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PREFACE

One of the objectives of IIASA's study, *Chemical Pollution and Its Sources in Dutch Estuaries and Coastal Regions*, is to characterize the emissions of six environmentally harmful pollutants in the Basins of the Rhine, Meuse, and Scheldt Rivers for the period from 1970 to the present. One of the major parts of this task is to estimate the levels of aqueous emissions from industrial point sources in the basins in previous decades. Information on this topic is surprisingly sparse, and the references 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 of "environmental histories" are rare in the environmental literature. The task is daunting because information is required on historical levels of industrial production, emission factors per unit of production and how these factors have changed over time, and the locations of the industrial point sources.

This paper, by reviewing the relevant literature and synthesizing data on economics, 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 paper not only provides valuable input to the Dutch Estuaries study, but also demonstrates a methodology by which "environmental histories" may be reconstructed and utilized in assessing long-term environmental trends.

ABSTRACT

This report contains an overview of the development of aqueous point source emission factors for cadmium in the Rhine River basin in the period 1970 — 1988. Based on these emission factors the aqueous emissions of cadmium for different industrial activities in the basin are calculated. For some activities defining emission factors does not make sense, since their cadmium emission is determined by e.g. ore or scrap purchase policy and not by the applied process technology.

The overall cadmium emission to the Rhine and to its tributaries is compared with the point source component of in-basin cadmium monitoring data. The results show reasonable agreement. Further study is required to include hydrological characteristics in a tributary-Rhine model, in order to justify the comparison of monitoring data and emission estimates. In the table below, a summary of all the calculated point source emissions in time and per branch is given. A second table provides an overview of the development of emission factors for point source emissions in the Rhine River basin in time.

Aqueous point source cadmium emissions in the Rhine River basin in the period 1970 — 1988 per branch[1]

branch	1970—1972	1973—1977	1978—1982	1983—1987	1988
non-ferrous mining	0.4	0.4	0.1	0.1	
other mining		0.5	0.5	0.5	0.5
primary Zn/Pb	2.0	1.6	1.0	0.5	0.1
secondary zinc	50	50	50	10^2	0
sec. cadmium	3	3		0	0
secondary lead	0.6	0.6	0.6	0.6	0.6
pigment manuf.	9.0—18.0	4.0—10	1.3	0.3	0.2
stabilizer m.	0.9— 1.7	0.4— 0.9		0	0
PVC manuf.	0.5— 1.0	0.5— 1.1	0.6— 1.4	0.4— 0.9	0
battery prod.	2.4	1.3— 1.6	0.9— 1.3	0.5— 0.7	0.3
plate	7.7—11.6	4.0— 7.7	2.0— 4.4	0.1— 0.7	0.1
phosphoric acid manufacturing	25.9	24.8	15.6	13.7—15.6	9— 10.3
coke production	10.3	8.9	3.5	0.5	0.6
iron & steel	17.8	18.7	15.4	7.6	1.7
SUM	130.5—144.7	118.7—129.7	91.5 — 95.1	34.8 — 38.0	13.1— 14.4

[1]   Blank spaces indicate that no data were available to justify any estimate.

[2]   Estimate, based on the assumption that in 1983 and 1984 together 50 tons of cadmium were emitted.

The evolution of emission factors for aqueous point source cadmium discharges in time in the Rhine River basin for the period 1970 – 1990

	1970–1972	1973–1977	1978–1982	1983–1987	1988
non-ferrous mining[1]	2.4	2.4	1	1	
other mining[1]	0.1	0.1	0.1	0.1	0.1
primary zinc[1,3]	16	10	10	5	0.5
secondary lead[1]	6.2	6.2	6.2	6.2	6.2
pigment manuf.[2]	10 – 20	4 – 10	1.5	0.5	0.3
stabilizer m.[2]	10 – 20	4 – 10	2.0	0.6	0.4
ind. stab. use[2]	1.2 – 2.4	1.2 – 2.4	1.0 – 2.0	0.8 – 1.6	0
battery manuf.[2] pocket plate sintered plate	8 15	4 10 – 15	3 5 – 10	1.5 2 – 3	1.0 1.0
plate manuf.[2]	20 – 30	15 – 25	10 – 20	1 – 6	0.3
iron and steel[1] BO-steel EA-steel	0.4 0.4	0.4 0.4	0.45 0.45	0.2 0.2	0.05 0.05

[1]   the unit of the factor is g Cd / ton material processed

[2]   the unit of the factor is g Cd / kg Cd processed

[3]   this factor only applies to pyrometallurgical winning processes

CONTENTS

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Industrial Discharges of Cadmium in the

Rhine River Basin in the Period 1970–1990:

an Inventory

F. Elgersma[1], B.S. Anderberg, & W.M. Stigliani

1   INTRODUCTION

1.1   Framework

The framework of this paper is the study of "Chemical Pollution and Its Sources in Dutch Estuaries and Coastal Regions" which is a collaborative research effort between RIVM and IIASA.

Principal investigator for RIVM is J.M. Knoop and for IIASA it is R. Shaw. The task of the International Institute for Applied Systems Analysis (IIASA) is to trace the upstream sources of the pollutants lead, zinc, cadmium, some organochloro compounds and dissolved nitrogen compounds and phosphates in estuaries and coastal regions of the Netherlands. It is relevant to assess trends in source loadings and to establish a relationship between manufacturing, processing and transporting potentially hazardous chemicals on the one hand and inputs from long range atmospheric transport from outside the basin on the other hand to downstream environmental effects.

The main sources of the above mentioned pollutants to the Dutch estuaries and coastal regions are located in the basin area of the rivers Rhine, Meuse and Scheldt. Therefore the study of transboundary and Dutch water pollution is the key to assessing the environmental impact created in the Dutch estuary. The three rivers mentioned will all be studied in a separate time schedule. The total study has been divided in three main parts considering the Rhine, the Meuse and the Scheldt basins. It was decided to start investigating the Rhine river basin first which will quantitatively probably be the most important one.

This paper is limited to the pollution of the Rhine river basin with cadmium, which was receiving the highest priority due to the relatively large hazards related to cadmium. In the following sections of this section the functions of the Rhine river will be discussed, as well as some definitions required for this work and the justification for the time period chosen.

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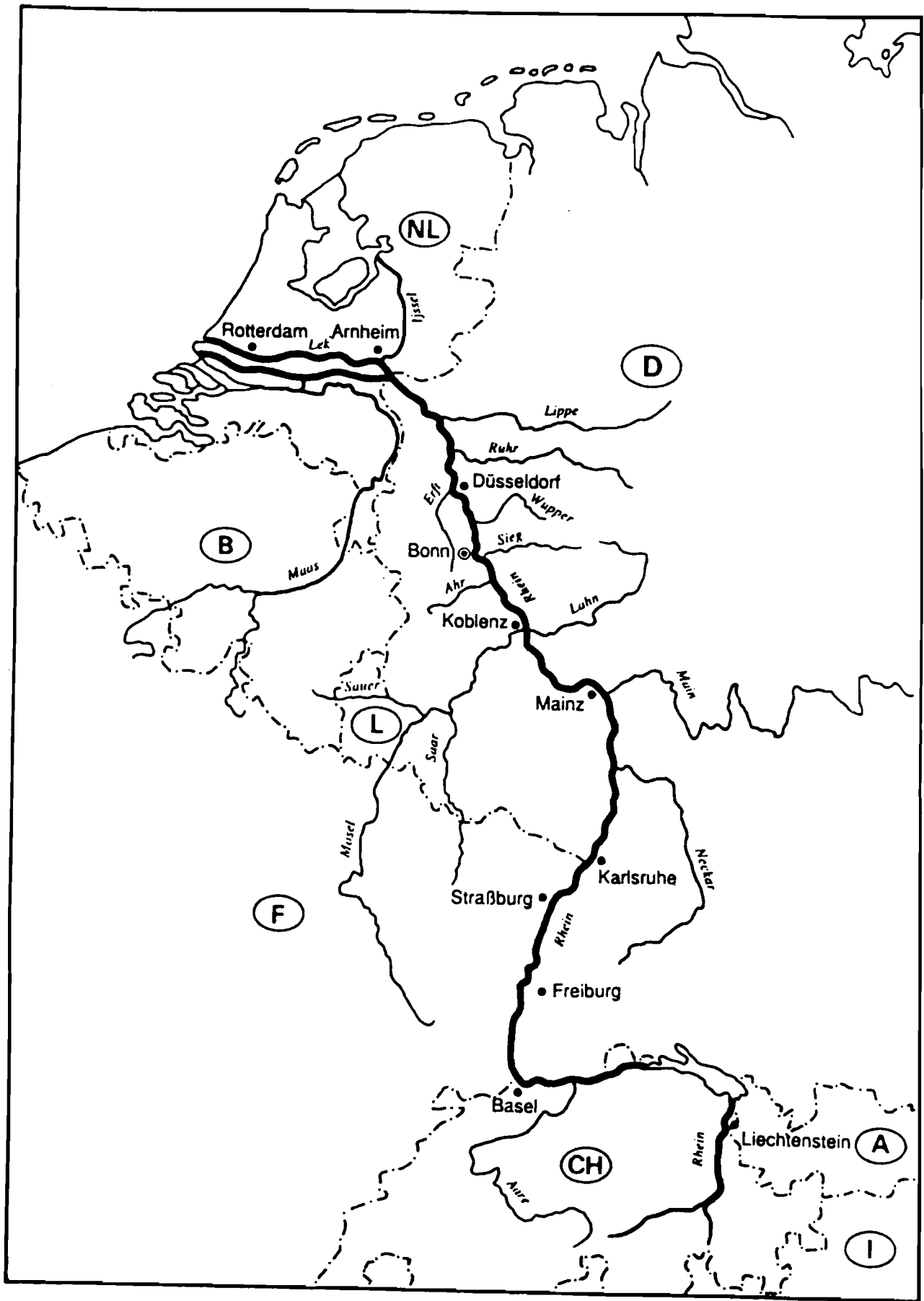
Figure 1.1 Rhine river and its main tributaries.

1.2 The River Rhine and its Functions

The Rhine River finds its origin in the Swiss Alps and is a so-called combined river, meaning that its water resources are both rainfall and the melting of ice in the mountains (see figure 1.1). In Switzerland the Rhine river passes Lake Konstanz. After the waterfall at Schaffhausen the Rhine river can be used for shipping. The river passes through Switzerland, France, the Federal Republic of Germany, Luxembourg and finally at Hook of Holland in the Netherlands ends up in the North Sea. From Schaffhausen to Hook of Holland the Rhine river has a length of almost 900 km. Along this part of the main stream and its main tributaries which are the Neckar, the Main, the Mosel (including the Saar and the Sauer), the Sieg, the Wupper and the Ruhr, this water basin has to fulfill quite contradictory functions. The most important of these are:

1) ecological functions
2) fisheries
3) shipping
4) (drinking) water supply
5) tourism
6) waste water discharge

Each of these functions will be discussed in more detail now.

Ad 1. Ecological function

The ecosystem Rhine is part of a complex system which supplies many animal species with food and space. Many of the human activities in the river basin area relate to this in a negative way. Therefore the ecosystem Rhine as such needs protection in order to at least maintain it at its current level.

Ad 2. Fisheries

In 1988 the Rhine supported approximately 31 different species of fish [1]. In the Rhine river basin 37 large companies and 100 smaller companies are still engaged in commercial fishing. However, they are practically only operating in those branches of the river, where the main stream is canalized, because in the main stream fishing is practically impossible due to the high stream velocity and the shipping intensity.

Apart from that, in the FRG alone, around 60.000 people have legal permission for fishing as a sport in the river.

Ad 3. Shipping

Shipping on the Rhine river and its main tributaries is of the utmost importance for the industry in the region. In 1985 the total Rhine fleet consisted of 11.419 ships with a total loading capacity of 10.5 million tons. For 1986 the amount of goods transported over the river equalled almost 100 million tons. It is evident that both regular transportation and accidents have an environmentally significant impact, although no further attention will be paid to this topic here.

Ad 4. (Drinking) water supply

The Rhine river is used for supplying 5.5 million people with drinking water and another 14.5 million people are depending on its tributaries for their supply [2].

If Rhine water is to be used for human consumption, without extraordinary clean up expenses, a high water quality standard has to be met.

Apart from municipal water use, the industry is also a major water consumer. In 1977 the FRG industry was estimated to use 12 billion m^3 water, a great deal of it for cooling purposes. In 1977 the FRG households used 4 billion m^3 [3]. In table 1.1 a few specific water consumption figures for some industrial products are shown [2]. These data are valid for the beginning of the 1980's. Table 1.2 provides the 1986 water use data for the Netherlands [4].

Table 1.1   The specific water consumption for some industrial products

Product	Required amount of water (liter)
1 liter beer	20
1 can for beer	40
1 liter oil	180
1 kg steel	25 to 200
1 kg paper	400 to 1000
1 automobile	380000

Table 1.2   The water winning and use in the Netherlands in 1986
(all figures in billion m3)

Household	0.7
Industry and Mining	4.3
Power Stations	9.2
Others	0.3
of which:	
Surface Water	13.4
Ground Water	1.1

Ad 5. Tourism

Tourism on the Rhine, Mosel and Neckar is an important economic branch in the FRG. Obviously, polluted water, toxic to fish and other aquatic life diminishes the attraction of these areas to tourism.

Ad 6. Waste water discharges

Waste water discharges in the Rhine are the main topic of this study. The origins of waste water discussed here are industrial discharges, municipal waste water treatment effluents and other

indirect discharges. The definitions of the individual sources and of waste water itself are presented in Section 1.4.

The annual water flow of the Rhine constitutes only 0.2 percent of total flow of all rivers in the western world, however, 20 percent of all chemical industries in the west are located within its basin. Moreover, other industrial branches like metallurgical industries, iron and steel manufacturers and paper works contribute significantly to the overall load, each with a specific contaminant spectrum.

In the FRG the Rhine was loaded with a pollution of 78 million inhabitant equivalents in 1986.

1.3   The time horizon

This paper will focus on the development of environmental protection measures and its effects with respect to the aqueous discharges of cadmium. For that reason a time period of interest had to be chosen. This period extends from 1970 to 1990. The choice to start the period under consideration at 1970 is justified as follows:

1)   Analytical methods which are required for determination of heavy metals in very diluted form and in the presence of many other interfering components are only available since the Atomic Absorption Spectroscopy - technique became operational. In the beginning of the 1970's with the introduction of this advanced analytical technique detection limits for heavy metals lowered drastically, enabling water quality data to be measured with much higher accuracy.

2)   Monitoring data, either from the water quality control point of view, or from direct discharges are only available since the beginning or middle of the 1970's. The policy debate for decreasing heavy metal concentrations in (waste) water was preceded by measures to decrease the nutrients, resulting from among others the overuse of chemical fertilizers in agriculture. This source caused a very visible degradation of the ecosystem, resulting in many rivers becoming practically anaerobic, with many subsequent severe ecological effects.

3)   Apart from studying the development of the discharges in time for the analysis of the effectiveness of the applied policy, it is also required to know historical emissions data for estimating the sludge contamination with pollutants.

Heavy metals in neutral water strongly attach to the particulate content in the water which has a long residence time in the estuary. A retrospective analysis thus is required to explain the current situation and to predict the future outlook.

This typically is the case with Rotterdam harbor sludge which since 1984 has not significantly decreased in pollutant concentrations, despite of the fact that the Rhine water as well as the Rhine sludge in that period has on average improved in quality [5]. Sludge contamination is also of major importance in tributaries to the Rhine.

1.4   Basic Definitions

Waste water discharges are distinguished in three different categories, based on their origin. The definitions for the individual categories are not standardized, and for the sake of clarity we have

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chosen the definition provided by the FRG Minister of the Economy in 1955:

" Waste water is water that originates from households, industry or other human activities and due to its physical, chemical and/or biological properties can cause damage to the water, the waste water canal or the waste water treatment plant in which it is discharged.

This waste water definition therefore among others includes water that during its use in household, industry or other human activities has been changed in physical, chemical and/or biological properties (e.g. also cooling water), deposition runoff and - in case it shows detrimental properties - also the water that is formed during production processes" [6].

The different categories of waste water discharges are in this context for practical reasons chosen as follows.

Category I refers to industrial discharge. This discharge has in geographical sense one origin, namely the industrial process site and mostly its subsequent waste water treatment plant, and one discharge point. The industry is discharging either directly to the Rhine or to a tributary to the Rhine. This is an important difference, since discharges to tributaries do mostly not directly end up in the main stream due to accumulation in the sediments of the tributary. Therefore direct discharges to the Rhine, in which sedimentation is practically negligible, are distinguished from discharges to tributaries. The Rhine River and its network of tributaries together forms the Rhine River basin.

Category II includes municipal discharges. In the geographical sense it has an urban origin, namely the city area of which the collected waste water is the input to a waste water treatment installation, whose effluents constitute the discharge. Although the sources of the waste water are spread over a certain region it is regarded as a point source discharge.

Category III includes all non-point source discharges. Their main characteristics are that the discharges are diffuse spatially and occur randomly over time. The most important sources are atmospheric deposition over the land and inputs of agrochemicals.

These categories have been defined in the references [1] and [7]. Another important criterion for waste water classification is the source of the pollutant. Two categories are generally distinguished.

Category A is pollution from point sources. These sources include e.g. chemical industries which emit a certain amount of hazardous chemicals per unit of product even after waste water treatment. In this category there is a direct relation between the plant location, the chemicals used and the pollutant.

Category B consists of all other pollution sources. Despite the fact that a municipal waste water treatment plant is discharging at one point, its influence has a wide spatial origin and an array of pollutant inputs. Thus sewage treatment plants are included in this category.

In this paper the emphasis is on describing Category I discharges.

1.5 Set-up of the Inventory

This study only concentrates on industrial cadmium discharges. In order to estimate these, it is helpful to distinguish between industrial emissions in which cadmium is processed as a product with a value added, i.e. in cadmium winning, pigment manufacturing etc. and in which cadmium is present as an undesired impurity. The first category is called the intentional use of cadmium: the second category is called the inadvertent use. Previous studies [8,9] have identified those industrial activities of branches that are of major importance for water pollution studies. The industrial activities studied here are presented in table 1.3.

Table 1.3 Industrial Activities of Major Importance for Cadmium Studies

Intentional Use of Cadmium
Zinc and lead mining industry Zinc and lead winning industry Battery manufacture Pigment manufacture Stabilizer manufacture Stabilizer application in the PVC industry Cadmium plating Cadmium alloying: production and application in manufacturing
Inadvertent Use of Cadmium
Wet phosphoric acid manufacture Cement manufacture Iron and steel industry Other non-ferrous metal industry Other mining activities

This inventory for aqueous cadmium emissions uses the following methods for emission (factor) estimation:

-1-   direct measurement of emissions
-2-   literature data on emissions
-3-   literature data on emission factors
-4-   legislation on maximum allowed emissions

Although most of the branches are covered by this approach, for some branches (e.g. alloy manufacturing and cement manufacturing) emission estimates have not been found. These branches are fortunately of minor importance.

Emission estimates are mostly given for individual years. Emission factors also relate to the state of the art of technology in a particular well defined period. However, economic fluctuations are of influence to emissions as well. In order to cover the period 1970 − 1990 it

is not required to present all individual annual figures. In this paper all branches are characterized by average periods of a few years which better reflect the development of the emission controls and the emission factors in time. The following periods are chosen (which are characterized by a specific year):

Year	Period
1971	1970—1972
1975	1973—1977
1980	1978—1982
1985	1983—1987
1988	1988

The year 1988 has been added in order to give an idea of the state of the art by then.

Heavy metals in Rhine water have been monitored since the beginning of the 1970's. These monitoring data are collected to investigate the water quality of the river, a.o. to ensure safe drinking water production. For the basin these monitoring data offer a unique source for determining the trends of the aquatic pollution in time.

The monitoring data are used as a reference which gives the overall discharge of cadmium to the River Rhine. Since monitoring data exist for different locations along the River Rhine, These data also reveal in which parts of the river the major cadmium emissions have taken place. More attention to monitoring data is paid in Section 3.

The following sections of this study contain:

- the properties and uses of cadmium metal and cadmium compounds
- an overview of cadmium monitoring data for the Rhine River for 1970-1990.
- the inventory of aqueous cadmium emission factors for individual branches in time
- an estimate of the industrial cadmium discharges in the basin for 1970—1990 based on the emission factors

2   CADMIUM; WINNING, PROPERTIES, USES AND ENVIRONMENTAL EFFECTS

2.1   Discovery, historical development and natural occurrence

Although cadmium is contained in practically all zinc ores, its discovery is only relatively recent. This is explained by the fact that it is only present in very limited concentrations and that it has a low standard electrode potential at 298 K (−0.403 V) [11,12].

In 1818 Stromeyer in Gottingen, Germany, detected in a slightly yellow zinc carbonate ore an unknown oxide, which resembled arsenic and iron oxides. Meanwhile Hermann in Schonebeck, Germany, had also detected that the unknown oxide that colored zinc oxide slightly yellow, could be dissolved in diluted acid and, after precipitation with hydrogen sulfide, yielded a bright yellow precipitate. In a reductive atmosphere and during heating, Stromeyer was the first to convert the newly discovered oxide into its metallic form. A white tin-like metal was produced. This newly discovered metal needed a name. Although Klaprothium was suggested, which relates to the brightly colored cadmium compounds, the metal was named cadmium. Cadmium originates from "Cadmia Fossilis" which is the latin name for Galmei, the type of zinc

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ore (zinc carbonate) in which cadmium was first discovered.

Cadmium has been produced on an industrial scale since 1827. The first applications were limited to the production of low melting alloys and pigments. During the First World War the production of cadmium increased dramatically because the United States Army required very large quantities of high quality zinc, which stimulated the technical development of electrolytic zinc production, a process known for its high purity zinc production. The large scale application of electrolytic zinc production caused large amounts of cadmium containing residues at these plants, which could be treated economically to produce pure cadmium as a by-product. Since then cadmium has been the "little sister" of "big brother" zinc, since cadmium production has become invariably linked to zinc production.

Zinc ore typically contains 0.3 % cadmium by weight [10,11,13], although certain zinc resources contain up to 5 % Cd. The zinc carbonate ore (Smithsonite) that was generally processed in the past contains more cadmium than the zinc sulfide (Sfalerite) that is being processed nowadays.

Cadmium, however, is not only present in zinc ore. Two individual cadmium containing minerals are known: Greenockite, a hexagonal cadmium sulfide with 77.8 % Cd and Otavite, a cadmium carbonate with 61.5 % Cd. These minerals have no economic importance.

Apart from minerals and other natural resources in which cadmium is present in relatively large (economically recoverable) amounts, cadmium is also present in resources in which its concentration is too low to be economically recovered (e.g. around 0.1 ppm). Cadmium in such resources constitutes mobilization of unwanted waste products. Examples are fossil fuels, sedimentary apatite ores and some cuprous, lead and ferric ores. Table 2.1 gives the typical cadmium contents of some natural resources [8,10,11,13,14,15,16,17,18,19,20].

Table 2.1   The typical cadmium content of some natural resources

Name	Content (ppm)	ref.
Greenockite (Cadmium sulfide hexagonal)	778000	[11]
	615000	[11]
Otavite (Cadmium carbonate)	10000	[11]
Smithsonite (Zinc carbonate)	5000	[13]
Wurtzite (Zinc sulfide hexagonal)	2000	[10]
Sphalerite (Zinc sulfide cubic)		
(Fluor-) Apatite (= Phosphate rock)		
origin: USA, Florida	6 – 16	[14]
Morocco	8 – 75	[14]
Senegal	70 – 90	[14]
Togo	50	[14]
Naura Island	80 – 90	[14]
USSR, Kola peninsula	0.1 – 0.4	[14]
Israel	27 – 33	[15]
Iron ore	0.5	[8]
Coal		
power stations UK	0.3	[8]
" " elsewhere	0.5	[8]
other applications	1.0	[8]
general specification	0.22	[17]
Coal Fly Ash	0.2 – 4	[16]
		[18]
	0.82	[19]
Refuse Fly Ash	449	[19]
Crude Oil (average)	0.011	[20]

2.2   Winning processes

2.2.1   Primary winning

The commercially applied processes for the production of cadmium metal are linked to zinc winning processes. In the winning of copper and lead only minor amounts of cadmium are recovered [21]. In this section the discussion will be limited to the description of processes that are or have been in use for cadmium winning during zinc winning processes. Processes aiming at winning both zinc and cadmium have to be very selective, because the two metals exhibit highly similar chemical behavior. The properties that offer the possibility for separating the two

are the difference in standard electrode potential at 25 °C (Cd: -0.403 V, Zn; −0.763 V) [12], the difference in boiling temperature (Cd: 1038 K, Zn: 1179 K) [8] and the different solubilities of some of the metal salts in diluted acidic solutions.

