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#### Appendix A List of chemical formulas of nitrogen and phosphorus compounds

N	nitrogen
N <sub>2</sub>	dinitrogen (molecular N)
NO <sub>x</sub>	nitrogen oxides (NO and NO <sub>2</sub> )
NO	nitric oxide
NO <sub>2</sub>	nitrogen dioxide
N <sub>2</sub> O	nitrous oxide
NH <sub>3</sub>	ammonia
NH <sub>4</sub> <sup>+</sup>	ammonium cation
HNO <sub>3</sub>	nitric acid
NO <sub>3</sub> <sup>-</sup>	nitrate anion
P	phosphorus
H <sub>3</sub> PO <sub>4</sub>	phosphoric acid
Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> F	apatite
NaNH <sub>4</sub> HPO <sub>4</sub>	ammonium phosphate
Na <sub>5</sub> P <sub>3</sub> O <sub>10</sub>	sodium tripolyphosphate
AlPO <sub>4</sub>	aluminum phosphate
FePO <sub>4</sub>	iron phosphate

## 26

### Trace Pollutants

HALINA SZEJNWALD BROWN ROGER E. KASPERSON SUSAN SWEDIS RAYMOND

For purposes of this analysis, we define trace pollutants as *the undesired contaminants present in an environmental medium at concentrations ranging from less than a part per billion to parts per million*. Even with this definition, the potential list of agents is virtually unlimited. To bound the task and to focus on those trace pollutants with the greatest potential contribution to global transformation during the past 300 years, we limit our analysis to agents generated by the large-scale human activities of metal mining and utilization and organic chemical manufacturing and use (Fig. 26.1). These activities, in addition to energy generation (whose effects are discussed elsewhere in this volume), in our view carry the greatest potential for human action to transform the long-term global configuration of trace pollutants.

The relationship among these broadly defined human activities and the generation of pollutants is not unique, we hasten to note. A particular environmental pollutant usually originates from multiple activities, and conversely, any one activity commonly generates multiple pollutants. The multiplicity of causal relationships between human activities and the trace pollutants calls for multiple data bases and diverse analytic tools. Our data base draws upon the results of environmental monitoring as well as production, consumption, and emission

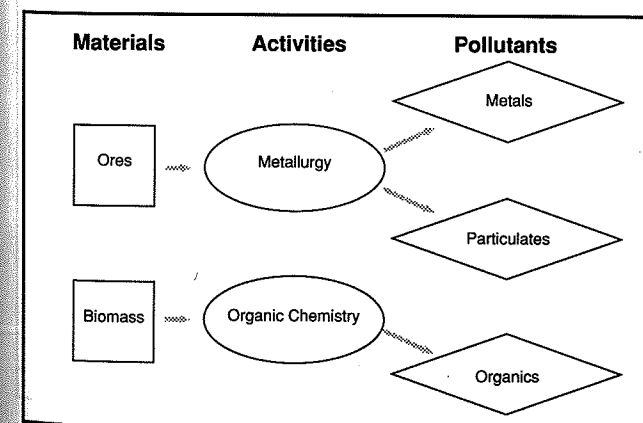


Figure 26.1 Relationship between industrial activities and environmental releases.

		Spatial	
Temporal	Local Short-lived		Global Short-lived
	Local Persistent		Global Persistent

Figure 26.2 Patterns in environmental fate of trace pollutants.

information. Each source has its limitations, and typically the data are fraught with gaps and inconsistencies.

The patterns of environmental movement and accumulation in environmental compartments and biota can be characterized in many ways. We have chosen to focus on two that are central themes of this symposium – the spatial and the temporal. Thus, we group the trace pollutants broadly into (1) locally concentrated and globally diffuse and (2) short-lived and persistent. Conceptually, the possible combination of these characteristics suggests a simple two-by-two matrix (Fig. 26.2).

The two sets of variables – spatial and temporal – are not independent. For instance, one would expect pollutants with short residence times in the environment to have mostly localized effects, and conversely, the persistent pollutants certainly to have a greater potential for global distribution and global effects. We should expect, therefore, most trace pollutants to cluster in the two diagonally located quadrangles – the upper left and the lower right.

The structuring of the analysis points to certain research questions. For trace pollutants with global/persistent effects, geographic shifts in the centers of production may be less important than cumulative worldwide production trends. For trace pollutants with local/short-lived effects, the reverse is true. For the pollutants with the other two combinations of effects, both types of data may be equally important. Within the limits of this analysis, we assess what is known about the

temporal and geographic patterns of these pollutants in the environment, and their effects on humans, ecosystems, and the planet Earth generally.

**Mining and Use of Heavy Metals**

World production of most metals has grown rapidly during the past 300 years (Fig. 26.3). Not only have production volumes increased exponentially, but the number of metals produced in large quantities has multiplied over time. This growth in total quantities and in the variety of metals produced has been linked in part to the demands of the electronics and space industries and to military uses (Huisken 1975; Nriagu 1980).

Both natural and human activities introduce trace metals into the environment. Anthropogenic sources include production-related activities such as mining, smelting, energy generation, manufacturing, and agriculture; and consumption-related activities such as use, wear, and disposal of consumer and commercial products. Among the production-related activities, the high-temperature processes are significant contributors to metal pollution, mainly through direct emissions of fine particles and gases into the ambient air. Activity-specific, high-temperature emissions are listed in Table 26-1 for a select group of heavy metals. The relative contributions of the individual activities differ among metals.

