

**EMISSION FACTORS FOR AQUEOUS INDUSTRIAL  
CADMIUM DISCHARGES TO THE RHINE BASIN**

**A Historical Reconstruction of the Period 1970–1988**

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# Foreword

One of the objectives of IIASA's study, "Sources of Chemical Pollution in the Rhine Basin," has been to characterize the historical aqueous emissions of selected heavy metals in the Rhine River. A major task in this endeavor has been to estimate how aqueous emission factors from industrial point sources have changed in previous decades. Information on this topic is surprisingly sparse, and the data which are available are not organized in a coherent way that allows one to trace readily the historical trends in aqueous emissions. In fact, it should be noted as a general statement that studies documenting historical pollution in specified regions are rare, even in relatively data-rich areas such as the Rhine Basin. The task of reconstructing past pollution is daunting because information is required on historical levels of industrial pollution, emission factors per unit of production and how these factors have changed over time, and the locations of the industrial point sources.

This report, by reviewing the relevant literature and synthesizing data on economic technologies, trade, and environmental monitoring, provides an analysis of the aqueous emissions of cadmium from industrial point sources in the Rhine Basin from 1970–1990. The report not only provides valuable input to our study of the Basin, but also demonstrates a methodology by which historical reconstructions of aqueous pollution can be attained and utilized in assessing long-term environmental trends.

As a final point, one may question the rationale for expending such an effort to obtain a regional environmental history. Rather than dwelling on the past, are not the present and future more important? We would argue, however, that history is a good teacher from which one may learn valuable lessons. This historical Rhine Basin study provides a much needed data base for further understanding of the institutional, political, and social factors that shaped the pollution landscape in previous decades, and led to the remarkable cleanup that has occurred more recently. In so doing, perhaps we can learn more than we now know about how societies pollute

their environment and how they go about cleaning it up. Such information is urgently needed for guiding policies, particularly in the newly industrialized regions of the world such as southeast China, and in highly polluted river basins such as in Eastern Europe.

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Sources of Chemical Pollution  
in the Rhine Basin

## 1. Introduction

An emission factor is defined here as the emission of a particular pollutant (in this case cadmium) to the environment per unit of production of a given product. The product can be either one in which the pollutant is deliberately embodied (e.g., cadmium in nickel-cadmium batteries) or one in which the pollutant is an unwanted waste material released during production (e.g., cadmium in steel production).

Emission factors are useful in quantifying the environmental burden of (industrial) activities. The factors are not constant over time, due to ever-improving process technologies which reduce hazardous emissions to the environment, yet little attention has been paid in the literature to historical changes in emission factors. This study analyzes such changes for the aqueous industrial cadmium discharges to the Rhine River basin (see *Figure 1*) over the period 1970–1988. This study is part of a wider investigation of chemical pollution in the Rhine basin currently being undertaken at IIASA. Cadmium is a priority substance in environmental policy in the EC because the metal and its compounds are toxic to humans and many other species. The period 1970–1988 is of particular interest because during this time the industrial aqueous cadmium emissions to the Rhine decreased by over 90%. The emission factors obtained in this study may well be applicable for studying historical aqueous emissions in other industrialized river basins.

## 2. Methodology

*Table 1* provides an overview of the cadmium-processing industries that are relevant to this study. It also indicates the locations of most of these industries in the basin.

Statistical data on the manufacturing of cadmium-containing products, as well as on the use of cadmium-containing raw materials, were collected. In order to eliminate short-term market fluctuations, the period 1970–1988 is divided as follows: 1970–1972, 1973–1977, 1978–1982, 1983–1987, and 1988. The periods 1973–1977, 1978–1982, and 1983–1987 were chosen so that comparisons with monitoring data which were available for these particular periods could be made.

In this study, the Rhine River basin is divided into three sectors: upstream of Koblenz, between Koblenz and Lobith, and downstream of Lobith. Aqueous emission factors for cadmium were obtained from the literature. As

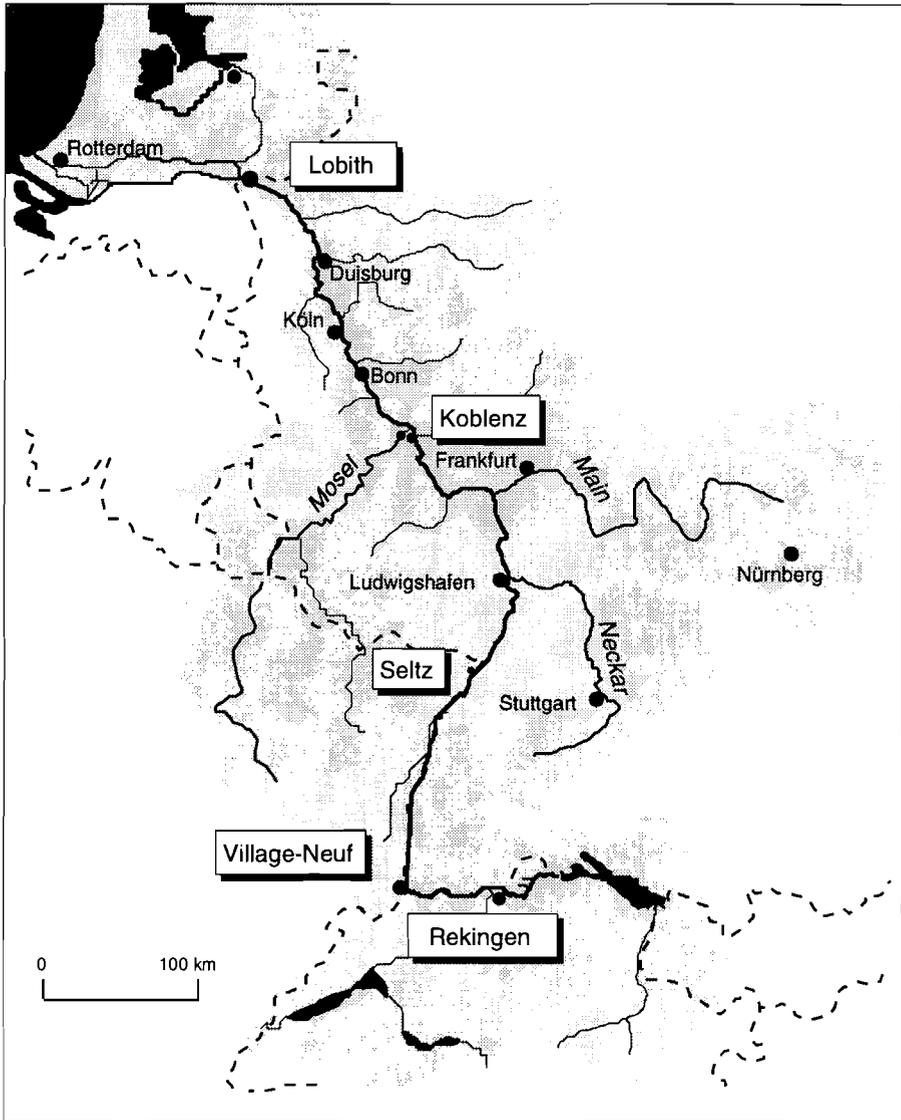


Figure 1. The River Rhine and its main tributaries.

**Table 1.** Relevant cadmium-processing industries and their locations.

	Main location
<i>Intentional use of cadmium</i>	
Zinc and lead-mining industry	Ruhr area, Germany
Zinc and lead-winning industry	Duisburg, Germany
Battery manufacture	Ruhr area, Germany
Pigment manufacture	North Rhine-Westphalia and Stuttgart, Germany
Stabilizer manufacture	Stuttgart, Germany
Stabilizer application (PVC) industry	North Rhine-Westphalia, Germany
Cadmium plating	Ruhr area, Germany
<i>Inadvertent use of cadmium</i>	
Wet phosphoric acid manufacture	Rotterdam, Netherlands
Iron and steel industry	Saar area, Lorraine, France; North Rhine-Westphalia, Germany
Other nonferrous metal industry	North Rhine-Westphalia, Germany
Other mining activities	Strasbourg, France

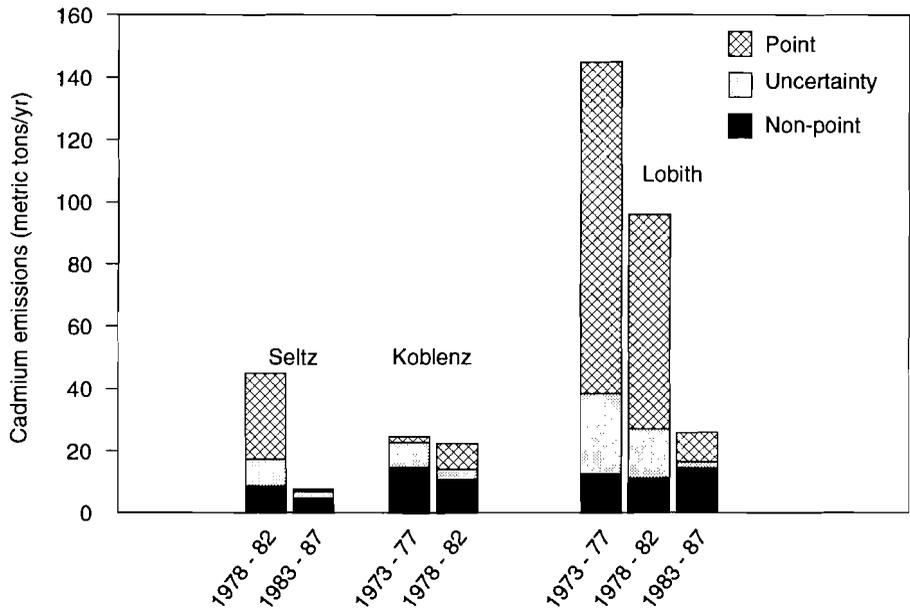
will be shown, the factors reported in different sources may differ by more than one order of magnitude for the same industrial activity. However, rather uniform changes for the different types of industry in the period 1970–1988 are expected for two reasons:

- Increasing regulatory pressure was exerted on cadmium-emitting industries (see section 4 of this article).
- The use of industrial wastewater treatment plants started in the 1970s and was greatly expanded in the 1980s. Thus, technology was available and was applied for improving the water quality in the Rhine basin.

