

Working Paper

Industrial Metabolism at the Regional Level: The Rhine Basin

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PREFACE

This working paper is a draft submitted for a chapter in the forthcoming book *Industrial Metabolism--Restructuring for Sustainable Development*, R.U. Ayres and U.E. Simonis, editors. *Industrial Metabolism* is a new concept, proposed in 1989 by R.U. Ayres as a new analytical framework for assessing environmental problems. Borrowing a metaphor from biology, it takes cognisance of the fact that effective strategies for the reduction of pollution must consider all the processes by which an industrial society, like a living organism, takes in substances, and uses and disposes of them. As noted by Ayres, the current metabolism of industrial societies behaves more like organisms that existed before the evolution of photosynthesis. Those organisms obtained their sources of energy from anaerobic fermentation of organic materials stockpiled in the biosphere through natural geophysical processes. They excreted wastes which were at the same time noxious and non-renewable. The current biosphere, however, based on respiration and photosynthesis, is an almost perfect recycling system. Thus, the challenge for modern industrialized societies is to create a new metabolism that can begin to approach the metabolism of the natural environment.

This study, on the industrial metabolism of the Rhine Basin is interesting from several different aspects. The basin has undergone a significant evolution over the last several decades. Until about the mid-1970s, production and consumption were more or less coupled to the level of pollution. The Rhine Basin up to that time was undoubtedly one of the most productive and at the same time most polluted basins in the world. Now that is no longer true--the economy has continued to grow and the level of pollution has subsided significantly. Understanding how this decoupling came about could provide a wealth of information that could be applicable to other regions still trapped in the production-pollution syndrome.

On the other hand, the problem of chemical pollution in the basin is far from being completely solved. Tens of thousands of tons of toxic chemicals, the legacy of previous decades of high levels of pollution, have been deposited in the forests, agricultural lands, and urban areas in the basin. Does this toxic load constitute a problem now, or has it been safely immobilized or dispersed in the environment? The analysis described in this paper on the effects of the cumulative cadmium load in agricultural soils suggests that indeed, the risk to human health from crop uptake of cadmium is significantly greater now than it was in 1960.

Another use of studies in industrial metabolism is to provide a context within which policies for reducing emissions can be assessed. They expose important gaps in information and are useful in setting priorities for a range of policy options. And by presenting the "big picture" they help planners avoid costly mistakes based on a too narrow assessment of the sources and flows of toxic materials.

The analysis of industrial metabolism of the Rhine Basin is one of several other studies which will be presented in the book mentioned above. The hope is that the examples provided by these studies will encourage more such analyses and will help in the formulation of policy alternatives that are better integrated and more directed toward the goals of long-term economic and ecological sustainability.

INDUSTRIAL METABOLISM AT THE REGIONAL LEVEL: THE RHINE BASIN

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INTRODUCTION

In November, 1986, an accident at a pharmaceutical company located on the Rhine River at Basel, Switzerland resulted in the inadvertent release of 33 tons of toxic materials. The effects were immediate and dramatic--one-half million fish and eels died and local residents could not use the river as a source of drinking water for about one month. This accident, highly publicized in the world press, raised a major public outcry calling for an action plan for reducing the risks of such accidents in the future.

Historically, however, the impact of chemical accidents on the overall pollutant load to the river has been relatively minor. For example, in 1980 about 27 tons of toxic materials daily (10,000 tons per year) were transported by the Rhine into the Dutch Delta and the North Sea. This toxic load was not the result of accidents, but rather, due to normal industrial, commercial, agricultural, and urban activities conducted within the Rhine Basin on a routine basis. The effects of such chronic pollution are not as obvious or spectacular as those occurring after industrial accidents. Much of the daily inputs ends up in sediments of the Dutch Delta, and the rest is washed out to the North Sea. Even today the sediments in the Delta are so polluted that the spoils, collected during dredging operations to keep navigation lanes open, are too toxic to be applied to polder lands in the Netherlands as had been the practice in the past.

On the other hand, the Rhine River today transports far less pollutants to the Netherlands than it did in 1980, even though the level of industrial and economic activities in the basin has not changed very much since then. Analyzing the history of pollution in the Rhine Basin, including the recent clean-up, can provide valuable insights into the linkages between economic activities and chemical pollution, and the opportunities for decoupling economic growth from environmental degradation. The research described in this paper, while not addressing all possible aspects of this history, hopefully can provide a basis for further in-depth studies.

COMPONENTS OF THE IIASA STUDY

IIASA's Rhine Basin Study includes analysis of seven chemicals: cadmium (Cd), lead (Pb), zinc (Zn), nitrogen (N), phosphorus (P), lindane, and polycyclic chlorinated biphenyls (PCBs). The time horizon is the period from 1950 to 2010. All sources of pollution are considered, including atmospheric and aquatic emissions from point sources, generation of industrial and municipal solid wastes, application of agrochemicals, sewage effluents, corrosion of materials, and traffic-related emissions. The major output of the study will be basin-wide deposition maps portrayed in decade time slices for each chemical. Estimated inputs of pollutants to the river from point sources and terrestrial runoff are being computed with assistance of researchers from the Research Center for Water Resources Development (VITUKI), Budapest, Hungary. These estimates have been calibrated in accordance with the statistical analysis of Behrendt and Boehme (1992), by which point and diffuse loads to the river can be calculated from river monitoring data. In-stream transport and ecological effects

in the Dutch Delta are being modelled by scientists from the National Institute for Public Health and Environmental Protection (RIVM) in Bilthoven, the Netherlands, and Delft Hydraulics, in Delft, the Netherlands. Major funding for the project has been provided by RIVM.

GEOGRAPHIC FEATURES OF THE RHINE BASIN

As shown in Figure 1, the Rhine Basin extends over five European nations. Included are most of Switzerland, the north-east corner of France, Luxembourg, most of the southwestern lands (provinces) of Germany, and most of the Netherlands. The population in the basin is about 50,000,000 and the area is about 220,000 km². (By way of comparison, the density of population in the basin is about 10 times higher than that of the United States.) About half of the land is used for agriculture, one third is forests and the remainder is urban and suburban areas. The basin is perhaps the most heavily industrialized in the world. Although the stream flow of the Rhine comprises only about 0.2% of the flow of all rivers, about 10% to 20% of the total western chemical industry (OECD countries) is located in its basin. Industry is particularly concentrated in the catchment areas of the Ruhr, Neckar, Main, and Saar tributaries. With regard to in-stream transport of heavy metals in the Rhine, little net sedimentation occurs until the flow reaches the Dutch Delta, which extends from the German-Dutch border to the North Sea. About 75% of the metals are deposited in the sediments of the Delta, and the remainder disperses into the North Sea.

METHODOLOGY

The study analyzes the entire system by which resource inputs to the industrial economy are converted into outputs that must be absorbed and processed by the environment. For analyzing a given chemical, this systems approach can be divided into three steps:

1. Identification of materials in which the chemical is embodied, and the pathways by which they flow through the industrial economy.
2. Estimation of emissions and deposition to air, water, and soil for each material at each stage of its life cycle.
3. Construction of a basin-wide pollution model for assessment of proposed emission reduction policies, environmental impacts, or other relevant issues related to the chemical in question.

In step 1, it is essential not to miss any important sources of pollution. In this regard, it should be noted that many chemicals enter the industrial economy inadvertently as trace impurities of high volume raw materials such as fossil fuels and iron and non-ferrous ores. Moreover, a full accounting should be made of all stages of the material's life cycle. These include not only the stage of industrial production, but also the later stages of use and disposal. Overlooking important sources of emissions can be costly. For example, Tschinkel (1989) has noted that billions of dollars have been spent in the U.S. on the construction of secondary sewage treatment plants. Much of the benefit gained from this technology, however, has been nullified because discharges of untreated storm waters containing toxic urban street dust continue to flow into lakes, rivers, and estuaries. Such an omission may

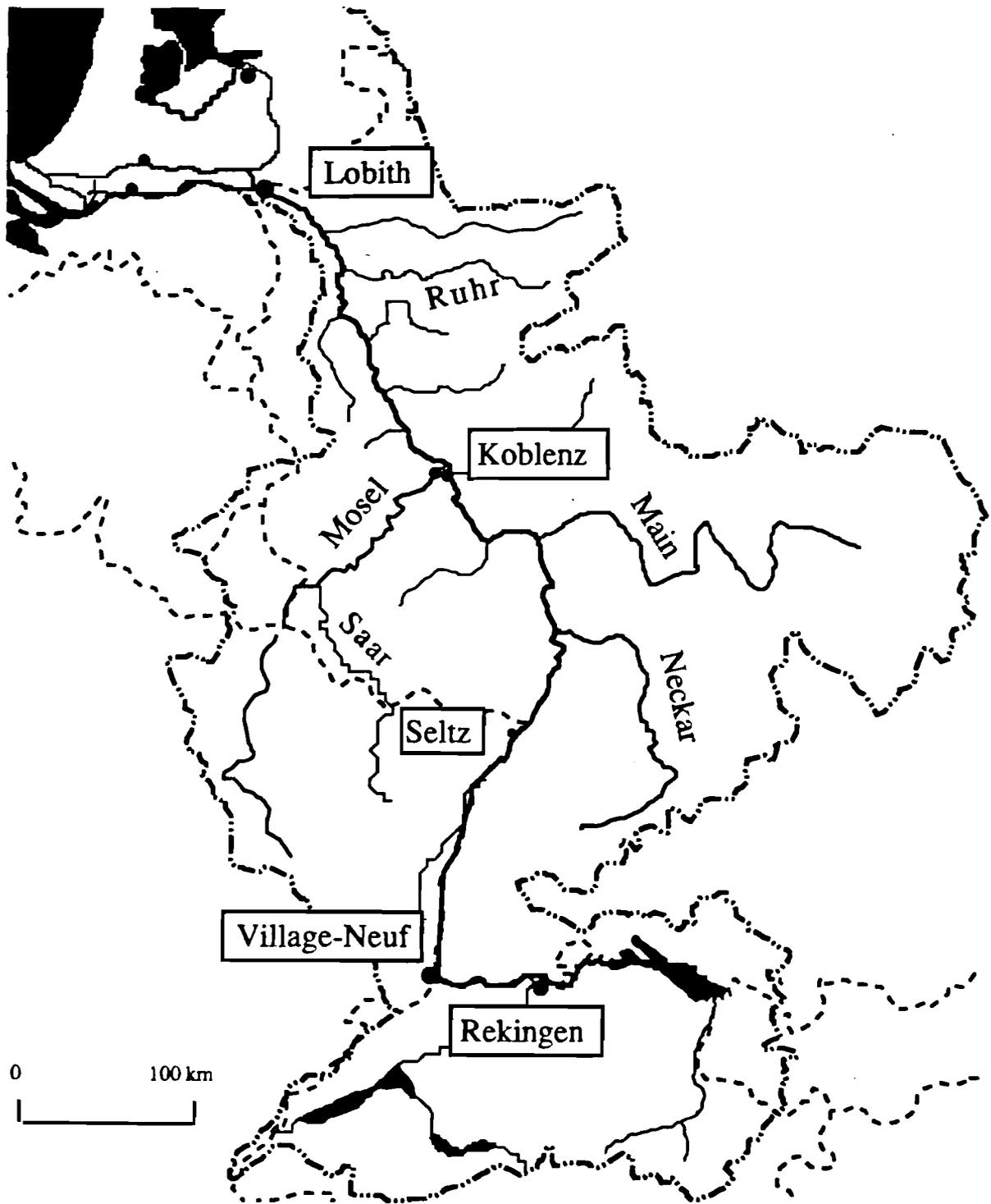


FIGURE 1: The Rhine Basin. Place names in boxes signify locations of monitoring stations of the International Commission for the Protection of the Rhine.

not have happened had planners been more aware of the significance of street dust as a major source of toxic materials.

In step 2, emissions and deposition are estimated quantitatively. Emissions may be classified broadly into two categories: *point source*, and *diffuse*. Point sources include electric power plants, industry, incinerators, and sewage treatment plants. Their emissions are typically highly concentrated and confined to a specific location, usually within an urban area. For each type of point source *emission factors*, generally expressed as weight of pollutant per unit weight of material consumed or produced, are assigned for emissions to air, water, and land. Emission factors will change over time, decreasing as cleaner technologies are implemented. Total emissions are calculated as the product of the emission factor and the weight of material consumed or produced.

Particularly in the case of atmospheric pollution, it is important to make a distinction between emissions and deposition. Via the mechanism of long-range atmospheric transport, emissions may be deposited hundreds or even thousands of kilometers from their sources. Thus, some emissions generated in the basin are transported and deposited outside the basin, and some emissions from outside the basin are transported into it. A long-range atmospheric deposition model has been developed at IIASA (Alcamo et al., 1992), for estimating deposition in the basin.