As shown in Table 26-1, the bulk of the arsenic and cadmium emissions comes from metal smelters, whereas selenium is primarily contributed by coal combustion. Lead is introduced mostly by combustion of leaded gasoline. Finally, environmental mercury is introduced by a mixture of technologic activities, with energy generation responsible for approximately 50% of the total. Combining the emissions from coal, wood, and petroleum combustion (excluding lead) also shows that, with the exception of selenium, energy generation by direct combustion of wood and fossil fuels contributes only a small part of total anthropogenic loading of heavy metals into the environment and that most of it originates from other activities, as graphically illustrated for arsenic, cadmium, lead, and mercury in Fig. 26.4. Table 26-1 also shows that the contribution from natural sources is an order of magnitude smaller than that from high-temperature industrial activities, and most likely represents only a very small fraction of the total anthropogenic loading.

In addition to the production-related processes, the normal use and wear of consumer and commercial products are an important source of these releases. According to Tarr and Ayres (chap. 38), the dissipative consumption includes: weathering of paints and pigments (silver, arsenic, chromium, cadmium, copper, mercury, lead, and zinc); incineration of discarded pharmaceuticals (silver, arsenic, chromium, and zinc), batteries (mercury, cadmium), electronic tubes (mercury), plastics (zinc), and photographic film (silver); wear and weathering of electroplated surfaces (cadmium), leather (chromium), plastics (zinc); and decomposition or combustion of treated wood (arsenic, chromium, copper). Whereas ambient air is the principal initial target of metal emissions from some of these processes, such as incineration of discarded materials and combustion of treated wood, it is the

soil and surface waters that receive the bulk of the emissions from dissipative consumption, mainly via surface runoff and sewage-treatment plants.

The relative contributions of consumption-related and production-related emissions to the total environmental loading of metals, either in the United States or worldwide, are largely unknown. In the United States, the environmental agencies traditionally have focused their attention on emissions from industrial and energy-generating sources into the air and surface waters, such as those listed in Table 26-1. More recently, discharges into soil and groundwater from agricultural activities and landfills have also become of concern. The inventories thus collected over the years provide information primarily on emissions from these activities and ignore the ubiquitous, highly diverse, and dissipated sources of metals associated with weathering and wear of myriads of consumer products. Comparison of the 1983 worldwide production of lead and mercury (Fig. 26.3), with their respective annual emissions from mining, smelting, and industrial processes combined (Table 26-1), shows that, at least for these two metals, most of the mass present in consumer and commercial products is not accounted for by emission inventories such as that shown in Table 26-1. Their ultimate environmental fate is not known. Tarr and Ayres (chap. 38) argue that a significant fraction of that unaccounted mass of material is mobilized and introduced into the environment through consumption-related processes. That these processes may in some areas be the primary source of trace-metal pollution is illustrated by Tarr and Ayres for several metals in the Hudson-Raritan basin.

Clearly, the contribution from dissipative consumption will vary with the industrial and agricultural traditions of a region, population density, technological development, wealth, and other variables. Therefore, although the data for metal emis-

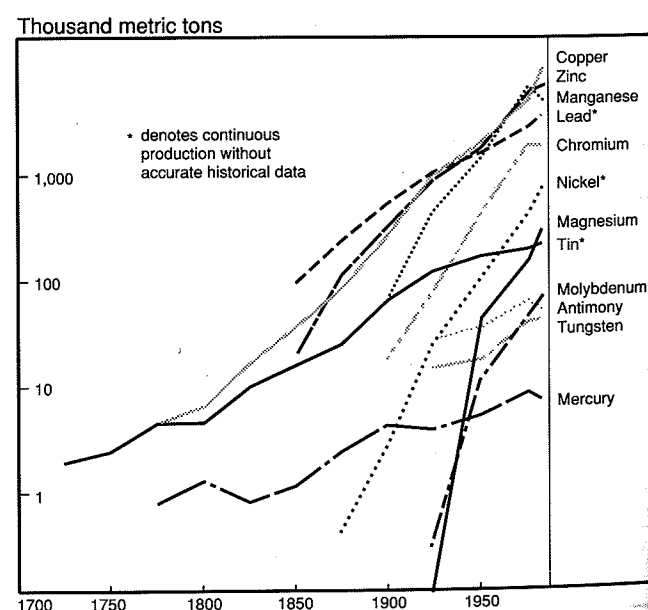


Figure 26.3 Annual worldwide production of selected metals from 1700 to 1983. Data from Schmitz 1979 and Minerals Yearbook 1984.