Emission factor estimates are based on data obtained from the literature, taking into account the two reasons for a rather uniform change of the factors over the period, regardless of the type of industry.

### 3. Monitoring Data

The Rhine River basin supplies drinking water for parts of western Germany[1] and the Netherlands and therefore the water quality is monitored extensively at a number of locations. Cadmium-monitoring data have been collected since 1973. The locations of Village-Neuf, Seltz, Koblenz, and



**Figure 2.** Cadmium-monitoring data for the Rhine basin over time.

Lobith are indicated in *Figure 1*. The monitoring data refer to the overall aqueous pollutant loads, regardless of the phase in which cadmium is present. This overall load is the sum of all pollutant inputs into the river, regardless of origin. Two source categories are distinguished:

- Point sources: including both industrial and nonindustrial point sources such as sewage treatment plants treating municipal wastewater.
- Non-point sources: runoff, natural origin, air pollution, etc.

A statistical method for analyzing the monitoring data developed by Behrendt (1993) distinguishes the fractions of a given overall pollutant load into a river from the two pollutant source categories. Discussing this method is beyond the scope of this report, however. *Figure 2* shows time trends in cadmium emissions based on monitoring data; it can be seen that there was a strong decrease in cadmium concentrations in the Rhine over the period 1973–1987, and that this decline was due mainly to reduced point source discharges. *Table 2* presents the point source emissions calculated according to this method, showing the importance of the Rhine sector between Koblenz and Lobith.

**Table 2.** Cadmium point source discharges to the Rhine, 1973–1987, in metric tons/yr.

Location	1973–1977	1978–1982	1983–1987
Village-Neuf	–	0	0
Seltz	–	23–28 <sup>a</sup>	1–2
Koblenz	2–7	6–9	–
Lobith	109–123	72–77	6–9

<sup>a</sup>The fact that the cadmium load decreased between Seltz and Koblenz in 1978–1982 is in disagreement with the assumption that no net accumulation occurred in this part of the river.

Source: Behrendt (1993).

Monitoring data from the Netherlands, downstream of Lobith, have not been used because extensive sedimentation and resuspension of cadmium are known to occur in this part of the river. Thus, measurement of cadmium concentrations of the river water is no longer directly correlated with aqueous emissions from point sources. In contrast, very little cadmium accumulates in the Rhine between Village-Neuf and Lobith (Hellmann, 1987). This is not true for the main tributaries of the Rhine, in which net sedimentation of cadmium occurs because the flow is regulated and is thus slower (Hellmann, 1987; Imhoff *et al.*, 1984).

## 4. Legislation

In 1976 the Commission of the European Communities published Directive 76/464/EEC on the prevention of water pollution, which contained two lists of chemicals: list 1 (often referred to as the “black list”) and list 2 (the “grey list”) (EC, 1976). These lists were also accepted in the international negotiations on the prevention of the pollution of the River Rhine (Treaty Papers, 1977). Cadmium and its compounds were among the first chemicals to be included in the black list. EC member states were obliged to prevent pollution with black list chemicals using the best technical means available. In 1983 the Commission of the European Community published a revision of this directive (83/513/EEC), which contained specific limit values according to the type of industry concerned and quality objectives for the aquatic environment into which cadmium is discharged by such industries (EC, 1983). The limit values had to be met by January 1986 and replaced earlier limit values (Verband der Chemischen Industrie, 1987). In addition, in 1982–1986

the German government increased the fees for residual discharges of cadmium considerably (Pohl, 1982). The fee for the discharge of 1 kg Cd/year was increased from DM 180 in 1982 to DM 400 in 1986. The first 10 kg Cd discharge per year remained free of charge. In the Netherlands between 1970 and 1988 there were no fees for aqueous heavy metal discharges. In 1992, however, the Dutch parliament introduced legislation to prevent the pollution of surface water (Wet Verontreiniging Oppervlaktewater), under which the fee for the discharge of 1 kg Cd/year was Hf1 420 ( $\simeq$  DM 375) (van der Hoogt, 1991).

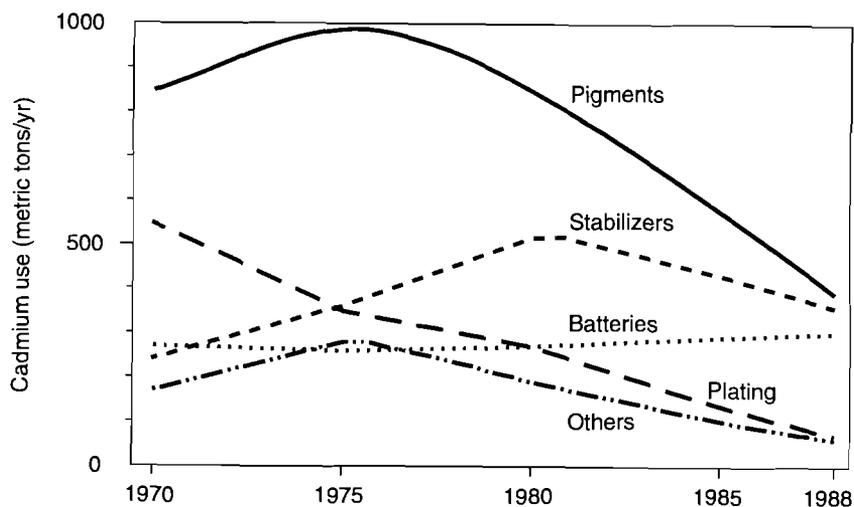
It is obvious that the discussion of emission factors for aqueous heavy metal discharges would have been helped if the authorities had published the fees received from emitting industries. If, in addition, the legal discharge permits issued to individual companies had been available, a much more accurate and detailed analysis of aqueous heavy metal discharges could have been made. However, the fees paid and the discharge permits are confidential and were therefore unavailable for use in this study.

## 5. Industrial Overview

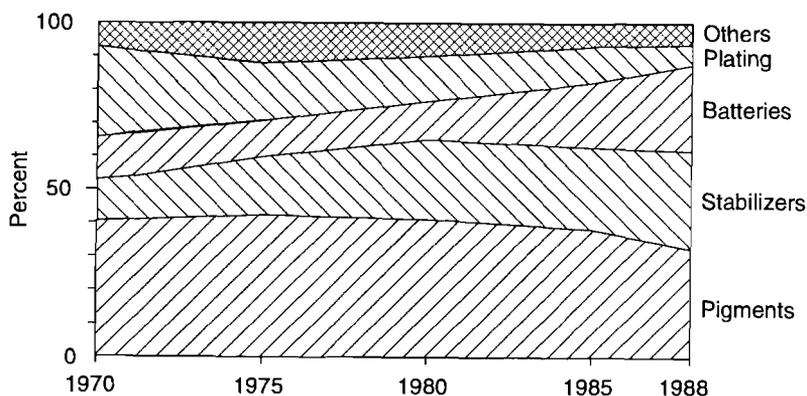
All branches of the cadmium-processing industries listed in *Table 1* are represented in the Rhine basin. The nonferrous metal industry includes zinc and lead mining, winning, and recycling. The iron and steel and the wet phosphoric acid industries are relevant because of the cadmium impurities in their raw materials. In this study, the cadmium product manufacturers and industrial users in the basin were divided into six categories:

- Cadmium pigment manufacturing.
- Cadmium stabilizer manufacturing.
- PVC manufacturing.
- Cadmium plating.
- Alloy manufacturing and processing.
- Nickel-cadmium battery manufacturing.

The pigment, stabilizer, PVC, and battery-manufacturing industries are all represented by a few large companies, whereas the plating industry is represented by a large number of generally small companies concentrated in the Ruhr area. The alloy manufacturing and processing industry is not an important source of aqueous cadmium emissions, and is not considered here. *Figure 3* shows the quantities of cadmium in products (in metric



**Figure 3.** Quantities of cadmium used by German industry, 1970–1988.



**Figure 4.** Relative levels of cadmium used by German industry, 1970–1988.

tons Cd/yr) in Germany over the period 1970–1988, and *Figure 4* shows the relative importance of these products in percentages.[2] *Figures 3* and *4* show that the use of cadmium for plating decreased over the period, whereas that for battery manufacturing increased. The overall use of cadmium fell by 47% over the period, from a peak of over 2200 metric tons in 1975 to about 200 metric tons in 1988.

Section 6 presents a description of the various cadmium-processing industries in the Rhine basin, their locations, the production data obtained, the estimated aqueous emission factors, and the calculated emissions.