These differences create the basis for three different cadmium winning processes: 1) the dry distillation process, 2) the combined process and 3) the hydrometallurgical process.

Ad 1) The dry distillation process

The dry distillation process is based upon the difference in atmospheric boiling temperature of the two metals and has been in use in combination with pyrometallurgical zinc winning processes in horizontal or vertical retort ovens, which were operated batchwise.

After loading the oven the temperature of the concentrate is increased by heating in a reductive atmosphere. Thus the sulfidic compounds are reduced to the metallic form. As temperature rises up to 1000 K and beyond the cadmium content is vaporized to a much larger extent due to its higher escaping tendency than the excess zinc load present. Therefore the first droplets formed in the condenser are strongly enriched in cadmium. By appropriate temperature control it was possible to distinguish between so-called "first run" (Vorlauf) which contains the majority of the cadmium and the rest of the charge. The "first run" charge forms the feed of a fractional distillation process, which step-by-step, increases the cadmium content of the product, until finally the required quality standard is met.

However, during this labor intensive, fractional distillation process very large quantities of volatile cadmium are emitted to the air, which also had a drastic influence on the winning efficiency which is reported to have been as low as 30 % . This "criminal" (from an environmental point of view) process has been in operation in the first half of this century, being more and more abandoned, for economical reasons, in the 1950's. The dry distillation process also caused severe water pollution.

Ad 2) The combined process

The combined process was developed to improve the cadmium winning efficiency. After the "first run" enriched zinc/cadmium dust is obtained, it is leached with (dilute) sulphuric acid, exploiting the higher solubility of zinc (sulphate) to enrich the remaining solid sludge in cadmium. The cadmium rich sludge then only requires a one step distillation to yield a sales quality cadmium metal product.

Despite the fact that this process leads to a higher cadmium winning efficiency, it creates a zinc sulphate solution, for which pyrometallurgical companies have no direct application. In order not to lose the valuable zinc content it is either used for wetting the concentrates entering the oven or is precipitated and recycled as a solid material. The overall process needs substantial amounts of chemicals (sulphuric acid, precipitation agent), whereas the cadmium winning efficiency still is not satisfactory.

The combined process was improved by using cadmium electrolysis. This process leaches the zinc and separates the remaining solids from the zinc sulphate solution. Thereafter the solids are leached by increasing the acidity of the bath and the cadmium is electrolytically won in rotating cathodes baths.

Despite the rather complicated process technology required, and the labor and equipment intensiveness, the cadmium winning efficiency remains limited to 80 % . This limit is dictated by the pyrometallurgical distillation. Given these limitations it was increasingly realized that a further improvement could be obtained by abandoning the high temperature step and switching to hydrometallurgical integrated winning. Already in 1928, 75 % of all cadmium produced was obtained by hydrometallurgical processes.

Ad 3) The hydrometallurgical process

The hydrometallurgical process is preferentially applied in combination with a hydrometallurgical zinc winning process. This zinc winning process consists in its most usual form (see figure 2.1) of a (fluid bed) roast oven which burns the zinc sulfide (sfalerite) concentrates at 1170 - 1220 K to zinc oxide yielding a sulfur dioxide off-gas which is perfectly suited for sulfuric acid production in a contact - process plant. The roasted concentrate, called calcine, is fed into a leach solution containing diluted sulfuric acid which is referred to as neutral leach. The operation temperature is 353 K and the pH ranges from 3 to 5. The neutral leach is carried out in a cascade of large stirred cylindrical vessels, each with a typical size of 50 to 100 m^3. The sulfuric acid required for dissolving the zinc oxide is formed during the zinc sulfate electrolysis.

The neutral leach is filtered yielding a neutral leach solution containing up to 85 % of zinc and cadmium and a sludge consisting of zinc ferrite and the majority of the ore impurities. This zinc ferrite is leached with strong sulfuric acid solutions (pH 0.5 - 1, T = 368 K) giving a ferric-zinc solution out of which the iron has to be precipitated selectively before this solution is added to the neutral leach solution. For precipitating the iron content three different processes are in use on an industrial scale: the jarosite, the hematite and the goethite process [22,23].

The neutral leach solution consists of zinc sulfate ions with cadmium, copper and cobalt ions as commercially interesting impurities. To this solution zinc dust is added, in order to precipitate cadmium, cobalt, copper and other impurities. The processing of the precipitate generally follows the flow sheet shown in figure 2.2 [24,25,26].

The precipitate itself contains four to twenty-nine times more zinc than cadmium and still contains other impurities like cobalt and copper. It is dissolved in a sulfuric acid solution made up by mixing spent cadmium electrolyte, spent zinc electrolyte and sulfuric acid at 318 - 355 K. The copper is removed by cementation with a small amount of zinc dust. After the copper cake is filtered, cadmium is re-precipitated, usually in two stages, by the addition of zinc dust. The so-obtained solid sponge product contains about 80 % Cd and less than 5 % Zn. After dissolving the separated solids once more in spent cadmium electrolyte and sulfuric acid a cadmium solution with approximately 200 g/l Cd is obtained.

This solution is mixed with spent cadmium electrolyte. The electrowinning is carried out at 293–298 K in cells equipped with silver-lead anodes and aluminium cathodes. The cathode deposits are stripped, washed, dried and melted at 653 - 673 K under sodium hydroxide, which prevents oxidation and effectively removes zinc and arsenic which may still be present. Thereafter the metal is cast into shapes. Two grades are commercially available: High Grade cadmium containing at least 99.99 % Cd and Super High Grade cadmium containing at least 99.9999 % Cd.

2.2.2 Secondary winning

The secondary winning or recycling of cadmium is practically limited to the use of waste that is formed during its primary production and to nickel/cadmium battery recycle. Therefore it is of minor importance and in 1984 only 5 - 10 % of the produced cadmium had a secondary origin. The recycling of cadmium from steel with a cadmium coated top layer is technically possible but has a narrow processing window.

Table 2.2 shows the total cadmium production worldwide since 1900 [13,20,27].

Table 2.2   The cadmium production in tons worldwide since 1900 [13,20,27].

Year	Amount
1900	14
1910	43
1913	63
1917	172
1930	2000
1936	3665
1945	6000
1960	12000
1969	17311
1973	17905
1981	17192
1984	19529
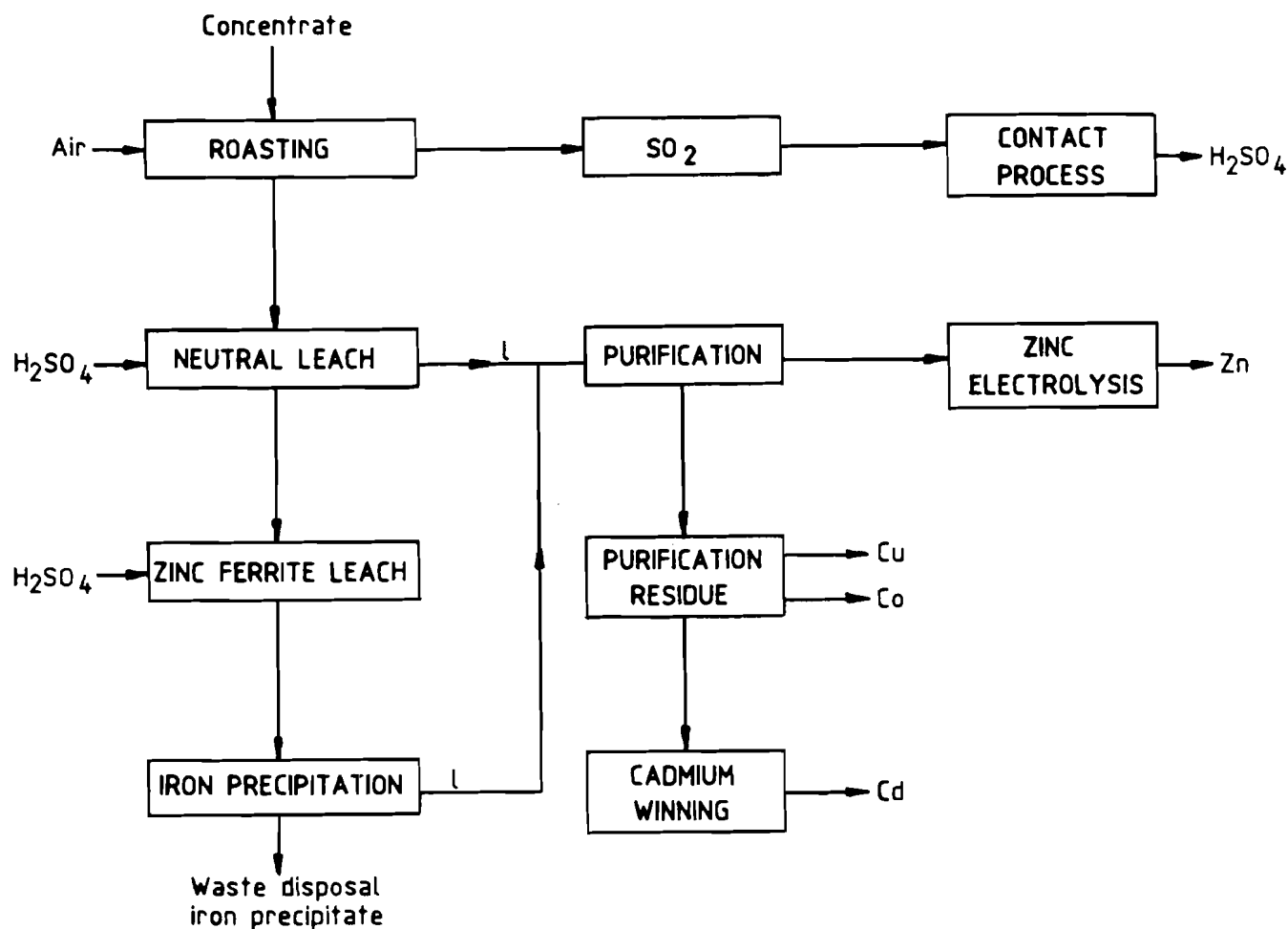
Figure 2.1   An outline of a hydrometallurgical zinc winning process.

2.3   The properties of cadmium metal

2.3.1   Physical properties and alloys

Table 2.3 summarizes some physical properties of cadmium. The metal crystallizes dihexagonal bipyramidal and as such is isomorphic with zinc. Its color is similar to zinc and tin. Pure cadmium is at room temperature very ductile. At temperatures just below its melting point it is easily pulverized. The alloying behavior is practically equivalent to that of zinc. The main impurities in industrial produced cadmium are zinc, lead and iron.
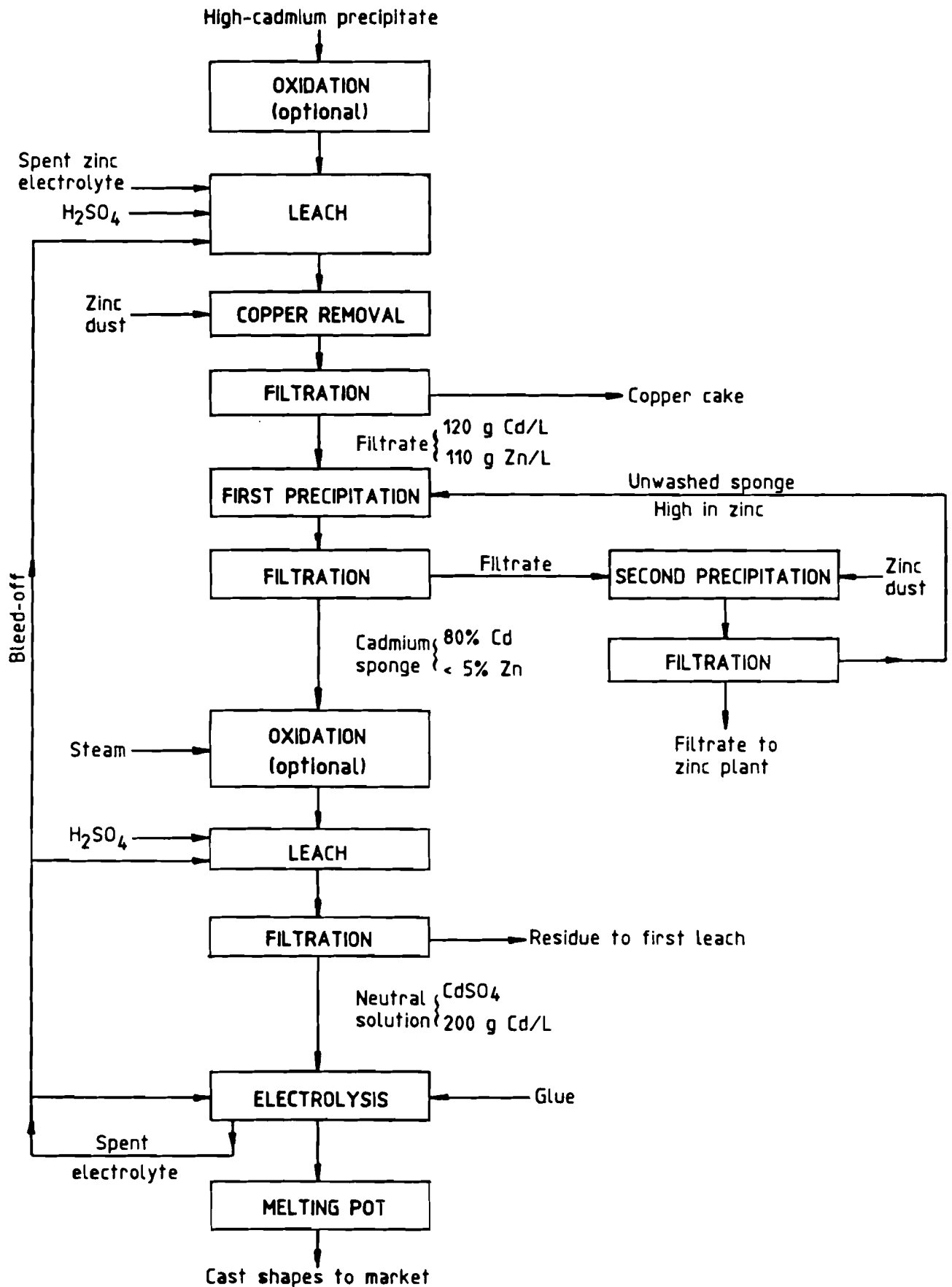
Figure 2.2   Electrolytic production of cadmium from zinc electrolyte purification residue.

In liquid cadmium zinc is dissolved infinitely, without the formation of chemical intermediates. The eutectic point of zinc-cadmium is 17.4 % zinc and 539 K [11]. The solubility in the solid state is practically zero. The presence of cadmium in zinc metal, used for galvanizing is not desirable because it increases the risk of intercrystalline corrosion.

In liquid cadmium lead behaves equivalently to zinc. The eutectic point of lead-cadmium is 82.5 % lead and 521 K. Solid lead dissolves approximately 3 % cadmium at 293 K. Solid cadmium dissolves about 0.1 % lead at 293 K. The mutual solid solubilities increase with rising temperature to the eutectic point.

Important alloys are nickel-cadmium, silver-cadmium, iron-cadmium, copper-cadmium and bismuth-cadmium mixtures, of which the last ones exhibit special properties, e.g. eutectic temperatures ranging from 320 to 413 K, depending upon the composition and the eventual addition of other elements like lead, zinc and tin.

Table 2.3 The physical properties of cadmium [13,20]

Symbol	Cd	
Relative Atomic Weight	112.41	
Specific density (298 K)	8640	kg/m^3
Melting point	594	K
Boiling point (101325 Pa)	1038	K
Specific Resistance	63	mOhm/m
Specific Heat	231	J/kg/K
Melting Heat	56.4	kJ/kg
Heat of Evaporation	88	kJ/kg

2.3.2 Chemical properties of cadmium metal

When exposed to dry air cadmium is covered with a cadmium oxide layer. Since the formed layer protects the cadmium from further degradation, the most remarkable property of cadmium is its high resistance to corrosion. A cadmium carbonate layer is formed when excessive amounts of carbon dioxide are present in the air. In aerated water a cadmium hydroxide layer is formed.

Liquid cadmium reacts with dry hydrogen chloride or chlorine to form cadmium chloride. Melting cadmium in the presence of sulfur leads to the formation of cadmium sulfide. A similar behavior is observed with selenium. Since both reaction compounds are completely insoluble in the solid and the liquid phase of the other compound, this reaction is only possible at the interface of the melting phases. Cadmium sulfide is also formed by contacting cadmium vapor with hydrogen sulfide or by dissolving cadmium in hydrochloric acid solutions under addition of sulfur dioxide gas. In nitric acid it dissolves quickly, even at room temperature, under formation of nitrous oxides. At elevated temperatures cadmium dissolves quickly in all three solutions.

Alkali or alkali-like reacting solutions do not react with cadmium, although zinc is quite easily dissolved. This is caused by the fact that cadmium, unlike zinc, is not markedly amfoteric. Cadmium forms many other complexes with cyanides and halides.

2.3.3 The applications of cadmium metal and alloys

Cadmium has some applications in consumer products. In table 2.4 the main uses of cadmium metal and alloys in the Rhine River basin are summarized quantitatively [28,29,30,31,32]. It has been suggested to buy and store cadmium in its metallic form as a strategic product [33]. This storage inhibits a further uncontrolled spread of cadmium in the environment and on a long term enables the use of cadmium for those applications where no substitutes are available.

Table 2.4 Domestic use of cadmium metal in the Rhine River basin in ton

"year" period	1971 (1970–1972)	1975 (1973–1977)	1980 (1978–1982)	1985 (1983–1987)	1988 (1988)
plate FRG NL	512 60^1	354 50^1	261 5^1	140 3^1	72 2^1
alloys FRG NL	67 25^1	63 25^1	67 30^1	52 15^1	31 10^1
battery FRG NL	203 40^1	225 45^1	236 109^1	333 86^1	393 —

[1] estimates based on [30,31,32]

Cadmium metal is used in coating processes, during which a cadmium surface layer is attached to another (metallic) product. Cadmium is favorably used for corrosion protection because of its high corrosion resistance and its ease of processing which is caused by its high ductility, its good solderability as well as its durable brightness. These properties enable applications for e.g offshore equipment. Some applications of cadmium surface layers are given in table 2.5 [34].

Table 2.5 Some applications of cadmium surface layers [34]

car brakes products in use on offshore platforms central heating installations valves and appendages aircraft applications space applications electrolytic baths for chlorine/caustic soda production radar equipment radio equipment for military, aircraft and shipping purposes optical instruments hearing aids

Cadmium as a metal is also used in batteries. These batteries are divided in two categories: the "open", large size batteries, which are used for industrial and military purposes and the "closed" small size batteries (capacity 0.5 Ah). The small size batteries are usually applied in small domestic appliances, like flashbulbs for photographs, calculators etc. They contain 20 % cadmium by weight [35]. Both types of batteries have the unique property that they can be re-used. The chemical system which constitutes these batteries is reversible and thus by using an adaptor these batteries can be recharged. The chemical reaction of this system is [36]:

$$Cd + 2\ Ni\ O\ (OH) + 2\ H_2O \rightleftharpoons Cd\ (OH)_2 + 2\ Ni\ (OH)_2$$
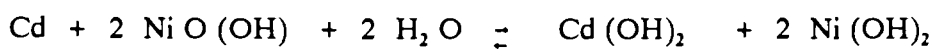
Moreover, relative to other types of batteries, NiCd-batteries have excellent technical properties:

-1- The battery's voltage-time curve is very flat. This means that most of the battery's capacity is supplied at its design voltage

-2- The battery can produce a very high current during a short time, which for instance is required for flashlights

-3- The battery loses its capacity during storage relatively quickly, even at 293 K, but can be easily recharged

-4- The battery is very well sealed against leakage

-5- The battery is suited for producing a relatively high current for a long time

-6- The battery is guaranteed to be rechargeable up to at least 500 times

Due to their long lifetimes, small NiCd-batteries are much cheaper to use than others, despite of their higher price. The costs per kWh are estimated to be only about 2 % (using 1982 figures) of the costs of zinc - manganese dioxide or alkaline batteries for the same purposes [35]. Nevertheless the specific cost per kWh for small NiCd-batteries is still two orders of magnitude higher than the specific cost of 220 V household electricity.

Cadmium alloys are used in applications where a low melting solder is required [10,36]. Especially Zn-Cd alloys are used for soldering aluminum [24]. The cadmium alloying behavior in general resembles that of zinc. Another important application of cadmium alloys is their use in low melting wires. These wires can be designed for any (melt-) temperature in the range of 313 to 393 K. Therefore they are applied as devices in tailor-made fire detection circuits. Cadmium -silver alloys are used in electrical and electronics industries, as well as in producing electrical contacts. The most common composition is 10 % cadmium oxide, dispersed in silver [21].

Currently cadmium-copper alloys dominate the market [9]. An alloy of cadmium (0.2 %) with copper has been applied since the late 1960's in automobile radiators to improve performance. For other purposes cadmium (0.5 to 1.2 %) is alloyed with copper to increase strength and wear resistance, e.g. in overhead wires.

In high speed and high temperature applications, which are too severe for tin or lead bearings, Cd-Ni- or Cd-Cu-Ag-alloys are employed.

Other applications include the use of Ag-In-Cd-alloys as control rods in nuclear reactors and CdS, CdSe and CdTe as semiconductors.

Cadmium is also used to improve the evenness of corrosion on zinc sacrificial anodes. Silver for chain making may contain up to 5 % cadmium.

2.4 The properties and uses of cadmium compounds

2.4.1 Introduction

Although many cadmium compounds are known, only a few are of commercial interest. Most of the cadmium salts are white or colorless and are easily dissolved in neutral or slightly acidic water. Table 2.6 shows the melting point, the boiling point and the solubility in water at 298 K of some cadmium compounds [11,12]. For the production of most industrial cadmium chemicals the metal is first converted into cadmiumoxide as an intermediate. Cadmium practically always has a plus two valency state in its compounds. Cadmium chemicals of importance are either inorganic or organic. The following two sections are based on reviews by Parker [37], Roskill [38] and others [11,21,39].

In Table 2.7 the applications of some cadmium chemicals are given. Category A 6) includes: pharmaceutical products, shampoos and polymer/rubber additives. Category C) includes: photography, lithography, engraving, photocopying, printing and dyeing. Category D) includes: fluorescence, flash powder, phosphors, pyrotechnics, and luminescence. Category E) includes: photodetectors, semi conductors, research, nuclear reactor control, infrared optics and radiation detection. Category F) includes: lubricants, fungicides, pesticides and heavy media mineral flotation. Table 2.8 gives an overview of the domestic use of different cadmium chemicals in the basin in time.

Table 2.6 Melting point, boiling point and solubility of
         some cadmium compounds

Cadmium compound	Melting point	Boiling point	Solubility
	K	K, 1 bar	kg/m^3 water
acetate	529		good
bromide	840	1136	570 − 1620
carbonate	decomp. 770		insoluble
chloride	841	1233	1400 − 1500
cyanide	decomp. 470		17
fluoride	1370	2031	43.5
hydroxide	decomp. 570		0.026
nitrate (hydrated)	332	405	2150
oxide (crystalline)	sublim.1663		insoluble
sulfate	1273		608 − 755
sulfide	sublim.1253	2023 (100bar)	0.0013

Table 2.8 Domestic use of cadmium compounds in the Rhine River basin in ton

"Year" period	1971 (1970−1972)	1975 (1973−1977)	1980 (1978−1982)	1985 (1983−1987)	1988 (1988)
pigment FRG	616	630	510	344	232
NL	—	100[1]	53[1]	27[1]	—
stabs FRG	283	304	402	287	241
NL	—	48[1]	24[1]	20[1]	—
others[2] FRG	162	155	163	127	77
NL	—	—	—	—	—

[1]   estimates based on [30,31,32] and unpublished results by Elgersma and Stigliani

[2]   For the period 1970 − 1990, pigments, plating, stabilizers, batteries and alloys
       together account for over 90 % of the domestic cadmium use in the FRG. For
       the other in-basin countries the situation is probably the same.

Table 2.7 The applications of some cadmium chemicals.

