

Working Paper

**Industrial Metabolism: A New
Approach for Analysis of Chemical
Pollution and Its Potential
Applications**

William M. Stigliani and Peter R. Jaffe

WP-92-6
January 1992



International Institute for Applied Systems Analysis □ A-2361 Laxenburg □ Austria

Telephone: +43 2236 715210 □ Telex: 079 137 iiasa a □ Telefax: +43 2236 71313

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PREFACE

Traditionally, studies of the environmental effects of chemical pollution have been conducted mostly by environmental scientists (usually after detrimental effects have been observed) and focussed mostly on the environment. Relatively little attention has been paid to the anthropogenic activities which have caused the pollution in the first place. There are, of course, many studies concerning sources of pollution, usually related to emissions from industrial point-sources. Far fewer studies exist on diffuse sources of emission generated during the normal use and consumption of materials, even though recent studies have indicated that the main sources of pollution in western industrialized nations are shifting away from industrial and manufacturing processes to the use and disposal of consumer and commercial goods. Even fewer studies have been conducted which analyze the economic and environmental spheres as a single entity. Much of the data required for these studies already exists, but has not been integrated over time and space to gain a deeper understanding of economy-environment interactions.

Analysis of material flows through the industrial economy can provide a rich, complementary data base for the analysis of flows through the environment. Detailed information may be gained, for example, on sources of emissions, the relative magnitudes of those sources, the paths of transport of chemical emissions from the industrial economy to the environment, historical trends in emissions, scenarios of future emissions, and socio-economic and political factors influencing emission trends. In addition, this approach provides the means for testing the effectiveness of proposed management strategies for reducing emissions. Since the analysis is based on the principle of mass balance, strategies that do not reduce emissions, but rather, shift them from one pollution pathway to another are readily exposed.

Finally, it should be noted that the environmental impact of broad-scale, long-term chemical pollution from routine, daily activities is probably far greater than the impact from highly-publicized industrial accidents. Despite this, there is a scarcity of data on the rates at which chemicals are building up in forest lands, agriculture, and urban areas, and on the potential effects of these cumulative loads on the environment or human health. The approach of industrial metabolism provides a means for estimating the loads and evaluating their impact. As an example, in this paper an analysis is presented of cadmium inputs to agricultural lands in the Rhine Basin over a 40 year period. The analysis indicates that cadmium inputs have built up to such levels that shifts in pH that are quite feasible may pose a public health problem today, while comparable shifts in 1960 would not have done so.

The object of this paper is to demonstrate the merit of studies in industrial metabolism as a new analytical tool for assessing the sources and flows of toxic chemicals, from which rational decisions can be made for their control and reduction.

Industrial Metabolism: A New Approach for Analysis of Chemical Pollution and Its Potential Applications

William M. Stigliani

International Institute for Applied Systems Analysis

Peter R. Jaffe

Princeton University, Princeton, New Jersey

1. Introduction

As industrial societies generate and use materials, some of these materials enter the environment and may thereby directly or indirectly alter the environmental quality. Over the last fifty years we have progressively recognized the effects from releases of large amounts of specific substances on relatively small ecosystems, and have developed and partially implemented the appropriate technology to mitigate these effects. Well known examples include: the discharge of organic wastes into surface waters, which depletes their dissolved oxygen content, and which was remediated in part through the construction of sewer collection systems and sewer treatment plants; use of sulfur containing fossil fuels for electric power generation, which is a main contributor to acid precipitation, and which was remediated in part by a shift towards fossil fuels with a lower sulfur content; disposal of toxic wastes on soils, which resulted in ground water contamination and severe illness of the population exposed to these wastes, and which was remediated by implementing a more appropriate disposal of hazardous wastes and massive site decontamination efforts. These are of course still actual problems that receive the majority of the attention from the public, governments, and industry.

In addition to the acute problems described above, some pollutants disperse in the environment and, depending on their degradability, may either reach a quasi steady-state (e.g., organic trace pollutants in urban air) or they may build up slowly (e.g., heavy metals). Heavy metals are of special concern. They are being mined from deep deposits in which they are abundant and relatively immobile, and are then, through a series of mechanisms described later, released into the environment. This slow and dispersed accumulation of trace pollutants may be called a chronic problem as opposed to the acute problems referred to earlier. To date we have not conducted many rigorous and comprehensive analyses to evaluate this type of pollution, but several important questions need to be addressed: Do we have a problem, and are trace pollutants building up in large regions of the environment to levels that are detrimental? How is this buildup, if it occurs, related to the activities of industrial societies? How can this buildup be prevented or minimized?

The objective of this paper is to review the current procedures used for analyzing the flow of materials through an industrialized society, how estimates of the rate at which these materials enter and disperse in the environment are being conducted, and how the long-term effects of these trace pollutants on the quality of specific environmental compartments is evaluated. We will review typical assumptions that are made for the purpose of such an analysis, and how they relate to the dynamics of trace pollutants in the environment. Finally, we will attempt to identify the gaps in our knowledge and weaknesses in the current procedure used to analyze these dynamics.

2. Pathways of Chemical Pollutants through the Industrial Economy

2.1. Categorization of sources of pollution

As shown in *Figure 1*, chemical pollutants are ubiquitous in industrial societies, with multiple sources of emissions and numerous pathways by which they cycle through the economy before entering the environment. Industrial and energy production result in *point source* emissions. These sources are typically confined to specific locations, usually in urban areas. Pollutants can be in the form of solid wastes, aqueous emissions, and atmospheric emissions. Point sources, in fact, are responsible for almost all atmospheric emissions of inorganic pollutants such as heavy metals, sulfur, and nitrogen (lead from leaded gasoline being a notable exception). Pollutants may be deposited via long-range atmospheric transport hundreds, even thousands, of kilometers from the source. Deposition from long-range atmospheric transport is a major source of pollution to remote forests and agricultural lands. With respect to urban areas, deposition from short-range atmospheric transport is important. Typically, about 10% to 15% of the total air emissions are deposited, usually in the form of dry deposition, within a radius of 20 kilometers from the point source. Pollutants are often present as unwanted trace impurities in materials with a high volume of use in the industrial economy. For example, coal contains trace amounts of heavy metals, which are mobilized during combustion.

Another important source of emissions is the application of *agrochemicals*, including fertilizers, sewage sludge, manure, and pesticides on agricultural lands. Crops take up trace amounts of toxic materials from the soil. Contaminated crops are a major source of pollution to humans. The soil contaminants that are not removed by crop uptake can accumulate in the soil, or they may be transported over the land by erosion, or they may seep into ground waters.

Industry, power production, and agricultural practices are not the only sources of toxic emissions. In fact, recent studies have shown that, relative to other sources of pollution, the use and disposal of commercial and consumer goods and materials are becoming increasingly important (Ayres and Rod, 1986; Anderberg et al., 1989, Stigliani and Anderberg, 1992a). Emissions released during consumption and disposal of commercial and domestic products are

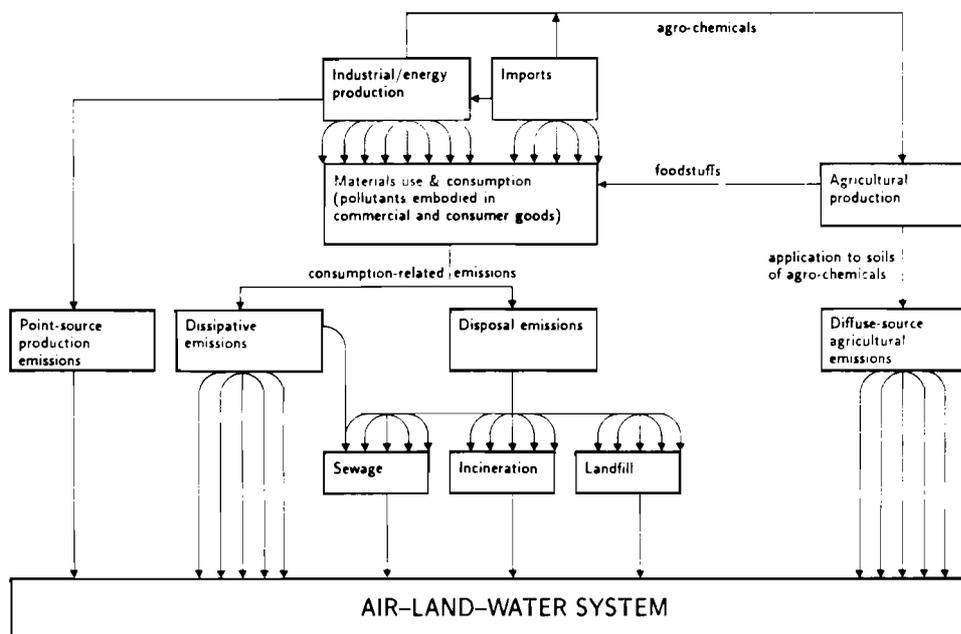


FIGURE 1: An integrated emissions classification scheme. (Source: Stigliani, 1990.)

mainly a problem of urban centers where most commercial enterprises are located and the great majority of the population resides.

For products and building materials containing toxic chemicals, emissions may be released and dispersed to the environment during normal usage. The importance of such emissions has been noted by Ayres et al. (1988) and Stigliani (1990), who have distinguished them as *dissipative* emissions, in contrast to emissions that occur after disposal. Included in this category are products such as fuels, agrochemicals, solvents and cleaning agents, chemical additives, pharmaceuticals, paints and other surface coatings, construction materials, and many uses of non-ferrous metals. In large urban areas, paints, construction materials, and traffic account for a major share of dissipative emissions. The extent to which toxic releases occur depends on how strongly the toxic chemical is bound within the product. For example, emission rates of toxic heavy metals such as chromium and lead contained in alloys are low during normal use, since they are incorporated as part of the alloy's molecular structure. In contrast, zinc as an additive in the rubber of automobile tires is released as the tire wears. Similarly, paints containing lead and zinc, and galvanized zinc surfaces are major sources of emissions of these metals in urban environments since they are susceptible to chipping, cracking, or corrosion as the material ages. Moreover, synergism between pollutants can play an important role. For example, the rate of corrosion of galvanized zinc is strongly coupled to SO₂ concentrations in urban air. The recent decline in zinc content in urban street dust in the Rhine Basin has been attributed to the large reductions in SO₂ emissions (Hrehoruk et al., 1992; Behrendt and Boehme, 1992).

A large fraction of the dissipative emissions ends up in street dust. The paved, impermeable surfaces that constitute approximately a third of the urban area serves as an efficient conduit for transporting the dusts to surface waters during storm events. Solids and dusts from paved urban areas have a runoff rate typically four or five times greater than agricultural lands and roughly 40 or 50 times greater than forest lands (Ayres et al., 1988). Thus, even though urban and suburban lands are typically 15% or less of the total area, their impact on the environment is disproportionately larger.

Landfills, incinerators, and sewage treatment plants, the final depositories of most consumer wastes that are not dissipated, may be classified as point sources. Unlike industrial or energy-producing point sources, however, these sites are receptacles for waste materials from a vast array of inputs. A study of toxic materials in domestic garbage in the U.S.A. revealed that the average American household discards approximately 55-60 g (about 0.35-0.40% by weight) of hazardous wastes per week (Rathje et al., 1987). Averaged on a national basis, that amounts to approximately 250,000 tons per year. Ideally, properly functioning sanitary and hazardous waste landfills should isolate toxic chemicals from the environment. Depending on the design and operation of the landfill, it may or may not leach and transfer the pollutants into ground waters. Toxic materials bound in certain products can be considered to be in safe, long-term storage. For example heavy metals bound in plastic products are relatively immobile (Bromley et al., 1983; Raede and Dornemann, 1981), and can be considered to be in long-term storage, regardless of their ultimate disposal, as long as the plastic is not incinerated. There is much current focus on devising new alternatives for the long-term storage of trace pollutants contained in solid wastes. One promising method, already practiced extensively in the Netherlands and Germany for solid wastes such as flyash from coal combustion, is their incorporation into building materials; e.g., cement and asphalt to name a few (MHPPE, 1988; Risse et al., 1991). Another possible option is deep subsurface injection in geologically stable areas where transport of the pollutants would be expected to be negligible.