## 6. Cadmium-Processing Industries

### 6.1 Nonferrous metal mining

During the period 1970–1987 three nonferrous metal mines were operational in the Rhine basin. Despite the rather fragmentary data, estimates of the zinc and zinc/lead concentrate production data were obtained (Hiscock, 1978; Roskill Information Services Ltd, 1974a,b, 1977, 1980a,b, 1984a,b, 1988, 1990; International Lead and Zinc Study Group, 1989). Waterborne dispersal is claimed to be the main route of cadmium loss from nonferrous metal mines (Hutton, 1982). For the mid-1970s overall aqueous cadmium emissions in the EC were estimated to be 60–150 metric tons/year (Hutton, 1982). Calculating the emission factor for western Germany, with 29.4% of the EC mining capacity, yields an emission factor of 74–176 g Cd/metric ton Zn concentrate produced. These numbers correspond to an accompanying zinc loss of 2.5–5.9% of the total concentrate production, which may be considered too high. It is estimated that a mine producing 120,000 metric tons of concentrate produces an overall cadmium emissions of 0.29 metric tons (von Röpenack, 1978); this yields an emission factor of 2.4 g Cd/metric ton Zn concentrate produced for the period 1970–1977, compared with 1 g Cd/metric ton Zn concentrate for the period 1978–1987. This reduction is justified by taking into account stricter environmental legislation and consequent improvements in on-site housekeeping. No estimate for 1988 is available due to the lack of data. *Table 3* summarizes the Zn concentrate production, emission factors, and emissions of cadmium due to nonferrous metal mining. *Table 3* indicates that nonferrous metal mining is not a major cause of cadmium emissions.

### 6.2 Other mining activities

Other mining activities in the Rhine basin include coal and salt mining. Overall cadmium emissions to the Rhine from coal mining have been estimated to be 30 kg/year in 1989 (International Centre for Water Studies,

**Table 3.** Zinc concentrate production, cadmium emission factors, and emissions from nonferrous metal mining in the Rhine basin, 1970–1987.

Period	Zn concentrate production (t/yr)	Emission factor (g Cd/t Zn concentrate)	Emissions (t Cd/yr)
1970–1972	146,000	2.4	0.4
1973–1977	148,000	2.4	0.4
1978–1982	135,000	1.0	0.1
1983–1987	100,000	1.0	0.1

**Table 4.** Aqueous cadmium emissions due to salt mining in the Rhine basin, 1973–1988.

Period	Chloride discharges (kg/Cl <sup>-</sup> )	Cd emissions (t Cd/yr)
1973–1977	114	0.46
1978–1982	133	0.53
1983–1987	130	0.52
1988	–	0.52

Source: Behrendt (1993).

1990), which suggests that coal mining is not a significant source of cadmium emissions in the basin.

For salt mining, aqueous cadmium emissions of 520 kg/year are reported for 1989 (International Centre for Water Studies, 1990), which originate in the French part of the basin. In order to backcast these emissions to the 1970s a linkage has been made between the point source chloride discharges to the Rhine and cadmium emissions due to salt mining. This is justified by the fact that the salt discharges are related to natural salt resources with an assumed constant composition. Using point source chloride discharge data, the results presented in *Table 4* are obtained (Behrendt, 1993).

The data in *Table 4* have been calculated using the proportionality constant of 0.13 g Cd/metric ton Cl<sup>-</sup>. Assuming the discharged salt to be sodium chloride, this gives 0.08 g Cd/metric ton salt. The average cadmium concentration in the earth's crust is 0.1–0.5 g Cd/metric ton (Hollander and Carapella, 1982), which is of the same order of magnitude as expected. The relative contribution of cadmium emissions due to salt mining was negligible in the 1970s but became significant by the late 1980s because of the large reduction in overall cadmium emissions.

### 6.3 Primary zinc winning

Aqueous cadmium emissions from the primary zinc-processing industry depends on the winning process applied. There are two primary zinc-winning plants in the basin: the Imperial Smelting Furnace (ISF) smelter in Duisburg, and an electrolytic plant in Datteln. The production statistics for these plants are based on incomplete data and estimates (Roskill Information Services Ltd, 1974b, 1980b, 1984a,b; International Lead and Zinc Study Group, 1989). The company operating the ISF smelter claims that in 1979 1 metric ton of cadmium was emitted (Hutton, 1982) in the simultaneous production of lead and zinc. Therefore the emission factor is linked to the joint production of lead and zinc, which was 95,400 metric tons in 1979. This yields an emission factor of 10 g Cd/metric ton (Zn+Pb). For the period 1970–1977 the emission factor is assumed to be higher. Although literature sources directly justify this statement, monitoring data indicate that there was a significant decline in point source discharges in the period 1975–1980 (see *Table 2*). Between Koblenz and Lobith over 110 metric tons of cadmium were emitted by point sources in the period 1973–1977, compared with 67 metric tons in 1978–1982. The emission factor for 1975 is calculated by multiplying the emission factor for 1978–1982 [10 g Cd/metric ton (Zn+Pb)] by (110/67). This yields an emission factor for 1970–1977 of 16 g Cd/metric ton (Zn+Pb).

According to the Deutsche Kommission zur Reinhaltung des Rheins (1989) the ISF smelter emitted 480 kg of cadmium in 1985. Given the production of 100,500 metric tons (Zn+Pb), the emission factor is 5 g Cd/metric ton (Zn+Pb). The International Centre for Water Studies (ICWS, 1990) independently measured all cadmium point source discharges to the Rhine by the nonferrous metal industries in 1989, giving total emissions of 90 kg Cd/yr. Thus, even if the ISF smelter is the primary emitter, the emission factor remains limited to about 0.5 g Cd/metric ton (Zn+Pb) for this last period.

For the electrolytic plant at Datteln, with a zinc production capacity of 105,000 metric tons, aqueous cadmium emissions were 10 kg Cd in 1977 (von Röpenack, 1978), which yields an emission factor of 0.1 g Cd/metric ton Zn. An emission factor of 0.02 g Cd/metric ton Zn has also been reported for a comparable 150,000 metric tons Zn plant in the Netherlands (van Vliet and Feenstra, 1982). Therefore the level of emissions from the plant at Datteln is assumed to be negligible. *Table 5* summarizes the primary lead and zinc

**Table 5.** Production of lead and zinc, cadmium emission factors, and cadmium emissions for primary lead/zinc winning in the ISF smelter in the Rhine basin, 1970–1988.

Period	Production lead (t)	Production zinc (t)	Emission factor g Cd/t (Zn+Pb)	Emissions (t Cd)
1970–1972	38,000	84,000	16	2.00
1973–1977	30,300	67,000	16	1.60
1978–1982	29,600	65,500	10	1.00
1983–1987	31,300	69,200	5	0.50
1988	30,000	70,000	0.5	0.05

production, the corresponding emission factors, and the resulting emissions of cadmium for the period 1970–1988.

Primary zinc and lead production in the Rhine basin in the period 1970–1988 remained approximately constant, but obviously the aqueous emissions of cadmium fell significantly. This is reflected in the change in the emission factors over the period from 16 to 0.5 g Cd/metric ton (Zn+Pb).

#### 6.4 Other nonferrous metal-winning industries

This category includes secondary zinc, cadmium, and lead winning. Secondary zinc winning was carried out in a large metal-recycling plant in Duisburg until 1984. Although no statistics on production and raw material use are available, this plant is assumed to have been the primary in-basin cadmium discharger until the early 1980s (Rauhut and Balger, 1976; Rauhut and Wiegand, 1981; Umweltbundesamt, 1981; von Röpenack, 1985). Two quotes illustrate this: “by the end of the 1970s one nonferrous metal company emitted 35–45 tons of cadmium annually, giving total emissions of 68 tons due to nonferrous metallurgy” (Umweltbundesamt, 1981) and “aqueous cadmium emissions have declined considerably in recent years mainly due to the closure of one plant which had been responsible for about 90% of the aqueous emissions” (von Röpenack, 1985). An emission factor for this plant is not defined, because the range of raw materials used is too wide to justify a generalized factor. Aqueous cadmium emissions were assumed to be 50 metric tons/year for the period 1970–1982 and 25 metric tons/year in 1983 and 1984. No emissions can be attributed to this source after its closure in 1984.

**Table 6.** Aqueous cadmium emissions from selected nonferrous metal industries in the Rhine basin, 1970–1988.

Period	Secondary zinc winning (t Cd/yr)	Secondary cadmium winning (t Cd/yr)	Secondary lead winning (t Cd/yr)
1970–1972	50	3.0	0.6
1973–1977	50	3.0	0.6
1978–1982	50	3.0 <sup>b</sup>	0.6
1983–1987	25 <sup>a</sup>	0	0.6
1988	0	0	0.6

<sup>a</sup>After 1984, this source equals zero.

<sup>b</sup>After 1979, this source equals zero.

Secondary cadmium winning was carried out during the period 1970–1979 by one company located in Bonn, whose cadmium production capacity was 300 metric tons (Roskill Information Services Ltd, 1974a). No data are available for emissions or emission factors. As a worst case scenario we used an emission factor of 10 kg Cd/metric ton Cd processed, which yields emissions of 3 metric tons/year during the 1970s.

Secondary lead winning is carried out at five plants: two plants in Duisburg and one each in Rommerskirchen, Braubach, and Nürnberg (Roskill Information Services Ltd, 1984b). No actual secondary lead production data are available. Assuming that all of these plants operate on average at 90% of their production capacities, annual production is about 100,000 metric tons. An emission factor of 6.2 g Cd/metric ton Pb has been reported (Environmental Resources Ltd, 1990), which gives emissions of 0.6 metric tons Cd/year for this industry. This figure indicates that these sources of cadmium are negligible compared with secondary zinc and cadmium winning. *Table 6* summarizes these data.

*Table 6* indicates that the secondary zinc-winning plants were dominant aqueous emitters of cadmium to the Rhine basin until the mid-1980s. These emission estimates have a large inherent uncertainty. This fact also greatly influences the accuracy with which other emission factors can be calibrated from river-monitoring data.