In contrast to point-source emissions, diffuse emissions are generally less concentrated, more dispersed spatially, and dependent on land use, which can be broadly categorized as forests, agricultural lands (both arable and grassland), and urban areas. The only inputs to forested lands are assumed to be atmospheric deposition via long-range transport. Chemical inputs to agricultural soils include not only long-range atmospheric deposition, but also agrochemicals, manure, and sewage sludge. Diffuse emissions from these two land uses are determined using a runoff export model (Jolankai et al., 1991). Transport of pollutants to surface and ground waters are much greater from agricultural lands than from forested areas. Transport occurs via storm runoff, erosion, and vertical seepage. The relevant parameters to be determined are the rates of applications of particular chemicals, expressed as weight per hectare, and the partition coefficient which determines the fraction of chemical that is mobilized and transported and the fraction that remains bound in the soil. Even if only a small percentage of the chemicals is mobilized, total emissions can be significant because of the enormous chemical inputs and the large spatial coverage of agricultural lands.

Another important source of diffuse emissions is transport of pollutants from paved urban areas to surface waters. This occurs by the buildup of toxic materials in street dust during dry periods, and the washing out of the dust during storm events. The pathways by which the transport may occur are shown in Figure 2. There are three main sources of toxic materials in urban dust: corrosion of building materials (particularly for heavy metals such as zinc used in galvanizing and surface materials), exhausts and tire wear from automobiles and other road vehicles (important for lead and zinc), and local and long-range atmospheric deposition (a dominant source of cadmium). When storm sewers are separate from municipal sewers (path SSS in Figure 2), the pollutants are transported directly to surface waters. Alternatively, storm sewers may be connected to municipal sewers that discharge to surface waters without treatment (path CSSW in Figure 2), or they may be connected to municipal sewers in which the effluents are treated (path WWTP). In sewage treatment plants with primary and secondary treatment, typically 50% or more of input heavy metals are trapped in sewage sludges. Even when the storm sewers are connected to sewage treatment plants, however, some fraction of the polluted street dust may be transported to the river unabated

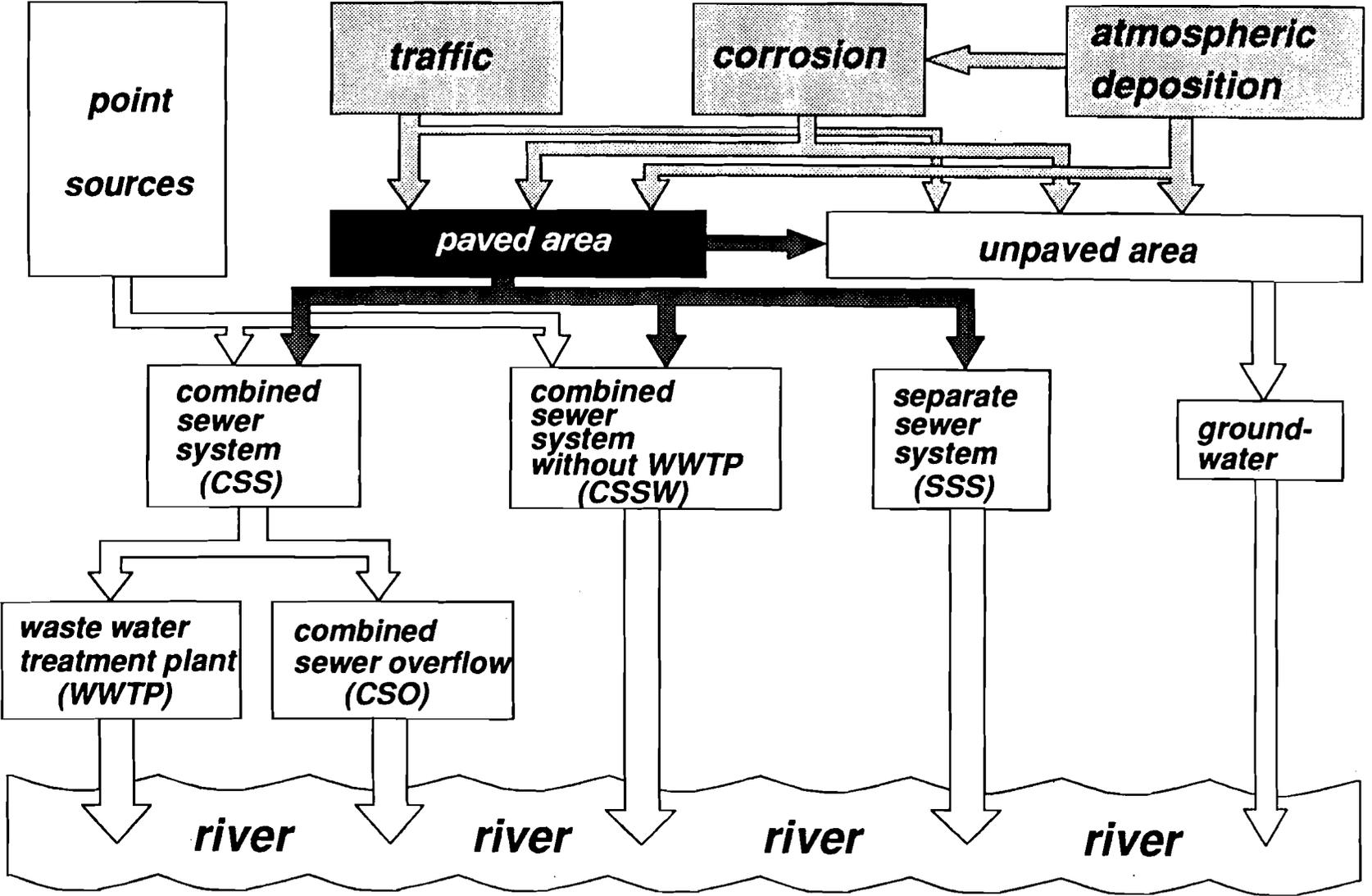


FIGURE 2: Pathways by which pollutants in urban areas are transported to surface waters. (Source: Behrendt and Boehme, 1992.)

if the volume of storm flow exceeds the flow capacity of the sewage treatment plant (path CSO in Figure 2), which is often the case. Another important source of pollution, also indicated in the figure, is the atmospheric deposition on unpaved urban areas with subsequent seepage to ground waters and transport to the river.

To calculate emissions from corrosion, it is necessary to determine rates of corrosion per unit surface of the corroded material and the total surface coverage of the material in question. Rates of zinc corrosion are strongly linked to urban SO₂ concentrations and will decrease over time as SO₂ levels are lowered. The following equation (ECE, 1984) shows the empirical relationship between SO₂ concentration and the rate of zinc corrosion from galvanized steel:

$$Y = 0.45 * [SO_2] + 0.7$$

where: Y = annual corrosion rate of galvanized steel (g/m²/yr)

[SO₂] = concentration of SO₂ in air (μg/m³)

Emissions from road traffic owing to tire wear may be estimated by determining emission rates per vehicle km, and multiplying this rate by vehicle km per year and the number of vehicles per year. Lead emissions from combustion of gasoline may be calculated by multiplying lead emitted per unit of gasoline burned and multiplying by annual gasoline consumption. The emissions are allocated spatially by apportioning them according to traffic density.

In urban areas, local atmospheric emissions are particularly important since a significant fraction, typically around 10% of the total emissions, are deposited within ten to twenty kilometers of the source. Factors affecting the proportion of local to long-range emissions include smokestack height, velocity of the gases and particulate matter leaving the stack, meteorological conditions, and particle size of emitted pollutants. The IIASA study includes an analysis of trends in local emissions as affected by changes in the above mentioned factors (Hrehoruk et al., 1992).

Lastly, it is necessary to employ an urban hydrology model that estimates the fraction of street dust that flows to the river. Even though urban and suburban areas occupy only about 15 % of total surface area in the basin, their contribution to the total diffuse load of aqueous emissions is significantly higher. This is so because of the prevalence of hard, impermeable surfaces in urban lands (typically around 33% of total urban area), from which runoff and transport of pollutants can be as high as 90%, compared to a maximum of about 25 % for agricultural lands (Ayres and Rod, 1986).

Completion of steps 1 and 2 for a given chemical provides a pollution model of the basin, including inputs and outputs for the chemical, its flows through the industrial economy over time, and its spatial allocation for each time period of interest. The model can be used for various purposes. For example, an historical analysis of pollution can provide information on changing trends in pollution sources. In the case of pollution in the Rhine River, the IIASA analysis indicates that since the mid-1970s diffuse sources of emissions of heavy metals have become increasingly important relative to point sources. Another useful application of the historical analysis is the possibility for estimating the *cumulative* buildup of toxic materials in soils and sediments. Currently, hardly any information exists on the rates of accumulation of toxic chemicals over wide spatial regions, or on the evaluation of resulting impacts to the environment and human health. (For a comprehensive discussion of cumulative chemical loading and potential environmental impacts see Stigliani (1988) and Stigliani et al.(1991).)

The pollution model can also be used to test the effectiveness of proposed policy options for reducing emissions of toxic chemicals. Because the model is based on mass balance analysis, all material flows to air, water, and land within the basin must be taken into account. The model will thus expose options that would not reduce overall emissions in the basin, but rather, would transfer them from one pollution pathway to another.

THE EXAMPLE OF CADMIUM

Step 1: Identification of Materials Containing Cadmium and Their Pathways Through the Industrial Economy

As an example of the approach taken in the study, the discussion focusses on the industrial metabolism of cadmium. Primary materials containing cadmium and its range of concentrations are shown in Table 1. Cadmium enters the industrial economy inadvertently as a trace impurity of high volume raw materials. The most important of these are phosphate ores, coal, oil, and iron ore. The production of phosphate fertilizer is a major source of aqueous cadmium pollution in the basin (Elgersma et al., 1991), and fertilizer application is now the major source of cadmium pollution in agricultural soils. Combustion of coal and oil are major sources of atmospheric cadmium pollution. Iron and steel production results in the generation of large volumes of solid wastes contaminated with cadmium, as well as atmospheric and aqueous cadmium emissions. An added source of cadmium pollution in steel production is the input of steel scrap treated with cadmium as a surface coating.

TABLE 1

Natural Occurrence of Cadmium

Material	Typical Range (ppm)
Soils, Global Average	0.01-0.7
Zinc Ore Concentrates	1000-12000
Lead Ore Concentrates	3-500
Copper Ore Concentrates	30-1200
Iron Ore	0.12-0.30
Hard Coal	0.50-10.00
Heavy Oil	0.01-0.10
Phosphate Ore	0.25-80

Source: Boehm and Schaefers (1990).

Cadmium contained in zinc ores is generally of sufficiently high concentration, that separating and refining it as a byproduct of zinc refining is economically feasible. In fact,

it has been via this route that all primary cadmium metal has been produced in the basin. There is some mining of Zn/Cd ores within the basin, but most of the ores, in the form of zinc concentrates, are imported. Inputs of cadmium to the Zn/Cd refinery are transformed into three outputs: refined cadmium metal; refinery emissions (to air, water and soil); and a trace component in refined zinc metal (0.15% - 0.50% in zinc produced at thermal refineries, and 0.02% or less in zinc produced at electrolytic refineries). Cadmium is also present in lead and copper ores but, as shown in Table 1, the concentrations are much lower than for zinc, and the production and use of lead and copper in the Rhine Basin is not an important source of cadmium pollution.

As shown in Figure 3, cadmium and zinc pollution are linked for at least two zinc-containing products, automobile tires and galvanized metals, which are significant sources of emissions, particularly in urban areas. Tire wear and corrosion of galvanized zinc cause the release of zinc and associated cadmium. The deposited metals accumulate in street dust and may be transported as aqueous emissions during storm runoff or dispersed as wind-blown dust. The amount of cadmium contained as an impurity in finished zinc metal has been decreasing since the 1960s as electrolytic refineries have accounted for an increasingly greater share of zinc production. Nevertheless, even in recent decades significant quantities of cadmium have entered the industrial economy by this route. In West Germany in the period from 1973 to 1986, it is estimated that 40 tons of cadmium per year on average (560 tons over the entire period) were contained in zinc products for domestic consumption (Rauhut and Balzer, 1976; Rauhut, 1978a, 1981, 1983, 1990; Balzer and Rauhut, 1987). Since the population of the West German part of the basin comprises about one-half of the total West German population and assuming an equal per capita distribution of zinc products, it is estimated that about 280 tons of cadmium entered the basin by this route from West Germany alone. When account is taken of the rest of the population in the basin (about two-thirds of the German population) a total of about 467 tons of cadmium is estimated to have been associated with zinc products over the 14 year period.