Incineration of wastes, the major alternative to landfills, is a source of air pollution comprised of heavy metals, polynuclear aromatic hydrocarbons, and dioxin. Moreover, the fly and bottom ashes left as residues of combustion contain high concentrations of heavy metals and toxic organic substances. Incineration residues are particularly problematic with respect to heavy

metals. Because of the presence of chlorine in municipal refuse, the metals form complexes with chlorine that are highly soluble (van der Sloot, 1991). Thus, in order to prevent the mobilization of the soluble complexes in the environment, incinerator ashes must be specially treated to reduce metal mobility, or disposed to safe landfills that will restrict their transport.

Municipal sewage treatment plants receive liquid wastes from households and small industries. Depending upon the sewer system, storm runoff containing polluted street dust from paved urban areas may either enter directly into surface waters or may enter a sewage treatment plant. Trace pollutants that tend to sorb will sorb strongly to the biomass, and will be concentrated in the sewage sludge. There are several routes of disposal for this sludge. These include: direct deposit in sanitary landfills; incineration; application as fertilizer on agricultural lands; and, finally, ocean dumping.

2.2. Obstacles to reducing emissions

Driven by economic and social pressures, strategies are focussing more and more on *pollution prevention* rather than "end of pipe" methods as a means for controlling toxic substances. Motivating this tendency is the enhanced realization that preventing the formation of pollutants can be ultimately more effective, practical, and cheaper than controlling pollutants escaping from the end of a pipe. In practice, however, it will not be possible to eliminate all toxic chemicals, and pollution prevention will have to encompass a hierarchy of reduction and management strategies. The U.S. Environmental Protection Agency (EPA) and others (OTA, 1986) have advocated four such strategies, listed below in order of decreasing preference:

1. Source reduction;
2. Environmentally sound recycling;
3. Treatment/stabilization;
4. Disposal.

The ultimate goal of this overall strategy, as noted by EPA Administrator William K. Reilly, is the attainment of a safe, sustainable environment (Ember, 1991).

There are many obstacles, however, in realizing this goal solely by implementing the four espoused strategies. Source reduction may be an effective strategy for reducing emissions from point sources, but it is not clear that it can be applied to consumer-related emissions. Emissions from production have been decreasing steadily over the last two decades, but consumption and disposal of materials have been increasing as affluence has bred an increasingly "throw away" mentality. As a result of these trends, the share of the total pollution load is shifting away from production, as emissions from consumption and disposal of materials are gaining in importance.

Although recycling can certainly play a large role in reducing the burden of toxic materials that end up in disposed wastes, many toxic chemicals are present in trace amounts, and recycling them may not be feasible or economically viable. A second and more overriding problem is that the toxic materials in disposal wastes stem from multiple sources, e.g., batteries, paints and pigments, wood preservatives, used motor oil, fire-retardant additives, etc. A careful book-keeping of these sources in municipal wastes is generally not available, and even if it were, sorting through the garbage to selectively remove the toxic-containing products is not usually undertaken. A notable exception is Japan, where toxic materials in garbage are sorted and removed and fully 50% of the garbage is recycled (Hershowitz and Salerni, 1987). Another factor acting against the recycling option is the increasing complexity of new materials, for which recycling is inherently more difficult than for traditional materials. For example, unlike the metals they will replace, the new high strength composites cannot be melted down and recast (Frosch and Gallopoulos, 1989).

Treatment, stabilization, or disposal of wastes is not at all applicable to dissipative urban and agricultural emissions, which are uncontrolled and unregulated. Moreover, the information base that would support possible control strategies is usually insufficient because of the difficulty of monitoring emissions of this type.

Another obstacle is that while point sources can be considered as closed systems amenable to control strategies such as reduction at source and closed-loop recycling, emissions from consumption and disposal processes occur in a more open system where the boundaries are less well defined. Major oversights can occur when policy decisions are based on an analysis that bounds the system too narrowly. For example, billions of dollars have been spent in the U.S.A. on the construction of secondary sewage treatment plants for improving water quality through reductions in BOD. As noted by Tschinkel (1989), however, much of the benefit gained from this technology 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 might not have happened had planners taken account of the multiple sources of toxic materials in street dust and the pathways by which these dusts are transported to the surface waters.

The most important obstacle, that hinders the effectiveness of all management strategies mentioned above, is the lack of a comprehensive accounting of the stocks and flows of chemical pollutants as they cycle through the industrial economy, and knowing the precise points in this flow at which they are emitted to the environment. Acquiring such a perspective for major classes of toxic chemicals such as heavy metals and organic micro-pollutants would greatly facilitate the formulation of prudent strategies for attaining the goal of the ecologically sustainable use of chemicals. Without such a base of information, management strategies may continue to be implemented on an *ad hoc* basis by which important sources and pathways of pollution remain unregulated.

3. Trace Pollutants in the Environment

3.1. The dispersion of trace pollutants in the environment

The dynamics of trace pollutants in specific environmental compartments such as streams, reservoirs, or soils have been studied in detail by environmental scientists for many years. The dynamics of a specific trace pollutant are tracked by a careful mass balance in which changes in mass per unit volume and time are equated to transport processes associated with the movement of fluids, mixing processes such as molecular diffusion and tidal mixing, chemical or biological transformations, phase changes such as volatilization and dissolution, and sources and sinks from and to other compartments. To make the analysis tractable, once the scale or compartment of interest is defined, the source term is assumed to be independent of the dynamics of the trace pollutant within the compartment.

For example, assume there is a landfill from which PCBs leach into a lake. The rate of leaching is the source term that will be used in the analysis of the PCB dynamics in that lake. A major sink term for the PCBs will be their volatilization across the water/air interface into the atmosphere. A small fraction of the PCB mass that volatilizes will sorb onto the surface soils surrounding the lake, and a fraction of that mass will enter the lake again with storm runoff as a non-point source. In the short term, this non-point source, which is in part directly related to the PCB dynamics in the lake, can be neglected for the purpose of our analysis since it is negligible compared to the main source. In the long term however, this non-point source might become an important source to the lake. If we now assume that there is another lake nearby, the non-point source described above might be the primary source of PCBs to that second lake.

This example illustrates that it is possible to isolate a specific environmental compartment in order to analyze the pollutant dynamics in that same compartment. Such

analyses are routinely being done, and are valuable tools to assess the impact of specific activities on the environmental compartment that is directly affected by them. Examples are the effect of agricultural practices on local soils and ground waters, the effect of discharges from point and non-point sources on local surface water and air quality, and the design of contaminated site remediation, to mention a few.

The example also shows that these analyses fall short in evaluating secondary effects that arise from the transfer of the pollutant from one compartment to another compartment. These are the long-term effects that arise due to the spreading of the trace pollutants in the environment. We can build further on our example of the dynamics of PCBs, which are known to be spreading throughout the biosphere. Atmospheric transport is one of the main mechanisms responsible for such spreading, and PCB residues have been detected in remote areas such as Arctic regions and Antarctica (Atlas and Giam, 1981; Tanabe et al., 1983; Murphy, 1984). It is obvious that in order to understand the source of PCBs to arctic regions, a complex analysis is required, which has to link the dynamics of PCBs in many compartments including soil, surface waters, air, and biomass. The scale of this problem is at least continental if not global. In order to track these dynamics mathematically, the environment needs to be discretized into a continuum of compartments that are all interconnected. In some of these compartments the PCB mass is decreasing while in others it is increasing. An overall mass balance will have to hold for the sum of all compartments. If we do not have an external source, mass conservation tells us that, for a stable trace pollutant (e.g., a metal), summing the mass in each compartment over all compartments has to remain constant over time. If a pollutant decays (e.g., radioisotopes or trace organics), the difference obtained from the sum of the mass in each compartment over all compartments at two different times has to be equal to the amount generated minus the amount that decayed during that time interval.

For an analysis of the long-term trends of specific trace pollutant levels in the environment as a function of the pollutant-release rate, it is essential to consider the link between a large number of environmental compartments. *Figure 2*, which is by no means complete, attempts to illustrate how pollutants released into the environment will be transferred between different compartments that are all interconnected. The transfer between compartments is driven by specific transport processes and the affinity of the individual trace pollutant to concentrate in a specific phase (i.e., aqueous, solid, or gaseous phase). Through these processes, trace pollutants will distribute themselves between compartments, and depending on their thermodynamic equilibrium between phases, they will tend to accumulate in specific compartments. For example, stable trace pollutants that sorb strongly onto soil and are not very volatile (e.g., most heavy metals) will accumulate in soils and sediments. On the other hand, pollutants that decay fast will not tend to accumulate in the environment. An interesting example is that of industrial solvents such as chlorinated ethenes, some of which are considered to be carcinogenic. These compounds are very volatile and tend to escape into the atmosphere, where they are relatively unstable and do not build up. The main problem with these compounds arises when they enter the ground water compartment, from which their volatilization into the atmosphere is very slow (Cho and Jaffe, 1990), and where their degradation under natural conditions is also very slow (Baeck et al., 1990). Chlorinated ethenes that enter the subsurface may therefore represent a long-term ground water pollution problem, even though they do not tend to build up in the compartment for which they have the highest affinity. These are therefore pollutants for which it is much easier to analyze their long-term fate in a specific environmental compartment without necessarily tracing their dynamics through all compartments to which they are transferred. Another interesting case is that of the chlorofluorocarbons (CFCs), which, similar to the chlorinated ethenes, tend to escape to the atmosphere, but which are very stable in most situations and are considered non-toxic. For a long time these compounds have therefore not been perceived as representing an environmental problem. We now know that as CFCs diffuse into the stratosphere, they do degrade, freeing

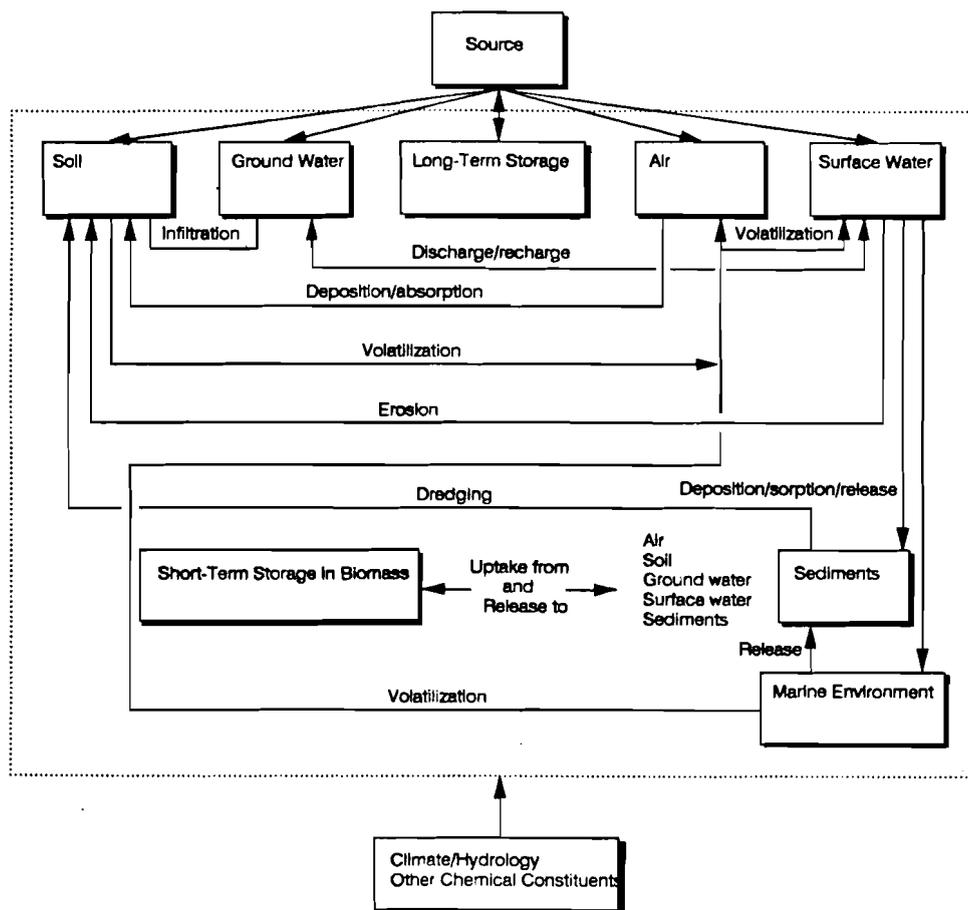


FIGURE 2: Interconnections and transfers between compartments of the biosphere.

chlorine that then reacts with ozone. This results in the well documented decrease of ozone levels in the stratosphere, and its related detrimental consequences for the biosphere (Cicerone, 1987).