Table 26-1 Global annual average contributions of trace elements from natural and anthropogenic high-temperature processes (1983)

	Arsenic	Cadmium	Lead (thousands of metric tons)	Selenium	Mercury
<i>Natural</i>					
Dust	0.24	0.25	10	0.3	0.03
Volcanoes	7	0.5	6.4	0.1	0.03
Forest fires	0.16	0.01	0.05		0.1
Vegetation	0.26	0.2	1.6		
Sea salt	0.14	0.002	0.1		0.003
Total	7.8	0.96	18.6	0.4	0.16
<i>Anthropogenic</i>					
Mining	—	—	8.1	0.005	—
Smelting of nonferrous metals	15.2	5.3	77.2	0.28	0.29
Iron production	4.3	0.1	50.0	0.01	0.45
Other industrial activities	—	0.04	7.2	0.05	—
Waste incineration	0.4	1.4	9.0	—	—
Phosphorus fertilizer production	2.6	0.2	—	—	—
Coal combustion	0.5	0.05	13.9	0.68	0.63
Wood combustion	0.5	0.2	1.0	—	—
Petroleum combustion	—	—	273.0*	0.06	0.27
Total	23.6	7.3	449	1.1	1.8

Source: Nriagu and Davidson 1986.

\*Lead is introduced into the environment primarily from combustion of leaded gasoline. Since this may be considered a secondary source, it may be listed under the category of "other industrial activities."

sions into the Hudson-Raritan basin cannot be generalized to the rest of the country or to the world, three important conclusions emerge from that study:

1. Dissipative consumption contributes a significant, and in some cases, the largest fraction of total loading of metals into the environment.
2. Efforts to decrease releases of metals by way of pollution-control technology and strict regulations address only part of the problem and, in fact, increase the relative contribution from consumption-related activities.
3. Mass balance of environmental pollution by metals must include the contribution from dissipative uses, in addition to the more obvious emissions from industry and power plants.

Metals emitted into the ambient air from various sources are carried different distances by the winds, depending on their state (gaseous, vapor, or particulate) before they fall or are washed out of the air onto land or the surface of the oceans. Deposition rates to soils from atmospheric lead in selected areas of North America and Europe are shown in Table 26-2. In the case of particulate matter, particle size is the decisive factor. Most metals associated with coarse particulate matter are deposited within 10 km of the point of emission. For the gaseous phase, deposition can take place 200–2,000 km from a source (Schroeder and Lane 1988). The gaseous phase is important for the aerial transport of mercury, arsenic, cadmium, lead, antimony, selenium, and zinc (Friberg, Nordberg, and Vouk 1979). The generally short atmospheric residence times for the large fraction of

Table 26-2 Deposition rates to soils from atmospheric lead in North America and Europe (mg/m<sup>3</sup>/yr)

	Deposition rates
<i>Industrial Areas</i>	
Toronto (smelter)	>6,000
Toronto (highway)	600
Missouri (800 m from smelter)	1,265
<i>Urban Areas</i>	
New York City	350–547
Los Angeles	17–8,000
London	54
Madison, WI	<25
<i>Rural Areas</i>	
	6.2–34.1
<i>Remote Areas</i>	
	0.01–4.2

Source: NAS, National Research Council 1980.

airborne metals mean that changes in human activities contributing to emissions to air are reflected fairly rapidly in local ambient concentrations (Woolson 1983). Figure 26.5 shows the effects of changes in the air emissions of lead in the United States on its ambient concentrations. Clearly, the gradient in average concentration followed that of emissions within a year. This change was accompanied by a drop in average blood concentrations of lead in the population.

In addition to the local deposition in the soils and surface waters adjacent to the emission sources, the elements introduced into the atmosphere are transported over longer

