 1985. The calculations were based on the usage of lead compounds and statistics on the gasoline consumption. The results of calculations are shown in Table 15.

Table 15: Lead content of gasoline in Europe between the 1950's and 1985 (per cent).

Country	1950-59	1960-69	1970-79	1980	1985
Albania	1.00	1.00	1.00	0.40	0.40
Austria	1.00	1.00	0.50	0.40	0.40
Belgium	1.00	1.00	1.00	0.40	0.40
Bulgaria	1.00	1.00	1.00	0.40	0.40
Czechoslovakia	1.00	1.00	1.00	0.40	0.40
Denmark	0.55	0.55	0.50	0.40	0.15
Finland	1.00	1.00	1.00	0.50	0.30
France	1.00	1.00	1.00	0.50	0.40
Fed. Rep. of Germany	0.55	0.55	0.40	0.15	0.15
German Democratic Rep.	1.00	1.00	1.00	0.40	0.40
Greece	1.00	1.00	1.00	0.84	0.40
Hungary	1.00	1.00	1.00	0.40	0.40
Iceland	1.00	1.00	1.00	0.40	0.40
Ireland	1.00	1.00	1.00	0.40	0.40
Italy	1.00	1.00	1.00	0.64	0.40
Luxembourg	1.00	1.00	1.00	0.40	0.40
The Netherlands	0.55	0.55	0.50	0.40	0.40
Norway	0.55	0.55	0.50	0.34	0.15
Poland	1.00	1.00	1.00	0.40	0.40
Portugal	1.00	1.00	1.00	0.40	0.40
Romania	1.00	1.00	1.00	0.40	0.40
Spain	1.00	1.00	1.00	0.60	0.40
Sweden	0.55	0.55	0.50	0.15	0.15
Switzerland	0.55	0.55	0.50	0.15	0.15
the United Kingdom	0.55	0.56	0.48	0.41	0.40
USSR-Europe	1.00	1.00	1.00	0.40	0.40
Yugoslavia	1.00	1.00	1.00	0.40	0.40

It is very difficult to obtain any means of verification of the data in Table 15. However, it was concluded that the Pb emissions in Rhine Area South (Cologne) due to traffic have decreased from 186.3 t/y in the period 1964-1974 to 63.4 t in 1980, thus almost 3 times (OECD, 1987). A decrease of total Pb emissions in the Federal Republic of Germany during this period was also 3-fold as seen from Table 2. Taking into account that gasoline combustion is the major source of lead emissions in the Federal Republic of Germany, the above described agreement between the data is quite interesting.

4 NON-FERROUS METAL PRODUCTION

Mining of ores and further roasting, smelting and refining processes in the non-ferrous metal production are the major sources of Cd and Zn production in Europe. A type of production process, efficiency of pollution control installations and contamination of ores by these elements are the most important parameters affecting the emission process.

There are two major types of technological processes employed in the non-ferrous metal production: pyrometallurgical (thermal) processes with high temperature during roasting and smelting and electrolytic extraction. Major source of atmospheric Cd, Zn and Pb (after gasoline combustion) is pyrometallurgical production of zinc and lead. Roasting of ore concentrates and low-grade ore enrichment are initial steps in the zinc and lead production. The zinc ore concentrates from roasters are then sintered and smelted to reduce zinc and cadmium oxides. The last step is purification.

The lead ore concentrate from roasting is extracted in a sintering plant. Sometime the sintering machine or electric furnace receives the lead sulfide ore directly. Lead sulfide is then oxidized in a blast furnace to lead oxide and reduced to produce lead metal. In the last step, the lead is refined either by electrolysis or by chemical precipitation.

The copper smelters can be significant sources of atmospheric emissions of Pb and Zn, and to less extent of Cd.

High efficiency control devices are presently employed in smelters. Roaster facilities, as well as sintering processes are controlled mainly with fabric filters and electrostatic precipitators. The control efficiencies of these installations in the non-ferrous metal production vary from 80 per cent up to 99.9 per cent with the values closer to 99.9 per cent nowadays.

Assuming that the same type of production process has been employed in a given smelter for several years in the past and that the ores have been delivered to a given smelter from the same mine (rather stable export-import market), the historical Cd, Pb and Zn emissions from smelters in Europe are mainly dependent on the progress of developing more efficient emission control installations and on the degree of control coverage of emission-generating processes within smelters. Therefore, the historical emissions of Cd, Pb and Zn need to be regarded separately for individual smelters in Europe, as far as information from these smelters exists.