	7.) Miscellaneous	C.) Electronic & instrumental appl.	D.) Phosphors and related applications	C.) Photography & Printing	3. Glass/Ceramic Manufacturing	2. Batteries	B.) 1. Plating	6. Others	5. Catalysts	4. Stabilizers (s.)	3. Stabilizers (l.)	2. Intermediates	A.) 1. Pigments	Cd-compound	formula
														Inorganic	
		x						x						Arsenide	Cd₃As₂
		x												Arsenide	CdAs₂
			x	x				x						Fluoborate	Cd(BF₄)₂
			x											Bromide	CdBr₂
	x				x									Borate	a.CdO.m.B₂O₃
														Borate	2CdO.B₂O₃, WO₃.18H₂O
	x		x	x				x						Chloride	CdCl₂
								x						Cyanide	Cd(CN)₂
	x		x						x			x		Carbonate	CdCO₃
		x	x		x									Fluoride	CdF₂
													x	Hg-sulfide	CdS.HgS
			x	x				x						Iodide	CdI₂
	x		x		x				x			x		Nitrate	Cd(NO₃)₂
		x				x	x	x	x			x		Oxide	CdO
						x						x		Hydroxide	Cd(OH)₂
	x													Phosphide	Cd₃P₂
	x	x						x				x		Sulfide	CdS
	x													Antimonide	CdSb
	x		x									x		Selenide	CdSe
		x							x					Silicate	CdSiO₃
		x							x					Silicate	Cd₂SiO₄
		x	x	x	x							x	x	Sulfate	CdSO₄
	x	x												Telluride	CdTe
		x							x					Tungstate	CdWO₄
														Organic	
			x	x				x		x	x			Acetate	
								x		x				Benzoate	
										x				Diethyl	
										x				Decanoate	
									x					Laurate	
									x					Myristate	
										x				Naphtenate	
										x				Octanoate	
									x					Palmitate	
x														Pentachloro-phenate	
										x				Phenolate	
									x					Ricolinate	
									x					Stearate	
x														Succinate	

2.4.2 Inorganic cadmium compounds

Arsenide

The cadmium arsenides are n-type semiconductors and have a high electron mobility. The main preparation step is either the heating of stoichiometric amounts of cadmium and arsenic in an inert atmosphere or the precipitation of ammoniacal cadmium sulfate solutions with arsine.

Fluoborate

Cadmium fluoborate only finds application in plating. It is used for cadmium electrodeposition on high strength steels, avoiding the hydrogen embrittlement involved in cyanide plating.

Bromide

Cadmium bromide, chloride and iodide are characterized by their partly covalent bonds. These halides are soluble in ethers, alcohols, ammonia and water. Anhydrous cadmium bromide is prepared by either a direct combination of the elements at elevated temperature or by mixing dry cadmium acetate with glacial acetic acid and acetyl bromide. It is also possible to dehydrate the tetrahydrate modification by calcining at 473 K. The tetrahydrate modification is easily formed by dissolving cadmium oxide in bromine water.
Cadmium bromide is applied in the manufacture of photographic films on a gelatin base, in photographic colloidon and in pyrotechnics.

Borate

Cadmium borate possesses fluorescent and phosphorescent properties. For this reason these compounds have been used for TV-screens and as a component of the coating powder. Borotungstate solutions with densities up to 3280 kg/m^3 are used for heavy media flotation of minerals.

Chloride

Cadmium chloride is formed through reacting chlorine or hydrochloric acid with metallic cadmium or cadmium oxide. It is also formed during zinc concentrate roasting if any sodium chloride is present. Other possible preparations include the reaction of hydrochloric acid with cadmium metal, carbonate, sulfide, oxide or hydroxide in aqueous solution, or the addition of dry cadmium acetate to a mixture of glacial acetic acid and acetyl chloride. The chloride is stable in air to 870 K. Under normal conditions of temperature and humidity, dicadmium chloride pentahydrate is stable.

Apart from the applications in photocopying, printing, photography and dyeing, cadmium chloride is used in metal finishing baths, because of its good throwing power and bright deposits. It replaces cadmium cyanide plating where the cyanide emissions are a particular problem.

The chlorides have found applications as phosphors, pesticides and as non-pasture turf fungicides. Cadmium chloride aerosols are among the most toxic cadmium compounds and should be handled with great care.

Cyanide

Cadmium cyanide has found major applications in cadmium plating, although their use has decreased significantly during the past decade, because of environmental risks.

Carbonate

Cadmium carbonate is obtained by addition of sodium, potassium or ammonium carbonate to a cadmium sulfide or chloride solution. It is used as an intermediate for the manufacture of other cadmium compounds and as a catalyst. It has also been used as a specialty fungicide.

Fluoride

Cadmium fluoride has an ionic structure. A cadmium fluoride solution is formed by the dissolution of cadmium carbonate in strong hydrofluoric acid. The pure fluoride is obtained by evaporating the so formed solution, followed by vacuum drying at 423 K.

Cadmium fluoride is also directly prepared by reaction of fluorine or hydrofluoric acid with either cadmium metal or with cadmium compounds such as the oxide, the sulfide and the chloride. The fluoride finds application as phosphor, as fluorescent, in electronics research and in nuclear reactor control.

Mercurous sulfide

Cadmium/mercury sulfide mixtures have been popular as pigments, due to their characteristically bright colors. For environmental reasons their use has been practically eliminated.

Iodide

Cadmium iodide is prepared by either dissolving cadmium metal, oxide, hydroxide or carbonate in hydroiodic acid or by heating the elements in an inert atmosphere. Cadmium iodide finds application in photographic collodion, catalysis and in pyrotechnics.

Nitrate

Three different cadmium nitrate modifications exist: the anhydrate, the di- and the tetrahydrate. The preparation method is the nitric acid digestion of cadmium metal, oxide, hydroxide or carbonate, followed by crystallization.

The nitrate has diverse applications. Its main use is starting material for the production of cadmium hydroxide which is used in NiCd-batteries. Minor uses are colorants for the ceramic industry, as flash powder with magnesium and as fungicide. It is or has been used as an intermediate for the manufacture of cadmium yellow pigments.

Oxide

Cadmium oxide is commercially formed by the reaction of cadmium metal vapor with air. The particle size distribution of the product is controlled by adjusting the ratio of cadmium over air. If required it is calcined to obtain uniform physical properties. Other synthesis routes include oxidation of the sulfide and thermal decomposition of carbonate, nitrate, sulfate or hydroxide. The heating of cadmium formiate or oxalate in an inert atmosphere results in a very fine powder. Cadmium oxide is a n-type semi conductor. In contrast to zinc oxide, cadmium oxide is not soluble in aqueous alkali solutions.

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The main use of cadmium oxide is as an intermediate for organic and inorganic cadmium compounds. Other major uses are cadmium plating and battery manufacture. It is also used as a catalyst and as an additive in nitrile rubbers and engineering plastics to improve their high temperature properties.

Hydroxide

Cadmium hydroxide is formed as amorphous white powder when precipitated from cadmium nitrate and sodium or potassium hydroxide. In an ammoniacal solution it is precipitated in a hexagonal crystalline form. The two applications of the hydroxide salt are intermediate for the production of other cadmium containing compounds and the use in NiCd-batteries as active anode material.

Phosphide

Cadmium phosphides are prepared by the direct union of cadmium with phosphorus in the desired ratio. Another synthetic route is the reaction of phosphine with solutions of cadmium salts. The phosphides are n-type semiconductors. In cadmium phosphides laser action is observed.

Sulfide

Cadmium sulfide is commercially and quantitatively the most important cadmium compound. Synthesis routes for the sulfides include the reaction of cadmium vapor and hydrogen sulfide at 1070 K or the reaction of cadmium or cadmium oxide with sulfur during heating. However, the usual preparation is carried out by precipitating the sulfides by adding sodium sulfide or hydrogen sulfide to a cadmium salt solution. By controlling the reaction circumstances and the cadmium salt either red of yellow modifications are obtained.

Cadmium sulfides are used as brilliant pigments with excellent physical properties. Other uses include fluorescent and phosphorescent pigments and soaps. It is also used, because of its semi conductor properties, in solar cells, radiation detection and the like.

Antimonide

Cadmium antimonide is formed directly from the elements. Monocrystals exhibit hole-type conductivity. It is a thermoelectric generator finding application in electronics.

Selenide

Cadmium selenide is a n-type semi conductor. It is made by the direct union of the elements at elevated temperatures or by precipitating the selenide from a cadmium salt solution by using either alkali selenide solution or hydrogen selenide gas. Cadmium selenide is a strongly colored pigment, which in mixtures with cadmium sulfide forms the so-called sulfoselenide group of pigments. Minor applications include the use as coloring agent in glass manufacture and the use in photocells.

Silicate

Cadmium silicates are formed either by reacting cadmium oxide with amorphous silicon or silica under pressure at 663 K or at 1170 K at atmospheric pressure. The silicates are fluorescent and phosphorescent and, after activating with traces of manganese ions, they are used as phosphors. They are also used as catalyst.

Sulfate

Cadmium sulfate solutions are prepared by dissolving cadmium metal, oxide, sulfide, hydroxide or carbonate in sulfuric acid. The precipitate is obtained by crystallization, if necessary using alcohol as salting-out agent.
Oxidation of cadmium sulfide at elevated temperatures yields anhydrous cadmium sulfate. The anhydrous modification is also obtained by the reaction of dimethylsulfate with finely powdered cadmium nitrate, halide, oxide or carbonate.
        Cadmium sulfate decomposes at 1100 K under sulfur dioxide emission.
Cadmium sulfate is used as an alternative to cyanide plating baths. Other applications are the use as pigment (intermediate), as intermediate for stabilizer production and as phosphor. It has been used in some pharmaceutical applications, which are now abandoned.

Telluride

Cadmium telluride is a n-type semiconductor, which is either prepared by the direct union of the two elements at high temperature or from solutions of cadmium salts by adding either hydrogen telluride gas or sodium telluride solution. Cadmium telluride is used in phosphors, photocells, as detector for nuclear radiation and in infrared optics.

Tungstate

Cadmium tungstate is a fluorescent compound which is used as such in X-ray screens and phosphors. It is also used as a catalyst in organic chemistry.

2.4.3   Organic cadmium compounds

Although a huge number of organic cadmium chemicals are known, only few have found any practical application. Two main applications are distinguished: catalysis and stabilizing of polymers.

Catalysis

In catalysis dialkyl- or diaryl cadmium compounds are in use. Dialkyl compounds are thermally less stable than organozinc or organomercury compounds. They are decomposed by light at room temperature, they react with air and water and in some cases ignite.
        The synthesis of these compounds is carried out by the reaction of cadmium halides with Grignard reagents, followed by distillation. They are used as polymerization catalysts and for

these purposes are made in situ, mostly for specialty chemicals. Diethylcadmium is also used as a catalyst for the polymerization of vinyl chloride, vinyl acetate and methyl methacrylate.

Stabilizers

The cadmium salts of organic acids are used as heat and light stabilizers in plastics like poly (vinylchloride). PVC-compounds degrade during processing at about 368 K by emitting hydrochloric acid and forming an unsaturated bond which is reactive and can cause further degradation. The emission of hydrochloric acid also causes discoloration (yellowing). Cadmium soaps are most frequently used in combination with barium soaps, which have complementary properties. Cadmium soaps prevent early discoloration whereas barium soaps are more helpful in preventing longer term degradation. The cadmium/barium soaps also improve the high temperature (processing) properties of the polymer in which they are applied. Their use provides better control of the rheology of the mixture and the reduction of the quantity of off-spec products. Due to their higher price and the environmental risks involved in using cadmium containing stabilizers, the cadmium stabilizers gradually lost their market share. The use of cadmium stabilizers is now limited to a few specific applications in which the substitution of cadmium stabilizers would lead to a serious worsening of the properties of the polymer. The major remaining application is the use in outdoor PVC window profiles.

The preparation of cadmium soaps is as follows. A suspension of cadmium oxide in a mixture of the organic acid and an inert organic solvent is heated during which an acid-base reaction slowly takes place.

The solid stabilizers include the soaps of lauric, myristic, palmitic, ricolinic and stearic acids. The liquid stabilizers are acetic, benzoic, decanoic, naphtenic, octanoic and phenolic acid soaps.

Apart from being used as a stabilizer, cadmium acetate is also used as intermediate for the manufacture of cadmium halides and finds application as colorant in glass, ceramics and textiles and as a catalyst.

Both cadmium pentachlorophenate and succinate are reported to be used as fungicides to protect cloth, wood and turf, particularly on golf courses.

2.5 Cadmium as environmental pollutant

2.5.1 Introduction

The environmental pollution of cadmium is known to have mainly an anthropogenic origin [41]. The annual cadmium discharge into the world's ecosystems is estimated to be of the order of magnitude of 39 kiloton/year (median value), whereas the overall cadmium emission due to natural sources is estimated only to be 1 kilotons/year.

Since, unlike many other heavy metals, cadmium is non-essential to life and possesses hazardous properties, it has all features required to become a priority substance to study. Despite of the fact that the toxic properties of cadmium have been known for a long time, it took a disaster to raise consciousness of its danger to humans. Cadmium originating from the effluent of a zinc smelter ended up in the food chain, causing the so-called "itai-itai" or "ouch-ouch" disease in which many inhabitants from a nearby village were afflicted. The event triggering public awareness occurred in Japan in the period 1945 - 1966.

This section will briefly discuss the human and ecological toxicity of cadmium and the risks involved in increasing the concentration of bio-available cadmium on earth.

2.5.2 Risks involved in human exposure

The human exposure to cadmium levels which have increased with relation to the natural background forms a direct risk to humans, since that there is a precarious margin of safety between natural background levels of intake and levels at which chronic toxic effects may be induced [38]. This was one of the conclusions based on the epidemiological research carried out after the outbreak of itai-itai disease in Japan. Human risks are both involved in cadmium exposure to a slightly higher concentration during a prolonged period of time, or to a high peak dosage which only occurs once. The two different possibilities will be discussed separately.

Acute cadmium poisoning

After acute oral poisoning with a high cadmium dosage (e.g. more than 0.35 gram) a healthy adult will die within 24 hours as a consequence of shock caused by dehydration. At lower doses the patient dies 7 to 14 days after the dosage, it is most frequently caused by kidney malfunctioning. Doses in the range of 3 to 350 mg can cause non-lethal diseases. Single doses below 3 mg are not believed to cause direct effects.

Inhalatory poisoning by exposure to 2500 mg/m^3 during 60 seconds or to 5 mg/m^3 during 8 hours will lead to breathing problems. As a consequence of the cadmium contamination, severe lung diseases are to be expected, which might be fatal. A no-effect level for 8 hours exposure is probably lower than 1 mg/m^3 for cadmium oxide vapor and lower than 3 mg/m^3 for respirable dust.

Chronic cadmium poisoning

Cadmium risks to human beings are nowadays almost exclusively related to chronic exposure, since acute poisoning, typically an industrial phenomenon of the past, has diminished due to increasing safety and hygiene standards.

Chronic cadmium exposure was one of the causes of the itai-itai disease in Japan and is currently one of the reasons that large populations in the direct surroundings of former (heavy metal) mining districts or (former) thermal smelters are not allowed to eat the vegetables they grow in their gardens. This is the case in (former) mining districts in a.o. England and Czechoslovakia as well as in the neighborhood of a former thermal zinc smelter in The Netherlands.

The resorption rate for oral uptake of humans with no diet deficiency is about 6 %. With some diet deficiencies, as for instance calcium, protein and vitamin shortage, it may increase up to 10 %. It is not clear how the resorption mechanism works and until 1984 no research had been carried out to define these chemical forms from which cadmium was more easily absorbed and those that were more inert [42].

For cadmium intake via breathing the resorption rate is estimated to be around 70 %, based on calculations carried out with smokers. Smokers, who smoke 25 cigarettes a day, increase their daily cadmium intake by 20 to 50 %. The relationship between cadmium and smoking is a consequence of the accumulation of cadmium available from the soil in tobacco plants. In general the intake via breathing in non-contaminated areas is less than 1 % of the total human intake.

The typical risk of cadmium intake is the fact that the biological half life time of the resorped part in human bodies is estimated to be between 10 and 30 years [43]. Therefore even small chronic exposures might in the long term present health consequences, due to accumulation. The lungs and the kidneys are the most sensitive organs to cadmium in the human body.

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The human body has a natural defense against cadmium. A small protein called metallothionein, is found in kidneys and binds cadmium well. Cadmium is stored in the kidneys in this way. The human body's defense is not prepared to store large dosages at once and has only limited overall storage capacity. For this reason especially old people are susceptible.

A lot of research has been carried out to describe cause and effects patterns with people that have been exposed to small amounts of cadmium for a long period. Unfortunately, it is very difficult to come to clear conclusions. This is caused by the fact that so many other health impacting factors differ over such a long time especially with regard to the size of the group that has to be checked, in order to obtain statistically sound results.

In 1980 the World Health Organization proposed a weekly maximum allowable dose of 0.4–0.5 mg Cd/person [44].

2.5.3 Environmental risks related to cadmium

Terrestric organisms

The intake and toxicity of cadmium is strongly influenced by factors affecting the bio-availability of the cadmium, like the pH, the organic matter content, the exchange potentiality for cations, the clay content, the presence of other metals, etc. The bio-availability is larger with a lower pH, a lower organic matter content and on a sandy soil. Small soil animals have no-effect levels ranging from 0.5 to 10 ppm Cd in dry soil.

The cadmium concentration of plants, originating from soil which has been polluted with 0.7 to 1.5 ppm cadmium, is still below the accepted limits for human consumption. Wheat and tobacco have relatively high uptake rates. Using strongly contaminated sewage sludge as fertilizer, containing 86 ppm Cd, for a prolonged period, leads to an increased cadmium uptake by the crops. This is not the case for sewage sludge which is polluted with less than 10 ppm Cd. Applying contaminated fertilizers resulting in a cadmium load of 13.5 - 40 mg/m² does not lead to a significant increase of cadmium uptake by the crops [20].

The intake of cadmium by domestic animals leads to accumulation in the kidneys and the livers. Cow feed containing 1.6 ppm Cd during 28 months leads to a cadmium concentration in the liver of 1.5 ppm and in the kidneys of over 6 ppm, however, without any biological damage being detectable. Biomagnification of cadmium in an animal food chain has not been detected.

In summary this part is concluded by the statement that a no-effect level for cadmium seems to exist, but that even minor increases in the natural background level, especially on sandy based soils, may have serious negative effects on the exposed ecosystem.

Aquatic organisms

The highest bio-availability and toxicity for aqueous species in salty water occurs with the highest temperature and lowest salt content. In non-salty waters a low concentration of calcium and magnesium and a low pH increases the toxicity, because the probability for cadmium/calcium exchange in vital functions gets proportionally higher. At low calcium and magnesium concentrations cadmium is already acutely poisonous to trout and salmon at concentrations around 1 ppb. The toxicity decreases at higher calcium and magnesium concentrations.

Salt-water organisms have a higher tolerance; typically acute effects occur at 10 − 20 ppb. This is caused by the lower bio-availability of cadmium in sea water. Algae, living in salty water, concentrate cadmium in their tissue up to more than three orders of magnitude, with respect to the salty water concentration of cadmium. Fish, living in non-salt water, concentrate cadmium up to one hundred times. Since the limit for human fish consumption is 50 ppb Cd (on fish weight basis) fish consumption is only allowed from waters that contain below 0.5 ppb cadmium.

The river Rhine in 1987 had an average concentration of 0.1 ppb at Lobith, so there is only a small margin of safety. In 1986 and 1987 the 0.5 ppb Cd concentration was passed three times in total [45].

2.5.4   Risks on a global scale

The Dutch committee for long term environmental policy (planning) has recently issued a report [33], based on a workshop entitled " To a cadmium-free society ". This report describes the tools for policy makers to avoid the steady increase of bio-available cadmium slowly moving from the boundary of the natural background concentration to the boundary concentration which is connected with chronic, irreversible environmental and thus human effects.

Although in many cases a closed loop material recycle from an environmental and a resource point of view would be most desirable, this is not the case for cadmium. The reason for that is the steady input of cadmium to the bio-available reservoirs by utilizing zinc concentrate which contains cadmium as a natural impurity. No closed loop can then be created since the input, linked to zinc winning and to a minor extent, to phosphoric acid production, is not directly controllable.

Facing the fact that the cadmium supply is inelastic, a cadmium containing product policy which is directed towards avoiding the use of cadmium, on a global scale, is ineffective, since the cadmium that does enter the loop has to end up somewhere. A policy that makes more sense is the use of cadmium in those applications and products where the risks involved in applying it are minimized. That is quite another optimization criterion than trying to ban the use per se. The new criterion leads to the following potential measures:

-1-   The product policy should be focussed on controlling the cadmium in the loop, e.g. the possibilities for recycling. This means that the dissipative uses of cadmium should be abandoned, whereas the use in batteries should be encouraged, under the strict constraint that a good recycling infrastructure is available.

-2-   Used batteries that are recycled would reintroduce cadmium back into the loop. Due to the inelastic supply, the width of the cadmium loop would thus continue to increase, and with it the environmental risks involved. It is therefore advocated to store e.g. used batteries safely and controlled as a strategic material. For that purpose also primary cadmium metal can be used which is a finite resource, worth preserving for essential applications for future generations.

-3-   The best strategy to reduce the cadmium supply is to reduce the global use of phosphate and zinc ore. Increasing process efficiencies and non-dissipative, recyclable uses of these commodities are desirable in a sustainable world anyway.

3   IN-BASIN MONITORING DATA FOR AQUATIC CADMIUM POLLUTION

3.1   Introduction

This section contains a short overview of the aquatic cadmium pollution as measured in the River Rhine and its main tributaries. The source of the data were the annual reports of the "International Commission for the Protection of the Rhine" (ICPR) and the German

Commission "Deutsche Kommission zum Schutz des Rheins gegen Verunreinigung" (DKSR).

These data-bases include monitoring cadmium data obtained during the period 1973 - 1987 at six different locations which are shown in table 3.1. Four stations took samples from the River Rhine, whereas two stations took samples from the tributaries Moselle and Main. Sampling data from other tributaries are rare. However, some available data are presented in the next section. No sampling data taken in The Netherlands have been used, since in the Dutch part of the Rhine basin pollution accumulation in the sediments occurs.

Table 3.1   The monitoring stations from which data have been used for further analysis

Rhine	Moselle	Main
Village-Neuf Seltz Koblenz Bimmen/Lobith	Koblenz	Kostheim

Obviously, monitoring data present the overall load to the river. This overall load as such is not specified into source categories. However, a statistical technique developed by Boehme and Behrendt in 1991 [46 a,b] enables the discrimination, within a given uncertainty range, between point-source and diffuse source discharges. It should, however, be realized that point sources include not only industrial emissions, but also emissions from (municipal) waste water treatment plants.

Discussing the statistical techniques as such is beyond the scope of this paper. For further details is referred to the work of Behrendt and Boehme [46 a,b]. In the next section their results for cadmium in the Rhine River basin are presented.

3.2   Cadmium monitoring data in the Rhine River Basin

Table 3.2, which is derived from ref. [46 a,b], presents the overall load of the river. The origin of the pollution is discriminated into point and non-point sources. Figure 3.1 gives a graphical representation of the data.

Data presented by Schleichert [47] are given in table 3.3. Data for the River Ruhr were obtained by Imhoff et.al. [48]. The figures which are given in table 3.3 represent the load of the tributaries to the Rhine. This load is significantly different from the cadmium discharge to the tributary. This is shown in table 3.4 for the River Ruhr.

The data presented in the tables 3.2 and 3.3 are in good agreement.

In general it is assumed that in the German part of the River Rhine no nett accumulation in the sediment occurs. This is somewhat contradicted by the monitoring data obtained at Seltz and Koblenz in the period 1978 - 1982. These data show that the measured cadmium load in the River Rhine decreases between Seltz and Koblenz in that period. This implies that some sedimentation has taken place in between the two stations.

All monitoring data for point source discharges are summarized in table 3.5. The sequence of the stations in the table corresponds to the sequence along the river, going downstream. From table 3.5 it is obvious that the significant point-source cadmium emissions to the Rhine have taken place between Koblenz and Lobith.

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Table 3.2   The Cadmium Monitoring Data for the Rhine River basin for the
period 1973 — 1987 [46 a,b]

	load t/a	point source	diffuse source
1973–1977			
Koblenz (R)	25	2 − 7	17 − 22
Lobith	145	109 − 123	22 − 36
Koblenz (M)	4.7	0.2 − 0.7	4.0 − 4.4
1978–1982			
Village–Neuf	4.7	0	4.7
Seltz	38	23 − 38	9 − 15
Koblenz (R)	24	6 − 9	16 − 18
Lobith	96	72 − 77	19 − 24
Koblenz (M)	4.1	0.4 − 0.6	3.5 − 3.7
1983–1987			
Village-Neuf	0.9	0	0.9
Seltz	7	1 − 2	5 − 6
Koblenz (R)	9	——	——
Lobith	20	6 − 9	11 − 14
Koblenz (M)	1.9	——	——
Kostheim	2.5	0.6 − 1.0	1.5 − 1.9

Table 3.3   Monitoring data for the Rhine River basin in 1976 [47]

River	Cd load (ton/year)
Rhine	
Koblenz	20
Lobith	135
Moselle	
Koblenz	2
Main	12
Neckar	4

Table 3.4   A Cadmium balance for the River Ruhr [48]

Sources of Cadmium	(ton/yr)	
Industrial discharges	6.6	
Domestic waste water	0.3	
Influent to waste water plants	6.9	
remaining in sludge	3.0	
Effluent from waste water plants to Ruhr		3.9
Storm water discharge		0.3
Surface Runoff		0.3
Wells and Groundwater		0.3
Sum		4.8

Sinks of Cadmium	(ton/yr)	
Accumulation in sediments		1.5
Processing and abstraction of drinking water		0.9
Effluent to the River Rhine		2.4
Sum		4.8

Table 3.5   The Cadmium point source pollution in the River Rhine in ton/yr

location	1973–1977	1978–1982	1983–1987
Village-Neuf (R)	—	0	0
Seltz (R)	—	23 – 28	1 – 2
Neckar[1]	4[2]	—	—
Main[1]	12[2]	—	0.6 – 1.0
Koblenz (R)	2 – 7	6 – 9	—
Koblenz (M)	0.2 – 0.7	0.4 – 0.6	—
Ruhr[1]	—	2[3]	—
Lobith (R)	109 – 123	72 – 77	6 – 9

[1] the tributaries were sampled at the point where they enter the Rhine

[2] overall load (diffuse sources included)

[3] based on [48]

For the period 1973 – 1977 the cumulative point source emissions at Koblenz, after the Moselle and the Rhine are joined, amount approximately 5 tons of cadmium. At Lobith this cumulative emission equals approximately 115 tons of cadmium. This shows that in this particular period between Koblenz and Lobith cadmium point source emissions up to about 110 tons have taken place.