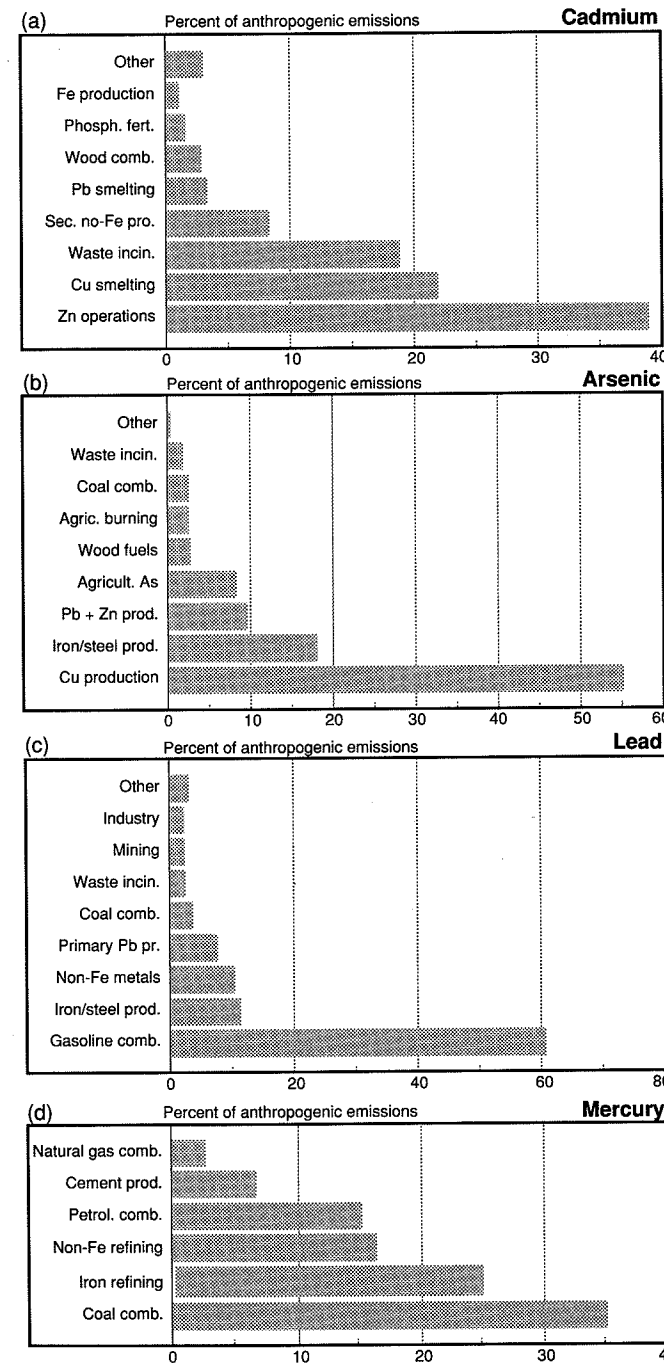


Figure 26.4 Relative contributions of various activities to total anthropogenic direct atmospheric emissions of individual metals. (a) cadmium; (b) arsenic; (c) lead; (d) mercury. Data from Nriagu 1979, 1980; Woolson 1983: 394-95.

distances and are deposited on distant soils and surface waters (Schroeder and Lane 1988). Recent measurements of concentrations of selected metals in polar snow (Table 26-3) illustrate that phenomenon. There has been a dramatic increase in the concentrations of lead, cadmium, and mercury at remote sites since ancient times. The trend is most pronounced for lead, with the current concentration being about 3 orders of magnitude higher than those in the earth's crust. Recent satellite data and other remote sensing data

Consumption of Lead in Gasoline and Ambient Air Concentrations of Lead

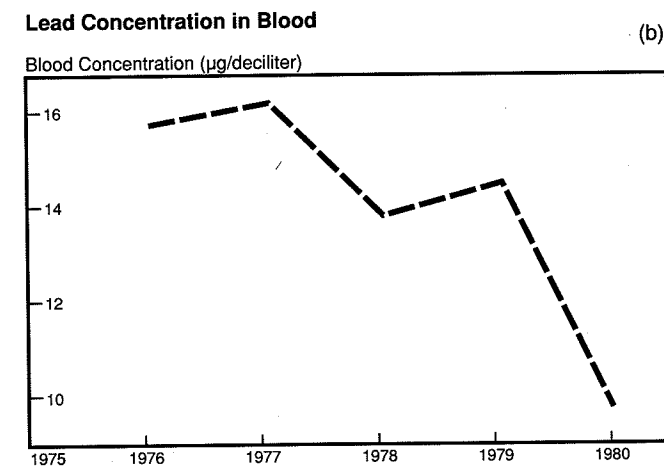
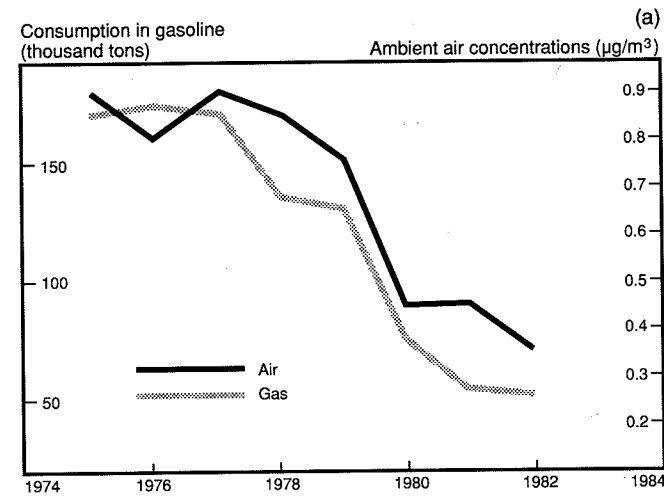


Figure 26.5 Trends in lead consumption and average concentrations in the United States, 1975-1982. (a) Consumption of lead in gasoline and ambient air concentrations of lead; (b) lead concentration in blood. Data from U.S. E.P.A. 1985.

have provided important information on the deposition of airborne particles, including metals. Two oceanic sinks for airborne particles have been identified, one located from Cape Hatteras to 1,500 km ENE of Newfoundland, and another one between southern Japan and the southwest Aleutian Islands (Chung 1986). Enrichment of lead and tin in these particular dumping grounds in the north Atlantic and the north Pacific already has been documented (Duce and Baut-Menard 1987). Lead concentrations in the waters of the

Table 26-3 Concentrations of selected metals in Arctic snow

Medium	Cadmium (picograms per gram)	Lead (picograms per gram)	Mercury (picograms per gram)
Modern, Greenland or arctic snow	5	200	10
Ancient Greenland ice		1.4	10
Modern antarctic snow	0.26	5	10
Ancient antarctic ice		1.2	2

Source: Wolff and Peel 1985.

Atlantic Ocean have been studied, and show a decreasing gradient with depth, substantiating the effects of the deposition of airborne metals on water (Langford 1973).