The largest inputs of cadmium to the Rhine Basin are not from inadvertent trace impurities, but rather, through the refining of cadmium metal, and the production, use, and disposal of cadmium products. As shown in Figure 4, cadmium metal, some of which is produced at the basin's zinc refineries and some of which is imported, is the input to plants that manufacture cadmium-containing products. The four major products are pigments (mostly for plastics), nickel-cadmium (Ni-Cd) batteries, plate (for surface protection of steel and other metals), and stabilizers (in PVC plastic). Emissions of cadmium occur for each of these manufacturing sectors.

The next stage in the material flow is the use of cadmium in the basin. Ayres et al. (1988) have noted the importance of *dissipative emissions*, referring to emissions that may occur during the normal use of products. Such emissions are important, however, only when the chemical is easily mobilized during use. Of the four major cadmium-containing products, only cadmium plate might be expected to generate emissions to the environment via corrosion when exposed to polluted atmospheres during use (Carter, 1977). In the other three products, the cadmium is tightly embedded in the matrix of the product, and emissions during normal usage would be expected to be negligible.

As shown in Figure 4, recycling is important for only two cadmium-containing products, large industrial batteries and cadmium-plated steel. Recycling of batteries back to the battery manufacturers by the industrial users, mainly the railroad industry and operations requiring emergency power supplies, is a long-established practice. This is not the case, however, for small, sealed batteries, used by consumers in personal computers and other

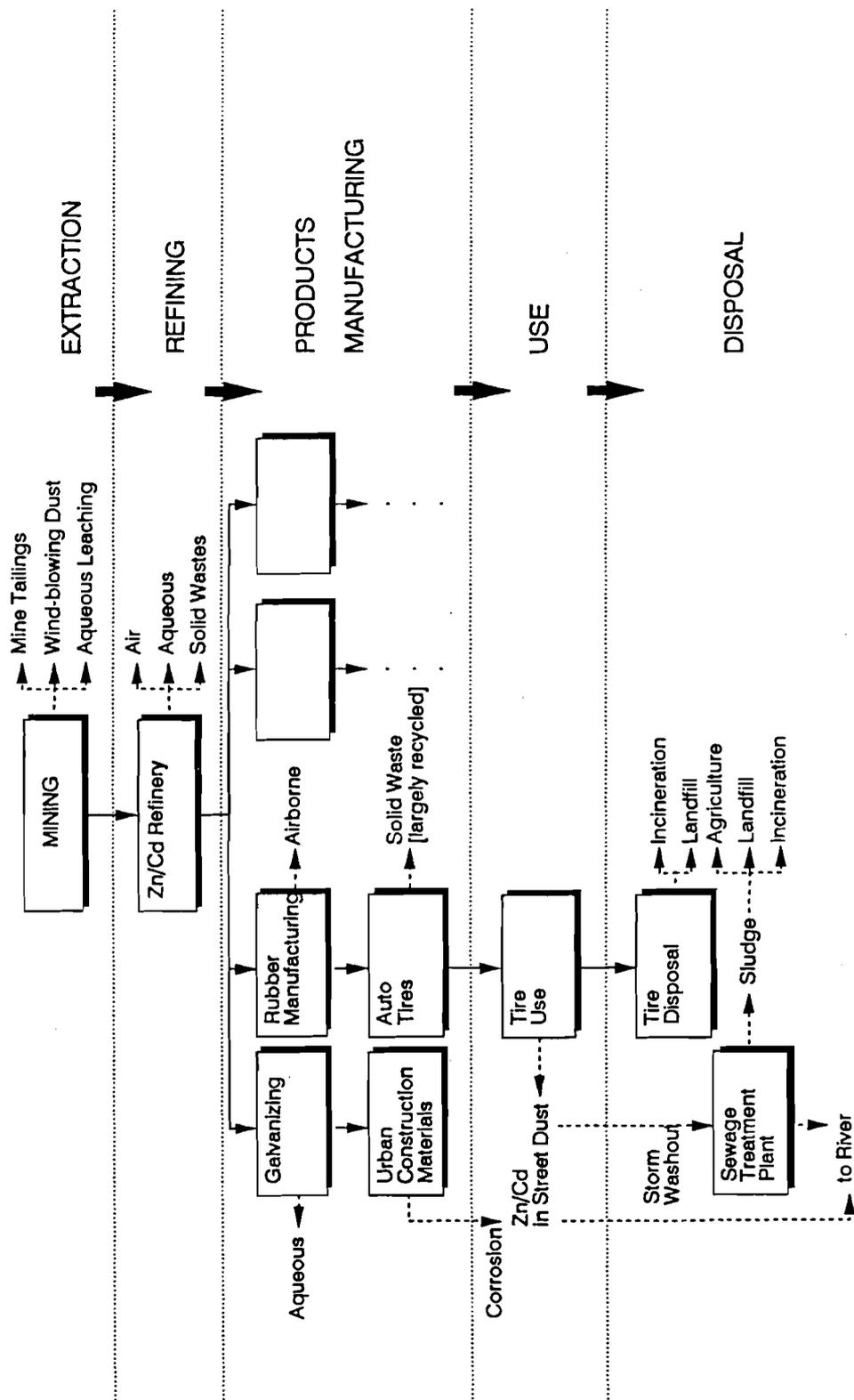


FIGURE 3: The coupling of zinc and cadmium pollution caused by the presence of cadmium as a trace impurity in zinc-containing products.

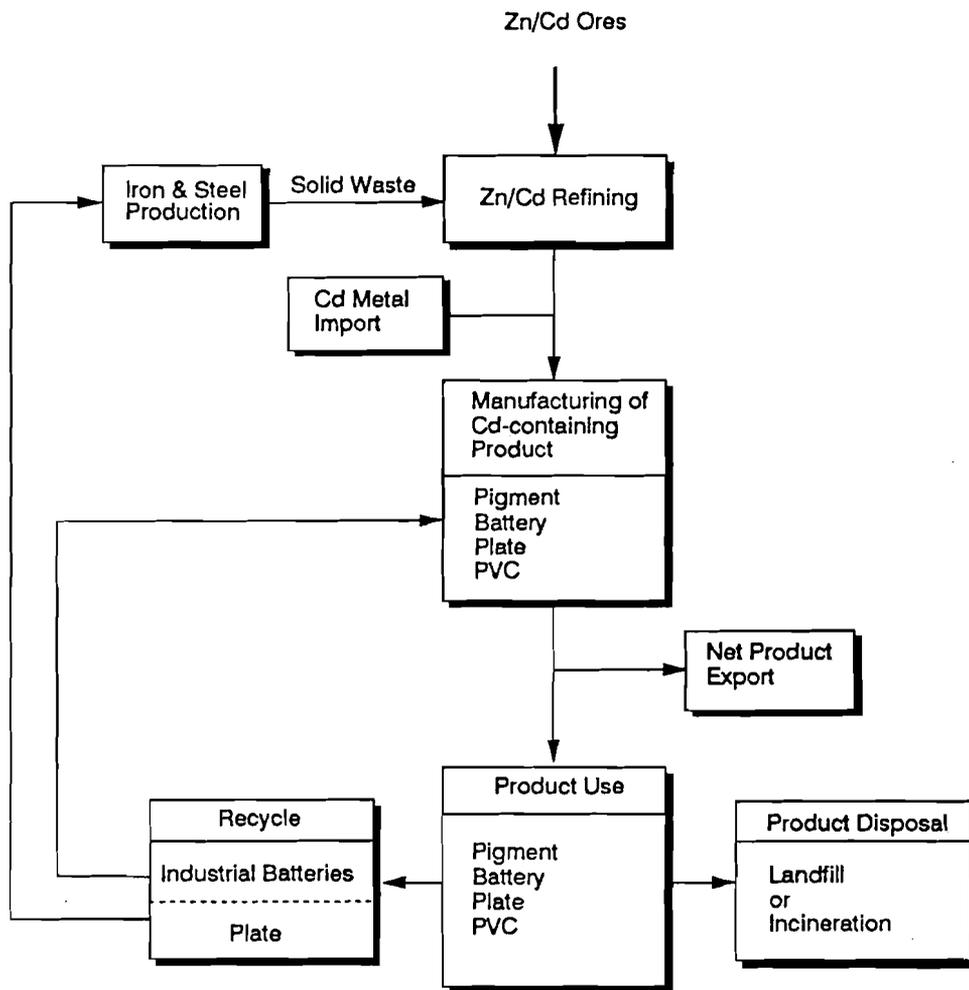


FIGURE 4: The flow of cadmium-containing products through the industrial economy.

light electronic equipment. Most of these batteries end up in municipal landfills or incinerators. An estimated 30% to 40% of cadmium-coated steel is recycled back to iron and steel producers as scrap. As noted earlier, this practice has been a major source of cadmium emissions in steel production. The remainder of the cadmium-plated metals ends up in landfills where most of the cadmium is corroded over time. Surface coatings for steel and other metallic substances were once the dominant use of cadmium in the basin. Currently, however, it is the smallest use, accounting for only about 20 tons used in 1988, compared to about 250 tons in 1970.

Cadmium as a pigment in plastics is a major source of cadmium in the consumer waste stream (Schulte-Schrepping, 1981). Since the cadmium is tightly bound in the plastic matrix, however, it is expected that very little of it would be mobilized if the wastes are directly landfilled (Raede and Dornemann, 1981). When the plastics are incinerated, however, (which is the case for about one-third of municipal wastes in the basin), they constitute a major source of atmospheric cadmium emissions, as well as cadmium concentrated in the residue incinerator ashes.

Cadmium as a stabilizer in PVCs is used almost exclusively in outdoor window frames. As in the case for cadmium-pigmented plastics, cadmium in this form is not likely to be appreciably mobilized, either during use or after disposal to landfills. Very little, if any, of the disposed PVC is incinerated, since most of it ends up in landfills or is recycled with other debris from demolition of old buildings.

Step 2: Estimation of Cadmium Emissions and Deposition to Air, Water, and Solid Wastes

Atmospheric Emissions and Deposition

Atmospheric Emissions within the Rhine Basin. Because atmospheric pollutants may be transported over large distances, a substantial fraction of emissions generated in the basin are transported and deposited out of the basin, and conversely, some fraction of emissions generated out of the basin are transported and deposited in the basin. Therefore, the calculation of cadmium deposited in the basin from the atmosphere requires the incorporation of emission sources both inside and outside of the basin. Such a European-wide data base was provided by Pacyna (1988) and Pacyna and Munch (1988) for the early-1980s. Historical emissions were calculated using available production statistics for the relevant sectors generating the emissions, and estimations of the evolution of emission factors per sector since the 1950s (Pacyna, 1991). Deposition was calculated using the TRACE 2 model developed at IIASA and described in detail in Alcamo et al. (1992). The model employs "transfer matrices" which convert emission inputs into deposition outputs.