## 6.5 Cadmium pigment manufacturing

The production process for cadmium pigments includes unit operations such as filtration and precipitation (Cadmium Association, 1978a), both of which give rise to aqueous pollution which is caused by residual dissolved cadmium

or very finely dispersed cadmium sulfide particles. Despite rapid improvements in wastewater treatment technologies, cadmium emissions to waters have not yet been completely eliminated.

Five chemical plants were manufacturing cadmium pigments in the Rhine basin in the 1980s (Stanford Research Institute, 1986). During the period 1970–1988, three plants dominated the market: Besigheim (close to Stuttgart), Bonn, and Leverkusen, (BASF, 1990). The accuracy of data on cadmium use in pigment production was confirmed by industry sources, and the levels of cadmium use per plant were obtained by dividing pigment production among the three plants (Rauhut and Balger, 1976; Rauhut, 1978a, 1981, 1982, 1983, 1990; Balger and Rauhut, 1987). A review of published emission factors is shown in *Table 7*. All sources refer to the Rhine basin except Yost and Greenkorn (1984), which refers to the USA.

Wastewater treatment units that efficiently capture low concentrations of heavy metals were not available in the early 1970s, so that the emission factor for cadmium-pigment manufacturing is expected to be high. The factor decreased significantly during the 1970s, in accordance with the trend observed in analyses in the literature. *Table 8* gives estimated cadmium pigment manufacturing data for the three plants, the estimated emission factors, and the resulting in-basin emissions for the period 1970–1988.

*Table 8* clearly shows the dramatic reduction in the emission factor in the period 1971–1988 by a factor of about 50, while production decreased by a factor of only about 2. The overall aqueous emissions of cadmium from pigment manufacturing were therefore reduced by about two orders of magnitude.

## 6.6 Cadmium stabilizer manufacturing

Cadmium stabilizer manufacturing involves a wet chemical process from which aqueous cadmium emissions are unavoidable (Cadmium Association, 1978b). The cadmium stabilizer industry in the Rhine basin is represented by just one plant, located in Besigheim in Germany in the 1970s (Harcros Chemicals BV, 1990). No data on the production of this plant or the year in which stabilizer production was terminated are available. It is assumed that this company, being one of four manufacturers of cadmium stabilizers in Germany, produced 25% of the total stabilizer output during the period 1970–1977. Data on cadmium use in the German stabilizer industry (Rauhut and Balger, 1976; Rauhut, 1978, 1981, 1982, 1983, 1990; Balger and Rauhut,

**Table 7.** Published emission factors for cadmium pigment manufacturing.

Date ref.	Emission factor (g Cd/kg Cd)	Source	Comments
1973	1.0	Rauhut and Balger (1976)	
1973	1.76	Rauhut and Balger (1976)	Calculated as emission/production
1978	20	Hutton (1982)	Without wastewater treatment
1978	10	Imhoff <i>et al.</i> (1984); Hutton (1982)	
		Ministry of Transport and Public Works (1986)	With wastewater treatment, eff. 50%
1979	1.46	Rauhut and Wiegand (1981)	Calculated as emission/production
1982	1.0	Rauhut (1982)	
1982	1.63	Rauhut (1982)	Calculated as emission/production
1984	8.2	Imhoff <i>et al.</i> (1984); Yost and Greenkorn (1984); Ministry of Transport and Public Works (1986)	With wastewater treatment, eff. 50%
1984	2.6	Yost and Greenkorn (1984)	With wastewater treatment, eff. 90%
1983–1985	0.7	Verband der Chemischen Industrie (1987)	Legal emission limit
1985	0.5	Deutsche Kommission zur Reinhaltung des Rheins (1989)	
Since 1986	0.3	EC Council (1983)	Calculated as emission/production Legal emission limit

**Table 8.** Relevant cadmium-pigment manufacturing plants, in the Rhine basin, their production, estimated emission factors, and related in-basin cadmium emissions, 1970–1988.

Period	Besigheim (t Cd/yr)	Leverkusen (t Cd/yr)	Bonn (t Cd/yr)	Total (t Cd/yr)	Emission factor (g Cd/kg Cd)	Emissions (t Cd/yr)
1970–1972	276	339	276	891	10–20	9–18
1973–1977	309	378	309	996	4–10	4–10
1978–1982	266	326	266	858	1.5	1.3
1983–1987	175	215	175	565	0.5	0.3
1988	178	0	201	379	0.3	0.1

1987) and emission factors are reviewed in *Table 9*. All sources refer to the Rhine basin except Yost and Greenkorn (1984), which refers to the USA.

As with cadmium-pigment manufacturing, the emission factor for stabilizer manufacturing in the early 1970s is expected to be high due to the lack of adequate wastewater treatment technology, but in the late 1970s it is assumed to have decreased significantly. The emission factor was derived by comparing the various sources in the literature. *Table 10* presents estimates of cadmium stabilizer production in the Rhine basin, the estimated emission factors, and the resulting emissions for 1970–1988.

The calculated emissions for the industry indicate that it did not contribute significantly to the aqueous cadmium pollution of the Rhine. The development of the emission factor is similar to that for cadmium pigment manufacturing.

## **6.7 Industrial uses of cadmium-based pigments and stabilizers**

Cadmium-based pigments are used in industry for coloring polymers and ceramics; formerly, they were used in lacquer manufacturing (Hiscock, 1978; Taubitz, 1985; Tötsch, 1989). Although other published cadmium emission inventories do not mention these uses (Hutton, 1982; Environmental Resources Ltd, 1990; Rauhut, 1978a,b), we have examined whether these industrial applications might be significant sources of aqueous cadmium pollution. The primary industrial use of cadmium pigments, ranging from 75% in the early 1970s to 90% in the late 1980s, is polymer coloring (Hiscock, 1978; Taubitz, 1985; Tötsch, 1989).

This industrial branch is not expected to cause aqueous cadmium emissions because polymer manufacturers send so-called master batches of polymers to pigment manufacturers, who color them on site and return them to polymer-processing plants, where they are used as color additives. This procedure restricts cadmium handling and processing to the site of pigment manufacturers, so that emissions from polymer-processing plants are expected to be negligible.

The industrial uses of (automobile) lacquer containing cadmium pigments as well as the use of cadmium pigments for coloring ceramics are not expected to cause significant aqueous emissions of cadmium. Automobile lacquer is dissolved in organic solvents, so that no water is involved in the

**Table 9.** Published emission factors for cadmium stabilizer manufacturing.

Date ref.	Emission factor (g Cd/kg Cd)	Source	Comments
1973	1–1.5	Rauhut and Balger (1976)	
1973	2.45	Rauhut and Balger (1976)	Calculated as emissions per unit of production
1978	20	Hutton (1982)	Without wastewater treatment
1978	10	Imhoff <i>et al.</i> (1984); Hutton (1982)	With wastewater treatment, efficiency 50%
1979	0.3	Ministry of Transport and Public Works (1986) Rauhut and Wiegand (1981)	Calculated as emissions per unit of production
1982	1.5	Rauhut (1982)	
1982	2.3	Rauhut (1982)	Calculated as emissions per unit of production
1984	1.0	Imhoff <i>et al.</i> (1984); Yost and Greenkorn (1984); Ministry of Transport and Public Works (1986)	With wastewater treatment, efficiency 50%
1984	0.2	Yost and Greenkorn (1984)	With wastewater treatment, efficiency 90%
1983–1985	0.8	Verband der Chemischen Industrie (1987)	Legal emission limit
Since 1986	0.5	EC Council (1983)	Legal emission limit

**Table 10.** Estimated cadmium stabilizer production in the Rhine basin, emission factor estimates, and related aqueous emissions, 1970–1988.

Period	Production (t Cd/yr)	Emission factor (g Cd/kg Cd processed)	Emission (t Cd/yr)
1970–1972	89	10–20	0.9–1.8
1973–1977	91	4–10	0.4–0.9
1978–1982	0	2.0	0
1983–1987	0	0.6	0
1988	0	0.4	0

processing, and ceramic-coloring processes require high temperatures that may cause atmospheric rather than aqueous emissions.

Cadmium stabilizers are used only in PVC processing. In the early 1970s many PVC products were stabilized by cadmium-containing additives, but increased environmental concerns have limited the number of PVC applications that utilize cadmium stabilizers. The market is now dominated by use in PVC window frames, which in 1989 had a market share of 75% in Germany (Tötsch, 1989). Only recently have PVC stabilizers been used in master batches (Nilsson, 1990). During PVC processing, aqueous emissions of cadmium may arise from processes such as the wet stripping of dust-laden air ventilation in systems.

In the Rhine basin eight companies are involved in PVC processing: one plant is located in Switzerland (Sins), six in Germany (Frankfurt am Main, Cologne, Ludwigshafen, Marl, Rheinberg, and Waldshut), and one in the Netherlands (Rotterdam). The Swiss plant has a PVC-processing capacity of 30 ktons, which is too small to justify further analysis. The German production capacity of PVC was 1445 ktons in 1983, of which 69% was located in the Rhine basin (Henz, 1983).

The plant in Rotterdam had a production capacity of approximately 200 ktons PVC. According to the Deutsche Kommission zur Reinhaltung des Rheins (1989), the PVC-processing plants in Ludwigshafen, Marl, and Rheinberg discharged more than 200 kg of cadmium in 1985.