Several studies have been carried out to assess emissions of heavy metals from smelters in FRG. In major smelters such as Stolberg and Duisburg emissions of Cd and other heavy metals peaked in the mid 1970's. They were 2 to 4 times higher than in the 1980's as concluded on the basis of various German and OECD documents (e.g. reports from Minister für Arbeit, Gesundheit und Soziales (MAGS) des Landes Nordrhein-Westfalen or from the OECD Chemicals Group and Management Committee). For example, industrial lead emissions in Duisburg have decreased from over 800 t/y in the mid 1970's to ca. 220 t/y in 1981. Cadmium emissions from the Stolberg smelter have been reduced from 900 kg in 1974 to a. 400 kg in the 1980's. It should be observed, however, that not only more efficient control technologies have been employed in smelters, but also less polluting production techniques in some smelters.

Concerning other countries in the studied region, reports from the Netherlands indicate that in the 1970's it must have been considerable Cd and other heavy metal emissions from the thermal zinc production processes operated in the Budel, Overpelt and Lommel areas of North Brabant and Limburg. Budelco BV is now the sole producer and since 1973 all production has been by the electrolytic process, in which process emissions of heavy metals to the atmosphere are insignificant.

Measurements carried out in the area of the copper smelter complex in Glogow in Poland and the Legnica lead smelter showed 2-fold decrease of heavy metal emissions into the atmosphere between the mid 1970's and the beginning of the 1980's (e.g. Pacyna et al., 1981).

It is very difficult to obtain detailed information on emissions of heavy metals from non-ferrous metal smelters during the period from the 1950's up to the 1970's. Therefore, it is suggested to use only two groups of emission factors for heavy metals. First group includes emission factors expected to be valid before the mid 1970's and the second group consists of factors for the situation in the 1980's. Thus, the first group of emission factors will be valid for the 1950's, 1960's, and 1970's, while the second group will be valid for 1980 and 1985. It was also assumed on the basis of the literature (e.g. various MAGS and OECD reports and the author own data) that the emission factors in the first group are three times (on average) higher than the emission factors in the second group. The emission factors are given in Table 16.

Table 16: Heavy metal emission factors for non-ferrous metal production before the mid 1970's and in the 1980's (in g metal emitted/t metal produced unless as indicated).

Operation	Before the mid 1970's			In the 1980's		
	Cd	Pb	Zn	Cd	Pb	Zn
Mining		2700 ^{*3}	240 ^{*1}		900 ^{*3}	80 ^{*1}
Primary copper production,	600	6000	2550	200	2000	850
Secondary copper production	15	390	1500	5	130	500
Primary zinc production	1500 ^{*2}	5700	48000	500 ^{*2}	1900	16000
Secondary zinc production			27000			9000
Primary lead production	30	9000	330	10	3000	110
Secondary lead production	7.5	600	900	2.5	200	300

*1 in g metal/t (Zn+Cu+Pb) mined

*2 This factor applies for pyrometallurgical processes other than:
 - Vertical Report (VR) process - 200 g Cd/t Zn produced, and
 - Imperial Smelting Furnace (ISF) process - 50 g Cd/t Zn produced.

*3 in g metal/t Pb processed.

5 IRON AND STEEL MANUFACTURING AND CEMENT PRODUCTION

Non-ferrous metal production is the major industry emitting heavy metals to the atmosphere, although not the only one. Other industries include iron and steel manufacturing and cement production.

5.1 IRON AND STEEL MANUFACTURING

The manufacture of iron and steel from iron ore or recycled scrap involves many processes with the potential of generating atmospheric pollution, including heavy metals. Concerning iron works, the major source of zinc and lead is blast furnace gas. The emission rates of Zn and Pb from blast furnace vary due to the type of ore operated and the type and efficiency of control devices. The lower values of emission factors are calculated for processes using haematite and ironstone and the higher ones are for siderite or magnetite.

The cupola furnace is the most important source of air pollutants in the production of iron castings, but emissions of Zn and Pb are insignificant.