In summary, as we have illustrated here through several short examples, trace pollutants released into the environment will tend to disperse in the environment, and if they are stable and have an affinity for a given phase, they will tend to accumulate in specific compartments.

3.2. Processes that disperse trace pollutants in the environment

Trace pollutants may enter the environment by being released directly into different compartments. This release may be due to natural sources (e.g., volcanic eruptions, weathering processes) and anthropogenic point and non-point sources. Through a series of mechanisms, the trace pollutants will then be transferred between compartments as illustrated in *Figure 2*. For example, trace pollutants such as heavy metals that are discharged into the air are transported by wind currents and deposited on surface soils, and surface waters including the marine environment.

Many trace pollutants including heavy metals and non-ionic organic substances such as PCBs will sorb strongly onto soil particles, which will have a strong effect on their transport from soil and ground water to other compartments. Movement of the trace pollutants from the soil to other compartments can occur via a series of processes: *volatilization* or *wind-induced erosion*,

by which either the volatile compound or dust particles containing the trace pollutants can be transferred into the air and can be transported over relatively great distances; *rain-induced erosion* and *runoff*, by which sorbed and dissolved trace pollutants can either enter surface waters directly, or can be redistributed to other soil compartments with a lower elevation; *infiltration*, by which dissolved-phase trace pollutants can be transported into the ground water; and *uptake* by plants from soils and sometimes shallow ground water (Hutton, 1982), followed by harvesting, by which dissolved trace pollutants may enter the food chain and be transferred to other compartments. In addition to these processes, transfers of pollution may occur from surface waters directly to ground waters in regions where the surface waters recharge ground waters, causing a transfer of trace pollutants to the ground water compartment.

In addition, there are several important types of point sources such as industrial sites and leaching landfills that contribute to the pollutant load of ground waters. Trace pollutants in ground water will slowly be transported to surface waters during ground water discharge into surface waters. Because ground water velocities are relatively slow, and the mean distance to the point of discharge to surface waters is usually long, transport of pollutants by ground water is a slow process compared to the transport in surface waters. Furthermore, because many trace pollutants sorb onto the soil, the velocity at which they move in the soil and ground water is even slower than the velocity at which the water moves. For these reasons, the dynamics of trace pollutants in the soil/ground water compartments usually do not have an immediate impact on the dynamics of these same trace pollutants in surface waters.

Because of the tendency of many trace pollutants to sorb onto particular solids, a large fraction of them that enters surface waters will be associated with bottom and suspended sediments. The cohesive sediments (i.e., clays and organic colloids) which are much smaller than non-cohesive sediments (i.e., silt), usually stay suspended in the water column rather than settling to the bottom until the turbulence decreases to levels that are commonly found only in lakes or river deltas. Most of the trace pollutants will be sorbed to the cohesive sediments because of their much higher organic carbon content and surface charges, which are the main properties of the sorbate (solid) that affect the sorption of non-ionic organic chemicals and trace metals (Karickhoff et al., 1979, Boeckhold et al., 1990). For this reason, sorbed trace pollutants in surface waters will tend to accumulate in regions of relatively low turbulence where the cohesive sediments can be deposited. An increase in turbulence, occurring, for example during a flood, can result in the resuspension of the sediments, thereby allowing the trace pollutants to reenter the surface water. In addition, slow leaching of trace pollutants can occur from bottom sediments into cleaner overlying waters. As will be discussed later, chemical alterations in the sediment-water column system can enhance leaching significantly. In large, navigable water systems, sediments are regularly dredged to keep shipping lanes open, and the spoils disposed on land. Through this process the trace pollutants can enter the surface soil compartment. If anaerobic conditions prevailed in the sediments prior to land disposal, the oxidizing conditions on land may cause rapid mobilization of pollutants that were tightly bound within the sediments (Gambrell et al., 1977; Khalid, 1980; see also discussion below on the effect of changing "redox potential"). Biological activity is another important mechanism by which trace pollutants may be mobilized in surface waters and bottom sediments. Uptake by microbes and other benthic organisms may subsequently lead to biomagnification of pollutants in the aquatic food chain. All the processes described above also pertain to the transport of trace pollutants to the marine environment, from which the main sinks are the atmosphere via volatilization, biomass via uptake in the food chain, and sediments via settling of suspended particulates.

The specific pathways of individual pollutants in the environment differ significantly depending on their thermodynamic properties. Most heavy metals, for example, do not volatilize under ambient conditions. For such pollutants the long-term dynamics in the water phase are more important than those in the gas phase. They only enter the atmosphere through

mechanical processes such as stack discharges or volcanic eruptions, and their atmospheric residence times are short. This order is reversed for very volatile pollutants.

3.3. The effect of environmental changes on the dispersion of trace pollutants in the environment

The dynamics of trace pollutants in the environment are of course strongly influenced by the presence of other factors. Changes in the chemical composition of a specific compartment can alter significantly their overall dynamics in the environment leading to an increased mobility (Stigliani, 1988).

As an example, one may consider *solubility* in water, and *sorption potential* of the dissolved trace pollutant onto soil and sediment, two parameters that have an important effect on the mobility of trace pollutants in the environment. Solubility of most metals increases as the pH decreases and is also strongly affected by changes in the redox potential. For example, at a pH in the range of about 8 to 10, cadmium precipitates in the presence of carbonate as cadmium carbonate, and in reduced environments (sulfate reducing conditions) cadmium precipitates as an cadmium sulfide (Hem, 1972). For this reason, alterations that result in a different pH and/or redox potential can result in a significant change of the solubility and therefore mobility of heavy metals such as cadmium (Gambrell et al., 1977; Kahlid, 1980).

Sorption of trace pollutants onto soil can also be affected by environmental changes. Cations of individual heavy metals compete with other cations for sorption sites. Therefore, as the concentration of other trace pollutants (specifically metal ions) increases, or as the salinity increases, or the pH decreases, the sorption of a specific heavy metal onto the soil is decreased (Prause et al., 1985, Boekhold et al., 1990). This is illustrated graphically in *Figure 3*, which represents two hypothetical isotherms describing the sorption of trace metals onto soil, and where isotherm 2 applies for conditions with a lower pH, higher salinity, and/or higher ionic concentrations of other trace metals. In addition to the effect of the competitive sorption between different ions, the formation of complex ions also affects sorption. A complex ion is a soluble species formed through the combination of two or more simpler species in solution. For example, mercury can exist in a solution in which chloride ions are present as Hg^{2+} , HgCl^+ , HgCl_2 , HgCl_3^- , and HgCl_4^{2-} . If a specific compound can be present as a free ion and in ion associations, as complex ions, the charge to mass ratio of the different ions associated with that compound can vary significantly. This can have a large impact on the sorption of that compound onto soil. The ions that react with a metal ion to form complex ions are called ligands. A few examples of inorganic ligands are Cl^- , H^+ , OH^- , HCO_3^- , CO_3^{2-} , SO_4^{2-} ions and NH_3 molecules. Naturally occurring organic compounds such as soluble humic and fulvic acids can also act as ligands in addition to synthetic substances such as EDTA (ethylene diamine tetraacetate). Finally, due to the non-linearity of the sorption isotherm of many trace pollutants onto soils, a gradual accumulation of the trace pollutant over time in soils may affect the fraction of the pollutant that is sorbed when an incremental amount of the trace pollutant is added or when other factors such as pH or salinity change. This is also illustrated by *Figure 3* for either isotherm, where one can see that if the total amount of trace metal present is very small (left side of the isotherm) changes in pH, salinity, amounts of other trace metals, or the amount of the trace metal itself will not have a significant impact on the overall fraction of trace metal of interest that is sorbed onto the soil, whereas if the total amount of trace metal present is very large (right side of the isotherm) the same changes will have a significant impact on the overall fraction of trace metal of interest that is sorbed onto the soil.

The behavior of non-ionic trace organics is somewhat different because changes in redox potential do not affect their solubility, but rather their potential for biodegradability. Also, their sorption isotherm onto soil is linear and is not affected by the presence of other trace organics,

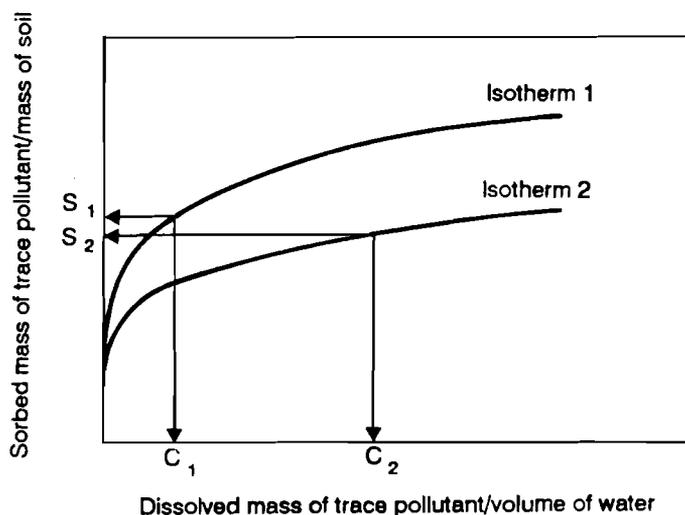


FIGURE 3: Freundlich isotherms illustrating the sorption of a trace metal onto soil. Isotherm 2 represents conditions with a lower pH, higher salinity, or higher concentration of competing cations than for isotherm 1. As environmental conditions for isotherm 1 change to those representing isotherm 2, the equilibrium represented by (S_1, C_1) shifts to that represented by (S_2, C_2) so that the total mass in both conditions remains constant.

although sorption onto soil can be decreased significantly in the presence of organic colloids and surface active agents.