Two approaches have been used to estimate an aqueous cadmium emission factor for PVC processing. In the first approach the use of cadmium stabilizers in Germany is assumed to be proportional to the PVC-processing capacity and is distributed over the three plants that are known to be dischargers (Deutsche Kommission zur Reinhaltung des Rheins, 1989). In the

**Table 11.** Estimated in-basin cadmium stabilizer use in the Rhine basin, emission factor estimates, and related aqueous emissions, 1970–1988.

Period	Stabilizer use (t Cd/yr)	Emission factor (g Cd/kg Cd processed)	Emissions (t Cd/yr)
1970–1972	245	5–7	1.2–1.7
1973–1977	251	4.2–5.8	1.1–1.5
1978–1982	366	2–3	0.7–1.1
1983–1987	292	1.4–1.9	0.4–0.6
1988	233	0.5	0.1

second approach the level of use of cadmium stabilizers by the three plants is assumed to be proportional to their PVC production capacities. The data for the PVC-processing plant in Marl are used to calculate the emission factor, assuming that PVC processing is the only cadmium-related activity on the site.

The resulting emission factor for the 1980s, using the first approach, is 1.4 kg Cd/metric ton Cd processed. The second approach yields an emission factor of 1.9 kg Cd/metric ton Cd processed. The company claims to have discharged 60 kg cadmium in 1990 (Hüls AG, 1990a). The emission factors for 1988 and 1990 are assumed to be equal: 0.5 g Cd/kg Cd processed. The emission factor is backcast for the 1970s based on wastewater treatment technology data supplied by the company in Marl.

It is claimed that over the period 1975–1990 organic water pollution was reduced by 90% (Hüls AG, 1990b). Assuming linear proportionality between organic pollutant reduction and cadmium removal, this leads to estimated emissions of 600 kg cadmium per year at Marl in the mid-1970s. This figure is related to the estimated cadmium stabilizer use in the 1970s and yields an emission factor estimate of 4.2–5.8 g Cd/kg Cd processed in 1973–1977.

*Table 11* presents the cadmium stabilizer use in the German part of the basin, the estimated emission factor, and the emissions. Emissions from cadmium stabilizer in the Netherlands are assumed to be negligible, compared with the emissions of two adjacent wet phosphoric acid production plants in Rotterdam. The use of stabilizers in PVC processing as sources of cadmium emissions to the Rhine basin is of relative minor importance.

## 6.8 Cadmium battery manufacturing

The manufacturing of nickel–cadmium batteries includes steps that give rise to aqueous cadmium pollution (Salkind and Pearlman, 1982). The only in-basin Ni–Cd battery manufacturer is located in the Ruhr at Hagen. Battery-manufacturing data for the period 1970–1988 were estimated (see *Figures 3* and *4*). There are two types of battery: vented or pocket-plate cells and sealed or sintered-plate cells. The manufacturing processes for these types differ, and so do the aqueous emission factors. The following production ratios were used (Rauhut and Balger, 1976; Rauhut, 1978a,b, 1981, 1982, 1983, 1990; Balger and Rauhut, 1987):

Period	Sealed	Vented
1970–1975	10%	90%
1976–1985	30%	70%
1986–1988	60%	40%

*Table 12* summarizes the emission factor estimates reported available in the literature. These estimates apply to the Rhine basin, except those of Yost and Greenkorn (1984), which are based on data for the USA. The figures in *Table 12* do not offer a consistent view, so that the accuracy of the estimated emission factors may be limited. It was assumed that the emission factors for battery manufacturing have decreased by about a factor of 10 over the period 1970–1988. *Table 13* presents calculations of Ni–Cd sealed and vented cell battery production in the Rhine basin, emission factor estimates, and the resulting aqueous cadmium emissions due to Ni–Cd battery production. The estimates of emission factors were based on the data in *Table 12*.

Although battery manufacturing has become the major cadmium application (see *Figure 4*), aqueous cadmium emissions have remained limited.

## 6.9 Cadmium plating

In the early 1970s cadmium plating was the most important use of cadmium by a large number of companies throughout the Rhine basin. Production data for Germany (Rauhut and Balger, 1976; Rauhut, 1978a,b, 1981, 1982, 1983, 1990; Balger and Rauhut, 1987), France, and the Netherlands (van Vliet and Feenstra, 1982; Feenstra, 1975; van der Voet *et al.*, 1988) are given in *Table 14*.

**Table 12.** Published aqueous emission factors for cadmium discharges due to Ni–Cd battery manufacturing in the Rhine basin, 1970–1988.

Date ref.	Emission factor (g Cd/kg Cd)	Source	Comments
1973	3.0	Rauhut and Balger (1976)	
1973	8.2	Rauhut and Balger (1976)	Calculated as emissions per unit of production
1975	2.0	Rauhut (1979)	
1975	3.1	CEC (1978)	
1979	3.6	Rauhut and Wiegand (1981)	Calculated as emissions per unit of production
1982	4.0	Rauhut (1982)	
1982	6.5	Rauhut (1982)	Calculated as emissions per unit of production
1982	2.9	Schulte-Schrepping (1983)	Calculated as emissions per unit of production
1982	3.0	Hutton (1982)	Vented battery manufacturing, no wastewater treatment
1982	1.5	Hutton (1982); Ministry of Transport and Public Works (1986)	Vented battery manufacturing, wastewater treatment efficiency 50%
1982	13.8	Hutton (1982)	Sealed battery manufacturing
1984	3.0	Yost and Greenkorn (1984)	Vented battery manufacturing, no wastewater treatment
1984	0.5	Yost and Greenkorn (1984)	Sealed battery manufacturing, wastewater treatment efficiency 50%
1986	1.5	EC Council (1983)	Legal emission limit

**Table 13.** Production of sealed and vented batteries, emission factor estimates, and aqueous cadmium emissions, 1970–1988.

Period	Production vented batteries (t Cd/yr)	Production sealed batteries (t Cd/yr)	Emission factor vented batteries (g Cd/kg Cd)	Emission factor sealed batteries (g Cd/kg Cd)	Emissions (t Cd/yr)
1970–1972	243	27	8	15	2.3
1973–1977	211	52	4	10–15	1.3–1.6
1978–1982	177	76	3	5–10	0.9–1.3
1983–1987	178	145	1.5	2–3	0.6–0.7
1988	136	205	1.0	1.0	0.3

**Table 14.** Use of cadmium in plating in the Netherlands, Germany, and France, 1970–1988.

Period	Netherlands (t Cd/yr)	Germany (t Cd/yr)	France (t Cd/yr)
1970–1972	50	508	324
1973–1977	50	355	322
1978–1982	5	261	271
1983–1987	1–3	140	242
1988	0	68	204

*Table 14* shows that there has been a strong decline in the use of cadmium plating. No data are available for Switzerland and Luxembourg, although it is expected that these countries produce less than 10% of the total in-basin production. Estimates of cadmium emissions due to plating in France are based on the percentage of population and industrial activities occurring in the part of France located in the basin. This is on the order of 5–10% of total French population and industrial activity. For the Netherlands it is assumed that 50% of all cadmium-plating companies are located in the Rhine basin, which is a worst-case scenario. In the FRG 75% of all plating companies are concentrated in the Ruhr area (Imhoff *et al.*, 1984).

*Table 15* gives an overview of emission factors for the cadmium-plating industry. The emission factors differ by two orders of magnitude. Much of this discrepancy can be explained by different levels of applied emission control technologies in the studies cited. Since the plating industry is known to have been a major source of aqueous cadmium emissions in the 1970s (Imhoff *et al.*, 1984), and since it is known from monitoring data that emissions from

**Table 15.** Published emission factors for aqueous cadmium emissions in the Rhine basin, due to cadmium plating, 1970–1988.

Date ref.	Emission factor (g Cd/kg Cd)	Source	Comments
1973	13	Rauhut and Balger (1976)	Calculated as emissions per unit of production
1975	12.6	Rauhut (1979)	
1979	4.7	Rauhut and Wiegand (1981)	Calculated as emissions per unit of production
1979	8–10	Imhoff <i>et al.</i> (1984)	
1981	1.5–1.8	Simon (1982)	Wastewater treatment efficiency 50%
1981	0.5–1.0	Simon (1982)	Best available technology by 1981
1982	25	Hutton (1982)	
1983	20	Imhoff <i>et al.</i> (1984); Ministry of Transport and Public Works (1986); Yost (1990)	Wastewater treatment efficiency 50%
1984	11.5	Imhoff <i>et al.</i> (1984); Yost and Greenkorn, (1984)	Wastewater treatment efficiency 50%
1986	0.3	EC Council (1983)	Legal emission limit

**Table 16.** Production of cadmium plating, estimated emission factors, and the resulting cadmium emissions in the Rhine basin<sup>a</sup>, 1970–1988.

Period	Netherlands (t Cd/yr)	Germany (t Cd/yr)	Emission factor (g Cd/yr/kg Cd)	Emissions (NL) (t Cd/yr)	Emissions (Germany) (t Cd/yr)
1970–1972	25	384	20–30	0.5–0.8	7.7–10.6
1973–1977	25	266	15–25	0.4–0.6	4.0–6.7
1978–1982	2.5	196	10–20	0–0.1	2.0–3.9
1983–1987	1	105	1–6	0	0.1–0.6
1988	0	54	0.3	0	<0.1

<sup>a</sup>Does not include France, Luxembourg, and Switzerland, which probably comprise less than 20% of the in-basin plate production.