Steel can be produced in open-hearth, electric-arc, and basic oxygen furnaces. A comparison of atmospheric emissions from electric-arc steelmaking (EAS) with those from basic oxygen (BOS) or open-hearth (OH) clearly indicates higher emission factors for the former technology due to high scrap charge loadings in the BOS process. The emission factors of Cd, Pb, and Zn for EAS are ca. one order of magnitude higher than those for BOS. These factors depend strongly on the efficiency of control devices, particularly when comparing the 1950's, 1960's, 1970's and 1980's emission factors.

On the basis of literature review, and particularly on research at the Midwest Research Institute (MRI, 1971) it can be suggested that the efficiency of control equipment to collect

metals emitted from iron and steel manufacturing was ca. 80% in the reference years 1960 and 1970. The technological advancement of control devices in the beginning of the 1980's resulted in obtaining 95% efficiency in 1980 and 97% in 1985. Taking into account this information, as well as the 1985 emission factors by Pacyna (1986), the historical evolution of emission factors is as presented in Table 17.

Table 17: Emission factors of Cd, Pb and Zn for iron and steel production (in g of metal/t of product).

Process	Cd	Pb	Zn
1960			
Iron	0.5	74.7	180
Steel: EAS	2.7	74.7	180
BOS	0.13	10.7	26
1970			
Iron	0.5	74.7	180
Steel: EAS	2.7	74.7	180
BOS	0.13	10.7	26
1980			
Iron	0.13	18.7	45.0
Steel: EAS	0.70	18.7	45.0
BOS	0.03	2.7	6.5
1985			
Iron	0.08	11.2	27.0
Steel: EAS	0.4	11.2	27.0
BOS	0.02	1.6	3.9

Very little is available on the efficiency of control equipment installed in the 1950's. Therefore, it is assumed here, that the Cd, Pb, and Zn emission factors calculated for the 1960's and 1970's can also be used for the 1950's.

5.2 CEMENT PRODUCTION

During cement production Cd, Pb and Zn can be emitted from the feed system, the fuel-firing kiln system, and the clinker-

cooling and handling system. The type of the production process (wet or dry), the type of fuel used in the grinding mill, the type of fuel-firing system employed, and the type of control equipment, all affect the emission rates of Cd, Pb and Zn. The most efficient control devices are baghouses controlling emission effluents from wet-type cement production process. In contrary, multicyclones and ESP's allow for more emissions to the atmosphere.

Emission factors for Cd, Pb and Zn have been published by Pacyna and Munch (1988) and Pacyna (1988) for cement plants in Europe equipped with 97% efficiency ESP's. Assuming, that the degree of dust removal from exhaust gases in cement plants during the last three decades followed the trend as for iron and steel production, the Cd, Pb and Zn emission factors for the reference years 1960, 1970, 1980 and 1985 developed as shown in Table 18.

Table 18: Emission factors of Cd, Pb and Zn for cement production (in g of metal/t of cement).

Element	1960	1970	1980	1985
Cd	0.3	0.3	0.07	0.04
Pb	7.3	7.3	1.8	1.1
Zn	73	73	18	11

Again, no information was available for the author regarding the control technology in the 1950's. Therefore, the 1950 emission factors can be assumed as those for 1960 and 1970 in Table 18.

6 WASTE-RELATED SOURCES

Two major types of waste-related sources include municipal waste incineration and sewage sludge incineration. In a view of the large amounts of wastes to be incinerated and their

chemical composition including heavy metals, incineration of wastes is now becoming one of the major sources of Cd and important source of Pb and Zn emissions to the atmosphere, particularly in Western Europe. Thus, incineration of wastes receives our attention, as a source of atmospheric contamination.

The emission rates for various pollutants depend on the type and amount of refuse to be incinerated and its chemical composition, as well as the type of burner and the type and efficiency of control equipment.

Recent OECD studies (OECD, 1988) on Control of Organic and Metal Emission from Municipal Solid Waste Incineration can be used to conclude as follows:

- Amounts of municipal wastes in countries of particular interest for this study, e.g. Belgium, France, FRG, the Netherlands and Switzerland differ insignificantly between 1975, 1980 and 1985 (a few per cent difference) except for ca. 34% increase from 1975 to 1980 for Switzerland;
- amounts of municipal wastes per capita vary from ca. 260 kg/person in France to 350 kg/person in FRG considering the above mentioned group of countries, with exception of ca. 530 kg/person in the Netherlands; and
- composition of municipal wastes has not changed significantly between 1975 and 1985 for the above countries except for decrease of paper and glass in FRG.