Dredging, sewage disposal, industrial discharges, river drainage, and surface runoff (of industrial and consumptive origin) are, next to atmospheric deposition, significant contributors to metal pollution in surface waters. Data recently have been compiled comparing the relative contributions of metals to the waters of the North Sea from land-based sources and direct atmospheric deposition (Mance 1987). Table 26-4 presents the North Sea data for several metals in both absolute and relative terms. Land-based contributions to heavy metals in the North Sea exceed atmospheric contributions for all the metals listed except cadmium, for which land sources account for only one-half as much as atmospheric sources. It is important to note that for copper and mercury the relative contributions of the two sources are nearly equal. The data presented in Table 26-4 are consistent with the idea that consumption-related use of metals is a significant source of their total environmental emissions.

The elements introduced into the environmental compartments via atmospheric emissions and long- and short-distance transport and deposition, as well as direct discharges into soils and waters, are subject to global geochemical cycles that lead to continuous recirculation among these compartments (Fig. 26.6). The residence times of metals in environmental compartments (Table 26-5) indicate that, although sediments are the ultimate sink for these atmospheric emissions, soils and oceans also provide long-term storage.

The problem presented by the long residence times of metals in the environmental compartments suggests that the most appropriate approach to understanding the impacts of human activities on their environmental dispersion would be to examine cumulative rather than annual production and/or consumption figures. This is shown in Table 26-6 for some metals. The results are dramatic. Over the past 150 years, for example, humans have mined and processed more than 182 million t of lead, 281 million t of copper, and 112 million t of manganese.

The transport of metals through the environment is dependent on their chemical and physical form and on the processes that act to change their form during transport.

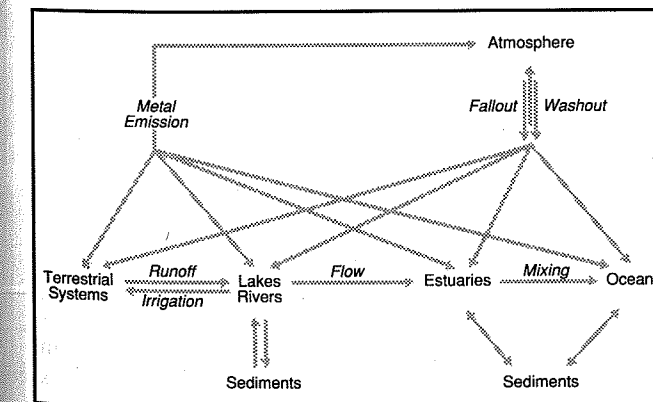


Figure 26.6 Routes of transport of trace metals in the environment.

Table 26-4 Land-based and atmospheric contributions to heavy metals in the waters of the North Sea

Metal	Land-based (t/day)	Atmospheric (t/day)	Relative contribution (land atmospheric)
Arsenic	2.2	0.63	3.5
Cadmium	0.68	1.56	0.4
Chromium	18.3	1.83	10.0
Copper	12.9	10.8	1.2
Lead	17.9	8.0	2.2
Mercury	0.18	0.14	1.3
Nickel	11.1	4.3	2.6
Zinc	86.3	19.2	4.5

Source: Mance 1987: 324-27.

Table 26-5 Residence times of metals in environmental compartments

Residence times (yr)	Arsenic	Selenium	Mercury	Cadmium	Lead
Atmosph.	0.03	0.03	0.1	0.02	
Land	2,400	4,600	280	3,000	3,000
Oceans	9,400	2,300	880	2,100	
Sediments	$99.8 \times 10^6$	$93.5 \times 10^6$	$90.8 \times 10^6$	$99.8 \times 10^6$	$99 \times 10^6$

Source: As, Se, Hg: MacKenzie, Lantzy and Paterson 1979; col, Cd: Nriagu 1980.

Elements associated with particles in rivers are less accessible to biota than those existing in water-soluble forms. Alkylation of mercury and its tragic consequences have been demonstrated in Minamata Bay in Japan. Thus far, only mercury and possibly cadmium are known to exhibit enhanced bioaccumulation via alkylated forms. It has been suggested that several other elements may be mobilized in the environment in organometallic form, including arsenic, tin, selenium, lead, and tellurium (Andreae et al. 1984). Changes in soil alkalinity due to acid precipitation also are known to affect the mobility of metals in soils, and thus their availability to biota (Cowling 1982).

Water-soluble forms of metals present in surface waters are readily absorbed into the flesh of aquatic organisms and in some cases can serve as a historical record for human activities. The 300-year history of utilization of lead through human action has been inscribed in the coral reefs off the Florida coast (Fig. 26.7). The ratio of lead to calcium in the dated coral bands, constant until the 1920s, has been steadily increasing, along with the global use of leaded gasoline. After reaching a peak in the mid-1970s, it appears to be declining thereafter. Interestingly, the growth and decline of lead residues in the Florida coral coincide with the use of lead in gasoline in the United States (Fig. 26.5) and not with the global mining and smelting trends (Fig. 26.3). This is consistent with an environmental transport model, in which a relatively short-range aerial transport of lead from urban areas is followed by fallout on the ocean surface and subsequent incorporation by the organisms.