**Table 17.** Aqueous cadmium emissions due to wet phosphoric acid manufacturing in the Rhine basin, 1970–1988.

Period	Netherlands (t Cd/yr)	France (t Cd/yr)
1970–1972	22.7	3.2
1973–1977	21.8	3.0
1978–1982	13.7	1.9
1983–1987	13.7	<1.9
1988	9.0	<1.3

point sources have been reduced by more than 90% over the last two decades, it is reasonable to assume that there has been a large and rapid 50–100-fold decrease in emission factors over the period 1970–1988. *Table 16* provides an overview, consistent with the monitoring data, of how these emission factors and cadmium emissions may have changed in the Netherlands and Germany during the 1970s and 1980s.

### 6.10 Wet phosphoric acid manufacturing

Wet phosphoric acid manufacturing is a major source of cadmium discharges in the Rhine basin. Cadmium is a natural constituent of apatite ore, which is used as raw material in the production of phosphoric acid. The cadmium content of the ore ranges from 0.1 to 90 ppm depending on its origin (Feenstra, 1978). A fraction of the cadmium (typically 20–50%) contained in the ore ends up in gypsum, a waste product formed during the wet phosphoric acid manufacturing process. In the Rhine basin two plants are located in Rotterdam and one in Ottmarsheim (France), all of which discharge gypsum to the Rhine. Because the cadmium discharges depend entirely on the composition of the ore, estimation of emission factors is not a feasible approach. The combined cadmium emissions by the two Dutch plants are presented in *Table 17* (van der Voet *et al.*, 1988; Oltshoorn and Thomas, 1986; Ros and Slooff, 1987; VROM-DGM, 1990; Anonymous, 1987; State Water Authority, 1990). For the period 1970–1973 import/export statistics were used to estimate the Dutch emissions (Centraal Bureau voor de Statistiek, various years). The emission estimates for the French plant are based on data available for the Dutch plants and French apatite ore import data (Environmental Resources Ltd, 1989).

*Table 17* shows that these plants reduced their cadmium emissions by 60% over the period 1970–1988, yet in 1988 phosphoric acid manufacturing

still caused more aqueous cadmium emissions than all other industrial activities combined. It is the aim of the companies in question, however, to limit their combined emissions to less than one metric ton by 1992 (Anonymous, 1987).

### 6.11 Iron and steel industry, including coke production

The iron and steel industry utilizes raw materials that contain minor amounts of cadmium in the production of coke, sinter, crude iron, and, finally, steel. The two most relevant steps with regard to aqueous cadmium emissions are coke and steel production.

#### *Coke production*

In the manufacture of steel iron oxide ores are reduced using carbon in the form of coke. Coke is obtained by processing coal, which contains cadmium as an impurity in concentrations ranging from 0.22 to 1 ppm (Environmental Resources Ltd, 1990; Coles *et al.*, 1979). Part of the cadmium content is converted into flyash which is captured by wet scrubber devices, causing aqueous emissions. The emissions due to coke production are calculated for the 1970s using an emission factor of  $(0.281 \times C)$  g Cd/metric ton coke produced (where  $C$  represents the cadmium content of the coal in ppm). It is assumed that this emission factor correctly describes the emissions in the period 1970–1979, with  $C = 1$  ppm. For the period 1980–1988 the emission factor is divided by a factor of 10, to take into account improved process technologies.

During this period seven coke plants were operating in France and 23 plants in Germany. Twenty-seven plants are located on tributaries that flow into the Rhine between Koblenz and Lobith, and three on the Rhine itself between Koblenz and Lobith. *Table 18* gives the development of coke production (OECD Energy Statistics, various years; Eurostat Iron and Steel, various years; *Handbuch der europäischen Eisen- und Stahlwerke*, 1978; *Iron and Steelworks of the World*, 1983; *Jahrbuch Stahl*, various years; *Steel Statistical Yearbook*, 1985, 1989; International Iron and Steel Institute, 1982, 1989; Warren, 1974), emission factors, and the resulting emissions. The coke production in the Rhine basin fell by 50% in the period 1970–1988, but a major reason for lower emissions has been the rapid decrease in the emission factor. The emission estimates show the high levels of aqueous cadmium emissions due to coke production in the 1970s.

**Table 18.** Coke production, estimates of emission factors, and resulting aqueous cadmium emissions in the Rhine basin, 1970–1988.

Period	France (kt/yr)	Germany (kt/yr)	Emission factor (g Cd/t coke)	Emissions (t Cd/yr)
1970–1972	3,922	32,227	0.281	10.3
1973–1977	3,554	28,198	0.281	8.9
1978–1982	3,268	23,471	0.129	3.5
1983–1987	2,261	18,626	0.028	0.6
1988	2,414	15,587	0.028	0.5

**Table 19.** Steel production in France and Germany, 1970–1988.

Period	BO steel	EA steel	EA steel	BO steel	EA steel
	Germany (kt/yr)	Germany <sup>a</sup> (kt/yr)	Germany <sup>b</sup> (kt/yr)	France (kt/yr)	France (kt/yr)
1970–1972	24,466	688	3,217	14,594	1,469
1973–1977	25,541	718	3,355	15,270	1,536
1978–1982	23,729	667	3,119	14,159	1,425
1983–1987	21,061	592	2,768	12,569	1,265
1988	20,194	568	2,655	12,042	1,212

<sup>a</sup>EA steel produced in a plant located on the Rhine upstream of Koblenz.

<sup>b</sup>EA steel produced in plants located between Koblenz and Lobith.

### *Steel production*

There are three major steel production processes: open hearth furnace (OHF), basic oxygen (BO) and electric arc (EA) steel-making. OHF steel-making is not applied in the basin and so is not analyzed in this study. In EA steel-making, a large proportion of the input material is scrap, which has a relatively high cadmium content (up to 6 ppm) (Hutton, 1982) due to the cadmium that is often applied to steel as a surface protection layer. In the period 1970–1988 there were 22 steel-making plants in Germany and 6 in France. In Germany, one plant is located at Kehl, upstream of Koblenz, seven are located directly on the Rhine, and the others on tributaries that flow into the Rhine between Koblenz and Lobith. *Table 19* presents data on BO and EA steel production in France and Germany (OECD *Energy Statistics*, various years; Eurostat *Iron and Steel*, various years; *Handbuch der europäischen Eisen- und Stahlwerke*, 1978; *Iron and Steelworks of the World*, 1983; *Jahrbuch Stahl*, various years; *Steel Statistical Yearbook*, 1985,

**Table 20.** Published aqueous cadmium emission factors for EA and BO steel manufacturing in the Rhine basin, 1970–1988.

Date ref.	Emission factor (g Cd/t steel)	Source	Comments
1982	not available	Hutton (1982)	
1983	0.09–0.45	Reinders (1983)	Emissions/metric ton crude iron for entire plant
1983	0–0.28	Hutton (1982); Reinders (1983)	Emissions/metric ton crude iron, excl. coke prod.
1983	0–0.23	Hutton (1982); Reinders (1983)	Emissions/metric ton BO steel
1985	0.007–0.01	van der Voet <i>et al.</i> (1988)	
1989	0.18	Environmental Resources Ltd (1990)	Emissions/metric ton BO steel
1989	0.11	Environmental Resources Ltd (1990)	Emissions/metric ton EA steel

**Table 21.** Emission factor estimates and cadmium emissions from steel production in the Rhine basin, 1970–1988.

Period	Emission factor (g Cd/t steel)	Emissions (1) <sup>a</sup> (t Cd/yr)	Emissions (2) <sup>b</sup> (t Cd/yr)
1970–1972	0.4	0.3	17.5
1973–1977	0.4	0.3	18.3
1978–1982	0.4	0.3	17.0
1983–1987	0.2	0.1	7.5
1988	0.05	0	1.8

<sup>a</sup>Emissions to the Rhine upstream of Koblenz.

<sup>b</sup>Emissions to the Rhine between Koblenz and Lobith.

1989; International Iron and Steel Institute, 1982, 1989; Warren, 1974). During the period 1970–1988 total production fell by 20%.

*Table 20* summarizes the various estimates of aqueous emission factors for steel production reported in the literature. The emission factor estimates based on these scattered data are given in *Table 21*, together with the resulting emissions to the Rhine upstream of Koblenz (1) and between Koblenz and Lobith (2).

The emission factor for steel production is assumed not to have changed in the period 1970–1982, during which time environmental measures in the

iron and steel industry were focused mainly on air pollution control. By 1982, however, it had been recognized that aqueous pollution problems in the steel industry originated in the process of etching steel in hydrochloric or sulfuric acid. During the 1980s the reduction of aqueous pollution received higher priority (due to stricter environmental legislation) so that the estimated emission factors are assumed to have decreased. The emission factors for EA and BO steel are assumed to be equal, due to lack of data that would justify a more detailed approach.

### **6.12 Summary of aqueous cadmium emission factors for all industrial sources**

The database presented in sections 6.1–6.11 is summarized in *Figure 5*, which provides an overview of the changes in aqueous cadmium emission factors for selected industries. The figure shows that the emission factors for all cadmium-processing industries decreased dramatically in the period 1970–1988, in most cases by 90% or more.

## **7. Results and Discussion**

In the previous sections, the trends in aqueous cadmium emission factors for the relevant branches of industry were estimated. Based on these estimates an emission profile for the River Rhine as a function of time and location is shown in *Figure 6*. This emission profile is compared with estimates from analyses of water quality monitoring data (Behrendt, 1993), although it should be noted that this comparison is subject to the following uncertainties:

- The emissions from just one secondary zinc-winning plant during the period 1970–1984 accounted for a significant fraction (on the order of 45–70%) of total emissions. Available information on this source, however, is limited.
- It is assumed that 100% of the emissions to tributaries of the Rhine reach the main stream, but this is probably a crude simplification.
- The point source discharges to the Rhine as determined by the monitoring data method include, e.g., household discharges via sewage treatment plants, but these discharges are not accounted for in the present analysis.