Therefore, it can be assumed that the chemical composition of exhaust gases from incinerators will be similar for the countries of interest and should not change substantially between the reference years 1975, 1980, and 1985.

Less information is available on emissions of Cd, Pb, Zn from sewage sludge incineration. Even if the information is available, very often it comes from the United States, where the chemical composition of sewage sludge to be incinerated can be different than that in Europe.

In order to calculate emission factors for Cd, Pb, and Zn, from municipal waste incineration, the amounts of emissions of Cd, Pb and Zn from this source (reported by the countries mentioned above - (see Pacyna, 1988) were divided by the amounts of municipal wastes incinerated in these countries (as reported by OECD, 1988). The emission factors are presented in Table 19.

Table 19: Emission factors of Cd, Pb and Zn for municipal waste incineration (in g metal/t waste incinerated).

Country	Cd	Pb	Zn
Belgium	1.1	13.2	?
France	1.1	12.6	56.0
FRG	1.8	27.7	77.0
the Netherlands	0.8	20.0	45.0
Average	1.2	18.4	59.3

Earlier estimates of the above emission factors by the author (Pacyna, 1986) were 2.2 g Cd/t refuse and 18.4 g Pb/t refuse.

It is suggested here to use the emission factors in Table 19 for all three reference years 1975, 1980 and 1985.

No information, however, was available to the author in order to assess the emission factors in years earlier than 1975. Concerning sewage sludge incineration, it is suggested to use emission factors calculated earlier by the author (Pacyna, 1986). The emission factors are as follows:

- for Cd: 12 g /t sludge incinerated,
- for Pb: 140 g /t sludge incinerated,
- for Zn: 104 g /t sludge incinerated, and

It is difficult to assess to what extent these factors have changed over the years, thus there is no better choice as to accept them as valid for 1975, 1980 and 1985.

7 INDUSTRIAL APPLICATION OF METALS

7.1 INDUSTRIAL APPLICATION OF CADMIUM

Three major application processes of cadmium include:

- production of stabilizers,
- production of Cd pigments, and
- production of Ni-Cd batteries.

Cadmium stabilizers are compounds of cadmium with organic acids, usually in combination with barium or zinc compounds and they are exclusively used in polyvinyl chloride (PVC) plastics to suppress decomposition under the action of heat and light.

Cadmium sulphide and selenide pigments are used as colorants in plastics, paints, glass, textiles, rubber, inks, and glazes for ceramics.

Nickel-cadmium rechargeable batteries are the major growth area of cadmium. There are two types of Ni-Cd batteries: pocket-plate cells, which account for 50% of the cadmium consumed, and sintered-plate or sealed cells, which account for the other 50%.

It is suggested to use the following emission factors for the above sources, for all the reference years:

- for Cd stabilizers: ~ 120 g Cd/t Cd charged,
- for Cd pigments: ~ 210 g Cd/t Cd charged, and
- for Ni-Cd batteries: ~ 860 g Cd/t Cd charged.

7.2 END USES OF ZINC PRODUCTS

Zinc metal has been applied in galvanizing, brass and bronze products, castings and production of rolled zinc. In addition to metallic applications, significant quantities of zinc are consumed as pigments, zinc dust or other chemicals.

Galvanizing accounts for over 90% of the total zinc, used for protective coatings for structural steel, roofing, siding, guttering, and reinforcing bars.

Brass and zinc-bearing bronze find widespread use in architectural construction for various kinds of applications. Other sectors using brass and bronze include automotive industry, military-oriented industries and variety of home applications.

Rolled zinc is produced from pure zinc or zinc containing alloying metals and has specific applications, such as for dry cell battery cases, weather stripping and lithographic plates.

It is very difficult to assess emission factors for end uses of zinc products. Nriagu and Davidson (1980) reported that on global scale this category contributes ca. 8% of atmospheric zinc to the total emission of the metal. Of course this number may vary from one country to another. However, there is no information on what is the contribution of Zn emissions from end uses of zinc products to the total zinc emissions in the countries of interest for this study. Therefore, it is suggested to multiply the Zn emission from other sources by a factor of 0.09 in order to obtain the Zn emission from the end uses of the metal.