For 1978 – 1982 the emissions still equal about 67 tons. For 1983 –1987 the figures for Koblenz are available. Data for Seltz are used instead. These data show that between Seltz and Lobith around 6 tons of cadmium by point sources. Summarizing these figures:

area	period	emission
Koblenz - Lobith	1973 – 1977	110 ton Cd
"	1978 – 1982	67 ton Cd
Seltz - Lobith	1983 – 1987	6 ton Cd

This shows the enormous decrease of the cadmium point source emissions in time in the Rhine River basin, upstream of Lobith.

Conclusively for 1989 data for the tributary discharges to the Rhine were measured by the International Centre for Water Studies (ICWS) in Amsterdam. These data are presented in table 3.6.

Table 3.6 Tributary discharges to the River Rhine in 1989 [49].

Tributary	Cadmium load (ton/yr)
Neckar	0.6
Main	0.5
Nahe	0.4
Lahn	0.3
Moselle	1.2
Sieg	0.2
Wupper	0.1
Erft	0.1
Ruhr	0.3
Emscher	0.1
Sum	3.8
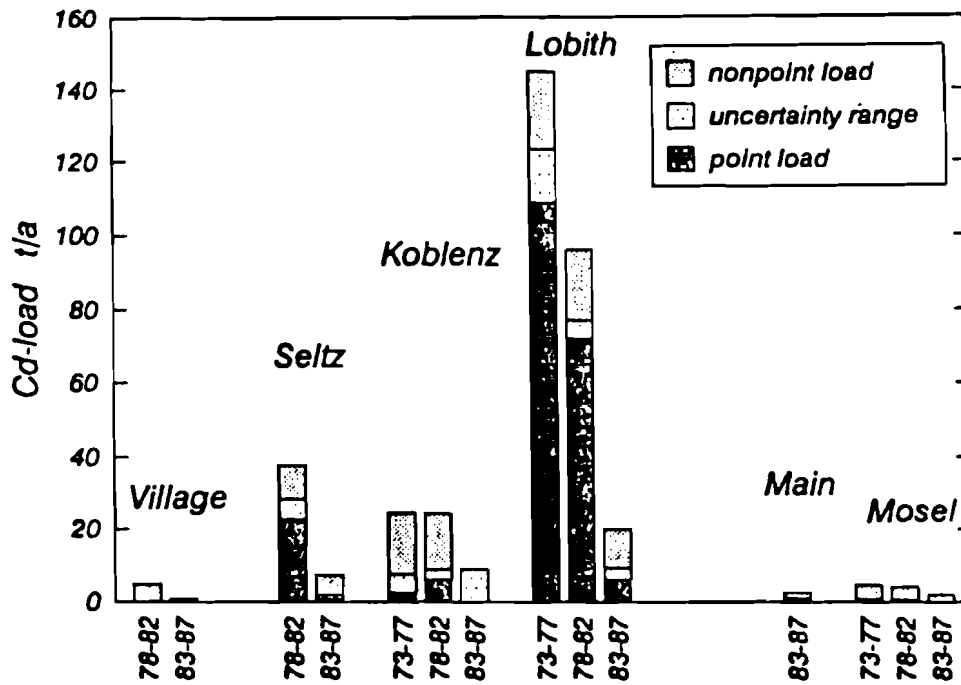
Figure 3.1   The cadmium monitoring data for the Rhine River basin in time, as processed by Behrendt and Bohme (46).

4 EMISSION FACTORS FOR RELEVANT INDUSTRIAL ACTIVITIES INSIDE THE BASIN

4.1 Introduction

This section provides emission factors for those individual activities that are responsible for the major part of the aqueous cadmium emissions in the Rhine River basin. The individual branches are mentioned in Section 1.5 and are discussed in more detail now.

4.2 Mining Industry

4.2.1 Non Ferrous Mining

In the Rhine River basin 3 non−ferrous metal mines were operational in the period 1970 − 1990. The Zn and Zn/Pb concentrate production data for these mines were obtained from the literature and are summarized in table 4.1 [38,50,51,52,53,54,55,56,57,58,59]. Despite the large number of sources, it has been hard to obtain all required data, because the data were very fragmentary. The in-basin non-ferrous mine production is summarized in Table 4.2.

Environmental Resources Ltd. has claimed [8] that on an EC-basis no serious estimates can be made of the aqueous cadmium emissions caused by the non-ferrous mining industry. To justify that statement the following arguments are given:

Uncertainties, per location, exist on:

- the proximity of mines and spoil deposits to flowing water,
- the nature of the underlying geology,
- the prevailing rainfall pattern,
- the historical legacy of previous mining activities and,
- the windblown dust transport to adjacent agricultural land and water.

Hutton [9] states that waterborne dispersal is the major route of cadmium loss from non-ferrous metal mines. Van Wambeke, cited in Hutton [9], estimates aqueous mine emissions for non-ferrous mines in the EC to be ranging from 60 to 150 tons/yr. The FRG's share of the total capacity of non-ferrous mining in the EC is 0.294 [38] in 1977. This would mean that the aqueous emissions due to non-ferrous mining in the FRG would have been 18 - 44 tons/yr. Taking into account that approximately 60 % of the non-ferrous mining production in the FRG [38] was inside the basin in the mid 1970's, the emissions would equal 11 - 26 tons/yr.

Based on this, the specific emission factor for non-ferrous mining for the period 1973 - 1977 would be 74 − 176 g Cd / ton Zn concentrate. Assuming the cadmium concentration in zinc concentrates to be 0.3 % this aqueous cadmium emission would require the loss of 3700 − 8700 tons of concentrate, which equals 2.5 − 5.9 percent of the production. These amounts seem to be far too large.

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Table 4.1 Non-ferrous mine production in the Rhine River basin from 1970 − 1990

Mine	Annual production of ton Zn or Zn/Pb conc.
Luderich Zn/Pb concentrate 1970 − 1972 1973 − 1977 1978 − 1982 1983 − 1987	 26,000 28,000 25,000[1] no data
Ramsbeck Zn concentrate 1970 − 1972 closed 1974	 30,000[1]
Lennestadt Zn concentrate 1970 − 1972 1973 − 1977 1978 − 1982 1983 − 1987	 90,000[1] 120,000[1] 100,000[1] 100,000[1]

[1] estimate based on incomplete data

Table 4.2 In basin Zn and Pb/Zn concentrate mine production between 1970 and 1987

Period	In-basin concentrate mining (ton/yr)
1970 − 1972	146,000
1973 − 1977	148,000
1978 − 1982	135,000
1983 − 1987	100,000

Von Roepenack claimed [60] that in 1977 the Lennestadt mine caused an aqueous discharge of 0.29 ton cadmium. Relating this figure to a production of 120,000 ton Zn-concentrate the emission factor equals 2.4 g Cd/ton Zn-concentrate. This estimate is used in this study for the periods 1970 − 1972 and 1973 − 1977. Since all other estimates are much higher, the emission factor as well as the aqueous emission might have been higher.

For the period 1978 − 1987 an emission factor of 1 g Cd / ton Zn-concentrate is used.

The choice for 1978 as discontinuity point in the emission factor estimation is made, because by then the West German government started to work out the so-called "Altlastsanierungsplan" which was meant to decrease a.o. heavy metal water pollution.

In summary this leads to the following discharges which are ascribed to non-ferrous mining activities in the basin:

period	production	factor	emission
1970 — 1972	146,000 ton/yr	2.4 g Cd/ton	0.4 ton
1973 — 1977	148,000 ton/yr	2.4 g Cd/ton	0.4 ton
1978 — 1982	135,000 ton/yr	1 g Cd/ton	0.1 ton
1983 — 1987	100,000 ton/yr	1 g Cd/ton	0.1 ton

4.2.2 Other in-basin mining activities

Two other mining activities are relevant in the basin. These are coal mining and salt mining. The only available data on coal mining are presented by ICWS [49]. ICWS reported for 1989 an aqueous cadmium emission, directly to the Rhine, of 30 kg/yr. Based on this figure, this branch was not regarded significant enough to warrant further analysis.

In the ICWS inventory [49] direct emissions to the River Rhine caused by salt mining have also been given. For 1989 these emissions equal 0.52 ton/yr. The emissions are located in the French part of the basin [49]. In order to backcast these emissions for the 1970's a linkage between the point source chloride discharge to the River Rhine and the cadmium emissions due to salt mining is made. This is justified by the fact that the salt discharges are related to natural salt resources with an assumed constant composition.

For the mid 1980's the emissions are calculated using the following data:

- the cadmium discharge is 520 kg/yr and assumed constant since the mid 1980's.
- the point source chloride discharges between the monitoring stations Village-Neuf and Seltz are assumed to be caused by this specific mining operation. These discharges amount 130 kg/s for 1983 — 1987 [46].

For the period 1973 — 1977 the point source chloride discharge between Village-Neuf and Seltz is 114 kg/s and for 1978 — 1982 it equals 133 kg/s. Assuming a linear proportionality between the chloride and the cadmium discharges the following data - in summary - are obtained:

Period	Chloride discharge (kg/s)	Cd-emission (ton/yr)
1973 — 1977	114	0.46
1978 — 1982	133	0.53
1983 — 1987	130	0.52

The proportionality constant is 0.13 g Cd/ton Cl⁻. Assuming the discharged salt to be NaCl this constant equals 0.08 g Cd/ton salt. Given the average cadmium concentration in the earth's crust which is between 0.1 and 0.5 g/ton [24] this figure seems to have the right order of magnitude.

4.3 Primary zinc industry

The aqueous cadmium emission of the primary zinc industry is strongly depending on the type of winning process that is being applied. Significant differences exist between electrolytic and thermal zinc winning plants.

In the basin an Imperial Smelting Furnace plant is located in Duisberg and an electrolytic plant is located in Datteln along the Dortmund — Ems canal. In table 4.3 the production of zinc and lead of these plants for the period 1970 — 1987 is given [55,56,57,58,61].

Table 4.3 In-basin primary zinc and lead production in ton/yr for the period 1970 — 1987

Plant	Zinc (ton/yr)	Lead (ton/yr)
Datteln electrolytic plant		
1970 — 1972	110,000	
1973 — 1977	105,000	
1978 — 1982	96,700	
1983 — 1987	103,000[1]	
Duisberg imperial smelting furnace	84,000	38,000
1970 — 1972	67,000	30,300
1973 — 1977	65,500	29,600
1978 — 1982	69,200[1]	31,300
1983 — 1987		

[1] estimate based on incomplete data. For this estimate the ratio of the individual plant production over the FRG production for the period 1978 — 1982 is calculated. For 1983 — 1987 the plant production is calculated by multiplying the production ratio (plant/FRG) for that period with the entire FRG production for that period.

Hutton [9] requested individual zinc winning companies to estimate their cadmium emissions. The Duisberg plant claimed to emit 1 ton/yr of Cd in 1979. With a production of 65,500 tons zinc this leads to the following emission factor: 15 g Cd / ton Zn for 1979.

However, the cadmium emission is caused by an Imperial Smelting Furnace, which is a lead and zinc winning plant at the same time. These plants process lead/zinc concentrates in one pyrometallurgical process. The emission of 1 ton cadmium for 1979 should thus be divided over the lead and the zinc production. The production capacity for lead was 29,600 tons in 1979. If the emission factor for lead winning (aqueous cadmium emission 8.3 g Cd/ton lead produced [8]) is used, the emission due to lead winning is (29,600 * 8.3 =) 246 kg/yr. Due to zinc winning the remainder, 754 kg Cd, is emitted. This leads to the following emission factor: 754 kg Cd/ 65,500 ton Zn = 11.5 g Cd/ton Zn.

This approach is rather artificial since lead and zinc winning are closely linked in an ISF-plant. A better approach is to add the lead and zinc production and then calculate an overall

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emission factor. Thus, 1 ton Cd is emitted as a consequence of the production of 95,400 ton lead and zinc. The emission factor then is 10 g Cd/ton (Pb+Zn) for 1978 − 1982.

For the periods 1970 − 1972 and 1973 − 1977 the emission factors have probably been higher. No literature sources are available to justify this statement. However, the monitoring data indicate that a considerable reduction of point source emissions has been realized from 1975 to 1980. Therefore it is assumed that the ratio of point source emissions in between Koblenz and Lobith for 1973 − 1977 (110 tons) and for 1978 − 1982 (67 tons) is representative for the technological improvement in this branch. Using these data an emission factor for 1970 − 1972 and for 1973 − 1977 is obtained. The factor equals (110/67 * 10 =) 16 g Cd/ton (Pb + Zn).

For thermal plants the emission factor for the period 1980 − 1990 is obtained by using data supplied by ICWS [49] and a document issued by the Deutsche Kommission zur Reinhaltung des Rheins [62].

In 1985 the cadmium emission for the ISF-plant is estimated to be equal to 480 kg [62]. Given a production capacity of 69,200 tons zinc and 31,300 tons lead this yields an emission factor of 480 kg Cd/ 100,500 ton (Zn + Pb) produced = 5 g Cd/ ton (Zn + Pb) produced.

The 1989 ICWS data are presented in aggregated form. For all direct discharges into the Rhine by non-ferrous metal industry an overall cadmium discharge of 90 kg/yr is given. Assuming this emission would only be caused by this ISF-plant, this would lead to an emission factor of 0.9 g Cd/ ton (Zn+Pb) produced. In practice this factor is probably still lower. In this study it is assumed to be equal to 0.5 kg Cd / ton (Zn+Pb).

Von Roepenack [60] estimated the total aqueous cadmium emission for electrolytic plants to be equal to 10 kg/year in 1977. The production by then was 105,000 tons, leading to an aqueous emission factor of 0.1 g Cd / ton Zn.

However, the ERL-report [8], consulting Belgian specialists, reports an emission factor of 5.7 g Cd / ton Zn for electrolytic production. Applying this factor would lead to a cadmium discharge at Datteln which equals 550 kg/yr. The ERL-figure is probably not applicable to the Datteln plant and therefore the von Roepenack estimate is used.

Additional evidence for the von Roepenack estimate is obtained by comparing the aqueous cadmium emissions caused by the Dutch hydrometallurgical zinc winning company and given in ref. [31]. This document claims that, after treatment, the 150,000 ton zinc plant emits 3.5 kg Cd/yr. This would lead to an emission factor of 0.02 g Cd/ton Zn in 1982. The same author [30] gives an emission estimate provided by an environmental pressure group, for 1974. Although the plant has not changed significantly in the period 1974 − 1982, as far as waste water is concerned, the difference in emission estimate is striking. Ref. [35] estimates an emission of 2,500 kg Cd/yr, equivalent to an emission factor of 17 g Cd/ton. This estimate is far too high. Therefore the estimate : 0.1 g Cd/ton Zn is regarded as the best estimate for the period 1970−1990.

In summary this leads to the following emission factors and emissions in time for primary zinc winning:
Thermal plants:

Period	Productivity ton (Zn + Pb)	Emission factor g Cd/ ton (Zn + Pb)	Emission ton Cd/yr
1970 − 1972	122,000	16	2.0
1973 − 1977	97,300	10	1.6
1978 − 1982	95,100	10	1.0
1983 − 1987	100,500	5	0.5
1988	100,000[1]	0.5	0.05

[1] estimate

Electrolytic plants:

period: 1970 − 1990; emission factor: 0.1 g Cd/ ton Zn; emission negligible

4.4 Other Non-Ferrous Metal Winning Industry

This category of industry includes secondary zinc winning, secondary cadmium winning, primary lead winning, secondary lead winning and primary and secondary cadmium production.

Secondary zinc winning

Secondary zinc winning has taken place in a large metal recycling plant in Duisberg. This company had a variable raw material spectrum and was producing a mixture of products. Statistics on production and raw material use are not available. It is assumed that this company has been a major cadmium discharger in the 1970's until the beginning of the 1980's [63,64,65,66]. Ref. [65] claims that by the end of the 1970's one non-ferrous metal company emitted 35 to 45 tons cadmium annually. All other non-ferrous metal industries would have emitted 23 to 33 tons, causing a total cadmium emission into the Rhine River of 68 tons. Von Roepenack [66] claimed in 1985 that the "... 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 cadmium emissions." This quote indicates that about 55 to 60 tons of aqueous cadmium emissions were caused by one plant.

The link between "the major discharger" and the Duisberg plant has not been stated directly in the references. The following two arguments justify the idea the Duisberg recycling plant caused major cadmium pollution:

-1- the recycling plant closed in 1984 and immediately afterwards the cadmium concentration in the River Rhine decreased significantly;

-2- the plant is located in that part of the Rhine River basin where, according to the monitoring data (Section 3), the major cadmium discharges have taken place.

The Duisberg plant had a 20,000 ton capacity of secondary zinc and by dividing the cadmium emission with the secondary zinc production an approximate emission factor for secondary zinc winning could be defined. However, since the raw material spectrum entering the plant is rather undefined, this emission factor is not of any value for other plants. It doesn't make any sense to define a factor which can not be generalized.

Considering the difficulties mentioned above, it is not possible to provide the direct aqueous emission factor for secondary zinc winning. Regardless of any emission factor, as long as no more detailed information on this branch of industrial activity is available, the following emission estimates are made:

period	aqueous cadmium emission (ton/yr)
1970 - 1982	35 − 45 tons; 55 − 60 tons : 50 tons Cd
1983 − 1984	no data
1984 − 1990	no more cadmium related activities

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Secondary cadmium winning

Secondary cadmium winning was applied by one company in Bonn, in the basin until 1979. Their production capacity was approximately 300 ton cadmium [38]. The raw materials that were used were recycled cadmium containing products. No aqueous emission factor is reported in literature. Even if the cadmium emission would have been as high as 10 g Cd/kg Cd processed, the overall cadmium emission (3,000 kg) would still be of minor importance in the 1970's.

The company, stated not to have direct aqueous emissions, due to the fact that all process water was recycled [67].

If as a first assumption a worst case scenario is made, the following emission factor is defined:

1970 – 1979: emission factor 10 g Cd/kg Cd processed; emission: 3 tons of Cd annually
1979 – 1990: no emission due to termination of the activities

Primary lead winning

Part of this subject is covered in Section 4.3 on primary zinc winning. Another primary lead winning plant is located in Arnhem. The Dutch Central Bureau of Statistics issues the annual water quality statistics for The Netherlands since 1976. Since 1976 no industrial cadmium discharges of more than 100 kg/yr have been registered in the province in which Arnhem is located [68]. This indicated that no further research needed to be carried out.

Secondary lead winning

In the Rhine River basin five companies are involved in this business, with a total production capacity of 110,000 tons/yr. Two companies are located in Duisberg, one in Nurenberg, one in Rommerskirchen and one in Braubach [61]. No actual recycled lead production data are available. If the companies all operated at 90 % of their capacity, the total production of recycled lead has been 99,000 tons.

In ref. [8] an aqueous emission factor of 6.2 g Cd/ton Pb processed is given. Using this factor would result in a total emission due to this activity of 0.6 ton Cd/yr in the basin.

No more details are currently available. It is assumed that the recycling of lead-scrap, which to a major extent consists of waste batteries, causes no significant cadmium emissions, since lead batteries do not, as a product, contain cadmium in a significant amount.

Primary and Secondary Copper production

For primary and secondary copper production two plants are operated in the basin. Their total production capacity equals 120,000 ton electrolytic copper. The companies are located in Rastatt and in Luenen. No emission factor estimates are available in literature.

The plant in Luenen has the major share of the production capacity with a 110,000 ton production capacity of secondary copper. Luenen is located near a tributary to the River Rhine. Therefore no direct emission data (e.g. ICWS) are available.

The plant is equipped with a pyrometallurgical smelter and an electrolytic copper refining section. The process is handling a highly variable raw material spectrum. Cadmium might be part of the feed of this plant via waste copper railroad overhead conductors and other copper alloys to which cadmium is added in order to improve mechanical strength. In these overhead

conductor alloys cadmium has a typical concentration of 0.8 to 1.2 percent [69]. These alloys are also used in copper radiators in automobiles.

It is not possible to determine which part of the secondary copper materials processed at the plant in Luenen has been alloyed with cadmium. Although quantitative estimates for the cadmium flow through this process are obtained, the aqueous cadmium emissions are assumed to be small, due to the pyrometallurgical feed processing. Any cadmium present in the feed will probably be volatilized, together with waste zinc, and end up in a zinc oxide rich dust, which is sold as secondary zinc containing raw material.

Although no details on the production process operated in Rastatt are known, the following worst case scenario is used:

- 20 % of the secondary copper is alloyed with 1 % cadmium
- the average copper content of the raw materials of this plant is 70 %
- the annual High Grade copper production is 10,000 tons.

This leads to the following figures:

- annual raw material consumption: 14,000 tons
- annual cadmium flow: 20 tons

As with the plant in Luenen it is most probable that the feed is processed pyrometallurgically. Practically all of the cadmium will then end up in a zinc rich fly ash, which might be processed as secondary zinc raw material, or might end up in a solid waste landfill. Aqueous emissions for this plant are not expected to be of any significance.

This assumption is confirmed by the fact that, according to the monitoring data (Section 3), no significant aqueous cadmium discharges have taken place in the part of the Rhine between Seltz and Koblenz.

4.5 Pigment Manufacturing

During pigment manufacturing aqueous emissions of cadmium are mainly caused during the precipitation and filtration step of the pigments. The pigment production scheme is given in fig. 4.1 [70].

Cadmium or cadmium oxide is dissolved in sulfuric acid to yield a cadmium sulfate solution. For particular colors like yellow and primrose, zinc salts are added. The cadmium sulfate is then precipitated by adding a sulfide salt. The color of the pigment is determined by the sulfide salt that is used. Sodium sulfide is added to produce a yellow pigment, mercuric sulfide or mercuric selenide/selenium is used to give a red pigment and barium sulfide gives lithopones.

The so-produced cadmium sulfide crystals are of a very small size (approximately 1 um) due to the high supersaturation that is created during the precipitation.

After filtration and washing the crystals are calcined. During this step the crystals are heated up to 550 - 650 °C in order to convert them from the cubic (zinc blende) to the more stable hexagonal (wurtzite) structure. After calcining, the crystals possess the required pigment properties. The calcined material is washed with diluted (0.1 mol/l) hydrochloric acid in order to remove 99.9 % of the residual soluble cadmium and subsequently filtrated and dried. Further handling of the pigments takes place without using wet process steps.