Based on the interactions of the solubility and sorption onto soil and sediments of trace pollutants with other chemical constituents, it becomes clear that specific environmental changes might significantly affect the dynamics of these trace pollutants in the environment. For example, a trace metal stored in the bottom sediments of an estuary can be released during a drought when the salt-water wedge moves upstream further than usual. A decrease in the river discharge due to an increased fresh water consumption can have a similar effect. Redox potential in bottom sediments may be shifted from sulfate reducing to nitrate reducing conditions, when large amounts of nitrate enter the environment due to excessive fertilization. This would again mobilize trace metals, such as cadmium, that were bound in bottom sediments. In general, changes in organic waste discharge practices have a severe impact on the redox conditions of environmental compartments, and therefore on the mobility of heavy metals. We also mentioned that a decrease in pH increases the solubility and decreases the sorption potential of trace metals. An acidification of the environment, such as is occurring in many forest soils in the northern hemisphere, will therefore result in an increased mobility of trace metals. Also of importance may be changes in the dynamics of trace metals due to a decreased sorption capacity of the soil. If, due to a long-term buildup of the trace metal itself, salinity, and other cations that compete for sorption sites, the sorption potential of the soil is decreased, any incremental amount of the trace metal that is added to the soil will have an increasing fraction that will remain in solution. This fraction in solution is available to be taken up by plants and to leach into the ground water. Significant increases in soil salinity, that could lead to a higher fraction of dissolved-phase trace pollutants, are occurring in many agricultural soils that are being irrigated with relatively highly saline surface or ground waters (Szabolcs, 1991).

This discussion illustrates that the dynamics of a trace pollutant can shift over time, and interactions with other compartments can become more important. Finally, it is necessary to mention that a climate change has to affect the dynamics of trace pollutants to some degree (Stigliani et al., 1991). Changes in temperature affect biological growth which affects the soil

and water chemistry (i.e., pH and redox potential). Changes in precipitation can affect a compartment's chemistry (i.e., as soils dry, their redox potential increases) and the physical transport mechanisms in and between compartments.

4. Concept of Industrial Metabolism

4.1. Background

There is an increasing recognition for the necessity of a "big picture" approach to environmental management, if we are to move beyond the current reactive phase of management often responding to the so-called "chemical of the month," to a more proactive phase in which policy alternatives are better integrated and more directed toward ecological sustainability. (See also the concept of "input management" advocated by Odom, 1989.) For reasons given previously, it is clear that new analytical tools are needed to achieve this end. One such tool is the concept of *industrial metabolism*, advocated by the National Academy of Engineering (Ausubel and Sladovich, 1989), the U.S. Committee on Global Change (Clark, 1988), and the International Institute for Applied Systems Analysis (Ayres et al, 1989). The concept embodies a systems approach to minimizing emissions of toxic chemicals by considering all sources of the chemicals, the pathways by which they flow through the industrial economy, and mechanisms by which they are transformed into outputs that must be absorbed and processed by the environment.

Analysis of material flows through the industrial economy can provide a rich, complementary data base for the analysis of flows through the environment. Detailed information may be gained on many important aspects of economy-environment interactions. These include: sources of emissions, the relative magnitudes of those sources, the paths of transport of chemical emissions from the industrial economy to the environment, historical trends in emissions, scenarios of future emissions, and socio-economic and political factors influencing emission trends. In addition this approach allows the estimation of decades-long cumulative loading of pollutants into various compartments of the environment, as well as a means for testing the effectiveness of proposed emission reduction management strategies. (The latter two aspects are discussed in detail in a later section of this paper.)

Despite the obvious benefits gained from complementary analyses of economic and environmental data, surprisingly few such studies have been undertaken. These few have focussed on the dynamics of relatively non-volatile trace pollutants over time horizons of 50 to 100 years (Ayres et al., 1988; Anderberg et al., 1989; Stigliani and Anderberg, 1992b). The preferred spatial scale for studies of industrial metabolism is the river basin. River basins have the advantage that the natural flux of the non-volatile trace pollutants across their boundaries is zero, except for the import and export of long-range atmospheric deposition, and the mass of pollutants that leaves the basin with the river flow, and for which data are relatively easy to obtain. Thus, after accounting for trans-boundary fluxes, the economic "space" where the sources of pollution reside corresponds precisely to the environmental "space" over which the pollutants are discharged and accumulated. Such overlapping of spatial domains greatly facilitates the calibration of economic and environmental data.

The information base for conducting studies in industrial metabolism to a large extent already exists. On the industrial economy side, data are available in statistical year books on materials production, population and land use, emissions and atmospheric concentrations of pollutants, traffic density, agricultural inputs, chemical industry (products and plant capacities), generation and disposal pathways of solid wastes, and the evolution of sewage treatment (e.g., OECD, 1991; SRI, 1990; Roskill, 1990; Eurostat, 1992; U.S. Bureau of Mines, 1992; FAO, 1992; UBA, 1989 to name a few). On the environmental side, there are literally thousands of studies on emissions of chemical pollutants from industrial plants, fossil fuel combustion, toxic waste

landfills, sewage treatment plants, incinerators, and so on. Environmental monitoring data are also often available (e.g., the Rhine River has been monitored since the early 1970s for numerous heavy metals and toxic organic compounds (ICPR, 1990). The problem has been that few researchers have attempted to integrate the available information over time (decades to a century) and space (river basins on the order of several hundred thousand square kilometers). One reason for lack of initiative in this area is that studies of this nature require a multidisciplinary team of researchers, and traditionally specialists have been reluctant, or have not been given sufficient professional encouragement, to delve in multidisciplinary research.

4.2. Methodology

The concept of industrial metabolism embodies three distinguishing principles:

1. Synthesis of economic data describing the flow of chemical pollutants through the industrial economy with environmental data analyzing the discharge, flow, and accumulation of the pollutants in the environment.
2. Integration of the analysis over space and time in order to assess the spatial allocation of pollutants and their cumulative load over time.
3. Evaluation of the policy implications arising from the analysis of the chemical flows.

The first step in an industrial metabolism study is to identify and quantify of all sources of emission. For each point source, it is necessary to determine its location, its annual material inputs or outputs, and an emission factor per unit of input or output. Historical emissions are estimated in the same way. Thus, it is necessary to obtain plant specific information on historical inputs or outputs and emission factors. *Table 1* illustrates the procedure for determining aqueous cadmium emissions from cadmium pigment production for the example of a plant in the Rhine Basin during the 1970s and 1980s.

Diffuse sources include application of fertilizers and pesticides on agricultural lands, and dissipative emissions in urban centers. Application of agrochemicals per hectare are readily available in agricultural statistical year books. The total spatial distribution of the chemical under analysis is obtained by integrating application rates over all agricultural lands in the region. In urban centers dissipation of heavy metals is caused by corrosion and traffic. Emissions from corrosion are obtained from an algorithm estimating the corrosion rate as a function of some influencing variable. For example, the annual corrosion rate of zinc in galvanized steel is related to SO₂ concentration by the following formula (ECE, 1984):

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

where: Y is the annual corrosion rate of zinc (g/m²/yr)
[SO₂] is the concentration of sulfur dioxide in air (µg/m³)

Emissions from traffic occur from tire wear and fuel combustion. Emission factors may be determined as a function of km per vehicle, or per liter of fuel consumed.

After the emissions have been quantified, the next step is to trace the emissions from their sources to their dispersion and deposition in the environment. The deposition of air emissions are estimated by short and long-range atmospheric deposition models. Examples are

TABLE 1
Aqueous Cadmium Emissions from Production
of Cadmium Pigments for a Plant in the Rhine Basin
(tons per year)

Year	Pigment Production	Emission Factor*	Cadmium Emission
1970	401	0.0150	6.0
1975	449	0.0070	3.1
1980	387	0.0015	0.6
1985	232	0.0004	0.1
1988	53	0.0004	0.0

*Equals tons of cadmium emission per ton of cadmium pigment produced; hence a dimensionless factor.
Source: Elgersma et al., 1991.

the short-range model developed by Hrehoruk et al. (1992), and TRACE2, the long-range model developed at IIASA by Alcamo et al. (1992), for heavy metal deposition. Deposition can be allocated according to land use, and if historical atmospheric emission factors can be determined it is possible to track the accumulation of deposition over time. In IIASA's study of *Sources of Chemical Pollution in the Rhine Basin*, historical factors of some heavy metals were estimated by Pacyna (1991), and the historical distribution of atmospheric deposition in the Rhine Basin was determined for cadmium, lead and zinc. *Table 2* shows the results for cadmium.

TABLE 2
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

Source: Stigliani and Anderberg, 1992a.

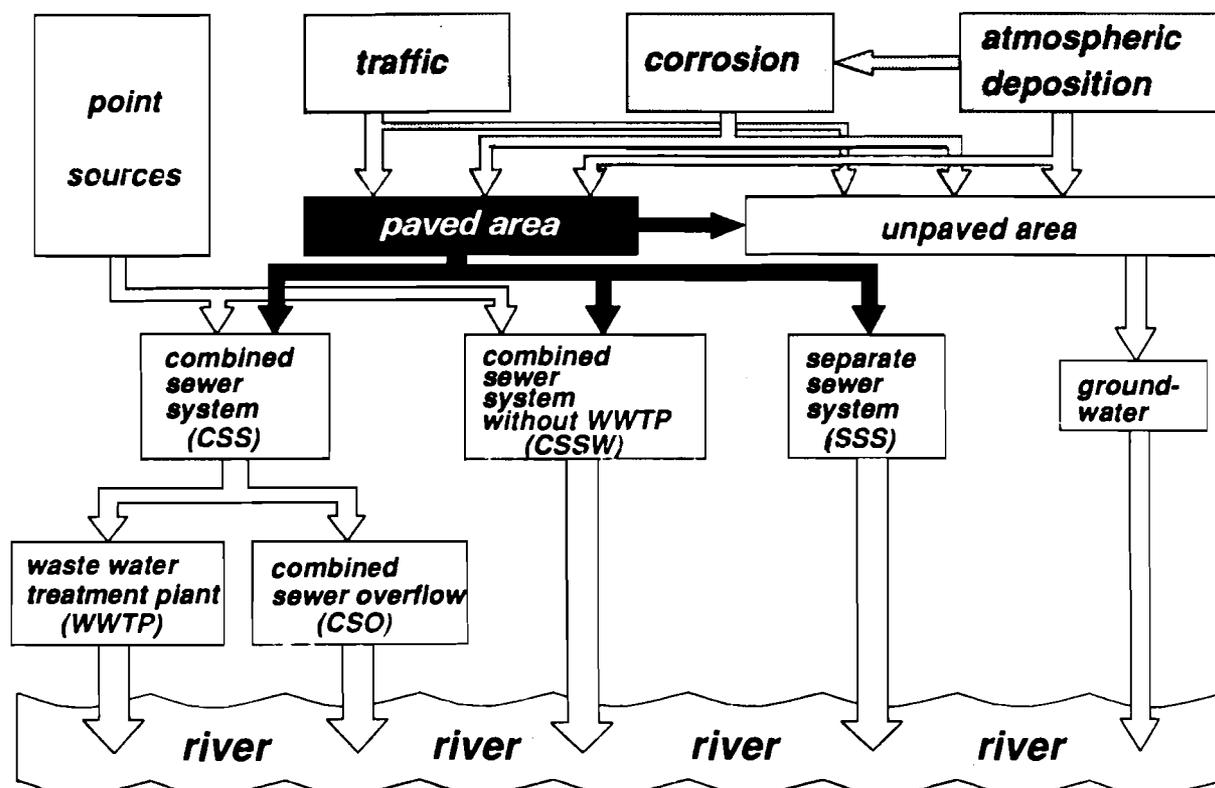


FIGURE 4: Scheme for a hydrologic urban pollution model. (Source: Behrendt and Boehme, 1992.)

Emissions from agricultural and forest lands to surface waters are calculated by a hydrological runoff model. In IIASA's Rhine Basin study, the SENSMOD model of the Research Center for Water Resources Development, Budapest, Hungary was adopted (Jolankai et al., 1991). Emissions from urban lands to surface waters require the development of a hydrologic urban pollution model. A schematic for the model used in the Rhine Basin study is shown in *Figure 4*. The inputs from atmospheric deposition, corrosion, and traffic are distributed among paved and unpaved areas. Paved areas are further subdivided into sewers in which storm waters and municipal wastes are either combined or separated. The estimated runoff from agricultural, forest, and urban lands to the Rhine River and its tributaries is in all cases calibrated with available river monitoring data (Behrendt and Boehme, 1992). Moreover, each step of the analysis is guided by mass balance principles.