Table 26-6 Worldwide cumulative production of selected metals for the period 1700–1986: their toxic effects upon chronic exposure and primary routes of exposure by humans

Metal	Cumulative production (thousands of metric tons)	Toxic effects <sup>1</sup>	Primary route of exposure <sup>2</sup>
Beryllium		respiratory cancer in humans (r), skeletal effects (o)	
Antimony	3,463	chromosomal breaks (r), emphysema (r), liver toxicity (o)	F,W,A?
Chromium	30,733	respiratory cancer in humans (r), renal toxicity (o)	W,F
Copper	281,875	aggravation of Wilson's disease (o)	F?
Magnesium	7,363		A
Manganese	112,035	neurotoxic effects (o)	F
Mercury	733	birth defects, neurologic effects (o, r)	F
Nickel	18,130	possibly cancer in humans (r), reproductive effects (o), dermatitis (o)	F,W
Tin	16,516	immunosuppression (o), metabolic disorders (o)	F
Lead	182,035	neurologic effects (r, o), developmental effects (o, r), possibly kidney cancer in animals	F
Arsenic		neurotoxicity, skin lesions (o), anemia, circulatory toxicity (o, r), respiratory cancer in humans (r), reproductive effects (r, o)	W,A?
Selenium		pancreas, kidney, and liver toxicity, retarded growth (o), developmental effects (o)	F
Cadmium		renal toxicity (r, o), respiratory cancer in animals (r), reproductive effects (o)	F

<sup>1</sup> Not all effects occur by all routes of exposure (r, respiratory; o, oral). From Friberg, Nordberg, and Vouk, 1979.

<sup>2</sup> A, air; W, water; F, food. From Andrae et al. 1984.

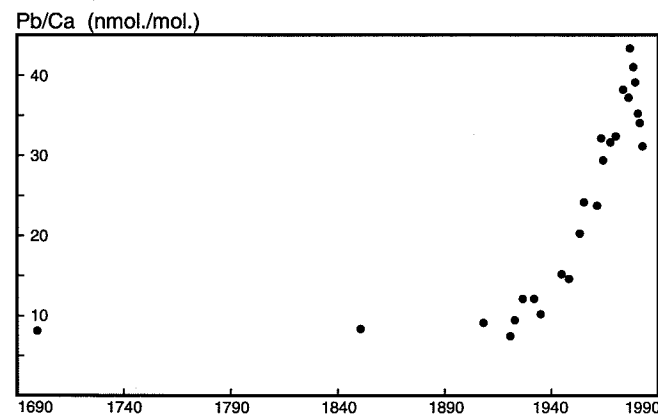


Figure 26.7 Lead concentrations in year bands of coral (*M. annularis*) from the Florida Keys. Source: Carpenter, Jickells, and Liss 1987.

Incorporation of metals residues into the flesh of aquatic organisms can also affect the food chain, where accumulation and biomagnification of the order of  $10^4$  to  $10^5$  times can occur and ultimately present a problem to humans. Recent measurements of metal concentrations on aquatic organisms in coastal and inland waters in the United States indicate that the process of food-chain contamination has been extensive. The 1976 National Marine Fisheries Service survey reported the presence of mercury, lead, cadmium, chromium, and arsenic in sea and freshwater fish at concentrations ranging from 0.12 ppm for mercury to 2.6 ppm for arsenic (Zook 1976). Some of the same metals, as well as additional ones (silver, cobalt, iron, manganese, nickel, and zinc), were found in several surveys of fish and shellfish in the New

England waters in concentrations ranging from 0.1 ppm for cobalt to 53 ppm for zinc (Capuzzo et al. 1987; Eisler et al. 1978). More recent studies of quahog clams from Narragansett Bay in Rhode Island showed contamination with cadmium, mercury, nickel, chromium, copper, zinc, and lead (Brown, Goble, and Tatelbaum 1988). Among those, cadmium, mercury, and lead have been judged to be above health-based acceptable levels for commercial use.

Adverse effects of some metals, derived mostly from observations made on occupational groups, are listed in Table 26-6. The environmental toxicology of metals is particularly complex. In addition to the limited understanding of the toxic effects of many metals at low doses and their toxicologically relevant chemical forms in the environment, risk assessors are confronted with variegated mutual interactions among metals that significantly affect the toxicity of each member in a complex mixture (Friberg, Norberg, and Vouk 1979; Liebescher and Smith 1968; Mertz 1981; Norberg 1978). Considering the undisputed global distribution of metals, especially through the food chain, further studies of their environmental fate and toxicity are among the most fascinating challenges to the risk-assessment community for the next several decades.

#### Organic Chemical Industry

The development of organic chemistry from its origins in the late eighteenth century has created substances entirely unknown in nature. The organic compounds present in biomass materials were the first to be exploited as feedstocks for the organic chemical industry. Fermentation, pyrolysis, and distillation of natural materials produced such new

products as alcohols, tars, shellac, and turpentine, consumed in large part as naval stores (Farber 1952; Ihde 1964; Reese 1976). Later, the introduction of coal decreased the relative importance of wood and cotton as raw materials for the chemical industry (Fig. 26.8). Since the 1930s, oil and natural gas have progressively replaced both cellulose sources and coal and have opened the way for an explosive growth of the petrochemical industry.

From the late nineteenth century until the 1920s, Germany was the undisputed world leader in synthetic organic chemistry, accounting for 25% of the world's chemical industry and 85% of its synthetic dyes (Hohenbery 1967). The major industrialized nations of Europe and North America also took up the industry, with the United States emerging as the greatest volume producer in the post-World War II era. During this period, the production both of organic chemical intermediates and of plastics and resins has increased dramatically (approximately 50- and 200-fold, respectively), whereas pesticides and medicinal chemicals have increased more gradually (Fig. 26.9).