Figure 5 shows the in-basin atmospheric emissions of cadmium for selected years in the 1970s and 1980s. West Germany has been the predominant source of emissions, accounting for between 75-80% of total emissions over the entire period. Table 2 shows the distribution of emissions by sector for 1970 and 1988. One may observe that over the 18 year time period there was an overall reduction of air emissions by 87%. This decrease occurred mostly from the implementation of emission control technologies. Additional factors, however, also were important. Emissions from coal and oil combustion declined because of the adoption of energy conservation measures, and the increased use of nuclear power. Emissions from iron and steel production declined in part because of the stagnation of production in the basin. The very large reductions in non-ferrous metal production (zinc,

Atmospheric Emissions of Cadmium

The Rhine River Basin 1970-1988

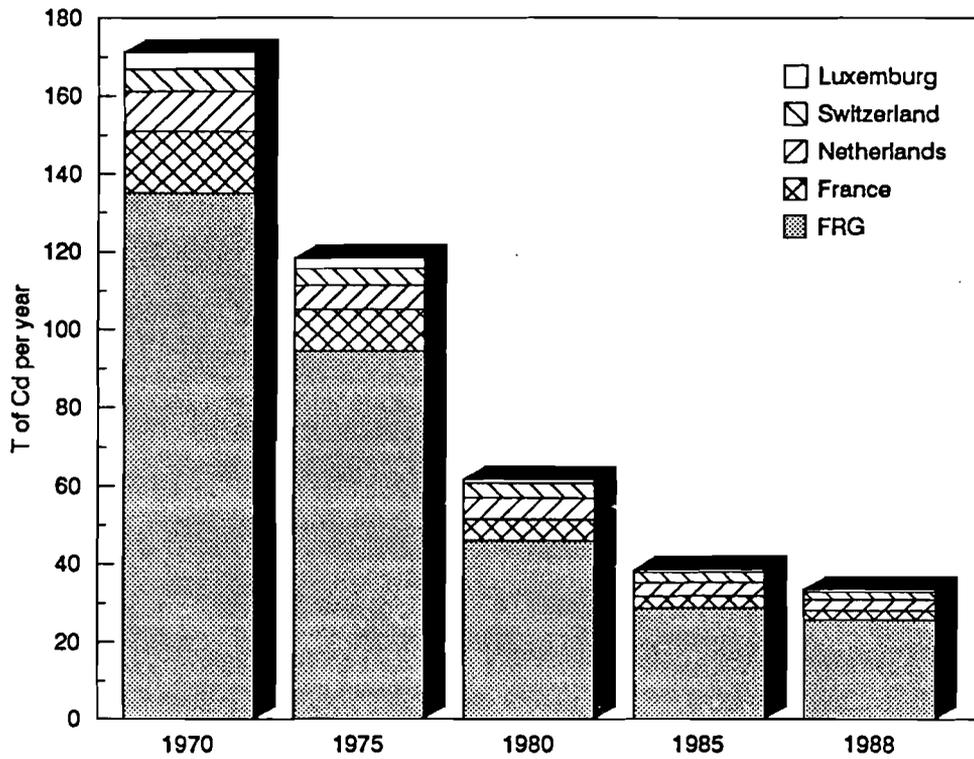


FIGURE 5: In-basin atmospheric emissions of cadmium.

copper, and others) was in part the result of the closing down of large pyrometallurgical smelters. Another significant trend was the increase in the relative share of emissions from incinerator wastes. In 1970 these emissions only accounted for about 5% of the total; by 1988 they accounted for 14% of total emissions.

TABLE 2
Atmospheric Emissions in the Rhine Basin
by Industrial Sector
(tons per year)

Process	1970(%)	1988(%)
Hard Coal Combustion	26.2(15.3)	10.1(30.2)
Oil Combustion	14.1(8.2)	4.6(13.8)
Other Fossil Fuel Combustion	4.7(2.8)	1.5(4.5)
Zinc Refining	31.6(18.5)	3.5(10.5)
Primary Copper Refining	25.2(14.7)	0.4(1.2)
Other Non-Ferrous Metal Refining	4.1(2.4)	1.1(3.3)
Iron & Steel Production	44.9(26.3)	6.3(18.9)
Coke Production	3.9(2.3)	0.5(1.5)
Cement Manufacturing	7.8(4.6)	0.8(2.4)
Waste Incineration	8.4(4.9)	4.6(13.8)
Sum	171.0(100)	33.5(100)

Atmospheric Deposition in the Rhine Basin. Table 3 lists total atmospheric deposition in the basin, and the calculated contributions to the deposition by countries inside and outside of the basin. One may observe that there was a 79% decline in deposition over the 18 year period, which is obviously related to the large decline in emissions within the Rhine Basin, as well as in the western European nations in close proximity to it. Deposition in the basin contributed by the formerly socialist republics of eastern Europe also declined during this period, although the decrease was not nearly as large as in the western European countries.

The share of total deposition attributed to the five Rhine Basin countries showed a slight, but continuous decline beginning in 1975 when they accounted for about 58% of the total deposition, until 1988 when they comprised about 50%. The share of total deposition from the three western European nations, Belgium, the United Kingdom, and Italy, dropped by about 37% between 1970 and 1988. In fact this trend was dominated by large decreases in Belgium's contribution, which was reduced from 25% in 1970 to about 12% in 1988. Belgium is one of the leading producers of zinc/cadmium in the world. Until the early-1970s, cadmium was produced solely at thermal zinc refineries with large atmospheric

TABLE 3

Atmospheric Deposition in the Rhine Basin
Contribution by Country
tons/year

Country	1970	1975	1980	1985	1988
West Germany	55.3 (39.4%)	41.2 (46.8%)	23.6 (43.4%)	13.9 (40.3%)	11.7 (39.3%)
France	8.5 (6.1%)	5.7 (6.4%)	3.9 (7.1%)	2.4 (6.9%)	1.8 (6.2%)
The Netherlands	14.6 (10.4%)	2.5 (2.9%)	1.9 (3.5%)	1.2 (3.4%)	0.9 (2.3%)
Switzerland	1.4 (1.0%)	1.1 (1.2%)	0.9 (1.7%)	0.7 (1.9%)	0.5 (1.6%)
Luxembourg	1.2 (0.9%)	0.8 (0.9%)	0.4 (0.7%)	0.2 (0.6%)	0.2 (0.6%)
Belgium	35.5 (25.3%)	15.3 (17.4%)	7.1 (13.1%)	3.6 (10.5%)	3.5 (11.8%)
United Kingdom	6.0 (4.3%)	3.8 (4.3%)	2.5 (4.6%)	1.7 (5.0%)	1.6 (5.3%)
Italy	1.4 (1.0%)	1.3 (1.4%)	0.9 (1.6%)	0.7 (2.0%)	0.6 (2.1%)
East Germany	5.1 (3.6%)	5.4 (6.2%)	4.8 (8.8%)	3.9 (11.3%)	3.5 (11.7%)
Poland	4.2 (3.0%)	5.3 (6.1%)	4.1 (7.5%)	3.1 (9.0%)	2.8 (9.4%)
Czechoslovakia	0.9 (0.7%)	1.0 (1.1%)	0.8 (1.5%)	0.6 (1.9%)	0.6 (2.0%)
Soviet Union	1.8 (1.3%)	2.1 (2.4%)	1.8 (3.4%)	1.4 (4.0%)	1.2 (3.9%)
Other	4.2 (3.0%)	2.7 (3.0%)	1.6 (3.0%)	1.1 (3.1%)	0.9 (3.1%)
Sum	140.3 (100%)	87.9 (100%)	54.4 (100%)	34.6 (100%)	29.8 (100%)

emissions of cadmium. During the 1970s the thermal smelters were phased out, in some cases by closing down and in others by switching to electrolytic zinc/cadmium production with greatly reduced air emissions. The opposite trend is shown for the eastern European countries. Emissions from East Germany, Poland, Czechoslovakia, and the Soviet Union contributed only about 9% of the total deposition in 1970, but the share increased to about 27% in 1988. This occurred not because emissions from eastern Europe increased, but rather, because total deposition in the basin decreased so rapidly, thus increasing the shares of contributions from eastern Europe. These shifts in percentage shares reflect regional differences in efforts to limit air pollution. While western European nations were able to reduce their emissions mainly through the extensive application of air pollution control equipment beginning in the 1970s, emissions in eastern Europe remained largely unabated during this time.

The estimated distribution of cadmium deposition among the three major land uses in the basin is given in Table 4. About 44% of the total deposition goes to agricultural lands, 31% to forests, and about 25% to urban areas. Relative to their spatial coverage in the basin (about 15% of the total land), urban areas receive more cadmium than forests or agricultural lands. This is so because most point sources are located in urban areas, and about 10 to 15% of atmospheric emissions are deposited locally within a radius of up to 20 km from the point source. As discussed below, urban atmospheric deposition constitutes a major source of diffuse cadmium loading to surface waters in the basin.

TABLE 4

Distribution of Atmospheric Deposition of Cadmium
in the Rhine Basin According to Land Use
(tons per year)

Year	Agriculture	Forests	Urban Areas	Total
1970	61.6	43.1	35.6	140.3
1975	38.0	26.6	23.2	87.8
1980	24.1	16.9	13.4	54.4
1985	15.4	10.7	8.5	34.6
1988	13.2	9.3	7.3	29.8

Point Source Aqueous Emissions in the Rhine Basin

Figure 6 shows the estimated annual loads of cadmium for the time periods 1973-1977, 1978-1982, and 1983-1987 at various monitoring stations on the Rhine and some of its tributaries. The station at Lobith is on the German-Dutch border. Since there is no net sedimentation of cadmium on an annual basis in the Rhine River¹ before the Dutch border,

¹This is not true for the tributaries of the Rhine, however, where significant sedimentation does occur.

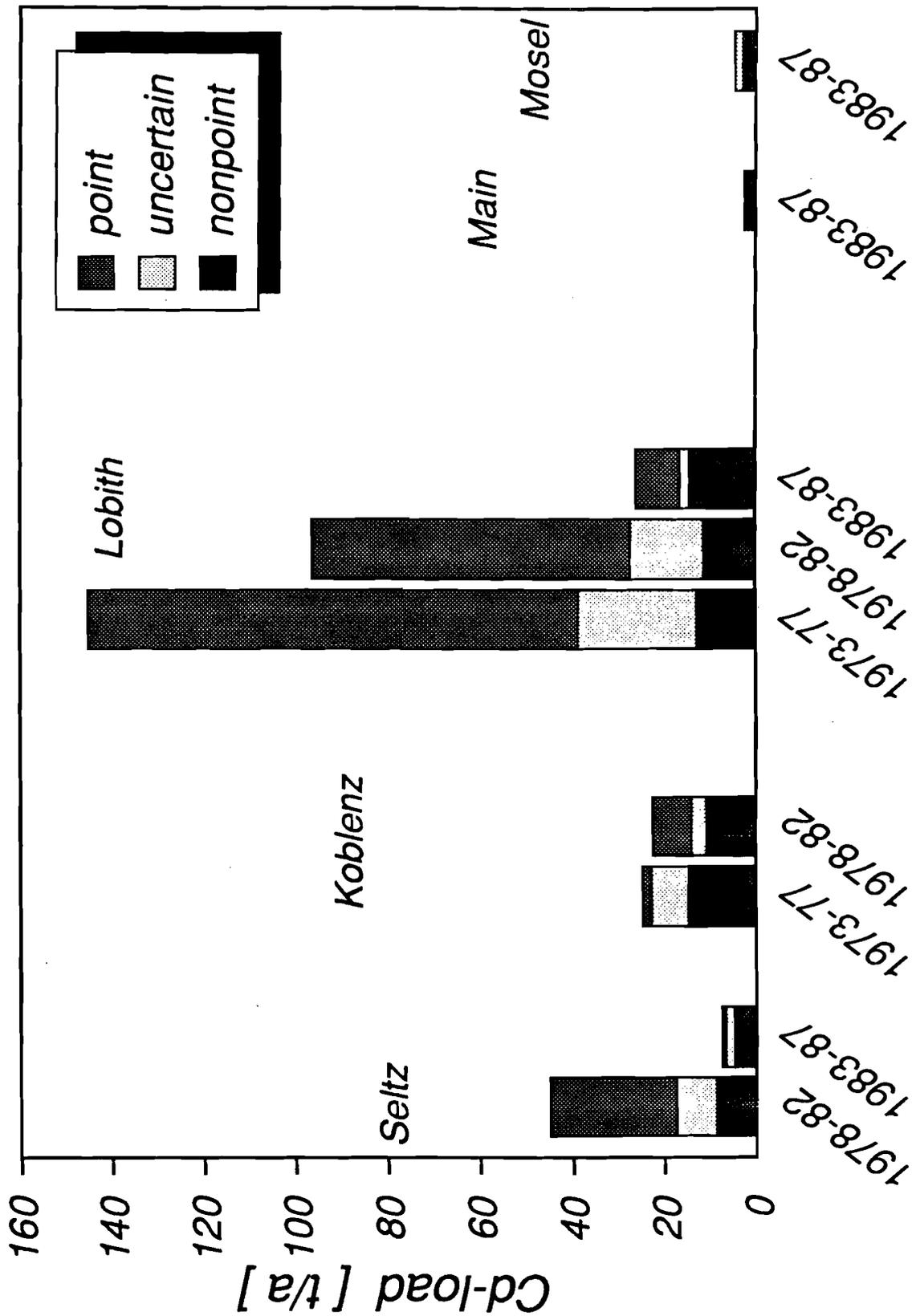


FIGURE 6: Estimated annual loads of cadmium at various stations on the Rhine River and its tributaries. (Source: Behrendt and Boehme, 1992.)

the load represents the total inputs to the river from all upstream sources. The analysis was conducted by Behrendt and Boehme (1992) and is based on monitoring data provided by the International Commission for the Protection of the Rhine in Koblenz, Germany. The analysis also included a disaggregation of the total load into point and non-point (diffuse) loads by a methodology developed by Behrendt (1992). One may observe the emergence of two major trends during this 14 year time period. Firstly, the cadmium load at Lobith decreased significantly over time, from 145 tons per year during the first period, to 96 tons per year in the second period, to 26 tons per year in the third period. Secondly, the relative contribution to the total load from point sources decreased from 82% in the first period, to 79% in the second period, to 42% in the third period, while the contribution from diffuse sources increased from 18% to 21% to 58%.