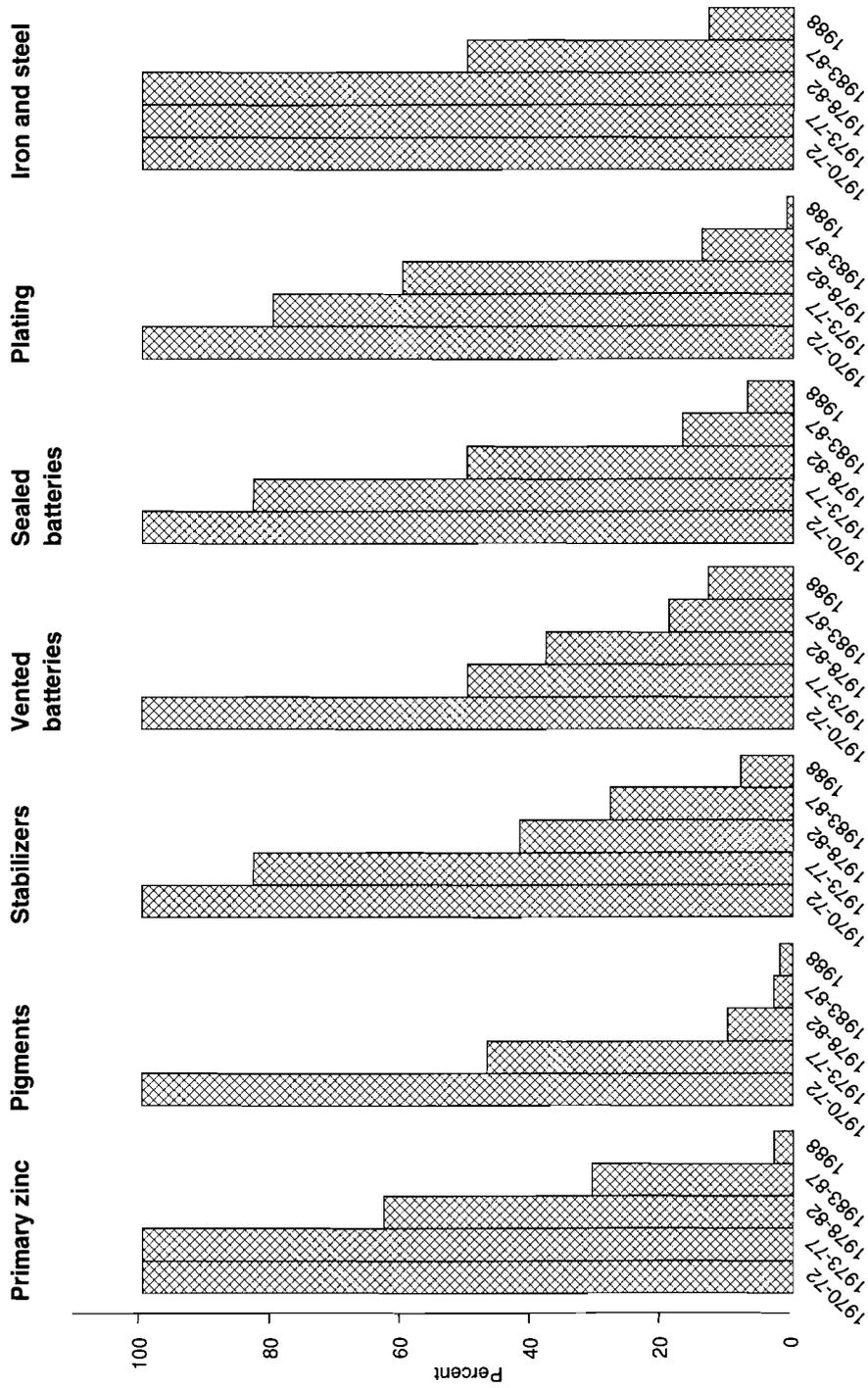
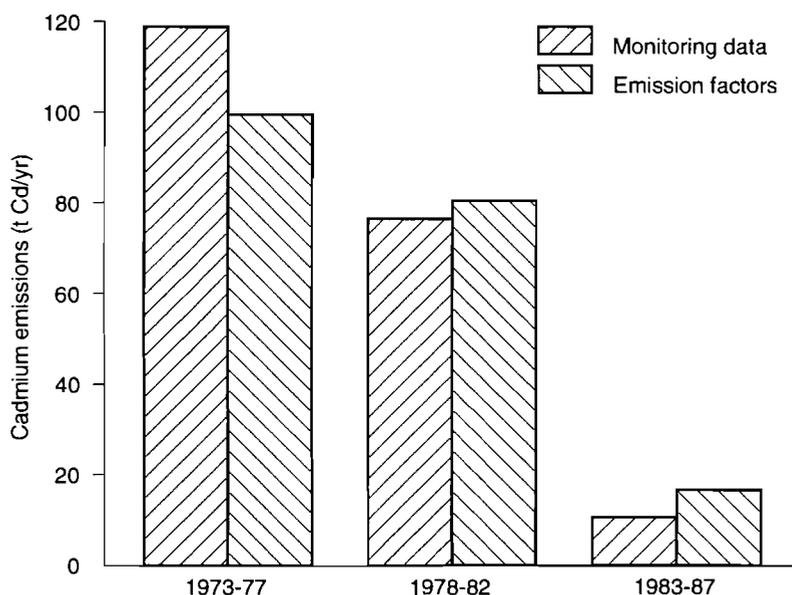


Figure 5. Development of emission factors for industries in the Rhine basin, 1970–1988.



**Figure 6.** Comparison of industrial cadmium emissions calculated via emission factors and via monitoring data for the Rhine basin, 1970–1988.

- Emission factors reported in the literature show a wide variation of values for some branches. These discrepancies introduce more uncertainty in the estimated values.
- In order to obtain emissions per industrial branch, estimated emission factors were multiplied by production quantities. In some cases production statistics were incomplete or unavailable, subjecting the emission estimates to further uncertainties.

Despite these sources of uncertainty, *Figure 6* clearly shows that the results based on emission factors are consistent with the trends based on monitoring data.

## 8. Conclusion

Aqueous emission factors are obtained for industrial cadmium discharges to the Rhine River basin over the period 1970–1988. The emission factors are calibrated by comparing the predicted cadmium emissions with monitoring data. The analysis suggests that there were large reductions in aqueous

emissions of cadmium from all sources over this 18-year period. Although part of this reduction has been the result of decreased industrial production, much of it is due to improvements in wastewater treatment technologies, as reflected by the large reductions in emission factors for the water-polluting industries.

## Acknowledgments

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## Notes

- [1] In this paper Germany and FRG refer to West Germany before reunification in 1990.
- [2] *Figures 3 and 4* are based on published data for 1973–1986 (Rauhut and Balger, 1976; Rauhut, 1978a,b, 1981, 1982, 1983, 1990; Balger and Rauhut, 1987). Data for 1970–1972 were estimated from Hiscock (1978). Data for 1987–1988 were obtained by extrapolation. The figures show connected lines between averages for the periods 1970–1972, 1973–1977, 1978–1982, and 1983–1987.

## References

- Anonymous, 1987, *Windmill bereid binnen 7 jaar cadmium in afvalgips te reduceren tot 0.6 ton/jaar*, Nederlandse Chemische Industrie (NCI), No. 14, p. 16.
- Balger, D., and Rauhut, A., 1987, Verbrauch und Verbleib von Cadmium und seiner Verbindungen in der Bundesrepublik Deutschland: Cadmiumbilanz 1981–1983, *LGA-Rundschau* **87-3**, Landesgewerbeanstalt (LGA), Nürnberg, Germany.
- BASF, 1990, personal communication, November.
- Behrendt, H., 1993, *Point and Diffuse Loads of Selected Pollutants in the River Rhine and Its Main Tributaries*, Research Report RR-93-1, International Institute for Applied Systems Analysis, Laxenburg, Austria.
- Cadmium Association, 1978a, *Cadmium Pigments*, London, UK.
- Cadmium Association, 1978b, *Cadmium in Stabilizers for Plastics*, London, UK.
- Centraal Bureau voor de Statistiek (NL), various years, *Foreign Trade Statistics for the Netherlands*, Annual Series, Heerlen, Netherlands.
- Coles, D.G., *et al.*, 1979, Chemical Studies of Stack Fly Ash from a Coal-Fired Power Plant, *Environ. Sci. Technol.* **13**(4):455–459.
- Commission of the European Communities (CEC), 1978, *Environment and the Quality of Life: Noxious Effects of Dangerous Substances in the Aqueous Environment*, EUR 5983 EN, Brussels, Belgium.
- Deutsche Kommission zur Reinhaltung des Rheins, 1989, *Schadstoff-Fracht des Rheins 1985 und Prognose der Reduzierung 1995*, Koblenz, Germany.