In the entire production process a number of steps are involved which might give rise to water pollution. The filtration and washing water directly after the precipitation is slightly contaminated with cadmium :

- because the reaction products have not been added perfectly stoichiometrically;
- because of bad mixing unreacted cadmium has remained in solution;
- because of the difficulty of filtrating (sub-) micron size cadmium sulfide particles and;
- since, due to the (strong) acidity of the solution cadmium sulfide has a certain, very low, solubility.
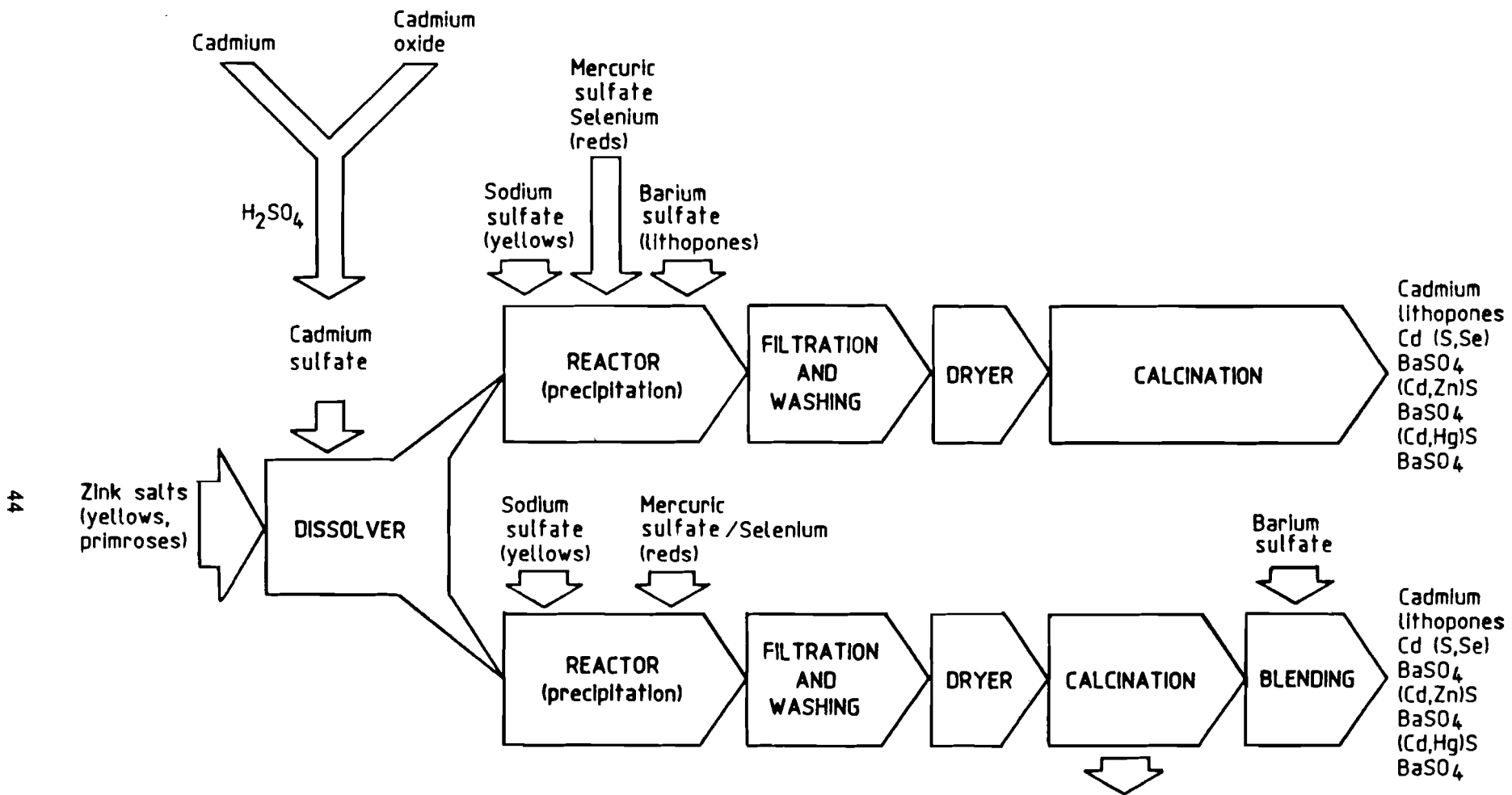
Figure 4.1. Manufacture of cadmium pigments

These causes also apply to the subsequent washing and filtering step after the calcination. The waste water that contains cadmium is usually processed in a waste water treatment unit. However, due to the limited efficiency of the methods which are usually applied, a residual amount of cadmium is discharged via the waste water treatment unit effluent.

Since no measuring data for cadmium concentrations in the different aqueous phases are available, it is obvious that one overall emission factor has to be defined. This emission factor gives the net emission of cadmium - in the solid as well as in the liquid phase - per weight unit of cadmium processed in pigment manufacturing.

The Directory of Chemical Producers [71] lists for the in-basin countries in 1986 four cadmium pigment manufacturers and pigment products which are given in table 4.4. Although registration in this directory is voluntary, in case of cadmium pigments and stabilizers, other sources confirmed the correctness of the contents. In the 1970's one manufacturing plant was located in Rotterdam.

Table 4.4   Cadmium Pigment Manufacturers

Cadmium Sulfide (orange cadmium) : 1,2 Orange 20   (cadmium sulfoselenide): 2,3 Red 108   (cadmium sulfoselenide): 1,2 Red 108:1   (cadmium sulfoselenide lithopone) : 1,2 Yellow 35   (cadmium zinc sulfide) : 1,4 Yellow 35:1 (cadmium sulfide lithopone) : 1 Yellow 37   (cadmium sulfide) : 1,3 Yellow 37:1 (cadmium sulfide lithopone) : 1
with: 1: Besigheim 2: Leverkusen (until 1988) 3: Bonn 4: Duisburg   Rotterdam (no details available)

Consulting specialists in this field the following information was obtained [72].

By 1970 the three main cadmium pigment producers in the FRG   (and in the whole basin) were:

Location	Pigment production	Cd content
Besigheim	500 tons	330 tons
Leverkusen	600 tons	400 tons
Bonn	500 tons	330 tons

For 1990 only two suppliers are left on the market.

Location	Pigment production	Cd content
Besigheim	220 tons	145 tons
Bonn	250 tons	165 tons

The producer in Duisburg and a producer in Rotterdam have not had a market share that justifies further analysis.

Stigliani [29] estimated the total amount of cadmium processed in pigment manufacturing at 844 tons in 1970. This figure is obtained by assuming the ratio of (the domestic processing / (the domestic processing + the imports)) for 1973 − 1980 (which is 0.96) to be applicable for 1970. The domestic processing + the imports for 1970 were equal to 879 tons. Multiplying 879 tons with 0.96 a total amount of 844 tons is obtained. For 1989 the cadmium quantity used in pigment manufacturing was estimated the same way at 334 tons.

For further analysis the figures derived by Stigliani are applied, using the following market shares for the individual producers:

Period	Besigheim	Leverkusen	Bonn
1970 − 1987	31 %	38 %	31 %
1988 − 1989	47 %		53 %

This leads to the production figures which are given in table 4.5.

Table 4.5   The major in-basin cadmium pigment manufacturing plant locations in the period 1970 − 1988 and their production in tons Cd/yr

Period	Besigheim	Leverkusen	Bonn	Sum
1970 − 1972	279	341	279	899
1973 − 1977	309	378	309	996
1978 − 1982	270	330	270	870
1983 − 1987	181	221	181	583
1988	185	0	208	393

The following emission factor and emission estimates are available.

For 1973 the maximum emission factor is given as 1 kg Cd/ ton Cd processed [64]. The total discharge of cadmium due to pigment manufacturing is estimated to be 2 ton [64]. This however, reflects that for 1973 with a total cadmium pigment processing of 1134 tons in the FRG [29] the actual emission factor has been (2000/1134=) 1.76 kg Cd/ ton Cd processed.

Hutton [9] gives an emission factor of 20 kg Cd / ton Cd processed for 1978, but does not include the waste water treatment unit in the factor. If the treatment unit has an efficiency of 90 %, the two estimates are in reasonable agreement, since then 2 kg Cd/ ton Cd processed is emitted.

However, the question is whether adequate (if any) waste water treatment plants were operating in the beginning of the 1970's. In waste water treatment plants which are designed to

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clean urban waste water, usually 40 to 60 % of the cadmium contained in the influent ends up in the sludge and 40 to 60 % is discharged with the effluent [48,73]. Considering Hutton's emission factor without treatment, it makes sense to assume that in the period 1970 – 1972 the aqueous emission factor for cadmium pigment manufacturing was 10 kg Cd/ton Cd processed or might even have been higher, up to 20 kg Cd/ton Cd processed.

For the period 1973 – 1977 the emission has probably decreased to about 4 to 10 kg Cd/ton Cd processed. This figure is significantly higher than the estimate given by Rauhut [64] and still accounts for the lack of adequate waste water treatment technology.

For 1979 the overall emission due to pigment manufacturing is estimated at 1.7 ton Cd [63]. Given a processing quantity of 1168 tons [29], this leads to an emission factor of 1.46 kg Cd/ ton Cd processed.

For 1982 the same author as for the 1979 survey provides an emission factor of 1 kg Cd/ ton Cd processed as well as a total emission of 1 ton Cd due to Cd pigment manufacturing [28].

For the period 1978 – 1982 it is assumed that the waste water technology has significantly improved. The emission factor, based on the refs. [28,63], is estimated for 1978 – 1982 at 1.5 kg Cd/ton Cd processed.

Yost and Greenkorn [74] claimed for the USA in 1984 that during pigment production the following partitioning of cadmium takes place:

- 94 % goes to the pigment product,
- 6 % is lost in production of which:
    4.47 % is reclaimed in the plant,
    1.4 % is emitted to municipal treatment plants and
    0.12 % is directly discharged to water.

This would mean that the total amount of the discharged cadmium would be about (1.4 * 0.5 + 0.12 =) 0.82 % . In other words: the aqueous emission factor would be 8.2 kg Cd/ ton Cd processed. This emission factor for 1984 is probably too high, since pigments are in the FRG manufactured in large chemical plants which by then were equipped with some sort of heavy metal removal process as part of the water treatment plant. This type of facility typically has an efficiency of e.g. 90 % . In that case the emission factor becomes (0.1 * 1.4 + 0.12 =) 0.26 or 2.6 kg Cd / ton Cd processed. Assuming higher efficiencies would even lower this factor, up to finally 100 % efficiency and consequently an emission factor of 1.2 kg Cd / ton Cd processed.

In the 1985 survey of the Deutsche Kommission zur Reinhaltung des Rheins [62] two pigment manufacturing plants are registered as major cadmium dischargers. These are the locations Besigheim (70 kg Cd/ yr) and Leverkusen (225 kg Cd/yr). In case of both locations the cadmium pigments are the only cadmium containing products that are being made [71].

The total amount of cadmium that is being processed for pigment manufacturing in 1985 is 636 tons [29]. Using the distribution percentages 197 tons are processed in Besigheim and Bonn and 242 tons in Leverkusen.

Assuming a direct relationship between the cadmium pigment manufacturing of these plants and their cadmium discharges such as mentioned by the Deutsche Kommission zur Reinhaltung des Rheins there is a surprisingly large difference between the efficiencies of the applied treatment methods. For the location Leverkusen the emission factor would become: 0.9 kg Cd/ ton Cd processed. For Besigheim the factor equals: 0.4 kg Cd/ ton Cd processed, whereas for the plant in Bonn the factor is probably smaller than 0.2 kg Cd/ ton Cd processed. For these rather unexpected results four explanations are suggested:

-1-   the emission document [62] is not accurate;
-2-   the discharges of cadmium in the plant in Leverkusen are also caused by other processes in which cadmium is emitted (e.g organic catalysis and PVC-processing);
-3-   the production assumptions are incorrect and;
-4-   the waste water treatment technologies are substantially different, which is not to be expected.

The legal emission limit for cadmium discharges due to cadmium pigment manufacturing in the EC was from 1983 until 1985: 0.7 kg Cd/ ton Cd processed [3]. In an EC - directive valid since 1986, this factor is lowered to 0.3 kg Cd/ ton Cd processed [75].

   If the emissions of the locations Besigheim and Leverkusen are added the total emission in 1985 is equal to 295 ton Cd. Given the production quantity of 636 tons [29] the so-obtained emission factor is equal to 0.5 kg Cd/ ton Cd processed. For 1989 the ICWS study [49] reveals that the total cadmium emission of all chemical industry discharging directly to the Rhine is equal to 330 kg. Since this figure does not include all manufacturers of pigments but does include other branches (e.g. PVC-manufacturing), it is of limited use.

   In table 4.6 the emission factors which are obtained for cadmium pigment manufacturing in the Rhine River basin for the period 1970 - 1990 are summarized. Based on the tables 4.5 and 4.6 the following summary of the emission and the emission factor estimates for the Rhine River basin between 1970 and 1988 is made.

Period	Production (ton Cd/yr)	Factor (kg Cd/ton Cd)		Emission (ton Cd/yr)
1970 − 1972	899	10 − 20		9.0 − 18.0
1973 − 1977	996	4 − 10		4.0 − 10
1978 − 1982	870	1.5	1.3	
1983 − 1987	583	0.5	0.3	
1988	393	0.3	0.1	

Table 4.6 Emission Factors for Cadmium Pigment Manufacturing

Date ref.	Emission factor kg Cd/ton Cd processed	Source
1973	1	[64]
1973	1.76	[29,64]
1978	20[1]	[9]
	10[2]	[9,48,73]
1979	1.46	[29,63]
1982	1	[28]
1984	8.2[3]	[74]
	2.6[4]	[74]
	1.2[5]	[74]
1983 − 1985	0.7[6]	[3]
1985	0.5	[29,62]
since 1986	0.3[7]	[75]

4.6   Stabilizer Manufacturing

The manufacturing of cadmium stabilizers is a wet chemical process which leads to waste water and aqueous cadmium emissions.

For liquid stabilizers the production process uses as raw materials barium and cadmium oxide and a heated organic acid like ethylhexanoic acid in the presence of solvents. The salts are dissolved directly and react to form finely divided cadmium/barium stabilizers. The reaction water is removed and the finished product filtered [76].

The solid stabilizer manufacturing process is given in figure 4.2 [77]. Stearic acid is mixed with water to give a stearic acid emulsion which is heated to 70 °C. This emulsion reacts with caustic soda to give a sodium stearate suspension in water. An aqueous cadmium chloride solution which is formed by dissolving finely divided cadmium metal or cadmium oxide powder in hydrochloric acid is added slowly to the suspension at elevated temperatures. Cadmium stearate precipitates and it is subsequently filtrated, washed and dried.

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[1] without waste water treatment

[2] with waste water treatment, efficiency 50 %

[3] with waste water treatment: efficiency 50 %

[4] with waste water treatment: efficiency 90 %

[5] with waste water treatment: efficiency 100 %

[6] legal emission limit

[7] legal emission limit
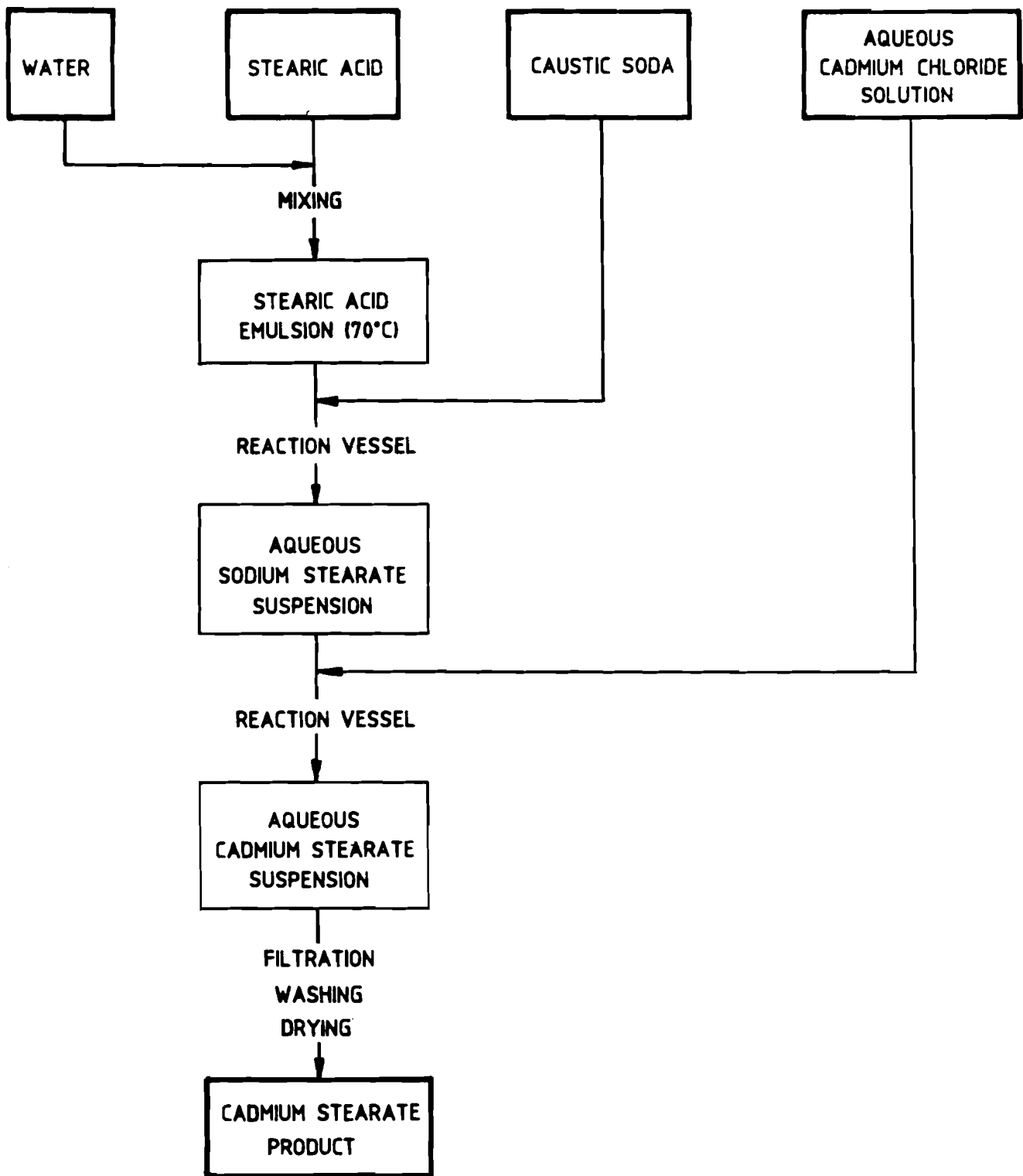
Figure 4.2   Cadmium stearate production.

Especially during these last three steps contamination of the process water occurs due to a.o.:

- bad mixing and consequently unconverted raw materials,
- the reaching of equilibrium solubilities and
- limited filtration efficiencies, especially for small particles which are typically formed during precipitation processes.

As with pigments it is not possible to estimate individual process step emissions. Therefore one overall emission factor, defined as kg Cd discharged per ton Cd processed will be used.

The Directory of Chemical Producers [71] does not mention any stabilizer manufacturing companies which are located in the basin. However, another source [78] claims that in the 1970's one company, located in Besigheim, also had a stabilizer production plant. No details on the production of this plant and the year of termination of their stabilizer related activities are available. Besigheim is located to a tributary to the river Neckar. In the river Neckar according to the monitoring data, significant point source discharges have taken place in the 1970's (see Section 3).

As a first estimate, it is assumed that the company has produced 25 % of all stabilizers in the FRG in the period 1970 − 1977. The figure 25 % is chosen because three other manufacturing companies were active in the FRG by then. The average annual FRG production of cadmium stabilizers in the period 1970–1972 was 343 tons on Cd basis [29]. For the period 1973 − 1977 this figure equals 363 tons.

The following data on emission factors are available.

Ref. [64] estimates the emission factor (after neutralizing the waste water and consequently cadmium hydroxide precipitation) still to be ranging between 1 and 1.5 kg Cd / ton Cd processed for 1973. A total emission for the FRG of 1 ton Cd is estimated for 1973 [64]. The total processing of cadmium stabilizers in 1973 in the FRG is estimated at 408 tons [29]. This leads to an emission factor of 2.45 kg Cd/ton Cd processed.

Hutton [9] gives an emission factor of 20 kg Cd/ton Cd processed for 1978, but does not include the waste water treatment unit in the factor. If the treatment unit has an efficiency of 90 %, the two approaches are in reasonable agreement.

However, as with pigments, it is questionable whether adequate waste water treatment plants were available in the early 1970's. Therefore, for the period 1970 − 1972 the emission factor is assumed to be equal to 10 to 20 kg Cd/ ton Cd processed. For 1973 − 1977, taking into account the introduction of waste water treatment plants, the factor is assumed to be 4 to 10 kg Cd/ton Cd processed.

For 1979 the aqueous cadmium emission due to stabilizer manufacturing in the FRG is estimated at 0.2 tons [63], which, given a production of 635 tons [29], leads to an emission factor of 0.31 kg Cd/ton Cd processed.

For the FRG in 1982 however, the same author as for the 1979 survey provides an aqueous emission factor of 1.5 kg Cd/ ton Cd processed, as well as a total emission of 1 ton Cd due to stabilizer manufacturing [28].

For the period 1978 − 1982 the aqueous cadmium emission due to stabilizer manufacturing is estimated at 2 kg Cd/ ton Cd processed.

Yost and Greenkorn [74] claimed in 1984 that during stabilizer production the following partition of cadmium takes place:

98 %	goes to the stabilizer product,
1.82 %	goes to landfill,
0.16 %	is emitted to municipal sewage water treatment and
0.02 %	is directly discharged to water.

The cadmium emission factor then depends on the removal efficiency which is assumed for the sewage treatment unit. If this unit is a municipal sewage water treatment plant the cadmium removal efficiency is typically 40 to 60 % [48,73]. In that case the overall emission factor equals (0.16 * 0.5 + 0.02 =) 0.1 % or 1.0 kg Cd / ton Cd processed. In case a specialized treatment unit is applied with 90 % removal efficiency the factor decreases to 0.018 % or say 0.2 kg Cd/ ton Cd processed.

The EC-legislation provided a legal emission limit of 0.8 kg Cd / ton Cd processed for the period 1983 − 1985 [3]. In a directive valid since 1986 this has been changed to 0.5 kg Cd/ ton Cd processed [75]. For the period 1983 − 1987 the aqueous cadmium emission factor is assumed to be equal to 0.6 kg Cd/ton Cd (on average).

In table 4.7 the obtained emission factors for cadmium stabilizer manufacturing are summarized. Using the average emission factors and the assumptions given above, the following estimates for the in-basin emission of cadmium due to stabilizer manufacturing is made.

Period	Production (ton Cd/yr)	Factor (kg Cd/ton Cd)	Emission (ton Cd)
1970 − 1972	86	10 − 20	0.9 − 1.7
1973 − 1977	91	4 − 10	0.4 − 0.9
1978 − 1982	?	2.0	?
1983 − 1987	0	0.6	0
1988	0	0.4[1]	0

[1] estimate, based on the legal emission limit

Table 4.7 :   Emission factors for cadmium stabilizer manufacturing

Date ref.	Emission factor kg Cd/ ton Cd processed	Source
1973	1 – 1.5	[64]
1973	2.45	[29,64]
1978	20^1	[9]
	10^2	[9,48,73]
1979	0.31	[29,63]
1982	1.5	[28]
1984	1.0^3	[74]
	0.2^4	[74]
1983 –1985	0.8^5	[3]
since 1986	0.5^5	[75]

4.7   The industrial use of cadmium pigments and stabilizers

4.7.1   Industrial use of cadmium pigments

Cadmium pigments are used in coloring polymers and ceramics, and as paint and artist's colors. In the period 1970 – 1988 by far the main use of cadmium pigments was the coloring of polymers, which had a market share of 75 % in the beginning of the 1970's up to 90 % in the late 1980's [59,79,80].

The importance of the polymer processing industry for aqueous cadmium emissions however, was unknown. No attention has been paid to this potential source in other emission inventories [8,9,81].

Consulting pigment specialists [72] it was claimed that this is due to the usual procedure of pigment application. Polymer manufacturers willing to color a plastic with cadmium pigments send a batch of the polymer to be colored to the pigment manufacturer. This batch is colored very intensely at the pigment manufacturing plant. It is then referred to as master-batch. The batch is returned to the polymer manufacturing plant in which this particular polymer batch is used as a coloring additive to large volumes of uncolored polymers. In this way emissions (if any) are concentrated at the pigment manufacturing plant, which, at least since the 1980's is better equipped for handling cadmium containing waste than polymer processing plant are.

It is not certain that the procedure has always been like this in the 1970's, but due to lack of data no more details are presently available.

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[1] before waste water treatment

[2] after waste water treatment, removal efficiency 50 %

[3] after waste water treatment, removal efficiency 50 %

[4] after waste water treatment, removal efficiency 90 %

[5] legal emission limit

[5] legal emission limit

For this emission inventory it is assumed that this procedure has been common practice. This means that no aqueous emissions of cadmium are to be expected from the application of cadmium pigments in the plastics industry.

The other uses of cadmium pigments are not considered as significant for the following reasons (apart from the small quantities):

-1-   the automobile lacquers which sometimes contained cadmium in the 1970's were not water-based. Aqueous emissions are not to be expected during lacquer use in automotive applications;

-2-   the use of cadmium pigments in ceramics requires mostly high temperature processes which would (if any) create atmospheric and not aqueous emissions;

-3-   the use in artist's colors would (if any) cause diffuse emissions, which are not discussed in this study.