Industrial Sources. Table 5 lists estimated aqueous emissions in the Rhine Basin during the 1970s and 1980s according to industrial sector (Elgersma et al., 1991). The estimates for a given point source were calculated by multiplying plant production by an assumed emission factor. Historical emissions were obtained from production statistics for the various industrial sectors, and an appraisal of changes in emission factors over time owing to the implementation of regulatory standards, and the adoption of water pollution control technologies. The assumptions applied in these estimations were calibrated by comparison with the estimates shown in Figure 6.

One may observe that during the 1970s, primary and secondary production of zinc was by far the most important source of aqueous cadmium pollution, accounting for more than 45% of all emissions. Most of the pollution from this sector can be attributed to two thermal zinc smelters that did not refine cadmium, but rather, treated it as a disposable waste. Reductions in emissions from these plants in the late-1970s and 1980s were achieved in part by recycling the wastes to an electrolytic zinc/cadmium refinery located in the basin. Further reductions were achieved when one of the smelters ceased refining zinc ore in the early-1980s.

The second largest polluting sector was the iron and steel industry, including coke production, which accounted for between 20% and 33% of the emissions during the 1970s and 1980s. Similar to the case for the thermal zinc refining sector, reductions in aqueous cadmium emissions were in part achieved by recycling the cadmium containing wastes to electrolytic zinc/cadmium refineries. In fact, recycling of industrial sludges and solid wastes increased significantly during the 1970s and 1980s for most industrial sectors in the basin. The wastes were either recycled as a feed stock to other industrial sectors, or they were used as filler in construction materials such as cement or asphalt. Another significant factor in reducing aqueous cadmium emissions in steel production was the reduction in cadmium-plated steel as a component in recycled steel scrap. Annual use of cadmium plate in the basin averaged about 300 tons/yr throughout the 1960s. By the early-1980s use had dropped to around 80 tons/yr, and by the late-1980s it was less than 30 tons/yr.

Historically, among the industries manufacturing cadmium-containing products, the production of cadmium pigments was a major source of water pollution. In the early-1970s the pollution load from this source comprised about 8% of the total from all point sources. By the early-1980s, however, pigment manufacturers accounted for less than 2%, and in the late-1980s they comprised less than 1% of the total load. These decreases occurred in part because of the implementation of more efficient pollution control technologies (thus lowering emission factors), and in part because of the decrease in production of cadmium-containing pigments. (Nearly 900 tons/yr of cadmium were used in pigment manufacturing in the early-

1970s; by the late-1980s cadmium use was reduced to under 400 tons/yr.)

Another major source of industrial aqueous cadmium emissions is the phosphate fertilizer manufacturing industry. It accounted for about 17-19% of the total industrial pollution in the 1970s, and in the 1980s was the dominant source of pollution, responsible for about 50% in the mid-1980s and 75% in the late-1980s. During the conversion of phosphate ore to phosphoric acid, gypsum, containing about 30% of the cadmium contained in the ore, is produced as a waste product. The largest polluters have been two fertilizer plants located in the Netherlands, both of which discharged the gypsum directly to the Rhine. It is the intention of these plants, however, to limit their combined emissions to less than one ton by 1992 (Elgersma et al., 1991).

TABLE 5

Aqueous Emissions from Industrial Point Sources in the Rhine Basin*

Activity	70-72	73-77	78-82	83-87	88
Zinc Production (Primary & Secondary)	74.0	63.9	40.4	2.8	0.1
Cadmium Production (Secondary)	3.0	3.0	1.2	0.0	0.0
Lead Production (Primary & Secondary)	3.7	4.3	1.6	0.1	0.0
Coke Production	10.7	9.5	4.3	1.0	0.9
Iron & Steel Production	21.4	21.4	19.5	8.5	2.1
Pigment Manufacturing	13.4	7.0	1.3	0.3	0.1
Stabilizer Manufacturing	1.3	0.6	0.0	0.0	0.0
Battery Manufacturing	2.4	1.5	1.1	0.6	0.3
PVC Manufacturing	1.4	1.2	0.9	0.4	0.1
Phosphate Manufacturing	27.9	26.9	15.2	15.1	9.8
Sum	159.2	139.3	85.5	28.8	13.4

* The emission values listed here are somewhat higher than the values for point sources shown in Figure 6 because not all of the aqueous emissions within the basin end up in the Rhine River. Some are trapped in sediments of tributaries. Also, this table includes point source emissions in the Netherlands, while Figure 6 includes emissions only up to the German-Dutch border.)

Source: Elgersma et al., 1991.

Emissions to Municipal Sewers. The two major point sources of cadmium emissions to municipal sewers are waste waters from households and small cadmium plating operations. The contribution of these two sources during the 1970s and 1980s is shown in Table 6. The table takes into account the evolution of primary and secondary sewage treatment plants in the basin over this time period. In 1970, only about 33% of the population in the basin was served by secondary treatment plants. By the end of the 1980s, this percentage had increased to about 84% (OECD, 1991). The introduction of secondary treatment has resulted in large reductions in aqueous cadmium emissions, since about 70% of the cadmium inputs is trapped in digested sewage sludges generated during treatment and about 30% leaves the plant as an aqueous effluent.

DeWaal Malefijt (1982), in a comprehensive Dutch study of sources of heavy metals in sewers, estimates the cadmium load from household waste waters to be 45 mg Cd per inhabitant per year. About 20 mg is directly from human wastes, another 20 mg is from corrosion of sewer pipes, and 5 mg is present in the waste water from other sources.

TABLE 6

Aqueous Emissions from Municipal Sewage:
Households and Plating Works
(tons per year)

Country	70	75	80	85	88
West Germany:					
Households	1.0	0.8	0.7	0.6	0.5
Plating Works	6.8	3.2	1.5	0.2	0.0
France:					
Households	0.1	0.1	0.1	0.1	0.1
Plating Works	1.8	1.3	0.7	0.1	0.0
The Netherlands:					
Households	0.4	0.3	0.3	0.2	0.2
Plating Works	1.4	0.7	0.1	0.0	0.0
Switzerland:					
Households	0.1	0.1	0.1	0.1	0.1
Plating Works	0.0	0.0	0.0	0.0	0.0
Luxembourg:					
Households	0.0	0.0	0.0	0.0	0.0
Plating Works	1.5	0.7	0.1	0.0	0.0
Totals:					
Households	1.6	1.3	1.2	1.0	0.9
Plating Works	11.5	5.9	2.4	0.3	0.0
Grand Total	13.1	7.2	3.6	1.3	0.9

As shown in Table 6, aqueous plating wastes were a major source of cadmium to sewers in the 1970s. In the 1980s, however, cadmium emissions were virtually eliminated. One reason for this was that production of plate decreased by more than 80% over this time period. Another reason was the implementation of strict regulations on emissions as required by the German Waste Regulation Act of 1978, and the EC directive of 1983, which called for reduction in three steps up to 1986. To comply with these regulations, aqueous emission factors were reduced from about 0.0250 tons Cd/(ton plate produced) in 1970 to about 0.0003 tons Cd/(ton plate produced) by the mid-1980s. These laws caused a rapid restructuring in the plating industry, forcing small firms, that could not afford to conform to these regulations, to cease production of cadmium plate.

Solid Wastes and Application of Agrochemicals

Industrial and Municipal Wastes. Solid wastes constitute, by far, the largest disposal pathway of cadmium in the Rhine Basin. The following are the four major source categories of wastes containing cadmium:

- Flyash from coal combustion.
- Flue dusts and slag from iron and steel production.
- Wastes from manufacture of cadmium plate.
- Disposal of consumer and commercial wastes to landfills, including flyash from incineration of consumer wastes.

It should be noted that thermal zinc smelting plants also generate substantial amounts of solid cadmium waste. Estimates of inputs and outputs of cadmium in the two thermal smelters in the Rhine Basin indicate, however, that in the 1970s their solid wastes were discharged directly to the river. This practice, in large part, accounts for the very large aqueous emissions from the smelters given in Table 5. By the early-1980s one smelter stopped producing zinc altogether and the other recycled most of its solid wastes to an electrolytic smelter.

Table 7 provides estimates of cadmium wastes disposed in the basin by sector. For most of the categories listed in the table, the tonnage of solid wastes declined appreciably over time. One exception was waste from coal combustion. The increase in this case resulted from increasing reductions in air emissions and concomitant increases in the collection of cadmium-containing dusts and particles. Most of this waste was flyash from combustion of lignite coal. With regard to flyash generated from combustion of hard coal, recycling became increasingly important. In 1970, about 50% of the flyash was recycled. The percentage increased to about 65% in 1980 and about 90% in 1990 (Risse et al., 1991).

Wastes from cadmium plate manufacturing decreased by nearly 80%, mostly because of large reductions in production, which declined from nearly 600 tons in 1970 to about 280 tons in 1980 and about 100 tons in the late-1980s. About half of the production was used in the basin, with the balance being exported. Thus, disposal of cadmium plate to municipal landfills also decreased substantially. The declining trend not only reduced the volume of cadmium waste in plate manufacturing and municipal wastes. As was the case for aqueous cadmium emissions, it also resulted in a substantial reduction of cadmium in solid wastes from steel production. Cadmium-coated scrap steel, although constituting only a small fraction of the total scrap, has been identified as the major source of cadmium pollution in steel production (Hutton, 1982). Assuming a ten-year life time of steel products coated with

cadmium plate, and a recycling rate of about 40%, it is estimated that about 125 tons of cadmium per year entered steel production from inputs of cadmium-coated scrap in the 1970s. By the late-1980s, however, the inputs had decreased to around 50 tons per year. Two other factors contributing to the decline of cadmium in steel wastes were a 20% reduction in steel production, and a significant increase in the recycling of cadmium-containing flue dusts and slags generated in production processes.

TABLE 7
Cadmium in Solid Wastes Disposed to Land in the Rhine Basin
(tons per year)

Activity	70	75	80	85	88
Coal Combustion					
Tons per Year	9.9	12.6	15.6	17.9	19.2
Percent of Total	(1.2)	(1.6)	(2.0)	(3.6)	(5.0)
Iron & Steel Production					
Tons per Year	68.3	67.0	51.9	18.5	14.0
Percent of Total	(8.6)	(8.4)	(6.8)	(3.7)	(3.7)
Cd Plate Manufacture					
Tons per Year	50.4	39.6	26.8	18.2	11.5
Percent of Total	(6.4)	(5.0)	(3.5)	(3.6)	(3.0)
Municipal Waste Disposal:					
Tons Flyash (Incineration)(a)	100.2	112.3	124.3	89.8	53.2
Tons Direct Landfill(a)	340.8	338.0	335.1	252.7	169.5
Tons Cd Plate(b)	216.0	223.3	205.2	100.5	112.0
Tons Sewage Sludge	4.1	3.7	3.1	1.9	1.7
Total Tons per Year	661.1	677.3	667.7	444.9	336.4
Percent of Total	(83.7)	(85.0)	(87.6)	(89.1)	(88.3)
Sum					
Tons per Year	789.7	796.5	762.0	499.5	381.1
Percent of Total	(100)	(100)	(100)	(100)	(100)

(a)Sources of cadmium in flyash and direct landfill are small consumer Ni-Cd batteries, and plastics containing cadmium pigments. Cadmium used as stabilizer in outdoor PVC window frames is not included here, since disposal of this source (in building demolition debris) is not likely to be mixed with municipal wastes.

(b)Includes cadmium plate *not* recycled to steel refineries. Most cadmium plate, used in automobiles, machinery, and electronic equipment is disposed in repositories with other hard goods and generally not mixed with municipal wastes. They are listed here because of their importance as a source of cadmium emissions.

Municipal wastes landfilled in 1988, including flyash from municipal incinerators, were about half of the quantity landfilled in 1970. These reductions occurred because of large reductions in consumption of cadmium-containing products over this time period. Of particular importance was the large decrease in the use of cadmium in pigmented plastics,

formerly the major source of cadmium in domestic wastes (Schulte-Schrepping, 1981). Use of cadmium pigments in the basin in 1988 (about 200 tons) was less than half the use in 1970 (about 440 tons). This trend was somewhat offset, however, by the increased use of small, sealed consumer Ni-Cd batteries, the cadmium content of which increased from less than 20 tons in 1970 to about 125 tons in the late-1980s.