After emissions and their dispersion and distribution in the environment have been determined, the result is a basin-wide pollution model that provides a wealth of information for environmental planning and assessment. As an indication of the model's utility, the following section describes some applications with respect to cadmium in the Rhine Basin.

4.3. The example of cadmium pollution in the Rhine Basin

4.3.1. General overview

Figures 5a and *5b* show the flows of cadmium in the Rhine Basin for the years 1970 and 1988. It is obvious from comparing these figures that cadmium pollution was much higher 20 years ago

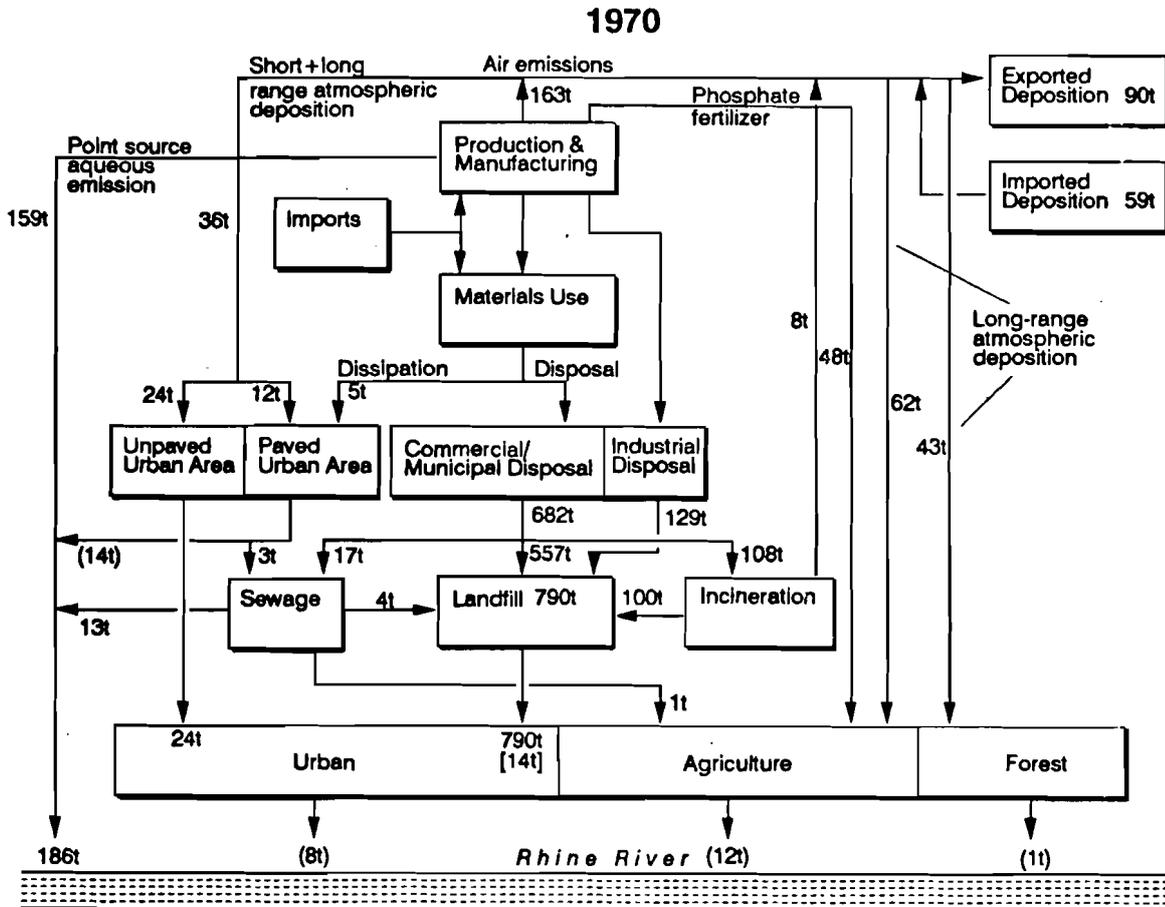


FIGURE 5a: Flow of cadmium (in tons per year) in the Rhine Basin, 1970. Numbers in parentheses indicate diffuse sources; number in brackets indicates annual availability.

than it is today. In-basin atmospheric emissions decreased from about 171 tons in 1970 to about 34 tons in 1988. This reduction occurred mostly from the implementation of pollution control technologies, forced by increasingly strict regulation.

Cadmium in solid wastes (including the increased generation of wastes caused by reduction of air emissions) declined as well, from 790 tons to 382 tons. The major reason for the decline of cadmium in industrial solid wastes (from 129 tons to 45 tons) was the increased effort on the part of industry to recycle their wastes. For example, almost all of the flyash generated from combustion of hard coal in the basin is now a feed stock in the production of cement (MHPPE, 1988; Risse et al., 1991). Cadmium in municipal solid waste generation (not including industrial solid waste) declined (from 661 tons to 337 tons) mainly because of an overall reduction of about 50% in the use of cadmium-containing products.

When assessing the environmental impact of solid wastes, total tonnage of cadmium contained in the wastes is not a good index of the availability of cadmium for mobilization and transport in the environment. Cadmium in plastics, for example, is tightly bound in the plastic matrix and its availability is relatively low (Bromley et al., 1983; Raede and Dornemann, 1981). In contrast, cadmium in surface coatings (Carter, 1977) and Ni-Cd batteries (Bromley et al., 1983) are susceptible to corrosion and leaching. Stigliani and Anderberg (1992a) have estimated

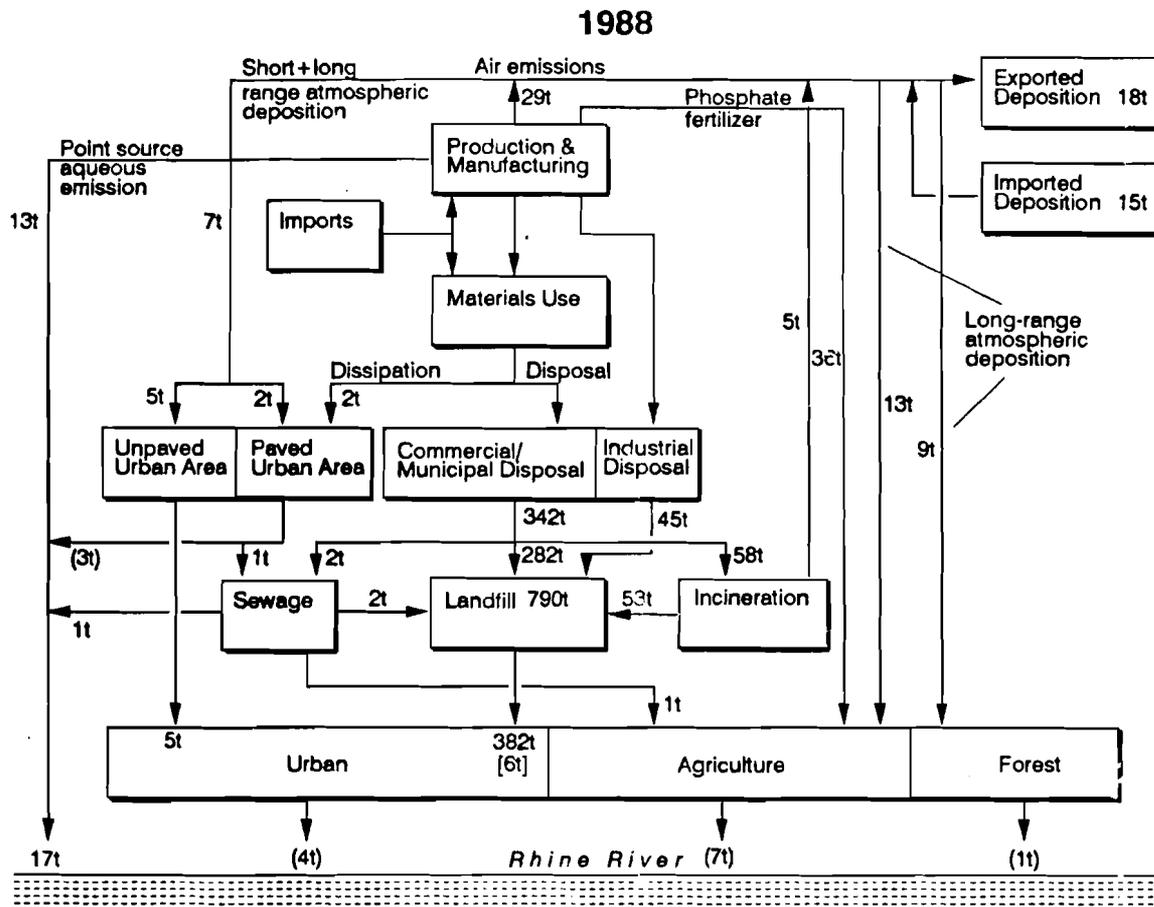


FIGURE 5b: Flow of cadmium (in tons per year) in the Rhine Basin, 1988. Numbers in parentheses indicate diffuse sources; number in brackets indicates annual availability.

the *maximum availability* of cadmium in the wastes¹, indicated in the figures as an annual average by the numbers in brackets under the numbers for total cadmium landfilled. Their estimates show that for 1970 the availability was 14 tons per year out of a total of 790 tons, and in 1988 it was 6 tons per year out of 382 tons. Thus, less than 2% per year of the total cadmium landfilled is available for transport in the environment. On the other hand, the availability of cadmium in the wastes may continue to pose a problem for several decades into the future, considering that the total availability over a 30 year period is calculated to be about 410 tons for wastes deposited in 1970 and 180 tons for wastes deposited in 1988.

Point source aqueous emissions of cadmium to the Rhine River (from production and manufacturing, and sewage) decreased from 172 tons to 14 tons. This reduction reflects the effect of increasingly stricter regulation of water emissions on the national and international level, beginning in the mid-1970s and accelerated in the 1980s. Diffuse sources of emissions, indicated by the numbers in parentheses, include runoff from paved urban surfaces, and runoff and ground water transport from unpaved urban surfaces, agricultural lands and forests. Two

¹Maximum availability is an operational parameter for estimating the mobility of cadmium in the environment under extreme environmental conditions, viz., a pH of 4 and a liquid to solid ratio of 100. It represents the maximum mobility over a 30 to 50 year period. The value of the availability in a particular kind of waste can be measured in the laboratory as described in van der Sloot, 1991.

distinct trends can be observed in the 18 year period. Firstly, total aqueous emissions of cadmium decreased from over 200 tons/yr to around 30 tons/yr. Secondly, the share of the diffuse sources to the total aqueous load increased from about 17% in 1970 to about 52% in 1988. The latter trend is due to the fact that diffuse sources have not been regulated as tightly as point sources.

One can observe in the figure that inputs of cadmium to urban, agricultural, and forest lands were much larger than the outputs in 1970. For unpaved urban lands there was a net increase of 30 tons/yr (counting *availability* rather than total cadmium in solid wastes), agricultural lands experienced a buildup of about 100 tons/yr, and forest lands about 42 tons/yr. On a per hectare basis, these net annual inputs correspond to 15 g/ha in unpaved urban areas, 10 g/ha in agricultural soils, and 6 g/ha in forest soils. By 1988, net inputs of cadmium to these lands were substantially decreased: for unpaved urban lands it was 7 tons/yr (3.5 g/ha), for agricultural lands it was 43 tons/yr (4.3 g/ha), and for forest lands it was 8 tons/yr (1.1 g/ha). These reductions in cadmium inputs are almost entirely due to reductions in air emissions. In 1970 total cadmium inputs to the lands of the basin were 192 tons. Of this amount 129 tons (67%) were attributed to air emissions. In 1988 total cadmium emissions were 70 tons, of which 27 tons (38%) were from air emissions. The largest single source of cadmium emissions to the environment is now phosphate fertilizer application, which causes an inadvertent input of 36 tons of cadmium per year to agricultural soils.