It is noteworthy that consumption of ethylene roughly parallels the production levels of the other two classes of chemicals. This is not surprising, because ethylene is a major chemical intermediate, usually consumed in the country of origin and mostly utilized by the synthetic organic chemical industry. Ethylene is, therefore, a reasonably good indicator of overall changes in synthetic organic production. Using ethylene as an indicator, trends in the worldwide production of synthetic chemicals between 1970 and 1983 are shown in Table 26-7. The table shows that although production has been concentrated in major industrial centers (such as the United States, Japan, West Germany, the Netherlands, and the Soviet Union), the recent rate of growth in some newly developing countries (such as Brazil, Mexico, Hungary, and China) has outpaced that in the established centers. As a result, the relative contribution to the world production by the major producers has dropped, and new centers of pro-

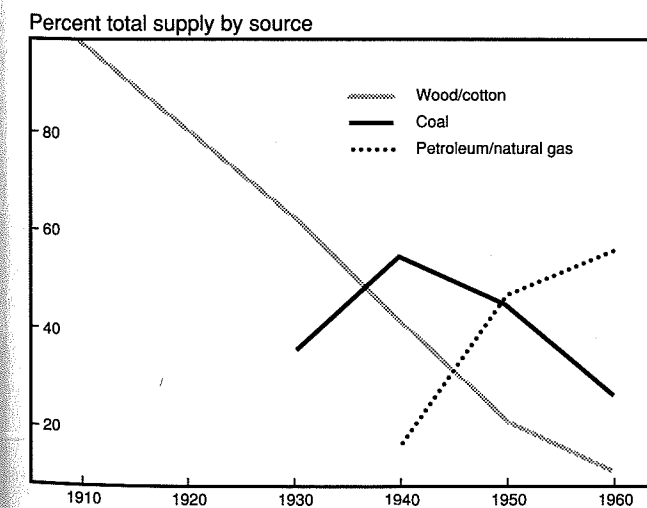


Figure 26.8 Relative contribution of fuel types as feedstocks for the chemical industry, United States and Europe. Data from Tillman 1978: 21.

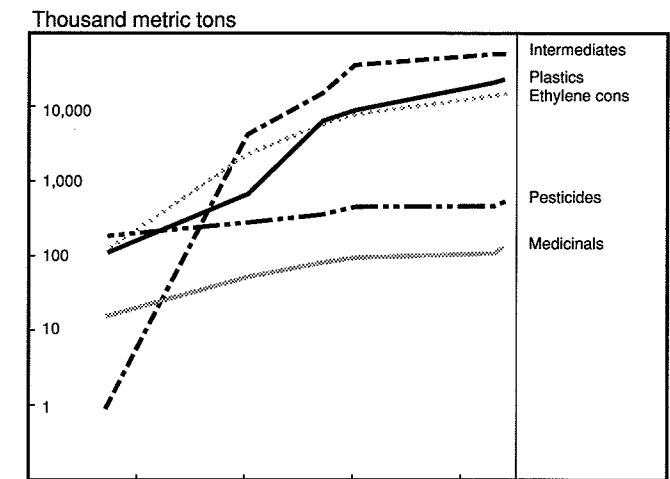


Figure 26.9 U.S. synthetic organic chemical production, 1947–1984, by production category. Sources: for 1947, 1960, Reese 1976; for 1969, 1970, U.S. Tariff Commission 1972; for 1967, 1983, 1984, U.S. International Trade Commission 1985.

duction of synthetic chemicals have emerged in eastern Europe, Asia, and possibly South America.

A similar picture of growth emerges for benzene (Table 26-8). The rate of growth in newly developing countries has outstripped that of the industrial countries, with an overall shift toward eastern Europe, Korea, India, and Brazil. Unlike ethylene, which is utilized mostly in the synthesis of other chemicals, the primary uses of benzene are in gasoline (78%) and as a solvent (13%). Benzene is, therefore, not a good indicator of chemical industry growth. Because more than 90% of benzene is ultimately released into the atmosphere, however, production levels and their geographic locations may be used to predict quite accurately atmospheric emissions of benzene.

With the exception of pesticides, most human-produced organic chemicals are not intended for release into the environment. Releases are typically the undesirable by-products of manufacturing, waste disposal, and the commercial uses of the substances. Among the organic chemicals unintentionally released into the environment, volatile organic compounds are by far the largest class. Used primarily as industrial solvents and synthetic intermediates (except benzene, which is used heavily in gasoline manufacturing), their main environmental sink is ambient air. The magnitude of emissions can be estimated from production volumes, using emission factors of the volatile intermediates. A case in point is plastics manufacturing from vinyl chloride. United States production of polyvinyl chloride in 1986 was 3,271,000 t, comprising approximately one-third of total world production. If global production is estimated at approximately 10,000,000 t and if the emission factor for vinyl chloride from polyvinyl chloride plants is assumed to be 35.5 g/kg (U.S. EPA 1978), more than 355,000 t of vinyl chloride were released into the atmosphere globally from polymer manufacturing in 1986.