Recycling of solid wastes (secondary materials) in the Rhine Basin has emerged as the major alternative to land disposal and incineration. The evolution in recycling noted above for flyash from hard coal combustion is typical for other industrial solid wastes as well. Flyash from coal combustion and slags from iron and steel production are used as feed stocks in the manufacture of bricks, cement, concrete, and asphalt road foundation. Flue dusts from iron and steel production and thermal zinc refining are recycled as inputs to non-ferrous electrolytic metal refineries. Recycling serves three purposes. Firstly, it replaces primary materials, thus conserving scarce resources. Secondly, it reduces the volume of solid wastes, thus reducing the amount of land that must be set aside for landfills. Thirdly, and most important from the environmental perspective, recycling the wastes into new products that effectively immobilize the cadmium may reduce the potential availability of leachable cadmium to the environment. Much research has been conducted for testing the leaching behavior of recycled products (Goumans et al., 1991). It appears that the recycling option may offer a viable alternative for managing cadmium-containing solid wastes, although more research is needed to determine the long-term leaching behavior (30 or more years) of recycled products.

An important factor that needs to be taken into account when assessing the environmental impacts of disposed solid wastes is the potential for the chemical in question to leach from the waste material in which it is embodied. The concentration of the toxic material in the waste is not a good index for such an assessment, since it is not necessarily proportional to the fraction of toxic material susceptible to leaching. Very few data are available that allow for assessment and comparison of the long term "leaching potentials" of different solid wastes under field conditions. There is, however, information from standardized laboratory leaching tests which provide estimates of leaching of heavy metals from waste materials under varying chemical conditions (van der Sloot, 1991). The waste material is ground to a specified particle size and then subjected to an acidic solution (pH=4) at a liquid/solid ratio of 100. The amount of heavy metal leached under these conditions is defined as the *maximum availability*, which refers to the total leaching that may occur over a period of 30 to 50 years. Table 8 lists values of maximum availability of cadmium in the four major categories of cadmium-containing wastes.

The table illustrates the wide variation in maximum availability among the various kinds of wastes. There is, for example, a striking difference between flyash from coal combustion, with a maximum cadmium availability of 10%, and flyash from incineration of municipal waste, with a maximum availability of 90%. The reason for the difference is the presence of chlorine in municipal wastes (from plastics and other consumer products), and the lack of chlorine in coal (van der Sloot, 1991). During incineration the chlorine forms complexes with cadmium that are appreciably soluble in water.

The factors for maximum availability given in Table 8 probably over estimate the availability that occurs under field conditions. This is particularly true in recent decades, during which solid wastes in the Rhine Basin have been increasingly disposed of in landfills engineered to restrict their mobilization by controlling the chemical conditions within the waste site, by the use of impermeable linings, and by treatment of drainage waters. Table 9 provides an estimate of the availability of cadmium from solid wastes, taking into account

the introduction of modern, safer landfills. For the new industrial landfills, it was assumed that the availability of industrial wastes was 10% of the maximum availability given in Table 8. For municipal landfills, however, the maximum availability was assumed, even for new landfills. This assumption appears justifiable because the pH of wastes in municipal landfills is typically in the range 4 to 5. (The maximum availability is based on leaching at pH=4.) Moreover, municipal wastes contain high concentrations of organic acids which can form complexes with heavy metals and increase their mobility.

Two trends are evident from Table 9. Firstly, there has been a better than 50% reduction in the availability of cadmium. Secondly, municipal waste disposal has been the major source of available cadmium, and its share of the total available cadmium has increased over time from about 75% in 1970 to about 96% in 1988.

TABLE 8

Estimated Maximum Availability for Cadmium in Various Solid Wastes
(over 30 to 50 year time period)

Activity Generating Waste: Type of Waste	Maximum Availability of Cadmium in Waste (%)
Coal Combustion: Flyash	10% (a,b)
Iron and Steel Production: Flue Dust Slag	50% (b) 100% (b)
Cadmium Plate Manufacturing: Plating Residues	100% (c)
Municipal Waste Disposal: Incineration: Flyash Bottom Ash Direct Landfill: Pigments (in plastics) Pigments (surface coatings) PVC Batteries Cadmium Plate Sewage Sludge	90% (b) 25% (b) 1% (c) 20% (c) 1% (c) 30% (c) 90% (c) 90% (c)

(a) Van der Sloot et al., 1985.

(b) Versluijs et al., 1990.

(c) IIASA, 1992.

The estimations given in Table 9 assume that the new landfills function without leaks or mechanical failures. In actuality this is not always the case, as leaks from presumably safe landfills have been reported in the literature (Hjelmar et al., 1988). Moreover, in the

long-term (more than 30 years) even correctly functioning safe landfills may begin to leak (Foerstner, 1991), resulting in emissions of toxic materials accumulated over previous decades. In addition, complex chemical reactions can occur in landfills, resulting in the generation, *in situ*, of toxic chemicals such as benzene, phenols, and vinyl chloride (Fleming, 1992). Hence, constructing the ideal landfill that is completely safe for current and future generations, is a daunting, if not impossible, task. Clearly, more research is required to understand the complex chemistry of landfills leading to generation and mobilization of toxic chemicals, and more thought must be given to engineering design for containing the chemicals over the long-term.

TABLE 9

Estimated Availability of Cadmium Contained in Solid Wastes
Generated in the Rhine Basin*
(tons)

Activity	1970	1975	1980	1985	1988
Coal Combustion Tons per Year Percent of Total	1.0 (0.2)	1.1 (0.3)	1.1 (0.3)	0.9 (0.4)	0.7 (0.4)
Iron & Steel Production Tons per Year Percent of Total	52.4 (12.7)	43.3 (10.7)	27.0 (7.4)	6.5 (3.1)	3.5 (2.0)
Cd Plate Manufacture Tons per Year Percent of Total	50.4 (12.2)	33.1 (8.2)	18.0 (4.9)	8.0 (3.8)	3.5 (2.0)
Municipal Waste Disposal: Tons Incineration (Flyash)	84.4	95.3	106.0	77.1	45.8
Tons Direct Landfill	27.4	25.9	24.5	25.7	22.1
Tons Cd Plate (a)	194.4	201.0	184.7	90.5	100.8
<u>Tons Sewage Sludge (b)</u>	<u>3.7</u>	<u>3.3</u>	<u>2.8</u>	<u>1.7</u>	<u>1.5</u>
Total Tons per Year Percent of Total	309.9 (74.9)	325.5 (80.8)	318.0 (87.3)	195.0 (92.7)	170.2 (95.7)
Sum Tons per Year Percent of Total	413.7 (100)	403.0 (100)	364.1 (100)	210.4 (100)	177.9 (100)

* Availability for a selected year is defined as the total amount of cadmium that may be leached to the environment over a 30-50 year period after the initial disposal.

As noted earlier, availability corresponds to the fraction of heavy metal that may leach from the solid waste over a 30-50 year time period. An important consequence of this long-term leaching behavior is that the waste may continue to be a source of toxic emissions for decades after it is deposited on the land. Thus, when assessing the total availability of a

heavy metal for a given year one must consider the *cumulative* availability of wastes deposited over the previous 30-50 years. Accounting for historical wastes is particularly important because until the 1970s most solid wastes were dumped on the land without precautions taken to ensure their containment. Table 10 compares the estimated annual availability, obtained by dividing the sums given in Table 9 by 30, with the estimated cumulative annual availability obtained by the following calculation for a given year=x:

$$\text{Cumulative Annual Availability (year=x)} = \frac{\sum_{i=x-30}^{i=x} (\text{Availability}_i)}{30}$$

Table 10 reveals a 15-year time lag between the year with maximum annual availability (1970) and the year of the maximum cumulative annual availability (1985). This result demonstrates the importance of considering long-term cumulative effects of toxic chemicals in the environment. It suggests that measures for reducing solid wastes may not always lead to immediate improvements because of the legacy of toxic materials deposited in past decades that are still environmentally active. (For a more detailed discussion of impacts of cumulative chemical inputs, see Stigliani, 1988.)

TABLE 10

Comparison of Annual and Cumulative Annual Availability of Cadmium in Solid Wastes in the Rhine Basin (tons per year)

Year	1970	1975	1980	1985	1988
Annual availability	13.8	13.4	12.1	7.0	5.9
Cumulative annual availability	218.0	267.8	307.7	323.1	320.5

Application of Agrochemicals. Three major inputs of cadmium to agricultural lands are via atmospheric deposition, application of phosphate fertilizer, and the spreading of sewage sludge. Once the cadmium is in the soil, it can be transported out of the soil by plant uptake, surface runoff, and erosion. The net accumulation of cadmium in agricultural soils can be determined by accounting for inputs and outputs as shown in Table 11.

Net cadmium inputs to the soil have been reduced by more than 50% between the early-1970s and the late-1980s. The most significant reduction has been in atmospheric deposition, which decreased by nearly 50 t/yr (80%) over this time period. In addition, there were more moderate reductions in inputs from phosphate fertilizer (25% reduction) and in sewage sludge (more than 50% reduction). Whereas atmospheric deposition was the largest source of cadmium to agricultural lands in 1970, by the mid-1970s phosphate fertilizer became the dominant source. By the late-1980s it accounted for more than 70% of the total inputs. Plant uptake of cadmium increased mainly because of increases in crop yields over the 18 year period. (The yield of cereal crops in the basin is estimated to have increased from about 2.7 tons/year in 1970 to about 5.6 tons/year in the late-1980s, WRI, 1988.) Runoff of cadmium decreased because of decreases in the concentration of cadmium in wet deposition. Erosion of cadmium increased slightly, reflecting the slow increase in the total soil cadmium content over time.

TABLE 11

Net Inputs of Cadmium to Agricultural Soils
(tons per year)

Source	70	75	80	85	88
Atmospheric Deposition	+61.6	+38.0	+24.1	+15.4	+13.2
Phosphate Fertilizer	+47.7	+43.0	+43.7	+38.0	+35.9
Sewage Sludge	+2.2	+2.3	+1.8	+1.1	+1.0
Plant Uptake	-2.2	-2.7	-3.3	-4.0	-4.1
Runoff	-6.8	-4.2	-2.6	-1.7	-1.4
Erosion	-2.0	-2.1	-2.3	-2.3	-2.4
Net Input	+100.5	+74.3	+61.4	+46.5	+42.2

An important question is whether the cumulative cadmium inputs to agricultural soils are causing significant increases in the soil concentrations of cadmium above background levels, and if so, whether these increases could lead to unacceptably high levels of cadmium in the crops grown in the basin. With this question in mind, the net inputs of cadmium to agricultural soils were estimated since 1950, using available information on historical phosphate use (Behrendt, 1988) and calculating atmospheric deposition². The net inputs were converted into soil concentration units, and the calculated increase in concentration was plotted over time as shown in Figure 7. Under the assumptions of the model, the average cadmium concentration in agricultural soils has risen from approximately 360 g/ha in 1950 to about 700 g/ha in 1988, corresponding to an increase of 94% in the 38 year period. A later section discusses the possible implications of this increase for crop uptake of cadmium and human health.

Eventually, a steady state will be reached between inputs and outputs and soil concentrations of cadmium will level off. Hutton (1982) has calculated a likely steady state concentration for the EC agricultural lands to be between 1,400 g/ha and 2,900 g/ha, for annual inputs of 8 g/ha of cadmium. If this value pertains to the Rhine Basin as well, then the current concentrations are still far from equilibrium and soil concentrations will continue to rise well into the next century if current annual inputs were to continue in the future.

²Historical atmospheric deposition was calculated from the TRACE 2 model (Alcamo et al., 1992) using historical emissions as input. Emissions were estimated from historical levels of production for the major industrial sectors, and historical trends in emission factors for these sectors as determined by Pacyna (1991).