Even though cadmium pollution is currently much less than it was in former times, the problem of cadmium in the environment cannot be considered to be solved. The analysis of the industrial metabolism of cadmium in the Rhine Basin provides a model for gaining a deeper understanding of the potential impacts of cadmium already accumulated in the basin, and the effect of proposed policies for further reductions of cadmium emissions. The next section provides two examples of the usefulness of the model for these purposes.

4.3.2. Industrial metabolism for assisting in the formulation of effective pollution prevention policies

One important application of industrial metabolism studies is testing possible pollution reduction strategies within the context of systems analysis. Because the industrial metabolism model is based on the principle of mass balance, the well known problem of reducing pollution in one medium by shunting it to another medium can be readily detected. For example, Stigliani and Anderberg (1992a) have analyzed the effectiveness of banning all cadmium-containing products except nickel-cadmium (Ni-Cd) batteries. *Figure 6* shows the materials flow of cadmium from refining, cadmium-product manufacturing, use, and disposal in the Rhine Basin in the mid-1980s. This figure is actually a detailed subset of *Figure 5*. It includes only the flow of the direct intentional use of cadmium-containing products, while *Figure 5* includes all sources of cadmium pollution, including products (e.g., phosphate fertilizer) in which cadmium is present as a trace impurity.

As shown in the figure, cadmium is refined almost exclusively as a by-product of zinc production. The demand for refined cadmium in the basin exceeded the supply by nearly 600 tons, and the shortfall was met by imports of cadmium metal. About 1,150 tons of cadmium were used in manufacturing four consumer products, viz., pigments in plastics, Ni-Cd batteries, surface plating for steel and other metals, and stabilizers in PVC. After exports, the cadmium in cadmium-containing products used in the basin totaled about 850 tons. Disposal of consumer

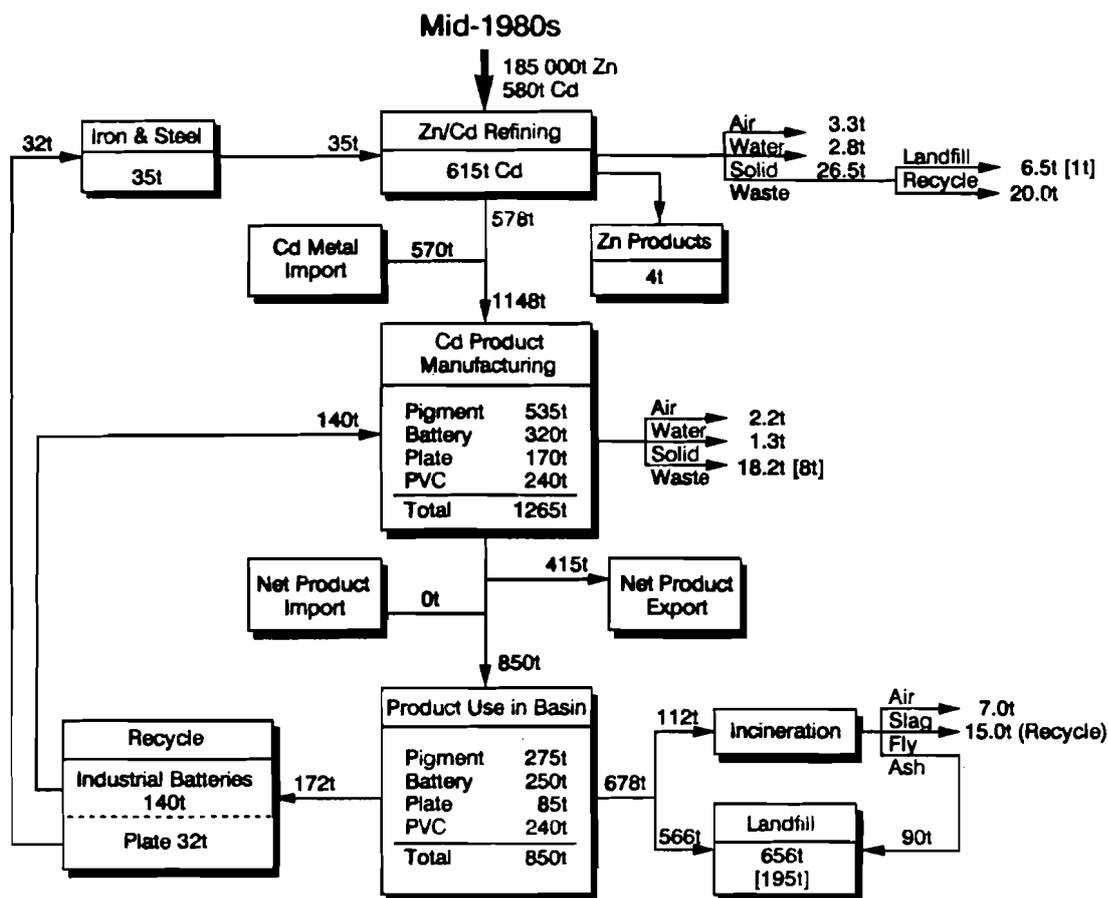


FIGURE 6: Balance of cadmium product use and disposal in the Rhine Basin, mid-1980s. (Source: Stigliani and Anderberg, 1992a.)

products totaled nearly 700 tons². In addition about 170 tons were estimated to be recycled³. Total air emissions for production, manufacturing and disposal was about 12 tons, water emissions totaled about 4 tons, and landfill totaled about 650 tons. As noted earlier, the *total availability* is a better index of environmental impact than the total tonnage of cadmium in solid waste. Stigliani and Anderberg (1992a) have estimated this to be 195 tons (shown in brackets in the figure) for a 30 year period. This equals an *annual availability* of about 6.5 tons. When assessing the relative effectiveness of pollution prevention policies, availability provides a measure by which the different policies can be evaluated.

By the late 1980s, in anticipation of bans on all cadmium products except for Ni-Cd batteries, major producers of other cadmium products had decreased production substantially. Projecting this trend into the future, a scenario was assumed for the late 1990s, in which the

²Disposal, as indicated in Figures 5 and 6 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.

³Unlike small consumer Ni-Cd batteries, for which recycling has been negligible, large industrial batteries have had a long history of recycling. About 38% of cadmium plate is assumed to be recycled along with other steel scrap.

bans had been realized. The results are depicted in *Figure 7*. Under this scenario, the only cadmium-containing product in use in the basin is Ni-Cd batteries, and it is assumed that 50% of the disposed consumer batteries are recycled. As shown in the figure, the strategy does achieve a significant reduction in the availability of cadmium in municipal solid wastes, from nearly 200 tons in 1985 to about 50 tons in the late 1990s. There is, however, a very large increase (estimated at about 425 tons) of cadmium wastes at the refinery. Currently, there is no information on the availability of cadmium in these refinery wastes. Nonetheless, it may be considerable, since cadmium in most solid wastes appears to be appreciably soluble in acids, or in the presence of commonly occurring complexing agents such as ammonia (Rauhut, 1978).

The overriding problem with any policy for curtailing consumer use of cadmium-containing products is that the supply of cadmium in the basin is essentially *inelastic* since it enters the basin as a by-product of zinc production. In contrast to the mid 1980s, rather than a deficit, there would be a large surplus of cadmium, which is enhanced by the recycling of consumer batteries. This analysis should not be construed to indicate that banning or recycling of 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 wastes at zinc refineries.

As noted by Stigliani and Anderberg (1992a), one possible option for reducing the surplus of 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 the use of cadmium for stabilization of PVC. If production of PVC stabilizer

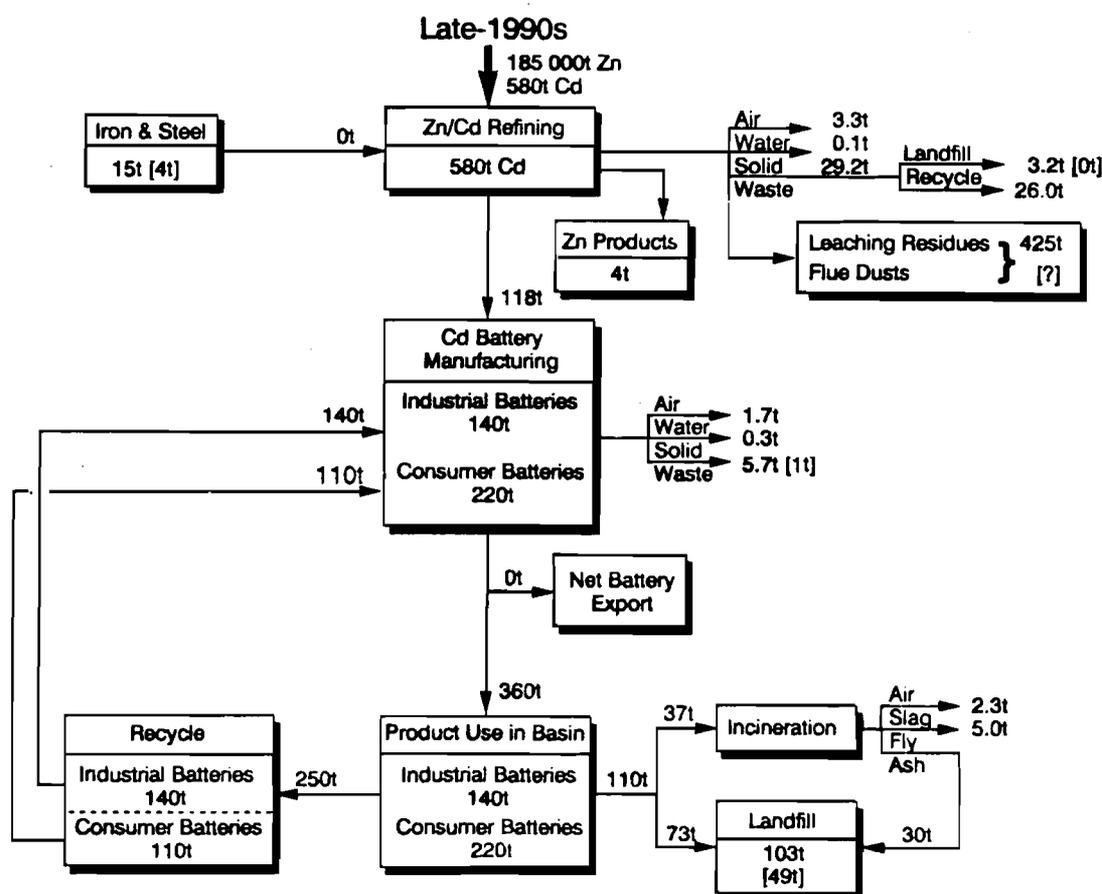


FIGURE 7: Scenario for balance of cadmium product use and disposal in the Rhine Basin, late 1990s. (Source: Stigliani and Anderberg, 1992a.)

were maintained at levels of the mid 1980s, about 240 tons, the surplus of cadmium in refinery wastes would decrease by more than 50%. The use of cadmium in PVC is now almost entirely for outdoor window frames. The availability of cadmium from this use is low as long as the PVC is not incinerated after disposal. This not likely to happen as the PVC would probably end up in building demolition wastes. Demolition wastes are either directly landfilled or recycled. Recycling of the wastes will increase in importance in the future. For example, in the Netherlands 45% of demolition wastes were recycled in 1986, and the projected goal for the year 2000 is to increase recycling to 80% (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, since such landfills have been reported to leak (Hjelmar et al., 1988), and the capacity for truly long-term storage, more than 50 years, is open to question. 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.