7.3 END USES OF LEAD PRODUCTS

There are several applications of lead products that generate emissions of the element to the atmosphere. However, these lead emissions have always been negligible compared to emissions from other sources (below 1% of total emissions globally, in Europe and North America, and in the countries of interest for this study). Anyway, these sources are shortly described here.

Lead is used as an alloying component to produce brass and bronze. The lead emissions from brass and bronze foundries vary with the type of furnace, the composition of lead in the alloy (ranging from 0.02% to 25%), pouring temperature and the foundry maintenance. Reliable data to estimate the lead emissions from brass and bronze foundries are difficult to obtain. Some literature data, mostly from North America seem to indicate an average emission factor of ca. 200 g Pb/1 t of brass and bronze ingots produced.

Lead has also been used in the production of lead alloys, manufacture of collapsible tubes, ammunition, pipes and sheets and coating of electrical cables. An amount of 2 kg of Pb was emitted to produce 1 tonne of the above mentioned goods. Soldering of metal products accounts for an emission of ca. 100 g of lead released per 1 tonne of the product.

Two major uses of lead have been storage battery production and lead alkyl manufacture. Emission sources of lead from storage battery production are grid casting furnaces and machines, paste mixers, plate dryers, and grinding and handling of dry metal and oxide powders prior to their formation into a paste. An emission factor of ca. 10 kg Pb/1000 batteries produced can be suggested on the basis of the statistical data for this source category.

Atmospheric lead emissions from lead alkyl manufacture consist of lead-bearing particles from melting and recovering the lead, and organic lead vapours from the manufacture, recovery, and

storage of alkyl lead compounds. An emission factor of ca. 2.5 kg Pb/1 t of lead used can be suggested for this source category.

Lead oxide has been used as a pigment in paints and ceramic glazes. Pigment dust lost during handling of the dry powder is minimal (ca. 4 kg/1 t of leaded paint produced).

Finally, lead oxide has been added to the major ingredients for the production of lead glass. Again, atmospheric emissions of lead from this source can be regarded as negligible.

8 CONCLUDING REMARKS

The following concluding remarks can be drawn:

1. It is very difficult to assess emission factors of Cd, Pb and Zn for various source categories with a view to estimate the historical trends in emissions of these metals. Even present emission factors are to be used with caution. Emission factors for the reference years 1950, 1960, and 1970 are often based on our current knowledge of industrial technologies and of advancement of control techniques. Generally, there is a lack of measured data on emissions in the 1950's, 1960's or even in the 1970's. Beside, some measured data cannot be trusted due to the low accuracy of analytical methods some 20 or 30 years ago, as well as a possibility of sample contamination, particularly when using zinc-containing samplers.
2. This study seems to be the first approach to the historical assessment of emission factors of Cd, Pb and Zn in Europe. The available data indicate that the emission factors for major source categories have gradually decreased from the 1950's up to the 1990's, mostly due to the improvement of collection efficiency of control devices. This, however, may not mean that emissions have decreased accordingly,

because the production and consumption statistics often peaked in the mid 1970's.

3. Non-ferrous metal industry and gasoline combustion are still the major emission source categories for Cd and Zn, and Pb, respectively. However, their contribution lowers while the contribution of emissions from waste incineration is increasing. This is particularly true for the countries of special interest for this study where, lead is being phased out from gasoline, and major part of non-ferrous metal production does not use the pyrometallurgical processes. At the same time the amount of wastes to be incinerated increases in these countries.
4. Emission factors presented in this work can be used together with the statistical data to estimate historical and current emission of Cd, Pb and Zn in Europe, and particularly in the studied region.

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TITTEL Emission factors of atmospheric Cd, Pb and Zn for major source categories in Europe during 1950-1985.		PROSJEKTLEDER Jozef M. Pacyna	
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TITLE	Emission factors of atmospheric Cd, Pb and Zn for major source categories in Europe during 1950-1985.
ABSTRACT	Emission factors of Cd, Pb and Zn for various source categories have been reviewed with major aim to assess their changes during the period from the 1950's up to 1985. A progress made in developing industrial technologies and emission control techniques has been considered when calculating emission factors applicable for the 1950's, 1960's, 1970's and 1989 and 1985. It was concluded that the atmospheric emissions of Cd, Pb and Zn in Europe peaked in the mid 1970's.

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