- EC Council, 1976, Directive on Pollution Caused by Hazardous Chemicals, which Are Discharged in the Aquatic Environment of Countries in the EC (76/464/EEC), *Official Journal of the European Communities*, L129/23.
- EC Council, 1983, Directive on Limit Values and Quality Objectives for Cadmium Discharges (83/513/EEC), *Official Journal of the European Communities*, No. L 291.
- Environmental Resources Ltd, 1990, *Evaluation of the Sources of Human and Environmental Contamination by Cadmium*, EC-contract no. B 6614-566-88(DG XI).
- Eurostat, various years, *Iron and Steel*, Office des Publications Officielles des Communautés Européennes, Luxembourg.
- Feenstra, J.F., 1975, *Gebruik en verspreiding van Cadmium in Nederland*, Institute for Environmental Studies, Free University of Amsterdam, Netherlands.
- Feenstra, J.F., 1978, *Control of Water Pollution due to Cadmium Discharged in the Process of Producing and Using Phosphate Fertilizers*, EC-Report ENV/223/74-E, Brussels, Belgium.
- Handbuch der europäischen Eisen- und Stahlwerke* (8. Auflage 1978), Montan- und Wirtschaftsverlag GmbH, Frankfurt am Main, Germany.
- Harcros Chemicals BV, 1990, personal communication.
- Hellmann, H., 1987, *Analysis of Surface Waters*, Wiley, New York, NY, USA.
- Henz, W.W. (ed.), 1983, *The Plastics Industry in Western Europe, Facts and Figures*, Hanser Publishers, Munich, Germany.
- Hiscock, S.A., 1978, *Production, Consumption and Uses of Cadmium in the European Community 1965-1976*, European Community Study Contract No. Env/223/74E, Cadmium Association, London, UK.
- Hollander, M.L., and Carapella, S.C., Jr., 1982, Cadmium and Cadmium Alloys, *Kirk Othmer Encyclopedia of Chemical Technology*, 4:387-396.
- Hüls AG, 1990a, *Umweltschutzbroschüre*, Marl, Germany.
- Hüls AG, 1990b, *Umweltschutz, wie wir unsere Verantwortung verstehen*, 1990, Brochure, Marl, Germany.
- Hutton, M., 1982, *Cadmium in the European Community*, MARC-Report, Contract No. 333-Env., Chelsea College, University of London, UK.
- Imhoff, K.R., et al., 1984, Cadmium Balance and Restoration Strategy for a River Basin, *Water Sci. Technol.* 16:315-325.
- International Centre for Water Studies, 1990, under assignment to Rotterdam Public Works, unpublished results, 1990, Netherlands.
- International Iron and Steel Institute, 1982, 1989, *Western World Cokemaking Capacity*, Brussels, Belgium.
- International Lead and Zinc Study Group, 1989, *Lead and Zinc Statistics* 29, No. 2. *Iron and Steelworks of the World*, 1983, 1986, Metal Bulletin Books, London-New York.
- Jahrbuch Stahl*, various years, Verlag Stahleisen GmbH, Düsseldorf, Germany.

- Ministry of Transport and Public Works and Water Management, 1986, Coördinatie Commissie Uitvoering Wet Verontreiniging Oppervlaktewater, Werkgroep VI, Diffuse Bronnen van Waterverontreiniging, The Hague, Netherlands.
- Nilsson, R., 1990, *Cadmium: An Analysis of Swedish Regulatory Experience*, KEMI-Report No. 6/90, Swedish National Chemical Inspectorate.
- OECD, various years, *Energy Statistics (Statistiques de l'énergie)*, 1970–1987, Paris, France.
- Oltshoorn, A.A., and Thomas, R., 1986, *Milieuverontreiniging door Cadmium 1981–2000*, Institute for Environmental Studies, Free University of Amsterdam, Report RIM-17, Netherlands.
- Pohl, W., 1982, Vorwort zum 9. Symposium über branchenspezifische Emission Cadmium emittierender Anlagen, *Gesundheitsingenieur, Haustechnik-Bauphysik-Umwelttechnik* **103**(6):281–283.
- Rauhut, A., 1978a, Verbrauch und Verbleib von Cadmium in der Bundesrepublik Deutschland im Jahre 1974 und 1975, *Metall* **32**:947–948.
- Rauhut, A., 1978b, *Industrial Emissions of Cadmium in the European Community, Sources, Levels and Controls*, European Community Study Contract No. ENV/223/74E, Cadmium Association, London, UK.
- Rauhut, A., 1979, The Cadmium Balance and Cadmium Emissions in the European Community, *Cadmium 1979, Proc. 2nd Int. Conf.*, Cannes, Metal Bulletin for the Cadmium Association, London, UK.
- Rauhut, A., 1981, Cadmiumbilanz 1976/1977 und Cadmiumverbrauch bis 1979, *Metall* **35**:344–347.
- Rauhut, A., 1982, Bilanz über Verbrauch und Verbleib von Cadmium und seine Verbindungen unter besonderer Berücksichtigung Cadmium emittierender Anlagen, *Gesundheitsingenieur, Haustechnik-Bauphysik-Umwelttechnik* **103**(6):284–289.
- Rauhut, A., 1983, Cadmiumbilanz 1978–1980, *Metall* **37**:271–275.
- Rauhut, A., 1990, *Cadmiumbilanz 1984–1986*, im Auftrag des Umweltbundesamtes, No. 1-5-97407-2/19, Landesgewerbeamt (LGA), Nürnberg, Germany.
- Rauhut, A., and Balger, D., 1976, Verbrauch und Verbleib von Cadmium in der Bundesrepublik Deutschland im Jahre 1973, *Metall* **30**:269–272.
- Rauhut, A., and Wiegand, V., 1981, Cadmiumabfälle und Möglichkeiten des Recyclings, *Metall* **35**(2):167–172.
- Reinders, M.E., 1983, *Handbook of Emission Factors, Part 2: Industrial Sources*, SDU, The Hague, Netherlands.
- Ros, J.P.M., and Slooff, W., (eds), 1987, *Ontwerp basisdocument Cadmium*, National Institute of Public Health and Environmental Protection, Report No. 758476002, The Hague, Netherlands.
- Roskill Information Services Ltd, 1974a, *The Economics of Cadmium*, 2nd ed., London, UK.
- Roskill Information Services Ltd, 1974b, *The Economics of Zinc*, 1st ed., London, UK.

- Roskill Information Services Ltd, 1980a, *The Economics of Cadmium*, 4th ed., London, UK.
- Roskill Information Services Ltd, 1980b, *The Economics of Zinc*, 2nd ed., London, UK.
- Roskill Information Services Ltd, 1984a, *The Economics of Cadmium*, 5th ed., London, UK.
- Roskill Information Services Ltd, 1984b, *The Economics of Zinc*, 3rd ed., London, UK.
- Roskill Information Services Ltd, 1984c, *The Economics of Lead*, 3rd ed., London, UK.
- Roskill Information Services Ltd, 1988, *The Economics of Cadmium*, 6th ed., London, UK.
- Roskill Information Services Ltd, 1990, *The Economics of Cadmium*, 7th ed., London, UK.
- Salkind, A.J., and E. Pearlman, 1982, Batteries, Secondary (Alkaline cells), *Kirk Othmer's Encyclopedia of Chemical Technology* **3**:596-609.
- Schulte-Schrepping, K.H., 1983, Cadmium Emissions and Immissions: A Local Problem, *Cadmium 1983, Proc. 4th Int. Conf.*, Munich, Cadmium Association, London, UK.
- Simon, H., 1983, Cadmium in der Galvanotechnik, *Metalloberfläche* **36**(1):1-6.
- Stanford Research Institute, 1986, *Directory of Chemical Producers: Western Europe*, SRI International, Menlo Park, CA, USA.
- State Water Authority, 1990, *Aqueous Emissions Data-Base*, South Holland, Netherlands.
- Steel Statistical Yearbook*, 1985, 1989, International Iron and Steel Institute, Brussels, Belgium.
- Taubitz, G., 1985, Cadmium-Farbpigmente: Anwendung und Alternativen, *Umwelt* **6**:499-502.
- Tötsch, W., 1989, Cadmium in der Kunststoffindustrie, *Kunststoffe* **79**(11):1209-1212.
- Treaty with respect to the protection of the Rhine against chemical pollutants (3rd December 1976), Treaty Papers (1977) No. 32.
- Umweltbundesamt, 1981, *Cadmiumbericht*, Berlin, Germany.
- van der Hoogt, A., 1991, Bureau Verontreinigingsheffing Rijkswateren, General Management, State Water Authority, Netherlands, personal communication, May.
- van der Voet, E., *et al.*, 1988, *Stroomschema's voor stoffen in economie en milieu van Nederland en Zuid-Holland, deel IIa: Cadmium*, Institute for Environmental Studies, Free University of Amsterdam and Centre for Environmental Problems, University of Leiden, Netherlands.
- van Vliet, H.P.M., and Feenstra, J.F., 1982, *Gebruik van Cadmium in Nederland, een Stofbalans voor 1980*, Institute for Environmental Studies, Free University of Amsterdam, Netherlands.

- Verband der chemischen Industrie, 1987, *Wasser, Reihe Chemie und Umwelt*, Frankfurt am Main, Germany.
- von Röpenack, A., 1978, Emission Control in Cadmium Metal Production, *Proc. 1st Int. Cadmium Conference "Cd 1977,"* San Francisco, Cadmium Association, London, UK.
- von Röpenack, A., 1985, *Cadmium in the FRG*, Report on Seminar "Cadmium Today," Brussels, issued by the Cadmium Association, London, UK.
- VROM-DGM, 1990, *Dutch Emission Registration Data-Base*, Leidschendam, Netherlands.
- Warren, K., 1974, *World Steel: An Economic Geography*, David and Charles, Newton Abbot, UK, and Crane, Russak, New York, NY, USA.
- Yost, K.J., 1990, *Source-specific Exposure Mechanisms for Environmental Cadmium*, Harcos Chemicals BV, Netherlands.
- Yost, K.J. and Greenkorn, R.A., 1984, *Source-Specific Environmental Impacts and Exposure Mechanisms for Cadmium: A Systems Study*, Purdue University, West Lafayette, IN, USA.