Moreover, a strategy for reducing cadmium inputs to the environment should not be narrowly framed in terms of tracing the flow of cadmium from the zinc refinery to final disposal. Other important sources of cadmium pollution exist, and if they are omitted from the analysis, even well-intentioned policies may not achieve the expected results. As we have seen, cadmium enters the industrial economy inadvertently as an unwanted trace contaminant of other high volume chemicals such as phosphate fertilizer, coal and oil. The IIASA model has estimated that currently about 35 tons of cadmium are deposited on agricultural lands from application of phosphate fertilizers. This is about three times the amount added by long range atmospheric deposition from all sources of air emissions. Thus, any strategy for safe-guarding the food supply from cadmium contamination should place the highest priority on reducing cadmium levels in phosphate fertilizer.

In summary, industrial metabolism studies as exemplified by the Rhine Basin study can serve as a useful analytical tool for developing strategies for pollution prevention. The method provides a context within which policies can be tested. It also may be useful for identifying important gaps in information and in setting priorities for a proposed range of policy options. Finally, by presenting the "big picture" it could greatly assist in avoiding the implementation of policies based on a too narrow assessment of the sources and flows of toxic materials in the environment.

4.3.3. Cadmium accumulation in soils and its relevance

It must be remembered that the environment of the basin has been a receptacle for high inputs of cadmium accumulated over many decades. A major question, still to be determined, is the potential impact resulting from such cumulative loading. Stigliani and Anderberg (1992a) have estimated that the cumulative inputs to unpaved urban areas, agricultural lands, and forests over the period from 1950 to 1988 were 830 tons, nearly 4,000 tons, and about 1,500 tons, respectively. On a per hectare basis the cumulative inputs were 420 g/ha for unpaved urban areas, 400 g/ha for agricultural lands, and 220 g/ha for forest areas.

The objective of this section is to assess the effect of cadmium accumulation in agricultural soils. Similar analyses should be conducted for impacts on urban areas and forest lands. We selected agricultural soil first because of its direct relevance to the food supply and human health.

Using the relation for sorption of cadmium onto soil as a function of the soil's pH and organic carbon content developed by Boekhold et al. (1990), we can develop a series of isotherms for the sorption of cadmium on soils with an assumed organic carbon content of 2%. *Figure 8* shows the effect of pH on the sorption of cadmium on soils in a 0.01 M CaCl₂ solution.

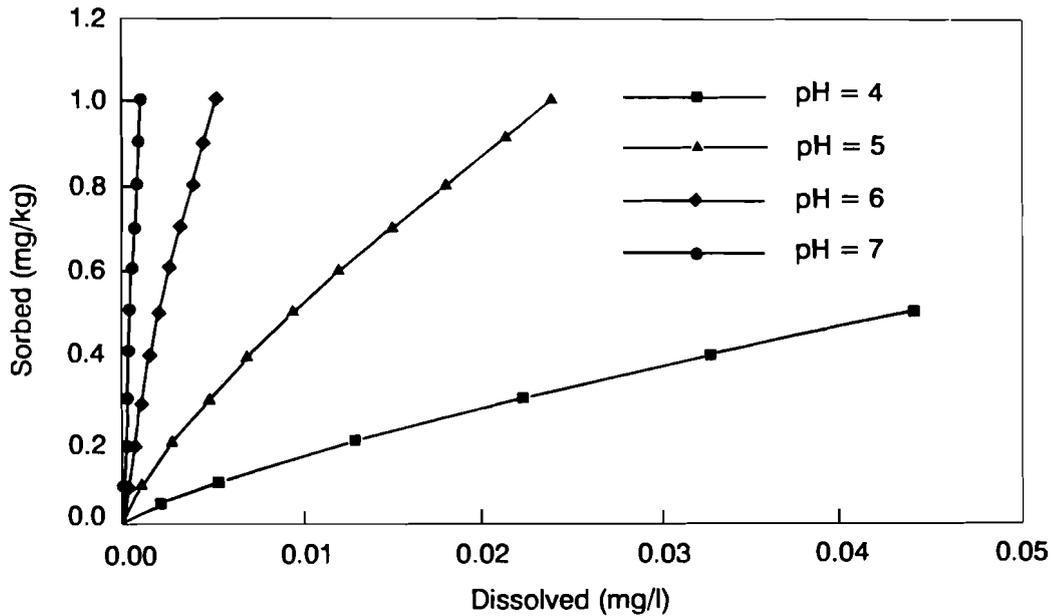


FIGURE 8: Ratio of cadmium adsorbed and mobilized in soils as a function of pH.

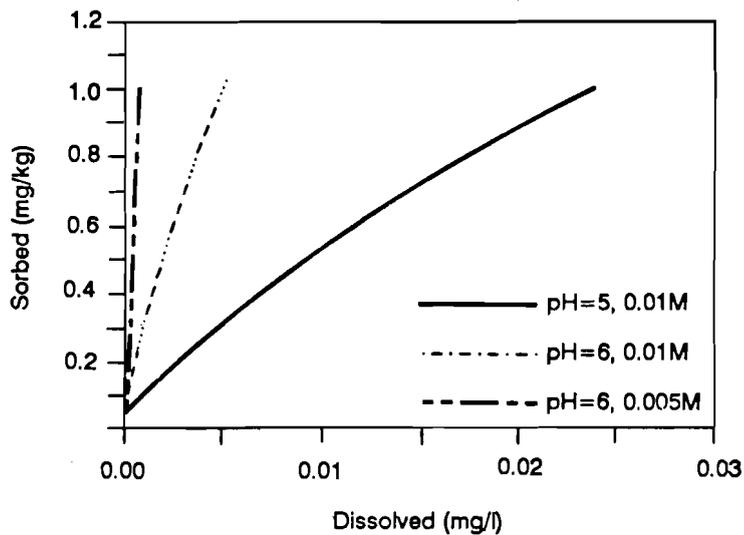


FIGURE 9: Sorption isotherms for cadmium on soil as a function of the soil's pH under varying CaCl_2 concentrations, for a soil organic carbon content of 2% (Boekhold et al., 1990)

Figure 9 shows the effect on the cadmium sorption on soil as the concentration of other ions (for this case CaCl_2) varies. If we take the load to agricultural soils, and assume that the pH of these soils is, due to liming, relatively high (pH = 6) then, because of the high fraction of Cd that is sorbed according to Figure 8, we can assume that almost all of the cadmium that was added to these soils is contained in the top 20 cm, or the depth of the soil that is tilled over. Nevertheless, there are some losses from crop uptake, surface runoff and erosion. Taking these outputs into account it is possible to estimate the *net buildup* of cadmium concentration in agricultural soils since 1950. The results, shown in Figure 10, indicate that the average soil

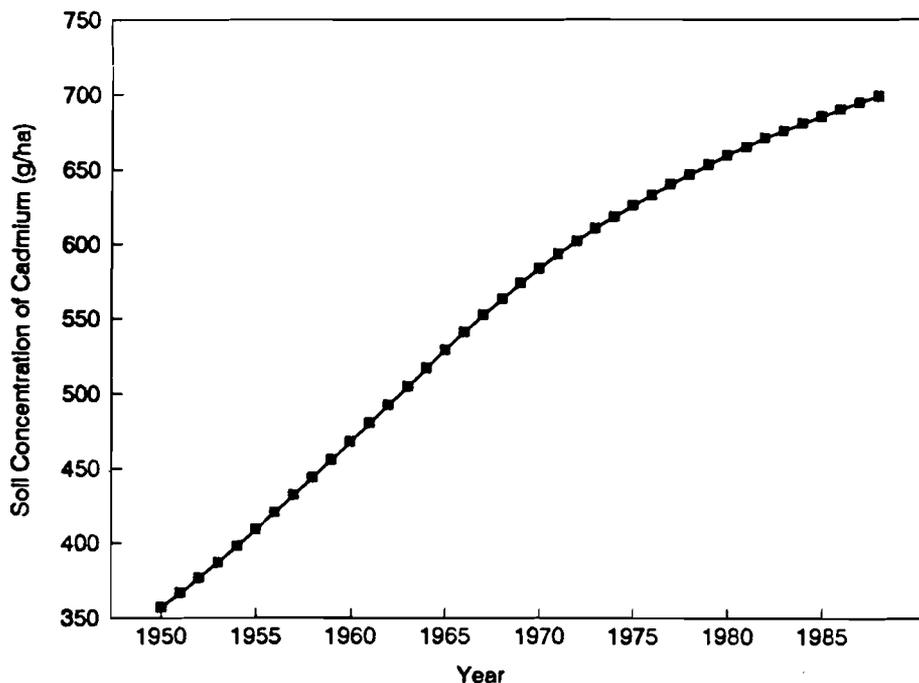


FIGURE 10: Estimated buildup of cadmium concentration in agricultural soils in the Rhine basin, 1950-1988.

concentration of cadmium doubled in the time period between 1950, when the average concentration was calculated at about 350 g/ha, and 1988, when the concentration was about 700 g/ha. A concentration of 700 g/ha is equivalent to 0.23 mg/kg if we assume a soil bulk density of 1.5 kg/l.

A major concern of the buildup of cadmium in soils is its effect on the cadmium content in foods and in ground water. The average cadmium intake for the population in the EC and the USA is on the order of 30 $\mu\text{g/day}$ or 210 $\mu\text{g/week}$, compared to the WHO recommended maximum intake which should not exceed 400 $\mu\text{g/week}$ to 500 $\mu\text{g/week}$ (Hutton 1982). For the first order calculations done here, we will assume that the cadmium intake is directly proportional to the cadmium content in crops. The cadmium content in crops is directly related to the dissolved cadmium in soils (Hutton, 1982), although it is known that atmospheric depositions also directly affect the cadmium content in crops (Keller and Brunner, 1983).

As shown in *Figure 10*, the cadmium content in agricultural soils has increased during the period of 1975 to 1988 from 625 g/ha to 700 g/ha. We assume here that the average cadmium intake reported above was roughly for 1975 cadmium levels in soil. If we assume a pH of 6 and use the isotherms shown in *Figure 8*, this will result in an increase of dissolved cadmium in agricultural soils by 13%. An assumed parallel increase of 13% in the average cadmium intake, will leave us still far from the WHO's recommended maximum intake. If we assume a cadmium increase in agricultural soils of 4.3 g/ha-yr, which was observed in the late 80's, it will take on the order of 120 years for the average intake of cadmium to reach the maximum allowable intake rate.

Changes in the pH of agricultural soils will have a much more important effect on the average cadmium intake. Following our simplified first order analysis, *Table 3* shows the estimated average cadmium intake for different years if the pH of agricultural soils deviates from 6.0. The calculations, for a constant pH of 6, are in agreement with those done by Keller

TABLE 3
 Estimated Average Intake of Cadmium ($\mu\text{g}/\text{week}$)
 at Different Values of pH of 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

*Assumes total food intake is from crops grown in basin.

and Brunner (1983) for Swiss soils, and show that the average cadmium concentration in agricultural soils has not built up to levels that would be considered unsafe, and will not reach such levels for many decades. What these calculations do show is that cadmium inputs have built up to such levels that shifts in pH that are quite feasible (e.g., from 6 to 5.5; corresponding to an average intake of $500 \mu\text{g}/\text{week}$) may pose a public health problem today, while comparable shifts in 1960 (corresponding to an average intake of $300 \mu\text{g}/\text{week}$) would not have done so. An increase over time in salinity of soils and buildup of other trace metals would increase the problem even more, as can be seen from the isotherms in *Figure 9*.