4.7.2   Industrial use of cadmium stabilizers

The use of cadmium stabilizers is exclusively connected to the manufacture of PVC. Many PVC-applications were stabilized with cadmium in the beginning of the 1970's. The number of applications and the production quantities have decreased since 1980, due to the increasing environmental concern with respect to cadmium.   The only large application in which cadmium stabilizers are still used, are outdoor PVC window profiles. These profiles had a market share of 75 % of the use of all cadmium stabilizers in 1989 in the FRG. Minor uses are roofing and swimming pool foil and other outdoor PVC profiles [80]. Substitutes for these applications are available, but due to the long-life guarantees which are common in the building industry, long-lasting tests with the substitutes must yield positive results, before substitution takes place [78,80].

Although PVC-stabilizers are now also used in master-batches, in order to reduce occupational health hazards and emissions in the PVC processing plants [82], this has not always been the case. For 1988 the master-batch procedure is assumed to be applied for all products which are being made in the basin.

Aqueous cadmium emissions were, using the old procedure, caused when wet scrubbers were used to clean (cadmium stabilizer) dust-laden gas. In case liquid stabilizers were used, minor amounts of the stabilizers might have ended up in the sewer.

In the basin 8 companies are manufacturing PVC. One plant is located in Sins in Switzerland, six are located in Germany (Marl, Koeln, Frankfurt am Main, Rheinberg, Ludwigshafen and Waldshut) and one plant is located in Rotterdam in The Netherlands. If it is assumed that

(i)   cadmium stabilizers are used in all plants and
(ii)   the magnitude of the stabilizer use is proportional to the magnitude of the PVC production capacity,

then the stabilizer use can be divided over the individual locations. For 1985 this leads for the FRG (in which additionally three production sites are located outside the basin) to the figures given in table 4.8.

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Table 4.8   The relative production capacities and the cadmium stabilizer use for 1985 for two different scenario's

Plant location	% PVC prod.[1]	Stabs use (1)[2] (ton Cd)	Stabs use (2) (ton Cd)
Marl	28.37	140	281
Koeln	11.76	58	0
Frankfurt	5.54	27	0
Rheinberg	11.07	55	110
Ludwigshafen	10.38	51	103
Waldshut	2.08	10	0
Not in basin	30.80	152	0

[1] the total PVC production capacity in the FRG in 1985 is 1445 ton [29].

[2] the total domestic cadmium stabilizer use is 494 ton [29].

The stabilizer use estimates, given in column (1), are of course very crude since the assumption that all PVC processing plants use cadmium stabilizers is probably incorrect. A PVC window profile is only one out of many PVC products. Companies specialize on certain products rather than cover an entire product's application market. The second point to make is that it is not sure that all plants indeed need stabilizers. If the manufacturing process stops at the point where the PVC resin has been formed, the use of PVC stabilizers is not always required.

Additional information for this inventory is offered by the Deutsche Kommission zur Reinhaltung des Rheins [62] which lists by 1985 three in-basin PVC manufacturing plants as major industrial cadmium dischargers. These companies are located in Rheinberg, Ludwigshafen and Marl. The following data are available.

Plant	Annual emission (kg Cd)
Rheinberg	130
Ludwigshafen	235
Marl	225

Based on the Directory of Chemical Producers [71] it is known that the plant in Marl is mainly concentrating on PVC, whereas the locations Rheinberg and Ludwigshafen have many other activities as well. Therefore the emission factor should be based on the plant in Marl.

Given the fact that only three out of six in-basin plants are mentioned as cadmium dischargers it is not convincing to suppose that all in-basin PVC plants actually used Cd-stabilizers in their PVC processing. An extra difficulty in this respect is the fact that PVC plants outside the basin have not been discussed by the Deutsche Kommission zur Reinhaltung des Rheins [62].

Two possibilities are discussed in this study:

-1-   all companies inside the FRG did use Cd-stabilizers and the use was proportional to the PVC production capacity;

-2-   only three companies, Rheinberg, Ludwigshafen and Marl, used Cd-stabilizers and their use was proportional to their PVC production capacity.

The figures corresponding with the second possibility are also given in table 4.8. Possibility -1- leads to the high extreme for the emission factor related to the PVC manufacturing plant in Marl, whereas possibility -2- leads to a lower value. The specific emission factor for 1985 is calculated as follows:

Possibility -1-

-    the cadmium stabilizer use was 140 ton Cd;
-    the emission (as given by ref. [62]) was 225 kg Cd;

-    the 1985 emission factor estimate then is 1.6 kg Cd/ton Cd processed or 0.5 g Cd/ton PVC processed.

Possibility -2-

-    the cadmium stabilizer use was 281 ton Cd;
-    the emission was 225 kg;
-    the 1985 emission factor estimate then is 0.8 kg Cd/ton Cd processed or 0.25 g Cd/ton PVC processed.

Based on these calculations the 1985 emission factor for the aqueous cadmium emission during PVC manufacturing is given as: 0.8 - 1.6 kg Cd/ton Cd processed.

The other two plants (Rheinberg and Ludwigshafen) would provide a higher emission factor. In case of Rheinberg this is due to potash production which is an additional minor source of aqueous cadmium emission. For the Ludwigshafen plant no explanation for the discrepancy is available. However, there's no evidence that the cadmium use of these plants is proportional to the production capacity. That assumption might also cause the discrepancy with the real data.

Backcasting the emission factor provided here, to the 1970's is even more tricky, due to lack of data. For two reasons, no spectacular decrease of the emission factor is assumed since the 1970's.

-1-   Until the 1980's the magnitude of the emission was such that it was not considered as significant;

-2-   as a consequence the cadmium emission due to PVC manufacturing has never been addressed, so there have been no incentives to improve the situation, apart from the tariffs in the German waste water legislation, which per unit emitted cadmium have increased significantly in the 1980's [83] [1].

Based on these two remarks the following estimated emission factors are given, based on an expected trend, without any supporting data:

Period	Cd-stabs-use (ton Cd/yr)	Factor (kg Cd/ton Cd)	Emission (FRG) (ton Cd/yr)
1970 - 1972	398	1.2 - 2.4	0.5 - 1.0
1973 - 1977	427	1.2 - 2.4	0.5 - 1.0
1978 - 1982	607	1.0 - 2.0	0.6 - 1.2
1983 - 1987	488	0.8 - 1.6	0.4 - 0.8
1988	398	0	0

For Switzerland the emission has been negligible [2]. For The Netherlands, using these emission factors, Dutch statistics on cadmium stabilizer use and the assumption that cadmium stabilizers are used, the emissions in Rotterdam have been negligible as well [3].

[1]   The German Waste Water Discharge Act of 13 september 1979 determines that per unit aqueous discharge a fee has to be paid. For cadmium discharges the unit is 100 g/yr. When the emission lies below 100 units/yr (or 10 kg/yr) the discharge is free of charge. The fee per unit is given here as a function of time.

1982	DM 18.—
1983	DM 24.—
1984	DM 30.—
1985	DM 36.—
1986	DM 40.—

[2]   The Swiss in-basin production capacity for PVC was 30,000 tons in 1985, which in case cadmium stabilizers had been used would have created an emission of the order of magnitude of ten to twenty kilograms cadmium per annum.

[3]   The Dutch in-basin production capacity for PVC was around 200,000 tons, which might have caused, if cadmium stabilizers had been used, an emission of about 100 kilograms. However, the plant is located next to two large wet phosphoric acid production plants which until 1988 together emitted at least 10 tons of cadmium per annum.

4.8   Alloy manufacturing and industrial use

The alloy manufacturing branch does not discharge cadmium to water [28]. This is due to the manufacturing process for alloys. Therefore, no reports on aqueous emissions as a consequence of alloy manufacturing are available.

During the use of cadmium alloys aqueous emissions are not be expected. The uses of cadmium alloys e.g. in the aircraft, railway and automotive sector as well as in jewellery do not cause significant emissions.

However, as a waste product these alloys still contain cadmium. Especially copper/cadmium alloys with 1 % cadmium which are recycled for their copper content might give rise to cadmium problems during secondary copper manufacturing. During secondary copper manufacturing cadmium might end up in waste streams which are landfilled. The cadmium content can also end up in a product primarily consisting of zinc oxide. This zinc oxide product is sold for further refining or used as a low quality pigment and/or a rubber additive.

4.9 Cement manufacturing

For cement manufacturing no aqueous emission estimates are known [8]. Due to the high temperature that is being applied during the cement manufacturing process and the low cadmium concentration in the raw materials aqueous emissions are not expected to be significant.

The emissions that are to be expected are atmospheric emissions. Waste material might end up on a landfill site.

It is significant to remark in this context that one of the German primary zinc smelters sends its 50,000 ton of hematite residue, which still contains up to 200 ppm cadmium to cement klinker manufacturing plants. This annual flow of up to 10 tons of cadmium might give rise to in-basin atmospheric cadmium pollution or to a diffuse spread of cadmium via building materials.

4.10 Battery Manufacturing and Use

The manufacturing of Nickel-Cadmium batteries is a process which includes steps that give rise to aqueous cadmium pollution. Since Ni-Cd batteries exist in different forms, these different forms are discussed separately [84].

a) Pocket Cells

The manufacturing of pocket cells proceeds as follows:

-1-   the construction of the positive electrode;
-2-   the construction of the negative electrode;
-3-   the joining of the electrodes to form an assembly;
-4-   the bolting of the interleaved electrode groups to a cover which is sealed to a container;
-5-   the filling of the cell with an electrolyte solution (mostly potassium hydroxide solution).

During this manufacturing process the only step during which cadmium is involved, is the second step; the construction of the negative electrode. A negative electrode is manufactured as follows:

-1-   cold-rolled steel ribbon is cut and perforated;
-2-   the steel ribbon is plated with cadmium and then formed into a trough shape which is filled with active material. Cadmium in its metallic form is the active material in the anode;
-3-   a cadmium-plated lid is formed which covers and locks with the filled trough;
-4-   the filled strips are then cut to length. An electrode sheet is formed by interleaving. In order to ensure good contact between ribbon and active material and to improve mechanical strength, a pattern is pressed into the electrode sheet;
-5-   the electrode sheet is finally cut to pieces of the desired size and bedding and lugs are attached to fit the electrode in a cold-steel ribbon frame.

The plating step (-2-) causes waste because the aqueous solution which is applied, can only be used a finite number of times. The filling of the anodes with active material step (-3-) is carried out by using either a briquetting or a powder filling technique. No details are known on how dust emissions are prevented and controlled. If wet scrubbers are applied in order to remove cadmium airborne dust, aqueous pollution is caused.

b) Tubular Cells

Tubular cells are mostly of the Nickel-Iron type. However, some Nickel-Cadmium cells are being produced as tubular cells. The manufacturing process for the cadmium anode is similar to that described for the pocket cell.

c) Sintered Cells

The manufacturing process for sintered cells consists of five major process steps:

-1-   preparation of sintering grade nickel powder;
-2-   preparation of the sintered nickel plaque;
-3-   impregnation of the plaque with active material;
-4-   assembling of the impregnated plaques into electrode groups and cells;
-5-   assembly of cells into batteries.

The only step in this process that is related to cadmium emissions is the impregnation. The impregnation method itself generally takes place as follows:

-1-   the plaques are submerged in an aqueous solution of the active material which is either a nickel or a cadmium salt;
-2-   after submerging an electrochemical or a (reaction) crystallization method is used to precipitate nickel or cadmium hydroxide. For cadmium anodes, cadmium nitrate solution with densities of 1800 kg/m^3 are used. The impregnation is carried out favorably in the presence of 3 to 4 kg/m^3 of free nitric acid. However, in order to prevent nickel to dissolve due to corrosion, a corrosion inhibitor is added. The anode functions best with half of the pore volume filled with active material;
-3-   the new anodes are combined with new cathodes in large temporary cells, filled with 20 to 30 % sodium hydroxide solution;
-4-   the sets are submerged to 1 to 3 charge-discharge cycles and subsequently washed and dried. This eliminates residual nitrates and poorly adherent particles and also increases the active surface. It is also used to regulate the state of charge of the electrodes prior to assembling the final sealed cell. This is important since the cell performance is improved, when 10 to 15 % of the anode mass is in the charged condition prior to the initial charging.

Having constructed the processed plaques the methods for cell assembly differ for sealed and vented cells. The operations that follow are not of direct interest to this study. The most commonly sold sealed cells contain only one plate of each polarity. Although many different forms of batteries are for sale the fabrication method as described in this section is universally applied.

In the basin one Nickel-Cadmium battery manufacturer is located in Hagen in the FRG [85]. For the FRG the total consumption of batteries is known or estimated for the period 1970 - 1989 [29]. For the battery processing in the FRG three sources are available [8,29,59] which give slightly different figures. For the sake of uniformity data provided by Stigliani [29] are used, which are based on detailed analyses by Rauhut [28,63,64]. The most accurate data are available for the period 1973−1986. In this period approximately 69 % of the consumed Ni-Cd batteries in the FRG are produced in Hagen. This percentage decreases slowly with time. This is caused by the fact that the Hagen plant has not gained the entire market for uses such as in toys,

hearing aids etc. In many of these applications the batteries are imported as part of the product. These types of applications have become more and more relevant during the 1980's. Therefore, the following assumptions have been made:

- backcasting to the period 1970 − 1972 the average ratio (domestic production/use) of the period 1973 − 1976 has been used, which is 0.83;

- for the period 1987 − 1988 a further decline of the relative use of locally produced Ni-Cd batteries is assumed, which is corrected for by further decreasing the ratio to 0.50.

- during the period 1970 − 1990 the relative importance of sealed and vented cells has changed considerably and so has their relative production. The following production ratio has been used:

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

This leads to the following production estimates for the Rhine River basin:

Period	Local processing of which: (ton Cd)	Pocket-plate (ton Cd)	sintered plate (ton Cd)
1970 − 1972	274	247	27
1973 − 1977	263	211	52
1978 − 1982	253	177	76
1983 − 1987	302	182	120
1988	313	125	188

For emission and emission factor estimation the following data are available.

Rauhut [64] claimed that for the FRG in 1973 a total aqueous emission of 3 ton cadmium as well as an emission factor of 3 kg Cd/ton Cd processed should be used. These data are conflicting since the total processing of cadmium for batteries in the FRG in 1973 was estimated at 365 ton, based on data by Rauhut [29,64]. Combining this 365 ton production with an emission of 3 tons the specific aqueous emission factor equals 8.2 kg Cd/ton Cd processed.

Rauhut [86] provides in a 1975 survey for the European Community an emission factor of 2 kg Cd/ton Cd processed. Another EC-document [87] uses EPA (US)-data for 1975 and provides an emission factor of 3.1 kg Cd/ton Cd processed.

For 1979 Rauhut [63] uses data provided by the Technischer Arbeitskreis Cadmium im Verband der Chemischen Industrie. It is claimed that in 1979 in the FRG 0.8 ton cadmium is discharged to water due to battery manufacturing. Using the battery processing data for 1979, as provided by Stigliani [29], it follows that, given the processing of 221 tons cadmium, the emission factor equals 3.6 kg Cd/ton Cd processed.

Rauhut [28] claims in a paper, issued in 1982, an aqueous emission factor of 4 kg Cd/ton Cd processed and an aqueous emission in the FRG of 2 tons Cd. Stigliani [29] provides for 1982 a total processing of 309 tons Cd (.69 * 461). Using this figure the aqueous emission factor increases to 6.5 kg Cd/ton Cd processed.

The Bundesverband der Deutschen Industrie, cited in Schulte-Schrepping [88], claims that for 1982 the cadmium emission due to battery manufacture in the FRG was 0.9 tons. Using Stigliani's data [29] this would result in an aqueous emission factor of 2.9 kg Cd/ton Cd

processed.

Hutton [9] in his 1982 EC-inventory on aqueous cadmium emissions distinguishes between pocket-plate and sintered plate cell manufacturing. Considerable differences exist between the aqueous emissions related to the two processes. The plant in Hagen is producing pocket-plate cells, as well as sintered cells [8].

For the pocket-plate process 3 % of the cadmium used is claimed to be lost in dust, of which 90 % enters landfill and 10 % is discharged to sewage treatment plants. In case of a direct discharge the emission factor would have been 3 kg Cd/ton Cd processed. Since Hagen is in the Ruhr River basin, the discharged cadmium is part of the influent of a waste water treatment plant [48]. Such a plant operates with a typical removal efficiency of 40 − 60 % and so the resulting emission factor becomes 1.2 − 1.8 or, in average, 1.5 kg Cd/ton Cd processed.

Yost and Greenkorn [74] claim for 1984 in the USA that 3 % of the cadmium is lost during pocket-plate processing, but divide it over three destinations:

- 50 % ends up in a landfill;
- 40 % causes atmospheric pollution and;
- 10 % (or 3 kg Cd/ton Cd processed) is discharged to water.

For sintered plate processing in 1982 Hutton [9] uses the following partition coefficient for the 5 % of the cadmium that is lost:

- 45 % is landfilled;
- 55 % (or 27.5 kg Cd/ton Cd processed) is discharged to sewage treatment plants. Given a typical removal efficiency of sewage treatment plants of 50 % the emission factor to the recipient water resource is 13.75 kg Cd/ton Cd processed.

Yost and Greenkorn [74] however, claimed for sintered plate processing in 1984 the following partition coefficient for the 5 % of the cadmium that is lost:

- 50 % is scrap which is recovered;
- 49 % is reclaimed as clarifier sludge and;
- 1 % is lost to aqueous waste streams.

This leads to an effective aqueous cadmium emission factor of 0.5 kg Cd/ton Cd.

The EC-directive (83/513/EEC), valid since January 1st 1986 [75], lays down limit values for cadmium discharges. The limit value is equal to 1.5 kg Cd/ton Cd.

An overview of all emission factors presented in this section is given in table 4.9. In this study the following emission factors are estimated based on the available literature and the references cited therein:

period	pocket-plate (kg Cd/ton Cd)	sintered plate (kg Cd/ton Cd)
1970 − 1972	8	15
1973 − 1977	4	10 − 15
1978 − 1982	3	5 − 10
1983 − 1987	1.5	2 − 3
1988	1.0	1.0

Using these emission factors and the production estimates given earlier the following emission estimates are obtained for the basin:

Period	Emission pocket-plate (ton Cd/yr)	Emission sintered plate (ton Cd/yr)	Emission sum (ton Cd/yr)
1970 − 1972	2.0	0.4	2.4
1973 − 1977	0.8	0.5 − 0.8	1.3 − 1.6
1978 − 1982	0.5	0.4 − 0.8	0.9 − 1.3
1983 − 1987	0.3	0.2 − 0.4	0.5 − 0.7
1988	0.1	0.2	0.3

The emissions calculated for the different types of batteries are somewhat artificial since they are linked to the activities of one company.

Table 4.9   Aqueous emission factors for cadmium dischargers due to Ni-Cd battery manufacturing in the Rhine River basin in the period 1970 − 1988

Date ref.	Emission factor (kg Cd/ton Cd processed)	Ref.
1973	3.0	[64]
1973	8.2	[29,64]
1975	2.0	[86]
1975	3.1	[87]
1979	3.6	[29,63]
1982	4.0	[28]
1982	6.5	[28,29]
1982	2.9	[29,88]
1982[1]	3.0[3]	[9]
1982[1]	1.5[4]	[9,48]
1982[2]	13.8	[9]
1984[1]	3.0[3]	[74]
1984[2]	0.5	[74]
1986	1.5	[75]

[1]   dealing with the manufacturing of pocket-plate cells

[2]   dealing with the manufacturing of sintered plate cells

[3]   without waste water treatment

[4]   with waste water treatment, efficiency 50 %

4.11 Cadmium plating

Corrosion was claimed to destroy one-fifth of the world production of ferrous metals annually [89]. Therefore corrosion protection of steel is of enormous importance. The usual method to protect steel is the use of a layer which covers the steel and inhibits the contact of corrosive environments with the steel surface. The materials used as layer are paints, polymer layers or metallic coatings. Cadmium is used as an anodic coating metal, because cadmium has compared with iron a superior corrosion resistance.

Four different plating techniques are used in cadmium plating: electroplating, mechanical plating, vacuum deposition and metal spraying. Only electroplating and to a minor extent mechanical plating are of commercial importance. Cadmium plating is, due to the high price and the environmental risks of cadmium, only applied in those applications where cadmium has no feasible substitutes. However, until the 1970's plate was the major use of cadmium in the basin.

Some of the specific advantages of the use of cadmium are [89]:

- cadmium offers a good protection in an alkaline, rural or marine environment as well as in the presence of detergents;
- cadmium coated steel is easily soldered and has a lower electrical contact resistance than zinc coated steel, which is important for electrical applications;
- cadmium corrosion products have a small volume. Therefore the products do not inhibit the functioning of a delicate mechanism (like a car-lock);
- cadmium can have an attractive polishable silvery finish;
- cadmium has a very low wear and is ductile.

The most common procedure for coating steel with cadmium is electroplating. The plating process is operated under either alkaline or acidic conditions.

-1- alkaline conditions

The usual alkaline solution contains dissolved cadmium cyanide. This solution is prepared by dissolving cadmium metal or oxide, cadmium or sodium cyanide and sodium hydroxide together with various additives. A plating bath contains typically:

- 20 g/l Cd^{2+}
- 120 g/l CN^-
- 15 - 20 g/l NaOH

The operating conditions are typically carried out at temperatures of 15 - 35 °C and at current densities between 0.5 and 5.0 amps/dm^2, usually 1.5 amps/dm^2. The plating time is about 10 − 15 minutes, depending on the layer thickness which is required. The minimum layer thickness is ranging from 5 to 25 um.

-2- acidic conditions

Acid cadmium fluoborate baths are used to reduce hydrogen entrapment in high tensile steels. The relative use of acidic cadmium plating has increased due to the serious occupational health risks involved in working with cadmium cyanide baths, as well as the problems related to discharging a waste liquor containing cadmium and cyanide ions. The acidic solution however, is corrosive towards the equipment and has less throwing power than the cyanidic bath. The operation temperature is 20 °C. A typical composition of a fluoborate bath is:

- 240 g/l $Cd(BF_4)_2$
- HBF_4 to pH 3.0 - 3.5
- 23 g/l H_3BO_3
- 60 g/l NH_4BF_4
- 1 g/l licorice

For some particular applications acidic cadmium sulfate plating baths are used.

The coating of steel products with cadmium is an aqueous chemical process. After the steel is coated, a cadmium containing solution is still entrained in the product or attached to the steel. In removing these residues rinsing water becomes contaminated with cadmium. Moreover, the plating bath liquor can only be used during a limited time, due to unavoidable contamination which increases in concentration in time. The two waste streams - the contaminated rinsing water and the polluted plating bath - require, due to the high aqueous cadmium concentration, a very efficient cadmium removal method and a special counter-current sequence of plating and rinsing baths, in order to cope with the present day environmental standards. In the past, when many small companies operated inadequate (if any) waste water treatment units, large aqueous cadmium emissions were caused due to plating.

A serious problem in analyzing the in-basin aqueous emission of cadmium due to cadmium plating is caused by the fact that the use data for the period 1970 - 1988 are only available for the FRG, for France (for 1975) and for The Netherlands (as estimates). No plant locations and no production capacities are known.

As noted by Rauhut, platers are mostly small operations and dispersed throughout the FRG. The Ruhr, however, may be particularly dense with respect to platers.

For Switzerland and Luxemburg no data are available. The in-basin cadmium use for plating in the period 1970 — 1988 in Switzerland and Luxemburg has probably been negligible. The data for France [29] do not enable to make any serious estimate. For the in-basin area in France no cadmium emissions due to plating are calculated.

For The Netherlands the use of cadmium for plating has been about 50 tons in the periods 1970 — 1972 and 1973 — 1977 [30]. In the late 1970's the use decreases significantly to about 5 tons in the period 1978 — 1982 and 1 — 3 tons in the period 1983 — 1987 [31,32].

For the FRG the most detailed use figures are presented by Stigliani [29]. The total processing in the FRG and The Netherlands for the different periods is summarized here.

Period	Use (NL) [1]	Use (FRG)	Use (F)
	(ton Cd/yr)	(ton Cd/yr)	(ton Cd/yr)
1970 — 1972	50	512	324
1973 — 1977	50	355	307
1978 — 1982	5	261	237
1983 — 1987	1 — 3	140	232
1988	0	72	167

[1] estimated values

For The Netherlands statistics are available on waste water discharges [68]. These statistics add the aqueous cadmium discharges by all Dutch metallurgical and metal industries inside and outside the basin. Insufficient details are available for determining individual sources, branches (like plating) and locations. However, the order of magnitude which equals 2.7 tons

of cadmium for 1976 — 1977, 1.2 tons for the period 1978 -- 1982 and 0.2 tons for the period 1983 — 1986 indicates that no significant discharges have taken place in the basin. Although these statistics unfortunately do not provide data earlier than 1976, it is assumed that aqueous in-basin emissions due to plating alone have not been higher than 1.0 ton of cadmium in The Netherlands in the 1970's.