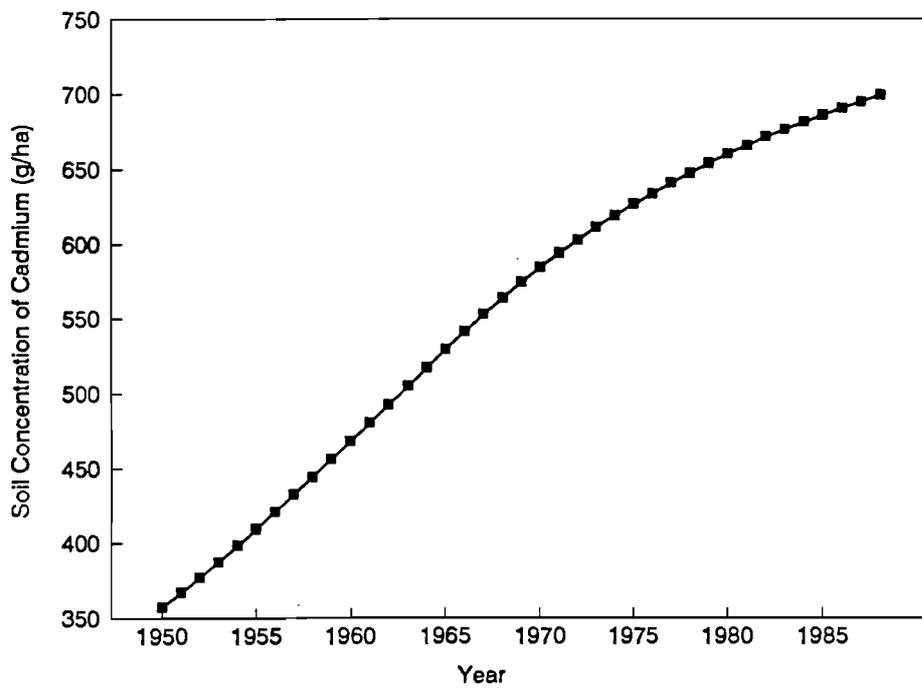


FIGURE 7: Estimated buildup of cadmium concentration in agricultural soils in the Rhine Basin, 1950-1988. (Source: Stigliani and Jaffe, 1992.)

Diffuse Sources of Aqueous Emissions

Diffuse sources of emission, as defined by Novotny (1988), may be differentiated from point sources in at least three ways. Firstly, the emissions occur at random, intermittent intervals; secondly, emissions can vary by several orders of magnitude from one event to another; and thirdly, the emission is usually closely related to meteorological variables such as precipitation. The load of diffuse sources to the Rhine River was estimated in two ways. The analysis of extensive river monitoring data by Behrendt and Boehme (1992) provided annual estimates of the diffuse load during the 1970s and 1980s. Their results are shown graphically in Figure 6. As a second approach, annual loads from the sources of diffuse emissions were estimated independently of the monitoring data. The results of the two approaches were then compared.

As was shown in Figure 2, in urban areas four major sources of diffuse emissions have been identified: atmospheric deposition, corrosion, and traffic in paved areas, and atmospheric deposition and landfills in unpaved areas. Given that most of the population in the basin is concentrated close to the river, it may be expected that a relatively high percentage of the cadmium deposited from these sources enters the river. Atmospheric deposition (wet and dry) on paved surfaces accumulates as street dust, is washed off during storm events, and is conducted to the river through storm sewers or through municipal sewage treatment plants. Cadmium emissions from corrosion occur mainly via the corrosion of galvanized zinc in which cadmium is present as an unwanted impurity. The corroded material accumulates in street dust and is washed out through the same pathway as atmospheric deposition. The main source of cadmium from traffic is through the wearing of automobile tires. Zinc is an additive in tires and a small fraction of cadmium is present as an impurity. The fragments from tire wear collect in street dusts and are transported to surface waters along with other cadmium dusts.

Unpaved urban areas have been the recipient of high loads of cadmium from both short range and long range atmospheric deposition. The cumulative load to all unpaved urban soils over the period from 1950 to 1988 is calculated at about 830 tons. In addition, solid waste landfills are concentrated in unpaved urban areas. As shown in Table 10, the cumulative leaching potential during the 1970s and 1980s is estimated to have been between 200 to 300 tons of cadmium per year. During storm events, cadmium stored in unpaved areas may be transported horizontally by surface runoff, or vertically through seepage to ground waters, where it may be transported to the river via subsurface flow. Leaching from landfills is more problematic for the older sites which were not constructed to contain the wastes. In the case of the new, safe landfills, drainage waters are collected and treated at municipal sewage treatment plants. Even so, the plant may only remove 50-70% of the cadmium. The balance of the cadmium leaves the plant in the aqueous effluent.

There are three sources of diffuse emissions from agricultural areas. One is surface runoff during heavy storm events. It is estimated that 10% of the river flow is contributed by such runoff. Cadmium, as wet deposition, is deposited during the storm and enters the river as a component of runoff. The second source is erosion of a thin layer of the surface soil. Cadmium contained in the layer is transported with the eroded soil. The third source is through subsurface groundwater flow. In this case the source of the cadmium is from natural geological deposits (Behrendt and Boehme, 1992). Most of the cadmium enters the river during heavy storm events when runoff and erosion are accelerated.

Table 12 gives estimates of the diffuse loads of cadmium to the Rhine River from urban and agricultural areas during the 1970s and 1980s. The total load decreased by more

than 60% during the two decades. The most important factor determining this trend was the reduction in atmospheric emissions, which led directly to reductions of atmospheric cadmium inputs to paved urban surfaces and agricultural runoff. Moreover, the reduction of SO₂ concentrations in urban centers greatly reduced the corrosion rate of galvanized zinc and its cadmium impurity (Hrehoruk et al., 1992).

During the early-1970s, paved urban areas are estimated to have been the most important source of diffuse cadmium emissions, responsible for more than 40% of the total load. In subsequent years this share declined sharply--36% in 1975, 27% in 1980, 22% in 1985, and 20% in 1988. In addition to reductions in air emissions, another mitigating factor with respect to cadmium from corrosion and traffic was the reduction in the concentration of cadmium impurity in zinc owing to the increase in production of zinc from electrolytic refineries, which produce a much purer zinc than do the thermal refineries. Despite this factor, cadmium emissions from traffic increased slightly because of the large increase in traffic in the 1970s and 1980s.

The estimated loads from unpaved surfaces are highly uncertain because no data are available for making direct calculations. Nevertheless, the estimates appear to be reasonable. As noted by Stigliani and Jaffe (1992), the vertical leaching velocity of cadmium is very much influenced by soil acidity. At a pH of 6, cadmium leaches at a rate of about 0.3 cm/yr. The rate increases to about 1.2 cm/yr at a pH of 5, and about 5.7 cm/yr at a pH of 4. Given that urban soils have received high loads of acidic deposition for many decades, a substantial fraction probably have pH values in the range between 4 and 5. Thus, it is most likely that shallow urban ground waters have been contaminated to some degree, and that transport of these ground waters to the Rhine River is a significant source of cadmium pollution. Assuming that half of the cadmium originates from the cumulative loading of atmospheric deposition on unpaved areas and half from cadmium-containing solid wastes, each source contributed between 2 and 4 tons/yr. With respect to solid wastes, this amounts to about 1% of the total cumulative annual availability given in Table 10. The fact that the load from unpaved areas appears to be decreasing may be due to both reduced atmospheric deposition of cadmium and better containment of solid wastes in new landfills. Because of the cadmium already present in unpaved urban soils, however, it is possible that continued leaching to the Rhine River may continue for decades into the future.

With regard to agricultural soils, runoff of cadmium decreased because of reduced cadmium concentrations in wet deposition. Erosion of cadmium increased slightly because the soil concentration of cadmium continued to increase over this time period, albeit at a slower rate than in previous decades. Cadmium inputs from ground waters were assumed to be constant because their origin is from natural geochemical sources unaffected by anthropogenic activities.

TABLE 12

Diffuse Sources of Aqueous Emissions of Cadmium
from Urban and Agricultural Areas
(tons per year)

Source	70	75	80	85	88
Urban Areas:					
Paved Areas					
Atmospheric Deposition	9.9	6.0	3.2	2.0	1.6
Corrosion	4.1	3.0	1.6	0.7	0.5
Traffic	0.4	0.4	0.5	0.6	0.6
Unpaved Areas					
Runoff & Leaching (a)	8.5	7.3	6.2	4.8	3.6
Agricultural Areas:					
Runoff	6.8	4.2	2.6	1.7	1.4
Erosion	2.0	2.1	2.3	2.3	2.4
Groundwater	3.2	3.2	3.2	3.2	3.2
Total Calculated Diffuse Emissions	34.9	26.2	19.6	15.3	13.3
Estimates of Behrendt and Boehme (1992):					
Range		73-77	78-82	83-87	
Mean		12.7-38.5	11.2-27.1	14.4-16.4	
		26.2	19.6	15.3	

(a)Determined as difference between sum of paved and agricultural areas and mean values determined by Behrendt and Boehme (1992).

**Step 3: Construction of a Basin-Wide Pollution Model for Assessment
of Proposed Emission Reduction Policies, Environmental Impacts,
or Other Issues Related to the Chemical in Question**

The result of completion of steps 1 and 2 is a basin-wide pollution model which provides an enhanced understanding of the "industrial metabolism" of cadmium in the Rhine Basin. Inputs and outputs have been quantified over time, and changing trends in the sources of pollution have been identified. The pathways by which cadmium moves from its introduction into the industrial economy of the Rhine Basin to its final destination in the environment have been delineated to the extent possible from available data.

Impacts of Cumulative Loading

One use of the model is to determine the long-term environmental impacts of cumulative loading of toxic chemicals in the soils and sediments of the basin. From 1950 to 1988, it is estimated that cumulative inputs of cadmium in unpaved urban areas, agricultural lands, and forests in the basin have been 830 tons, nearly 4,000 tons, and about 1,500 tons, respectively. Stigliani and Jaffe (1992) have examined the effects of cadmium accumulation in agricultural soils. Crop lands are particularly vulnerable to cumulative loading for two reasons. Firstly, inputs of toxic materials from application of agrochemicals and atmospheric deposition have been historically high. Secondly, the pH of the soils has been artificially maintained at around 6 by the addition of lime. Soils at a pH of 6 have a much higher capacity to adsorb heavy metals and pesticides than do soils at lower pHs. Thus, in contrast to the situation for acidified urban soils in which cadmium is rapidly leached out, the metal essentially accumulates in agricultural soils. The history of this accumulation was discussed previously with regard to Figure 7.

The next step in the analysis is to estimate the impact of the increased soil concentrations on plant uptake and food consumption. These aspects are discussed in detail in Stigliani and Jaffe (1992). Table 13 presents estimates of the average Cd intake in $\mu\text{g}/\text{week}$ per capita in the Rhine Basin assuming that all of the diet is obtained from food grown in the basin. The World Health Organization (WHO) recommends that maximum cadmium intake should not exceed 400 to 500 $\mu\text{g}/\text{week}$. The table shows that cadmium intake is still well below the recommended maximum, but only under the condition that the pH of the soils is maintained at 6 or above. If the pH were to shift from 6 to 5.5, however, the increased uptake of cadmium in the food supply could lead to levels that exceed the WHO recommended threshold standard for human consumption. A shift of pH to 5.5 is quite feasible, particularly in areas affected by acid deposition and given the fact that lime is often not applied continuously on an annual basis. The most important point of the analysis is that in 1960, a shift to a soil pH level of 5.5 would have resulted in consumption levels still well below the WHO standard. Thus, the major impact of the cumulative loading of cadmium in agricultural soils since 1950 has been a loss of resilience with respect to cadmium uptake during random fluctuations in pH. The safe functioning of the agricultural system now requires tighter constraints on the range over which such fluctuations may occur.

TABLE 13

Estimated Average Intake of Cadmium ($\mu\text{g}/\text{week}$)
at Different Values of pH in Agricultural Soils in the Rhine Basin

Year	pH=6.0	pH=5.5	pH=5.0
1960	140	300	660
1970	200	440	940
1988	230	500	1090

Source: Stigliani and Jaffe (1992).

Testing the Effectiveness of Proposed Pollution Reduction Policies

One important application of industrial metabolism studies is testing possible pollution reduction strategies within the context of systems analysis. Because this approach is based on mass balance, policies that do not reduce overall emissions, but rather, merely shift them from one pollution pathway to another can be readily exposed. By way of example, a policy for reducing inputs of cadmium to the environment via the banning of cadmium-containing products is discussed here. Although no such ban is yet in effect, perhaps the anticipation that it will be implemented has already resulted in a marked decline, since the early-1980s, in the production and use of all cadmium-containing products, with the exception of Ni-Cd batteries.

Let us assume that the policy under consideration is the banning of all cadmium products in the basin except for N-Cd batteries, for which there is a growing market and for which suitable substitutes have not yet been developed. Furthermore, it is proposed that by the late-1990s, at least 50% of the small sealed consumer Ni-Cd batteries entering the domestic disposal stream are recycled. To what extent will this policy serve the purpose of reducing cadmium emissions?

The first step in the analysis is to determine the flow in the production, use and disposal of cadmium products in the basin. Figure 8 portrays this flow for the mid-1980s³. Also shown are the emissions of cadmium to air, water, and solid wastes. The numbers in brackets beside the solid wastes are the estimated *availabilities* as previously defined. The sum of the availabilities of cadmium provides an approximate index by which the effectiveness of control strategies can be appraised. In the mid-1980s, this sum was 204 tons with waste disposal the largest contributor at 195 tons.