It is also possible to make some first order estimates of the leaching potential of cadmium to groundwater. The factor by which the velocity of a sorbing trace pollutant is retarded with respect to that of water (R) can be expressed as:

$$R = 1 + (K_p r / n)$$

where K_p is the partition coefficient, n is the porosity, and r is the soil's bulk density (Freeze and Cherry, 1979). Again, if we assume a soil porosity of 0.3 and a bulk density of $1.5 \text{ kg}/\text{l}$ we can use the isotherms shown in *Figure 8* to compute retardation factors for different soil pH. These retardation factors are shown in *Table 4*. Given these retardation factors, we can estimate an order of the average rate at which cadmium migrates through the soil. For this purpose we will

TABLE 4
 Estimated Average Partition Coefficient (K_p), Retardation Factor (R), and Leaching
 Velocity (v)* as a Function of Soil pH

pH	4.0	5.0	6.0	7.0
K_p	19	90	420	1940
R	98	450	2090	9710
v	5.7	1.2	0.27	0.06

* v is in units of cm/yr

assume that the net infiltration rate (infiltration - evapotranspiration) is 0.5 m/yr, and that the average soil moisture content is 30% of the field capacity. This will yield an average velocity for the infiltrating water of 5.6 m/yr. The corresponding average leaching velocity of cadmium is also shown in *Table 4* as a function of pH.

The results listed in the table show that cadmium essentially accumulates in agricultural soils with a pH of 6. From the isotherm in *Figure 8* we can see that the fraction of dissolved cadmium in soils with a pH of 6 is about 0.31%. For a net water infiltration of 0.5 m/yr this will result in a loss of cadmium from the top 20 cm on the order of 0.5% per year. A steady state of cadmium in the soil will be reached when the sum of anthropogenic plus natural cadmium inputs is equal to the amount that leaches. As opposed to cadmium that has been deposited on agricultural soils, cadmium that has over the last few decades been deposited on non-agricultural soils such as urban and forest soils, which may in some cases have a pH between 4 and 5, has most likely contaminated shallow ground waters to some degree.

In summary, the results from the industrial metabolism study on cadmium in the Rhine basin have been useful in identifying the environmental compartments where cadmium is building up and at what rate. The first order analysis conducted here was able to point to scenarios and timeframes for which this buildup may become a significant problem. Given that these results show that there may be a point where the cadmium intake for some segment of the population will be too high, and that cadmium in some shallow ground waters may very likely be increasing, it is clear that a much more rigorous analysis is warranted. Such an analysis will require a high spatial and temporal resolution of cadmium deposition, soil pH and organic carbon content, changes in soil salinity and concentrations of other trace metals, infiltration, transport of cadmium in soil, and plant uptake. Although we may understand the cadmium dynamics in a well characterized soil plot, the methodology on how to do such an analysis for a large watershed is non-existent. Meaningful scaling and averaging techniques have to be developed for these chemical interactions similarly as was and is being done in fields such as global hydrology and climate change.

5. Future Research and Applications of Industrial Metabolism Studies

The study of industrial metabolism is an emerging field with many possible applications. Furthermore, many important aspects of such studies need to be investigated before they will be used routinely by decision makers for policy setting and analysis. By way of example, we discuss below a few areas where industrial metabolism analyses may be applied, particularly in cases where little information is currently available because of the lack of appropriate analytical tools.

5.1. Cradle-to-grave emissions accounting for effective pollution control

As emphasized in the earlier discussion, pollution may occur at numerous stages in a material's life cycle in the industrial economy. Therefore, strategies for pollution reduction must emphasize controls during production and manufacturing, use, and disposal. As a major first step, the U.S. Environmental Protection Agency, under its "Industrial Toxics Project", has asked more than 600 companies to voluntarily reduce pollution caused by 17 toxic chemicals. Under this initiative, the companies would reduce their emissions (relative to 1988 levels) by 33% in 1992 and by 50% in 1995. A listing of the chemicals targeted for reductions is provided in *Table 5*.

Since industrial wastes constitute only one contribution to the total of wastes generated, a fundamental question is the importance of other sources. The German government has

TABLE 5
Chemicals Targeted for Reductions in Emissions
under the U.S. EPA's Industrial Toxics Project

Benzene	Methyl ethyl ketone
Cadmium	Methyl isobutyl ketone
Carbon tetrachloride	Nickel
Chloroform	Tetrachloroethylene
Chromium	Toluene
Cyanide	Trichloroethane
Dichloromethane	Trichloroethylene
Lead	Xylene
Mercury	

published a listing of the aqueous emissions to the Rhine River in 1985 for 27 chemicals (DKRR, 1989), 11 of which are contained on the EPA's list given in *Table 5*. The emissions were subdivided into direct industrial, sewage effluents, and diffuse. The results are shown in *Table 6*.

One may observe that only a little more than one third of the total aqueous emissions to the river stem directly from industrial point sources. The rest of the emissions are approximately equally divided between sewage effluents and diffuse sources.

Although no data are available for atmospheric emissions or solid wastes, it is obvious that while reducing industrial emissions is a necessary first step, it will be important to control sewage and diffuse sources as well. It is likely that the sources of inputs to the sewers are small industrial and commercial operations that are not tightly regulated. Since 85% to 90% of all industrial activities are conducted by very small, small, and medium-sized industries, it is not surprising that the load is so high. In this regard, it should also be noted that much of the chemicals produced by large industries are consumed by other industries and manufacturers, and data for tracking this "inter-industrial" movement of chemicals is usually not readily available. Finally, as noted earlier, toxic chemicals contained in consumer products may be emitted through dissipation or via household wastes.

One important application of the methodology described in this paper would be to track the flow of these chemicals from "cradle to grave" so that appropriate and effective strategies can be formulated for reducing emissions downstream from the large industrial producers. Even when there are gaps in data, the mass balance approach can provide valuable information on approximate quantities passing from one sector of the economy to another.

5.2. Accumulation of trace pollutants in the environment

An important task regarding the accumulation of trace pollutants in the environment is to gain better insight on where they are accumulating. As was described in previous sections, metals tend to accumulate in soils and ground water. This provides therefore the potential for an increasing uptake of these pollutants through food and drinking water by the population. In order to make an accurate assessment of the rate at which such trace pollutants are being taken up through food by the population, and in order to assess at what rate they are leaching into the ground water, it is necessary to understand their long-term dynamics in the soil environment better. For example, trace pollutants that are being deposited from the atmosphere onto the

TABLE 6
Chemical Emissions to the Rhine River
from Industry, Sewage, and Diffuse Sources
(tons/yr)

Chemical	Direct Industrial Inputs	Inputs from Sewage	Inputs from Diffuse Sources	Total Inputs
Benzene	2.970 (73.0%)	<	1.100 (27.0%)	4.070 (100%)
Cadmium	1.775 (27.8%)	2.460 (38.6%)	2.140 (33.6%)	6.375 (100%)
Carbon Tetrachloride	13.300 (70.9%)	3.975 (21.2%)	1.500 (8.0%)	18.750 (100%)
Chloroform	88.900 (85.5%)	7.600 (7.3%)	7.500 (7.2%)	104.00 (100%)
Chromium	220.40 (49.8%)	222.60 (50.2%)	<	443.00 (100%)
Lead	81.000 (29.7%)	126.00 (46.2%)	65.800 (24.1%)	272.80 (100%)
Mercury	0.725 (31.9%)	0.650 (28.6%)	0.895 (39.4%)	2.270 (100%)
Nickel	79.000 (25.1%)	236.00 (74.9%)	<	315.00 (100%)
Tetrachloro-ethylene	1.850 (6.9%)	10.050 (37.6%)	14.850 (55.5%)	26.750 (100%)
Trichloro-ethane	0.0 (0.0%)	1.200 (32.4%)	2.500 (67.6%)	3.700 (100%)
Trichloro-ethylene	0.810 (3.9%)	9.590 (46.6%)	10.190 (49.5%)	20.590 (100%)
Average %	36.8%	34.9%	28.4%	(100%)

< signifies "below detection limits"

Source: DKRR, 1989.

soil surface in a relatively uniform manner can migrate through erosion and runoff from areas with a higher slope to areas that are less steep, which could increase their concentration just in areas that are more likely to be used for agricultural purposes. Furthermore a more detailed vertical resolution has to be achieved. The long-term and seasonal accumulation of these trace pollutants in the root zone of the soil, and how the uptake by different crops responds to these changes needs to be understood. For this purpose one needs spatial and seasonal information

on the deposition of the trace pollutant on soils, precipitation, evaporation, pH, and soil properties including weathering to mention a few. In addition to the accumulation of trace pollutants in agricultural soils, their accumulation in urban soils may also merit further attention. It is clear that urban soils receive a much higher trace pollutant load, but associated health effects have not been investigated. Dynamics in forest soils are again quite different due to their higher acidity. These questions should be addressed through a series of rigorous analytical simulations in conjunction with properly planned laboratory experiments and field measurements.

Wetlands may have an important role in the overall dynamics of trace pollutants. Since wetlands often provide a buffer zone between land and surface waters, and since they are an important recharge point for ground waters, it is important to determine to what degree they can immobilize specific trace pollutants and to what degree organic trace pollutants such as PCBs may even be degraded or partially detoxified in wetlands. Once such wetland dynamics are understood, the effect on the trace pollutant distribution in the environment of a decrease of wetland areas due to increased farming or urbanization can be assessed. Wetland dynamics are rather complex and, similarly as for soils, studying the dynamics of trace pollutants in wetlands would require a combination of mathematical modeling, laboratory experiments, and field measurements.

It was mentioned in section 3.1 that many pollutants could contaminate ground waters for extended time periods, even though the pollutant may not have a high affinity for the aqueous environment and can decay rapidly in other compartments. It may therefore be important to focus on the deterioration of ground water resources due to contamination as a function of different human activities. In addition to groundwater contamination by diffused sources such as farming, contamination occurs through point sources such as industrial sites, landfills, accidents that may occur during the transportation of materials, as well as use and disposal of materials. An industrial metabolism-type approach in combination with ground water transport simulations should be a useful tool to assess different strategies on the quality of ground waters in a densely populated environment.

5.3. Methodology development

One important aspect regarding industrial metabolism studies is the relatively large scale of these analyses. Detailed analyses are common practice in the assessment of the dynamics of pollutants in soils, river sediments, and ground or surface waters. For many of these analyses processes that occur at a very small scale (e.g., colonization of soil grains by bacteria) are formulated in detail, and form the basis of these analyses. It is obvious that such a small-scale resolution is not needed, and in fact infeasible to track, for a river basin study such as that of the Rhine described above. Yet it is important to determine the level at which specific processes should be described for the large-scale studies, and at what resolution their spatial and temporal variability should be considered. A basin with the degree of information as exists for the Rhine is ideally suited to probe on a systematic basis the effects of averaging specific processes over different scales, and determine the effects of this averaging on different outputs of the model.

Once it is clearly understood at which scale information is needed, and over what scale transport processes can be averaged, one could more easily address the question of how to conduct industrial metabolism studies in different river basins, or extrapolate results from one basin to another one. Other questions regarding the transferability of analytical techniques between different geographical locations are also important. For example, can one extrapolate the results and the methodology from the Rhine study to basins with other climates (e.g., southwestern part of North America) or other economic settings (e.g., Eastern Europe or Third

World regions), and if so, how? Techniques to answer these questions need to be developed since it would take an extraordinary and perhaps unnecessary effort to conduct a large series of river basin studies independently without transferring our knowledge gained from other studies, if that is possible.

Because industrial metabolism studies provide information on where and how the environment is responding to changes in the discharge of trace pollutants, they could be used to design monitoring schemes to detect long-term trends in the quality of the environment. This would be an important outcome of the further development and refinement of the methodology applied for industrial metabolism studies, and it is linked directly to the question of the scale mentioned above (i.e., how many samples are required, where do we have to sample, and how long do we have to sample to detect a specific trend).

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