For the FRG data are provided by Imhoff [48] and Simon [90]. Simon [90] gives a total use of cadmium for plating in the FRG of 400 tons/yr for 1981. Imhoff [48] claims that 300 tons were processed in the 1970's in the Ruhr River basin. Imhoff also shows illegal discharges of some plating companies, which have been detected by secret sampling, carried out by the Ruhrverband. The data presented by Imhoff and Simon conflict with respect to the magnitude of the cadmium discharges. Simon claims that about 700 kg cadmium is discharged in the FRG in 1981, whereas Imhoff shows that the total industrial discharge to the Ruhr equals about 4 tons in the 1970's (see Section 3). Imhoff does not mention the presence of the Nickel-Cadmium battery plant in Hagen specifically. Nevertheless it is assumed that industrial emissions of 4 tons in the River Ruhr include the battery manufacturing plant. This would still leave about 2.5 — 3 tons of the cadmium discharges to plating.

The only useful data for the determination of the in-basin and not-in-basin cadmium plating activity in the FRG are presented above. It is assumed that 300 out of 400 tons cadmium are used in the Ruhr River basin and that no other cadmium plating industry is located in the Rhine River basin. In order to obtain the in-basin cadmium use for plating, the use figures for the FRG are multiplied by 0.75. Rauhut's data, used by Stigliani [29], however, provided as cadmium use figure for plating in the FRG in 1981 only 160 tons. The significant differences between these figures are explained by the fact that the Imhoff data are related to the 1970's. For the sake of uniformity Stigliani's data [29], such as presented earlier, are used, multiplied by a factor 0.75 to correct for the FRG plating companies, located outside the basin. The factor 0.75 is assumed not to depend on time, which means that it is assumed that the decreasing market for cadmium plated products has not specifically struck the Ruhr area.

Many references have provided emission and emission factor estimates for the cadmium plating industry, which are now reviewed.

Rauhut [64] claims that the total emission due to cadmium plating in the FRG in 1973 was about 5 tons. Given the use of 394 tons cadmium this leads to an emission factor of 13 kg Cd/ton Cd processed [64].

Rauhut [86] claims in an EC-survey a specific emission factor for 1975 of 12.6 kg Cd/ton Cd processed.

The Technischer Arbeitskreis Cadmium im Verband der Chemischen Industrie, cited in [63], claimed for the FRG in 1979 a total emission of 1.5 ton cadmium. Given the use of 319 tons of cadmium [29] for plating this leads to an emission factor of 4.7 kg Cd/ton Cd processed.

Imhoff [48] published the total discharge of all cadmium using industries in the Ruhr River area. Before waste water treatment the industries discharge 6.6 tons of cadmium in the 1970's. Given the Ni-Cd battery production plant in the area and some potential other emission sources in the Ruhr like coke and iron and steel plants, the aqueous emission described to cadmium plating before treatment is still about 5 tons. After treatment this means that at least 2.5 to 3 tons cadmium emission is caused by the branch. Given Imhoff's assumption that around 300 tons of cadmium were used in plating, the emission factor would be about 8 — 10 kg Cd/ton Cd processed. This figure is much higher than the figure presented in a paper by Simon [90] which, based on an inventory made throughout the entire FRG plating industry, provided an emission figure of 1.5 to 1.8 kg Cd/ton Cd processed. This figure however, does not include the illegal discharges detected and described by Imhoff. The paper by Simon (1981) also provides the emission factor for best technical means which equals 0.5 — 1.0 kg Cd/ton Cd processed.

Schulte-Schrepping [88] provides data supplied by the Bundesverband der Chemischen Industrie for 1981. The overall emission for the FRG is estimated to equal 0.7 tons. This figure

is based on the work by Simon [90]. Rauhut [28] in his paper presented in 1982, also refers to the emission factor provided by Simon [90] of 2 kg Cd/ton Cd processed.

Hutton [9] provides in his 1982 inventory the following emission estimates. It is assumed that 10 % of the cadmium used in cadmium plating is lost to aqueous wastes. The cadmium lost to aqueous wastes is recovered for 50 % and discharged for 50 % to sewage treatment plants. This means that 5 % or 50 kg Cd/ton Cd processed is lost. Assuming waste water treatment plants to have an effective removal efficiency of 40 to 60 % [48,73] an emission of 25 kg Cd/ton Cd processed is caused.

Yost [91] estimates for 1983 the following flow of cadmium in a cadmium plating unit per 1000 kg cadmium purchased:

- 900 kg is used on the products;
- 100 kg is lost of which;

-1-   10 kg is recovered electrolytically;
-2-   10 kg is recovered via evaporation;
-3-   55 kg ends up in a chemical destruct waste treatment;
-4-   25 kg is lost untreated.

Ad -1- The material that is recovered electrolytically is recycled for 50 %, or 5 kg Cd/ton Cd. The other 5 kg cadmium is divided equally over the chemical destruct waste treatment and the untreated flow.

Ad -2- The material that is recovered in the evaporative section is recovered for 40 %, or 4 kg Cd/ton Cd processed. The other 6 kg cadmium is divided equally over the chemical destruct waste treatment and the untreated flow.

Ad -3- The 55 kg of cadmium that ends up directly in a chemical destruct waste treatment is divided as follows:

- 50 kg is precipitated as solid waste;
- 4.4 kg ends up in the sewage treatment plant;
- 0.6 kg is discharged directly to natural waters.

Ad -4- The 25 kg of cadmium that is lost untreated is divided as follows:

- 22.5 kg goes to sewage treatment plants;
- 2.5 kg is discharged to natural waters.

Summarizing these data the following distribution of cadmium is obtained (per 1000 kg of cadmium used):

- 909 kg is used (of which 9 kg after recycling);
- 55   kg is precipitated as solid waste;
- 32.3 kg is discharged to a sewage treatment plant and;
- 3.7 kg is discharged to natural waters.

Using the usual removal efficiency of 40 − 60 % for sewage treatment plants [48,73] the aqueous cadmium emission factor to natural waters is equal to 20 kg Cd/ton Cd processed.

Yost and Greenkorn [74] revised the data given above for 1984. Summarized, the distribution is as follows:

- 10 % of the cadmium consumed is lost to the aqueous waste stream of which;
- 77 % becomes landfilled sludge and;
- 23 % is discharged in waste water.

These 23 kg Cd/ton Cd processed is discharged to waste water treatment plants, so the effective emission factor is about 11.5 kg Cd/ton Cd processed.

The EC-limit, valid since January 1ᵘ 1986, equals 0.3 kg Cd/ton Cd processed [75]. In table 4.10 the emission factors presented above are given in summary. There's a considerable difference between the different sources. The emission factors presented in this study for the Rhine River basin are estimated based on the above mentioned sources.

Period	In-basin use (ton Cd)	Emission factor (kg Cd/ton Cd)	Emission (ton Cd)
1970 – 1972	384	20 – 30	7.7 – 10.6
1973 – 1977	266	15 – 25	4.0 – 6.7
1978 – 1982	196	10 – 20	2.0 – 3.9
1983 – 1987	105	1 – 6	0.1 – 0.6
1988	54	0.3	< 0.1

Table 4.10   Emission factors for the aqueous cadmium emission due to cadmium plating

Date ref.	Emission factor (kg Cd/ton Cd proc.)	Ref.
1973	13	[64]
1975	12.6	[86]
1979	4.7	[29,63]
1979[1]	8 – 10	[48]
1981	1.5 – 1.8	[90]
1981[2]	0.5 – 1.0	[90]
1982	25	[9]
1983[1]	20	[48,73,91]
1984[1]	11.5	[48,74]
1986	0.3	[75]

[1] after waste water treatment, efficiency 50 %
[2] best available technology by 1981, according to the source

4.12 Wet phosphoric acid manufacturing

This section describes one of the major cadmium discharging processes in the Rhine River basin, which is due to inadvertent use of cadmium. Cadmium is a natural constituent of apatite ore which is of sedimentary origin. The cadmium content of the ore is strongly depending on the location where the ore is found. This is shown in table 2.1 in Section 2. Magmatic phosphate ores do not contain much cadmium.

The phosphate ore is processed in order to produce phosphoric acid. Phosphoric acid

is a raw material for fertilizers, which are of major importance for the agriculture in the Rhine River basin.

The cadmium that is enclosed in phosphate ore is dissolved during the digestion of the ore by a mixture of sulfuric and phosphoric acid. During this digestion the major waste product is calcium sulfate. Calcium sulfate dihydrate or gypsum is precipitated during the phosphoric acid processes in order to remove the calcium from the phosphoric acid solution. The gypsum is a waste product for which only low-grade applications exist. Gypsum has had applications in the building industry, but as a building material these applications are limited more and more by three serious drawbacks:

-1-   the gypsum originating from wet phosphoric acid processes is contaminated with cadmium, but more important for building applications, it is also polluted with polonium and radium. The radioactive decay of these elements causes radiation, which forms a health hazard in living areas.

-2-   due to the international concern about acidification of the ecosphere due to fossile fuel burning, many coal-fired power stations have been equipped with flue gas desulfurization plants. Gypsum is formed during desulfurization, because lime is added to capture sulfur dioxide. The demand for gypsum is overwhelmed by the current supply.

-3-   despite of the large supply, natural gypsum, which is a cheap commodity, is still preferred for many applications. These applications include the use in pigments and in products in which the impurities contained in phosphoric acid gypsum or flue gas desulfurization gypsum inhibit their use.

For these reasons many wet phosphoric acid plants are discharging or dumping their waste gypsum. In the Rhine River basin three companies are involved in wet phosphoric acid production which discharge their cadmium containing gypsum in the Rhine. One plant is located in France and two plants are located in The Netherlands. The French plant is located in Ottmarsheim. The Dutch plants are located in Vlaardingen and Pernis, opposite to each other, about 20 km upstream of the Rhine mouth. There are also a couple of German plants in the Basin, but their waste gypsum is used for construction or is dumped in storage ponds.

The 'production' of cadmium is inadvertent. The magnitude of the cadmium 'production' is determined completely by the origin of the ore. Wet phosphoric acid manufacturers determine to some extent the cadmium 'production', although ores containing practically no cadmium have a limited availability on the world's phosphate ore market. Therefore, cadmium emissions via gypsum are for many wet phosphoric acid manufacturers more or less unavoidable.

The distribution of cadmium over the gypsum waste and the fertilizer product is depending on the wet phosphoric acid process lay-out. Many different processes are currently operated commercially. The main difference is determined by the modification of calcium sulfate that is precipitated, and the possible presence of recrystallization steps. In general 20 to 50 % of the cadmium that enters a plant via the phosphate ore is discharged with the gypsum and 50 to 80 % ends up in the phosphoric acid [8].

Based on the arguments presented above, it is evident that defining an emission factor for wet phosphoric acid manufacturing is useless, since each plant is different and each plant determines its cadmium 'production' by its ore purchase policy.

-1- The Dutch wet phosphoric acid plants

Aggregated direct emission figures for the two Dutch plants are available for 1974 and since 1976. The Dutch Central Bureau of Statistics has collected data for the industrial emission of cadmium in the province South-Holland. Both plants are located in South-Holland and are the practically the only source of cadmium emissions. Other references also provide data on these emissions. The data are summarized in table 4.11.

In table 4.11 the cadmium emission is estimated for the early 1970's since no emission figures are available for that period. The estimates are based on ore import data provided by the Dutch Central Bureau of Statistics [95]. Table 4.13 shows the phosphate ore imports for the period 1970 to 1976. The cadmium content of phosphate ore is given in table 4.12, using data presented by Feenstra [14] and Becker[97]. Feenstra [14] shows for 1978 that the ratio of in-basin phosphate ore processing over the total phosphate ore processing in The Netherlands equals 0.86. Assuming this ratio to be correct the cadmium influx of the in-basin plants is calculated, assuming the ores to be distributed evenly over the different plants in the country. The 1974 and the 1976 import data are included in order to calculate the fraction of the cadmium that ends up in the gypsum, since for 1974 and 1976 emission figures are available as well. For 1974 and 1976 the fraction cadmium that ends up in the gypsum equals in average 0.46 . The emission estimates given in table 4.11 are calculated for 1970 − 1973 and 1975 using this factor.

The figures presented in table 4.11 are aggregated for the different periods, used in this study. For those years where more than one emission estimate is presented, the data presented by the CBS (source [68]) are used.

Table 4.11   Cadmium emission data for the Dutch wet phosphoric acid manufacturing plants for the period 1970 — 1989

Year	Emission (ton Cd)	Ref.
1970	20.9[1]	
1971	20.7[1]	
1972	26.6[1]	
1973	27.0[1]	
1974	23	[92]
1975	19.9[1]	
1976	24.1	[68]
1977	14.9	[68]
1978	10.0	[68]
1979	10.0	[68]
1980	16.3	[68]
1981	16.1, 11, 15.7	[68,92,15]
1982	16.1	[68]
1983	16.2	[68]
1984	16.1	[68]
1985	16.6, 15.6, 15, 14	[68,92,32,20]
1986	11.7	[68]
1987	7.7, 14.2, 18.8	[68,93,94]
1988	9.0	[94]
1989	3.9	[94]

[1]   estimated values

Table 4.12   The cadmium content of phosphate ore [14,97]

Country/Origin	Range (ppm)	Average (ppm)
Senegal	70 — 90	80
USSR	0.1 — 0.4	0.25
Maroc	8 — 75	25
Tunesia		25[1]
Togo	+ 50	53[2]
USA	6 — 16	10

[1]   estimated value

[2]   ref. [97]

Table 4.13   Phosphate ore imports and the resulting cadmium import and in-basin processing in The Netherlands (in ton)

	1970	1971[1]	1972[1]	1973[1]	1974[2]	1975[1]	1976
Senegal	203,706	179,689	239,969	236,244	275,118	155,666	44,400
USSR	43,090	64,080	55,519	82,827	55,350	25,822	48,931
Maroc	436,979	342,856	536,464	461,716	651,424	526,531	579,401
Tunesia	17,671						
Togo	382,674	379,681	526,436	536,827	692,743	385,190	479,260
USA	496,141	497,472	675,256	622,444	818,987	510,251	590,508
Cd-import	52.8[3]	52.4[3]	67.2[3]	68.1[3]	80.3[3]	50.4[3]	47.3[3]
in-basin proc.	45.4	45.0	57.8	58.6	69.1	43.3	40.7

[1]   import data were only available for the period january to november and are multiplied by 12/11 to compensate for december

[2]   import data were only available for the period january to october and are multiplied by 6/5 to compensate for november and december

[3]   In order to improve accuracy the (small) export is subtracted from the import assuming the average cadmium content of the imported ore to be representative for the export. The figure presented in the table represents the result of this subtraction.

export: 1970   6,379 ton
          1971   244 ton
          1972   3,102 ton
          1973   34,943 ton
          1974   85,882 ton
          1975   26,579 ton
          1976   73,676 ton

-2- The French wet phosphoric acid plant

No direct aqueous emission data are available for this plant. The production capacity of the plant in Ottmarsheim is 50 kton of phosphoric acid. Phosphate ore import data are available for France in 1987 [8]. In 1987 in France 3,699 kton of ore was imported. The ore contained 103.4 ton cadmium. The figures available for The Netherlands in 1987 [8] (1,906 kton of phosphate ore imported which contained 51.2 ton cadmium) are comparable. The total production capacity of the two Dutch plants equals 360 kton of phosphoric acid.

Assuming the plants to have comparable processes an indication of the cadmium discharge via the gypsum discharge in France is calculated. The ratio of production capacity equals 50/360. Multiplying the Dutch emissions in the different periods with this factor results in emission estimates for the Ottmarsheim plant, varying between 1.3 and 3.2 ton aqueous cadmium emission per annum.

Die Internationalen Kommission zum Schutze des Rheins gegen Verunreinigung [96]

shows that by 1985 the total French cadmium discharge equals 5.5 % of all direct cadmium discharges. The total sum of all discharges equals 24 tons, which shows that all French discharges together are equal to 1.3 tons of cadmium. This shows that the emission estimate for the period 1983 — 1987 is too high, since the sector mining also contributed about 500 kg cadmium/yr.

It is assumed that the calculated figure for 1988 is too high as well. This argument is based on data provided by ICWS [49] in which phosphoric acid manufacturing is not mentioned.

Due to the crude assumptions made and the very limited data, the figures presented for France only give the order of magnitude of the emissions.

Period	Aqueous cadmium emission	
	NL (ton Cd/yr)	F (ton 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

4.13 The iron and steel industry, including coke production

4.13.1 Introduction

The iron and steel production process includes a great variety of unit operations and the use of different raw materials in which minor amounts of cadmium are contained. In order to facilitate the discussion, this section is split up into different sub-sections, each discussing a separate step.

Figure 4.3 gives a scheme of an integrated iron and steel production facility.

4.13.2 The production of coke

Carbon, in the form of coke is essential for generating a reductive atmosphere which is required for converting oxidic iron ores into metallic iron. The most suitable raw material for the very large quantities of coke used in the iron and steel industry is coal. The most important reasons for choosing coal (in comparison to other hydrocarbons) are:

- it is cheap;
- it is relatively abundant;
- its supply is not determined by political conflicts and;
- it has an overall hydrogen/carbon ratio which is comparatively small.

Heavy fuel oil is rarely used for coke production.

The inadvertent use of cadmium in coke production is entirely due to the use of cadmium containing coal. Therefore, emissions due to coke production are determined by the cadmium content of the coal. In Section 2 of this study it is shown that the cadmium content of coal varies between 0.22 and 1 ppm [8,17]. Hutton [9] uses a cadmium content of 1 ppm in his analysis, using data supplied by Prater for the 1978 UK Iron and Steel industry. After correcting arithmetic errors in Prater's paper it is found that for 1978 the production of 7.27 Mton coke, based on 10.2 Mton of coal, results in an atmospheric emission of 1.53 ton cadmium and an aqueous emission of 2.04 ton cadmium. This aqueous emission is due to waste gas cleaning devices, in which wet scrubbers are operated.

The aqueous emission factor, based on these results equals (281 * A) kg Cd/Mton coke produced, in which A represents the cadmium content of the coal in ppm. This emission factor is the only available source and is used for the analysis below. If it is assumed that:

- the cadmium content of the coal is 1 ppm;
- the 1978 based emission factor is correct for the period 1970 - 1988;

a worst case or high scenario is obtained. Later a low scenario is defined.

Inside the basin many coke plants are and have been operational. Anderberg [98] has made an overview of these plants and their production (capacity) which has been used as a source for this work. Table 4.14 shows the production capacity of the different plants in time. No coke plants are located in-basin in The Netherlands, Switzerland or Luxemburg.

The 30 in-basin coke plants are aggregated to a more practical level, before the corresponding emissions, using the two scenario's, are calculated.

The aggregation level is based on the locations of the plants in the basin. Table 4.15 presents the calculated emissions for the basin and refers, via the plant numbers, to the original plants.

The values calculated for the high scenario are too high for the periods 1983 − 1987 and 1988. The figures for the period 1978 − 1982 are probably too high as well. The evidence for this statement is provided by the following sources.

The three plants in Duisberg have not been mentioned in the inventory by the Deutsche Kommission zur Reinhaltung des Rheins as major discharging plants [62] in 1985, which would have been the case if their total emission would have been equal to 1.1 ton.

The ICWS-inventory [49] lists (see table 3.6) tributary contributions to the River Rhine for 1989. All tributaries contribute significantly less cadmium than, even taking into account potential accumulation in the sludge, the calculated emissions would probably give rise to. This also indicates that the figures given in table 4.15 for the high scenario are too high for the 1980's.

Table 4.14   Coke production plants in the Rhine River basin and their production capacity in kton coke/yr during the period 1970 — 1988

Plant	1970–1972	1973–1977	1978–1982	1983–1987	1988
France					
1. Pont-a-Mousson	306	277	275	240	208
2. Seremange	306	277	534	564	669
3. Neuves-Maisons	242	219	204	0	0
4. Carling	1,515	1,373	1,296	1,255	1,493
5. Marienau	1,019	923	869	562	45
6. Joeuf-Hom	267	242	45	0	0
7. Hagondang	267	242	45	0	0
Sum	3,922	3,554	3,268	2,621	2,414
FRG					
8. Furstenhausen	1,716	1,501	1,250	1,432	1,318
9. Dortmund -1-	1,268	1,110	924	0	0
10. Dortmund -2-	2,425	2,121	1,766	1,618	1,017
11. Dortmund -3-	970	849	706	854	885
12. Dortmund -4-	1,455	1,273	1,059	1,020	715
13. Du-Huckingen	1,119	979	815	1,082	998
14. Du-Hamborn	2,723	2,383	1,983	2,447	2,259
15. Du-Rheinhausn	634	555	462	523	489
16. Datteln	671	587	489	0	0
17. Essen	3,767	3,296	2,744	3,043	2,730
18. Bottrop	2,611	2,285	1,902	1,208	1,242
19. Oberhausen-1-	2,089	1,828	1,521	785	0
20. Oberhausen-2-	1,343	1,175	978	0	0
21. G-Kirchen -1-	1,977	1,730	1,440	1,512	1,374
22. G-Kirchen -2-	448	392	326	0	0
23. G-Kirchen -3-	1,940	1,697	1,413	1,424	1,299
24. Erkenschwick	634	555	462	0	0
25. Hamn	709	620	516	325	0
26. Castrop-Rauxel	970	849	706	0	0
27. Voelklingen	821	718	598	379	0
28. Burbach	671	587	489	0	0
29. Neunkirchen	560	490	407	0	0
30. Dillingen	709	620	516	973	1,261
Sum	32,227	28,198	23,471	18,626	15,587

coal   ore   ore

side-products gaspu-rifica-tion   coke plants   sinter plants   pelleti-zing plants

coke oven gas   coke   sinter   pellets

process fuel   gaspu-rifica-tion   blast furnace

blast furnace gas   blast furnace slag   pig iron   oxygen making

road construction products slag proces-sing   oxygen steel factories

clinker

plaster of Paris   granu-lation

cement facto-ries   continu-ous cas-ting ma-chine   steel blocks

blast furnace cement

roll mill for thick plate   slabs   blooming mills   blooms

thick and medium plate

hot strip mills   billet mills

hot rolled thin sheet and sheet of medium thickness

cold re-ducing mills   tinning line   billets

cold rolled thin sheet

tin plate

billets

bar and wire mill

reinforced concrete steel, bar steel, rod wire

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Table 4.15   Aqueous cadmium emissions in ton/yr in the Rhine River basin due to coke production in the period 1970 - 1988

tributary/river	1970–1972	1973–1977	1978–1982	1983–1987	1988
Saar[1] High Low	2.0 2.0	1.7 1.7	1.5 0.7	1.3 0.13	1.2 0.1
Moselle[2] High Low	0.4 0.4	0.4 0.4	0.3 0.1	0.2 0	0.2 0
Ruhr High Low	1.1 1.1	0.9 0.9	0.8 0.4	0.9 0.09	0.8 0.1
DortmundEms High Low	0.2 0.2	0.2 0.2	0.1 0.1	0 0	0 0
Rhine High Low	1.3 1.3	1.1 1.1	0.9 0.4	1.1 0.11	1.1 0.1
Lippe[3] High Low	0.4 0.4	0.3 0.3	0.3 0.1	0.1 0	0 0
Emscher[4] High Low	4.9 4.9	4.3 3.6	3.6 1.7	2.4 0.24	1.8 0.2
Sum High Low	10.3 10.3	8.9 8.9	7.5 3.5	6.0 0.6	5.1 0.5

[1]   including the tributaries to the Saar

[2]   including the tributaries Orne and Fensch but excluding the Saar

[3]   including a tributary to the Lippe

[4]   including the Rhein - Herne Kanal

River	Plant no.'s
Saar	4, 5, 8, 27, 28, 29, 30
Moselle	1, 2, 3, 6, 7
Ruhr	17
Dortmund-Ems	16
Rhine	13, 14, 15
Lippe	24, 25
Emscher	9, 10, 11, 12, 18, 19, 20, 21, 22, 23, 26

A low scenario is obtained by dividing the figures for the 1980's by a factor of 10 correcting for:

- the improved environmental technology;
- the possibility that the cadmium content of the coal is lower than the 1.0 ppm that is assumed above.

The overall figures for a low scenario for the 1980's are added, assuming the emission factor (since 1980) to be equal to 10 % of the factor given for the high scenario.

It is assumed for the high and the low scenario that the French and the German plants used the same emission control technology. This is, for the 1980's, probably not correct, but hard to take into account in this analysis.

4.13.3 Sinter production

The second step in integrated steel manufacturing is the production of sinter. This step includes the agglomeration of the fine ore particulates to yield sintered ore. The increase of the particle size is required for the operation of a blast furnace. The sinter process is carried out at high temperatures and without any aqueous steps. Aqueous emissions of whatsoever material due to sintering are very unlikely.

4.13.4 Crude iron production

Crude iron is manufactured in a blast furnace. Raw materials for this process are iron ore, manganese ore, coke and sinter. No aqueous emissions of cadmium are ascribed to this process. The cadmium content of the ore is consequently transferred quantitatively to the crude iron out of which steel is produced.