Figure 9 is a flow diagram depicting the situation in the late-1990s assuming that the proposed mitigation strategy has been implemented. It is assumed that the use of small, sealed consumer batteries doubled relative to the mid-1980s. This represents a moderately reduced growth rate relative to the 1980s when consumer use doubled within ten years. One positive effect of the product ban is a large decrease in availability from solid waste disposal, from 195 tons in the mid-1980s to 49 tons in the late-1990s.

A problem still remains, however, because the supply of cadmium entering the basin is essentially inelastic since it is a by-product of zinc production. The production of zinc in the basin has been quite stable, averaging about 185,000 tons per year since the late-1960s. It is not likely that there will be any drastic reductions or increases in zinc production in the late-1990s. Thus, it seems reasonable to assume that about 600 tons of cadmium will be separated from zinc at the refineries. In contrast to the mid-1980s, when there was a shortage of cadmium in the basin, requiring the importing of 570 tons of cadmium metal, according to the scenario only 118 tons of cadmium would be required for battery production, resulting in a surplus of about 425 tons of cadmium at the zinc refineries. These are in the form of flue dusts at the thermal refinery and leaching residues at the electrolytic refinery. There are no data on the availabilities of cadmium in these wastes. It appears that they may be considerable, however, since cadmium in most solid wastes is appreciably soluble in acids, as well as in the presence of commonly occurring complexing agents such

³Disposal, as indicated in Figures 8 and 9, is actually the "disposal commitment" for the given years. Because the life cycle of cadmium-containing products varies from a few years (for cadmium pigments) to several decades (for cadmium in PVC), the numbers in the figures represent the disposal over years to decades in the future, from the products that entered the industrial economy in the years indicated.

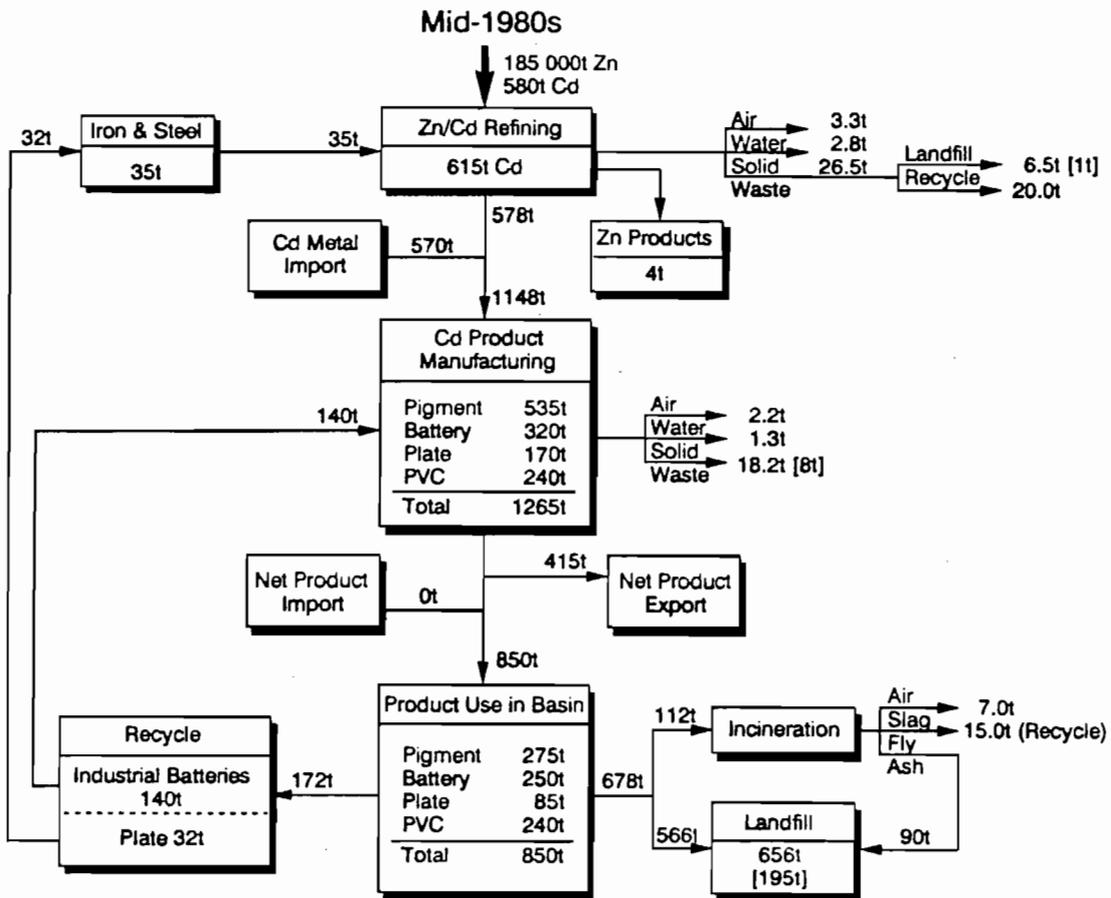


FIGURE 8: Balance of cadmium product use and disposal in the Rhine Basin in the mid-1980s.

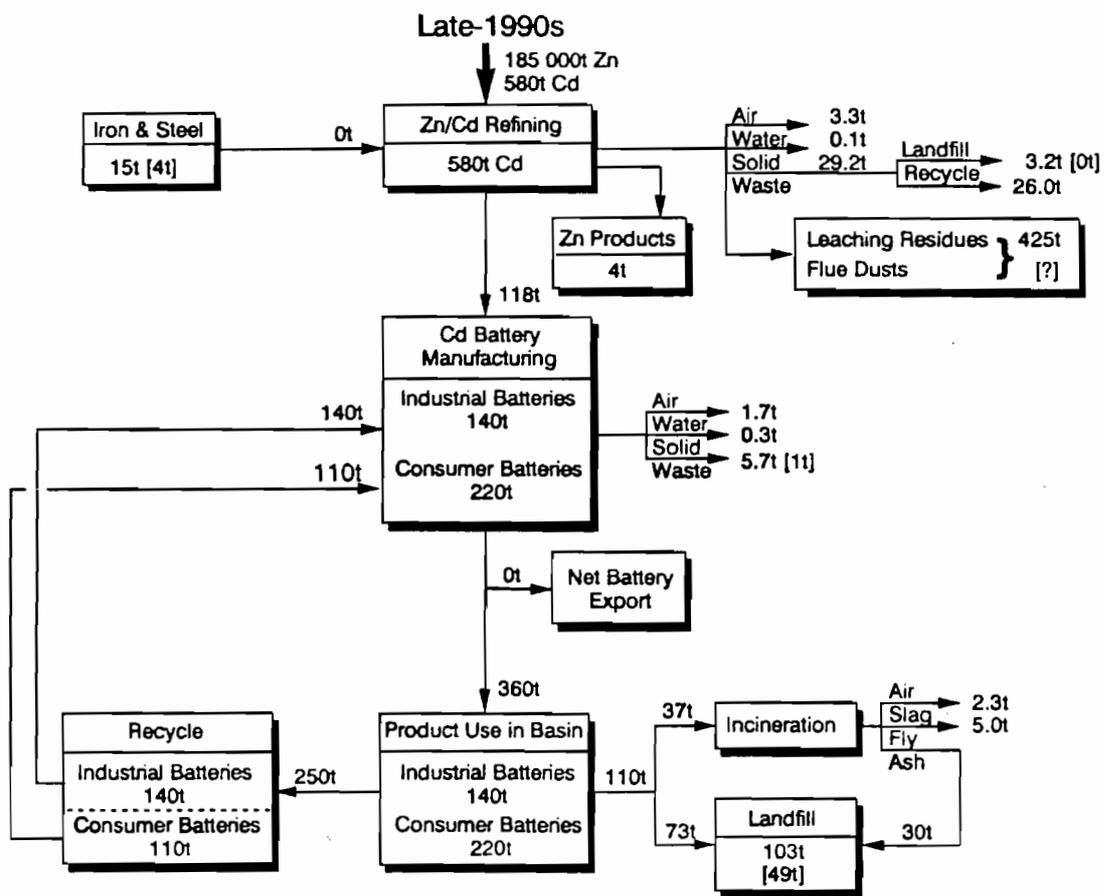


FIGURE 9: Scenario for balance of cadmium product use and disposal in the Rhine Basin in the late-1990s.

as ammonia (Rauhut, 1978b). In recent decades the flue dusts from the thermal smelter have been sent to the electrolytic refinery for processing into cadmium metal. (As noted earlier in the discussion, until the late-1970s, these flue dusts were discharged to the Rhine River, and constituted the largest source of water pollution.) About 95% of the cadmium in the leaching residues generated at the electrolytic refinery were refined to cadmium metal in the mid-1980s. Moreover, the iron and steel industry sent solid wastes containing about 35 tons of cadmium to the electrolytic refinery. Under the scenario shown in Figure 9, there will be a very low demand for recycled cadmium-containing wastes from the metallurgical industries. EC regulations regarding the disposal of solid wastes will require that they be stabilized (i.e., they must be treated to ensure a low cadmium availability). Stabilization of wastes is expensive and not always effective in reducing availability (Kosson et al., 1991). So the ultimate effect of banning most cadmium products and recycling 50% of the disposed consumer batteries may be to shift the pollution load from the product disposal phase to the zinc/cadmium production phase. This analysis does not imply that banning cadmium-containing products is not a wise strategy. Rather, it indicates that if such a ban were to be implemented, special provisions would have to be made for the safe handling of surplus cadmium wastes generated at the zinc refineries.

One possible option that would reduce the volume of surplus cadmium at the refinery would be to allow the production and use of cadmium-containing products with inherently low availability for leaching. A good candidate for consideration is cadmium used as a stabilizer in PVC. If production of PVC stabilizer were maintained at levels of the mid-1980s, about 240 tons, the surplus of cadmium in refinery wastes would decrease by more than 50%. Cadmium-stabilized PVC is used almost exclusively in outdoor window frames. Because the cadmium is locked into the PVC matrix, its availability is expected to be low, even when the product is disposed into landfills. (See Table 8.) Cadmium contained in plastic could be mobilized if the plastic were incinerated. This is a major problem with respect to plastics containing cadmium pigments. However, it is likely that the PVC window frames would be disposed along with other construction debris, which one would not expect to be incinerated. In fact, in 1986 in the Netherlands about 45% of demolition debris was recycled, and in the year 2000 it is projected that 80% will be recycled (MHPPE, 1988). Of course, further studies would be required to ensure that the cadmium in the recycled material is effectively immobilized and poses an acceptably low risk to the environment and human health. The other option, depositing the cadmium-containing refinery wastes in safely contained landfills, has other associated risks, as noted above. What is certain is that as long as zinc is produced in the basin, cadmium will be introduced either as a desired or unwanted by-product.

CONCLUSIONS

Analysis of the chemical "metabolism" of modern industrialized societies is very complex, requiring a sophisticated systems approach. Nevertheless, studies tracking the flow of toxic materials through the industrial economy and into the environment can be an indispensable tool for environmental management. Study of the Rhine Basin since 1950 is of particular interest because the region has passed through the phase in which high productivity is associated with correspondingly high levels of polluting emissions, and into a phase where production has been decoupled from pollution. Understanding the societal, economic, and technological driving forces that stimulated this transition could provide a rough blueprint for the clean-up of river basins that are currently trapped in the coupled

production-pollution syndrome. The insights provided by the Rhine Basin study, together with studies of the industrial metabolism of highly polluted regions such as eastern Europe, could provide a sound basis for the rational prioritization of actions required for restoring the environment to an acceptable level.

The Rhine Basin study has demonstrated that even regions in a more advanced stage of environmental management could benefit from such studies. Indeed, "input management" (e.g., Odom, 1989), rather than "fire brigade actions," will be of increasing importance in formulating action alternatives that are better integrated and more directed toward the goals of long-term economic and ecological sustainability.

Finally, it should be noted that one of the most useful functions of soils and sediments is their ability to serve as a "sink" for the retention of toxic chemicals. This sink, however, usually has a finite sorption capacity, the size of which is governed by fundamental chemical properties such as pH, organic matter content, etc. Hardly any information is available regarding the long-term, broad-scale cumulative loadings of toxic chemicals into the environmental sinks, and whether, and under which conditions, the sorption capacity might be transgressed beyond a threshold value considered to be safe to the environment or human health. The analysis presented in this paper on the effects of cumulative cadmium inputs to agricultural soils illustrates the usefulness of our approach in evaluating such long-term environmental impacts.

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