4.13.5 Steel production

Three different processes are operated for iron and steel production. These are:

- open hearth furnace (OHF);
- basic oxygen steel (BO) and;
- electric arc furnace (EA).

The OHF-method is not applied in the basin and is therefore not analyzed in this study. The BO-steel method is the usual method to convert oxidic iron ores via crude iron into steel. The EA-method is primarily operated for the recycling of steel. Recycled steel is a secondary source

of steel which is known to contain a relatively high content of cadmium compared to crude iron, produced from oxidic iron ores. The high cadmium content of the recycled steel is due to the application of cadmium as a steel surface protecting layer on a minor part of the steel that is recycled.

As with coke production the steel production is studied separately for the FRG and France. Stigliani [29] and Anderberg [98] have collected data on the production of steel in the basin as well as in France and in the FRG. The production capacities for the individual plants for EA- and BO-steel are known for a particular year and assumed to be constant.

Using these data the relative in-basin production capacity for BO-steel and EA-steel which respect to the overall production in France and the FRG respectively is obtained for each plant. These relative production capacities are multiplied by the overall production of EA- and BO-steel for an individual year in the period 1970 - 1988 in order to obtain an estimate of the actual annual production realized by the individual plants.

For the FRG the following data are available. Table 4.16 gives the relative production capacities for all FRG in-basin plants that produce EA- or BO-steel or both. The percentage of in-basin EA-steel production capacity is 0.6675, for BO-steel production capacity it is 0.6130. Table 4.17 gives the overall crude iron, EA-steel and BO-steel production in the FRG for the period 1970–1988. Table 4.18 gives the aggregated EA- and BO-steel production in time. Table 4.19 presents the production figures for EA- and BO-steel for the basins of the tributaries, the Rhine upstream of Koblenz and the Rhine between Koblenz and Lobith.

For France the data are more limited. Table 4.20 presents the relative production capacity of the French in-basin steel production plants. The percentage of in-basin EA-steel production capacity is 0.2394, for BO-steel production capacity it is 0.5536.

The only data source for the French total production of EA- and BO-steel were given for 1977. The total EA-steel production was 5,562,515 tons. The total BO-steel production was 23,902,484 tons.

In order to estimate the total production capacity for other years in France, it is assumed that the trend in time has been equal to the trend for the FRG.

The 1977 FRG BO- and EA-steel production is chosen as index 100 and for all other years production indexes are calculated. Multiplying these indexes with the French 1977 production data and aggregating the data in the usual periods, the results presented in table 4.21 are obtained. Table 4.22 presents the in-basin French production of EA- and BO-steel in aggregated periods.

Table 4.16   The relative production capacity of the FRG in-basin steel production plants

Plant	% EA-steel	% BO-steel
River Rhine A. Upstream of Koblenz 1. Kehl	0.1080	0
B. between Koblenz and Lobith 2. Rheinhausen 3. Duisburg-Huckingen 4. Duisbg-Bruckhausen 5. Duisbg-Beekerwerth 6. Duesseldorf -1- 7. Duesseldorf -2- 8. Krefeld	0 0.0178 0 0 0.0039 0.0020 0.0094	0.0679 0.0943 0.1321 0.1335 0 0 0
SUM (of B.)	0.0331	0.4278
River Ruhr 9. Bochum -1- 10. Bochum -2- 11. Hattingen -1- 12. Hattingen -2- 13. Witten 14. Duisburg-Ruhrort	0.0785 0.0097 0.0024 0.0677 0.0053 0	0.0095 0 0 0.0261 0 0.0243
SUM	0.1636	0.0599
River Emscher 15. Dortmund 16. Oberhausen	0.0248 0.0428	0.1064 0
SUM	0.0676	0.1064
River Sieg 17. Siegen -1- 18. Siegen -2-	0.1046 0.0310	0 0
SUM	0.1356	0
Rivers Saar + Moselle 19. Voelklingen (S) 20. Bous (S) 21. Trier (M)	0.0565 0.0262 0.0030	0.0734 0 0
SUM	0.0847	0.0734
River Lahn 22. Wetzlar	0.0194	0

Table 4.17   The overall crude iron, EA-steel and BO-steel production in the FRG in the period 1970 - 1988

Year	Crude iron (kton)	EA - steel (kton)	BO - steel (kton)
1970	36,908	6,666	38,375
1971	31,315	5,966	34,347
1972	31,211	6,468	37,237
1973	36,828	7,329	42,192
1974	40,221	7,878	45,354
1975	28,049	5,981	34,431
1976	31,629	6,277	36,136
1977	28,724	5,770	33,214
1978	29,939	6,105	35,148
1979	35,181	6,814	39,226
1980	33,873	6,488	37,350
1981	31,876	6,158	35,452
1982	27,621	5,310	30,570
1983	26,598	5,288	30,441
1984	30,203	5,830	33,559
1985	31,531	5,994	34,503
1986	26,712	5,496	31,638
1987	24,345	4,798	27,619
1988	26,667	5,255	30,253

Table 4.18   The aggregated production for EA-steel and BO-steel in the FRG in the period 1970 - 1988

Period	EA - steel (kton)	BO - steel (kton)
1970 - 1972	6,367	36,653
1973 — 1977	6,647	38,265
1978 — 1982	6,175	35,549
1983 — 1987	5,481	31,552
1988	5,255	30,253

Table 4.19(A)   The in-basin FRG production of EA-steel (in kton) in aggregated
                       periods

River (plant no.)	1970 − 1972	1973 − 1977	1978 − 1982	1983 −1987	1988
Rhine -A- 1.	688	718	667	592	568
Rhine -B-					
3.	113	118	110	98	94
6.	25	26	24	21	20
7.	13	13	12	11	10
8.	60	62	58	52	49
SUM	211	219	204	182	173
Ruhr					
9.	500	522	485	430	413
10.	62	64	60	53	51
11.	15	16	15	13	13
12.	431	450	418	371	356
13.	34	35	33	29	28
SUM	1,042	1,087	1,011	896	861
Emscher					
15.	158	165	153	136	130
16.	273	284	264	235	225
SUM	431	449	417	371	355
Sieg					
17.	666	695	646	573	550
18.	197	206	191	170	163
SUM	863	901	837	743	713
Saar & Moselle					
19.	360	376	349	310	297
20.	167	174	162	144	138
21.	19	20	19	16	16
SUM	546	570	530	470	451
Lahn 22.	124	129	120	106	102

Table 4.19(B)   The in-basin production of BO-steel (in kton) in aggregated periods

River (plant no.)	1970 – 1972	1973 – 1977	1978 – 1982	1983 – 1987	1988
Rhine -B-					
2.	2,489	2,598	2,414	2,142	2,054
3.	3,456	3,608	3,352	2,975	2,853
4.	4,842	5,055	4,696	4,168	3,996
5.	4,893	5,108	4,746	4,212	4,039
SUM	15,680	16,369	15,208	13,497	12,942
Ruhr					
9.	348	364	338	300	287
12.	957	999	928	824	790
14.	891	929	864	767	735
SUM	2,196	2,292	2,130	1,891	1,812
Emscher					
15.	3,900	4,071	3,782	3,357	3,219
Saar					
19.	2,690	2,809	2,609	2,316	2,221

Table 4.20   The relative production capacity of the French in-basin steel production plants[1,2]

Plant	% EA-steel	% BO-steel
1. Pompey	0.1387	0.0574
2. Gadrange/Rombas	0	0.2159
3. Hagondange	0.0647	0.0403
4. Neuves Maisons	0	0.0607
5. Thionville	0.0360	0
6. Seremange	0	0.1793
SUM	0.2394	0.5536

[1]   All plants are located to the Moselle, expect for plant 6. which is located to the tributary Fensch

[2]   The relative production capacities are based on data for 1977

Table 4.21   The aggregated production for EA-steel and BO-steel in France in the period 1970 - 1988, using FRG production statistic indexes

Period	EA-steel (kton/yr)	BO-steel (kton/yr)
1970 — 1972	6,135	26,364
1973 — 1977	6,419	27,583
1978 — 1982	5,952	25,576
1983 — 1987	5,284	22,707
1988	5,062	21,751

Table 4.22   The in-basin French production of steel (in kton) in aggregated periods

Plant no.	1970 — 1972	1973 — 1977	1978 — 1982	1983 — 1987	1988
EA-steel					
1.	851	890	826	733	702
3.	397	415	385	342	328
5.	221	231	214	190	182
SUM	1,469	1,536	1,425	1,265	1,212
BO-steel					
1.	1,513	1,583	1,468	1,303	1,249
2.	5,692	5,955	5,522	4,902	4,696
3.	1,062	1,112	1,031	915	877
4.	1,600	1,674	1,552	1,378	1,320
6.	4,727	4,946	4,586	4,071	3,900
SUM	14,594	15,270	14,159	12,569	12,042

The data on emission factors for steel production are limited. Hutton [9] claims that as of 1982, it is not possible to estimate the aqueous emission of cadmium from steel manufacturing, due to lack of data.

Yost [99] investigates the iron and steel industry in 1979. In his scenario, based on 1975 data, the following distribution of the different cadmium waste streams in the steel industry is given:

- 91.7 % goes to landfill;
- 1.1 % is recycled;
- 6.1 % is emitted to air and;
- 1.1 % is emitted to water.

However, it is not explained how these figures were obtained and whether these figures are related to EA- or BO-steel production.

The same author presents in 1983 [91] an overview of the emissions due to steel making, given the then current practice. In this reference the following figures are given:

- 89.1 % goes to landfill;
- 10.5 % is emitted to air and;
- 0.4 % is emitted to water.

As for ref. [99] no indication is given about the process for which these data are valid.

The Dutch Handbook of Emission Factors [100] gives for 1983 for an integrated BO-steel plant an emission factor of 0.1 − 0.5 g CdO or 0.09 − 0.45 g Cd to water per ton of crude iron. It is not clear whether the cadmium emission of the BO−steel unit which follows the crude iron unit is included in this factor and whether the coke production plant is excluded. In case this emission factor includes the entire plant the following nett emission of the BO-steel unit is obtained. Stigliani [29] shows that per ton of crude iron 0.597 ton coke is required. The emission factor for coke production equals (given a Cd-concentration of coal of 1 ppm): 0.281 g Cd/ton coke. Per ton crude iron this factor equals: 0.168 g Cd/ton crude iron. Given an overall emission of 0.1 - 0.45 g Cd/ton crude iron the nett emission due to crude iron and BO-steel production equals: 0 − 0.28 g Cd/ton crude iron. Although BO-steel is primarily made from crude iron a minor amount of scrap is usually added. The scrap is the major cadmium source in BO-steel production. However, assuming this contribution to be included in the figure given above, the emission factor only needs to be divided by the ratio of BO-steel/crude iron in order to obtain an emission factor for BO-steel production. The ratio BO-steel/crude iron equals typically 1.2 (taking into account the scrap). Finally, the emission factor for BO-steel production is then equal to: 0 - 0.23 g Cd/ton BO-steel.

A large BO-steel plant (out of basin) with an annual steel production of 5 to 7 million tons steel is known by 1985 to cause an aqueous emission of about 50 kg cadmium [32]. This indicates that the emission factor is equal to 0.007 − 0.01 g Cd/ton BO−steel. For the French part of the Rhine (1985) the aqueous cadmium emission is estimated to be equal to 100 kg for production and treatment of metals. The production of coke, together with mining and tar production is responsible for 300 kg Cd/year [101]. A similar study for Luxemburg showed that the total aqueous emission of cadmium by industry to the Rhine was equal to 66 kg/year for 1985 [62].

ERL [8] distinguishes separate emission factors for BO-steel and EA-steel. For BO-steel the factor equals 0.18 g Cd/ton BO-steel, for EA-steel it equals 0.14 g Cd/ton EA-steel. Table 4.23 gives a summary of the emission factors. Before estimating the emission factors, two trends in time regarding environmental protection in the iron and steel industry are mentioned.

-1-   Due to the increased environmental concern, higher legal standards to reduce the atmospheric pollution have been adopted in the in-basin countries. As a consequence of this, the use of wet scrubbers might have reduced the atmospheric pollution but actually increased the aqueous pollution.

-2-   The aqueous pollution in general has been reduced in the period 1970 − 1988 due to the availability of better pollution control devices and the increased environmental concern about heavy metal pollution.

It is assumed that in the period 1970 − 1982 efforts were made to control atmospheric pollution and from 1983 on efforts were made to control aqueous pollution as well. It is important to notice that a significant part of the iron and steel production capacity has been shut down in the period. Mostly these were the older, smaller plants, which a.o. for environmental reasons were no longer competitive. For these plants it was not possible to comply with the higher standards

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without investments that, given the size or the age of the unit, would never give satisfying returns.

Based on table 4.23 and the arguments presented above the following emission factors are estimated:

Period	Emission factor (g Cd/ton steel)		Total emission
	BO-steel	EA-steel	(ton Cd/yr)
1970 − 1972	0.4	0.4	17.8
1973 − 1977	0.4	0.4	18.7
1978 − 1982	0.45	0.45	15.4
1983 − 1987	0.2	0.2	6.6
1988	0.05	0.05	1.7

In table 4.24 the resulting in-basin iron and steel emissions are given for the individual rivers. The emissions for the period 1970 - 1982 have been considerable, but a significant decrease has taken place in the 1980's.

Table 4.23   Aqueous emission factors for cadmium due to EA- and BO-steel manufacturing in the Rhine River basin in the period 1970 − 1988

Year	Emission factor (g Cd/ton steel)	Ref.
1982	not possible	[9]
1983	0.09 − 0.45[1]	[100]
1983	0 − 0.28[2]	[9,100]
1983	0 − 0.23[3]	[9,29,100]
1985	0.007− 0.01	[32]
1989	0.18[4]	[8]
1989	0.11[5]	[8]

[1]   emission per ton crude iron (probably for the entire plant)
[2]   emission per ton crude iron (exclusive coke production)
[3]   emission per ton BO-steel (exclusive coke production)
[4]   emission per ton BO-steel
[5]   emission per ton EA-steel

Table 4.24(A) The in-basin aqueous cadmium emissions due to EA-steel production

River	1970 − 1972	1973 − 1977	1978 − 1982	1983 − 1987	1988
Rhine -A-	0.3	0.3	0.3	0.1	0
Rhine -B-	0.1	0.1	0.1	0	0
Ruhr	0.4	0.4	0.5	0.2	0
Emscher	0.2	0.2	0.2	0.1	0
Sieg	0.3	0.4	0.4	0.1	0
Saar & Moselle[1]	0.8	0.8	0.9	0.3	0.1
Lahn	0	0.1	0.1	0	0
SUM	2.1	2.3	2.5	0.8	0.1

Table 4.24(B) The in-basin aqueous cadmium emissions due to BO-steel production

River	1970 − 1972	1973 − 1977	1978 − 1982	1983 − 1987	1988
Rhine -B-	6.3	6.7	6.8	2.7	0.6
Ruhr	0.9	0.9	1.0	0.4	0.1
Emscher	1.6	1.6	1.7	0.7	0.2
Saar & Moselle[1]	6.9	7.2	3.4	3.0	0.7
SUM	16.4	16.4	12.9	5.8	1.6

[1]   including the French plants

5   CONCLUDING REMARKS

This section contains an overview of the aqueous point source cadmium emissions which are calculated in Section 4 of this study. Table 5.1 provides these data per branch. Table 5.2(A) and 5.2(B) show the geographical spread of the emissions in the basin. The emissions are related to a location, but due to sedimentation in the tributaries, there is no direct relationship between the point source emissions to a tributary and the contribution of the tributary to the River Rhine. Hydrological studies of the in-basin tributaries and the River Rhine itself are planned to bridge this gap in this study.

In table 5.3 the contributions of the tributaries are added to the direct emissions to the Rhine in the three Rhine sections:

(1)   upstream of Koblenz;
(2)   between Koblenz and Lobith and;
(3)   downstream of Lobith.

In this approach the potential sinks of cadmium in the tributaries are neglected. This is reflected in the magnitude of the figures, which for example for the period 1983 - 1987 are relatively high compared with the monitoring data given in Section 3. For the Rhine sections (2) and (3) together the overall point source cadmium emission is supposed to equal only 6 tons.

For section -2-, which is the only sector of serious interest, the figures for the periods 1973 — 1977 (monitoring data: 110 ton Cd, emissions: 90 — 100 ton Cd) and 1978 — 1982 (monitoring data: 67 ton Cd, emissions: 75 ton Cd) compare, given the limited accuracy, reasonably well.

Based on the emission overview the following conclusions are drawn:

- The aqueous point source cadmium emissions in the Rhine River basin have decreased by a factor of 10 in a period of 15 years. By 1988 the only significant emission is due to wet phosphoric acid manufacturing. In 1989 this emission has decreased to about 3 tons, which once more meant a decrease of 50 % of the overall emission.

- The contribution of wet phosphoric acid manufacturing to the total cadmium emission rises from 19 % in the early 1970's to 70 % in 1988, which justifies the current research investments and efforts undertaken to limit this emission.

- The importance of one plant in which zinc was recycled is striking; the closure of this single plant has decreased the in-basin aqueous cadmium emission by more than 50 %

- The point source emissions to the River Rhine itself contribute between 70 % in the early 1970's to more than 80 % in the 1980's to the overall emission of point sources in the basin.

- Inadvertent uses to a large extent dominate the aqueous emission of cadmium in the period 1970 - 1988. The production (via Pb/Zn) and recycling of cadmium as well as the four main uses (pigments, stabilizers, batteries and plate) contribute between 19 and 27 % in the early 1970's down to only 6 % to the total emission in the 1980's.

- The major part of the cadmium emissions to the Rhine itself are until 1984 located between Koblenz and Lobith. After 1984 more than half of the emissions take place downstream of Lobith.

Table 5.1   Aqueous point source cadmium emissions in the Rhine River basin in the period 1970 − 1988 per branch[1]

Branch	1970–1972	1973–1977	1978–1982	1983–1987	1988
non-ferrous mining	0.4	0.4	0.1	0.1	
other mining		0.5	0.5	0.5	0.5
primary Zn/Pb	2.0	1.6	1.0	0.5	0.1
secondary zinc	50	50	50	10^2	0
sec. cadmium	3	3		0	0
secondary lead	0.6	0.6	0.6	0.6	0.6
pigment manuf.	9.0–18.0	4.0–10	1.3	0.3	0.2
stabilizer m.	0.9– 1.7	0.4– 0.9		0	0
PVC manuf.	0.5– 1.0	0.5– 1.1	0.6– 1.4	0.4– 0.9	0
battery prod.	2.4	1.3– 1.6	0.9– 1.3	0.5– 0.7	0.3
plate	7.7–11.6	4.0– 7.7	2.0– 4.4	0.1– 0.7	0.1
phosphoric acid manufacturing	25.9	24.8	15.6	13.7–15.6	9– 10.3
coke production	10.3	8.9	3.5	0.5	0.6
iron & steel	17.8	18.7	15.4	7.6	1.7
SUM	130.5–144.7	118.7–129.7	91.5 -- 95.1	34.8 – 38.0	13.1– 14.4

[1]   Blank spaces indicate that no data were available to justify any estimate.

[2]   Estimate, based on the assumption that in 1983 and 1984 together 50 tons of cadmium were emitted.

Table 5.2(A)   Geographical spread of the aqueous point source cadmium emissions (ton/yr) in the Rhine River basin in time for the period 1970 − 1988[1]

A: Discharges directly to the Rhine

	1970–1972	1973–1977	1978–1982	1983–1987	1988
1. upstream of Koblenz					
other mining		0.5	0.5	0.5	0.5
PVC-production[2]	0.1 − 0.2	0.1 − 0.2	0.1 − 0.3	0.1 − 0.2	0
phosph. Acid	3.2	3.0	1.9	0 − 1.9	0 − 1.3
iron and Steel	0.3	0.3	0.3	0.1	0
SUM	3.6 − 3.7	3.9 − 4.0	2.8 − 3.0	0.7 − 2.7	0.5 − 1.8
2. between Lobith and Koblenz					
primary Zn/Pb	2.0	1.6	1.0	0.5	0.1
secondary zinc	50	50	50	10[3]	0
sec. cadmium	3.0	3.0		0	0
secondary lead[4]	0.4	0.4	0.4	0.4	0.4
pigment manuf.	6.2–12.4	2.8–6.9	0.9	0.2	0.1
PVC-production[2]	0.1− 0.2	0.1–0.2	0.1–0.3	0.1–0.2	0
coke production	1.3	1.1	0.4	0.1	0.1
iron and Steel	6.4	6.8	6.9	2.7	0.6
SUM	69.4 − 75.7	65.8 − 70	59.7 − 59.9	14 − 14.1	1.3
3. downstream of Lobith					
phosph. Acid	22.7	21.8	13.7	13.7	9.0
PVC-production	0 − 0.1	0 − 0.1	0 − 0.1	0 − 0.1	0 − 0.1
plate	0 − 1	0 − 1	0 − 0.5	0 − 0.1	0
SUM	22.7–23.8	21.8–22.9	13.7–14.3	13.7–13.8	9.0–9.1
Grand Total	95.7–103.2	91.5–96.9	76.2–77.2	28.4–30.7	10.8–12.1

[1]   Blank spaces in the table indicate that no data were available to justify any estimate.

[2]   The figures for PVC-production are obtained using "possibility -2-" in ch4.7, assuming the ratio of PVC-production and thus stabilizer use in time for the different companies to be constant. The ratio of cadmium stabilizer use is:
Ludwigshafen   21 %
Rheinberg   22 %
Marl   57 %

[3]   estimate, based on the assumption that in 1983 and 1984 together 50 tons of cadmium were emitted.

[4]   69 % of the production capacity is located directly to the Rhine [29] in the 1980's. This ratio is assumed to be constant for the whole period.

Table 5.2(B)   Geographical spread of the aqueous point source cadmium emissions (ton/yr) in the Rhine River basin in time for the period 1970 – 1988[1]

B: Discharges to tributaries

Tributaries	1970–1972	1973–1977	1978–1982	1983–1987	1988
1. upstream of Koblenz Neckar[2] pigment manuf. stabilizer m.	2.8 – 5.6 0.9 – 1.7	1.2 – 3.1 0.4 – 0.9	0.4	0.1 0	0.1 0
Main[2] secondary lead[3]	0.1	0.1	0.1	0.1	0.1
Lahn iron and Steel	0	0.1	0.1	0	0
SUM	3.8 – 7.4	1.8 – 4.2	0.6	0.2	0.2

2. between Lohith and Koblenz					
Moselle[2]					
coke production	2.4	2.1	0.8	0.1	0.2
iron and steel	7.7	8.0	4.3	3.3	0.8
Sieg					
non-ferrous mining	0.1	0.1	0		
iron and steel	0.3	0.4	0.4	0.1	0
Erft[2]					
secondary lead[4]	0.1	0.1	0.1	0.1	0.1
Ruhr[5]					
plate	7.7 – 10.6	4.0 – 6.7	2.0 – 3.9	0.1 – 0.6	0.1
coke production	1.3	1.1	0.5	0.1	0.1
iron and steel	1.3	1.3	1.5	0.6	0.1
battery	2.4	1.3 – 1.6	0.9 – 1.3	0.5 – 0.7	0.3
non-ferrous mining	0.3	0.3	0.1	0.1	
Emscher[6]					
coke production	4.9	4.3	1.7	0.2	0.2
iron and steel	1.8	1.8	1.9	0.8	0.2
Lippe[2]					
PVC-production	0.3 – 0.5	0.3 – 0.6	0.3 – 0.7	0.2 – 0.4	0
coke production	0.4	0.3	0.1	0	0
SUM	31 – 34.1	25.4 – 28.7	14.6 – 17.3	6.2 – 7.1	2.1

Notes with table 5.2(B)

[1]   Blank spaces in the table indicate that no data were available to justify any estimate.

[2]   Inclusive tributaries to a tributary

[3]   This plant has 21 % of the secondary lead production capacity

[4]   This plant has 10 % of the secondary lead production capacity

[5]   Inclusive the Dortmund-Ems Kanal and tributaries to the Ruhr

[6]   Inclusive the Rhein-Herne Kanal and tributaries to the Emscher

Table 5.3   The grand totals of the point source emissions of cadmium to the River Rhine
            (in ton Cd / year)

	1970 − 1972	1973 − 1977	1978 − 1982	1983 − 1987	1988
Rhine -1-	7.4− 11.1	5.7 − 8.2	3.4 − 3.6	0.9 − 2.9	0.7 − 2.0
-2-	100.4−109.8	91.2 − 98.7	74.3 − 77.2	20.2 − 21.2	3.4
-3-	22.7− 23.8	21.8 − 22.9	13.7 − 14.3	13.7 − 13.8	9.0 − 9.1

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