Among the largest-volume volatile organic compounds in the United States (Table 26-9), emission factors are also high. Over 90% of all the benzene, trichloroethylene, and trichloro-

Table 26-7 Major ethylene producers in 1970 and 1983 (unless otherwise specified)

Region	1970		1983		Growth factor relative to 1970
	× 10 <sup>3</sup> mt	% total	× 10 <sup>3</sup> mt	% total	
<i>North America</i>					
Canada	406	1.9	1,196	3.5	2.9
Mexico	60	0.3	645	1.9	10.8
U.S.A.	8,204	39.3	12,967	37.5	1.6
<i>South America</i>					
Brazil	349 <sup>b</sup>	1.7	1,163	3.4	3.3
<i>Western Europe</i>					
Finland	98 <sup>a</sup>	0.5	140	0.4	1.4
France	1,235 <sup>a</sup>	5.9	2,046	5.9	1.7
F.R.G.	2,020	9.7	3,172	9.2	1.6
Italy	900	4.3	1,063	3.1	1.2
Netherlands	1,406 <sup>a</sup>	6.7	1,747 <sup>c</sup>	5.1	1.2
Spain	92	0.4	235	0.7	2.5
U.K.	998	4.8	1,155	3.3	1.2
<i>Eastern Europe</i>					
Bulgaria	56	0.3	213	0.6	3.8
Czechoslovakia	122	0.6	543	1.6	4.5
Greece	13	0.1	14	<0.1	1.1
Hungary	2	<0.1	261	0.8	130.5
Poland	26	0.1	198	0.6	7.6
Romania	111	0.5	316	0.9	2.8
Yugoslavia	42	0.2	168	0.5	4.0
<i>Africa</i>					
Algeria	37 <sup>b</sup>	0.2	77 <sup>d</sup>	0.2	2.1
<i>Asia</i>					
China	65 <sup>a</sup>	0.3	654	1.9	10.1
India	39	0.2	102	0.3	2.6
Korea	90 <sup>a</sup>	0.4	491	1.4	5.5
Turkey	43 <sup>a</sup>	0.3	56	0.2	1.3
USSR	1,366 <sup>a</sup>	6.5	2,267	6.6	1.7
Japan	3,097	14.8	3,688	10.7	1.2
TOTAL	20,877	99.8	34,577	100.3	1.7

Source: United Nations 1984.

<sup>a</sup> 1975; <sup>b</sup> 1976; <sup>c</sup> 1981; <sup>d</sup> 1982.

ethane manufactured in this country is ultimately released into the ambient air. Nonetheless, the overall trend in the total emissions of volatile organics relative to the amounts produced has been downward since the early 1970s, possibly as a result of the implementation of the Clean Air Act. A striking illustration is the approximately 30% reduction in estimated emissions of total volatile organic compounds in the United States, despite the more than 50-fold increase in chemical manufacturing during the same time, as reflected by ethylene consumption (Fig. 26.10). This growing gulf between production and releases shows that changes in technology can have dramatic effects on total emissions. It also suggests that using consumption and production figures as indicators of emissions may not be appropriate for comparisons among countries that have vastly different regulatory and technological systems. It is also likely that the recent migration of

organic chemical production from developed to developing countries, in which more permissive regulatory frameworks and control technologies exist, may involve environmental problems greater than those suggested by the changes in the distribution of world production centers shown in Tables 26-7 and 26-8.

Atmospheric chemistry largely determines the environmental fate of volatile organics released into ambient air. Agents with short atmospheric half-lives (e.g., ethylene, propylene, styrene, or butadiene) are more likely to have short-term and more localized impacts than those with longer half-lives. Limited monitoring data consistently show higher concentrations of volatile organic compounds in urban and industrial areas than in rural and remote areas (Singh, Salas, and Stiles 1982).

The direct effects of inhalation of volatile organic com-

Table 26-8 Major benzene producers in 1970 and 1983 (unless otherwise specified)

Region	1970		1983		Growth factor relative to 1970
	× 10 <sup>3</sup> mt	% total	× 10 <sup>3</sup> mt	% total	
<i>North America</i>					
Canada	406	4.0	1,196	7.7	2.9
Mexico	77	0.8	139	0.9	1.8
U.S.A.	3,753	36.7	4,094	26.5	1.1
<i>South America</i>					
Brazil	121 <sup>a</sup>	1.2	1,436	2.8	3.6
<i>Western Europe</i>					
Belgium	64	0.6	41	0.3	0.6
France	385	3.8	627	4.1	1.6
F.R.G.	819	8.0	1,336	8.7	1.6
Italy	501	4.9	528	3.4	1.1
Netherlands	284	2.8	1,032	6.7	3.6
Spain	131	1.3	194	1.3	1.5
U.K.	463	4.5	726	4.7	1.6
<i>Eastern Europe</i>					
Czechoslovakia	106	1.0	268	1.7	2.5
Hungary	13	0.1	104	0.7	8.0
Romania	125	1.2	204	1.3	1.6
<i>Asia</i>					
India	21	0.2	92	0.6	4.4
Korea	8 <sup>b</sup>	<0.1	159	1.0	19.9
Turkey	8	<0.1	9	<0.1	1.1
USSR	1,366 <sup>b</sup>	13.3	2,267	14.7	1.7
Japan	1,585	15.5	1,938	12.6	1.2
TOTAL	10,236	99.9	15,433	100.0	1.5

Source: United Nations 1984.

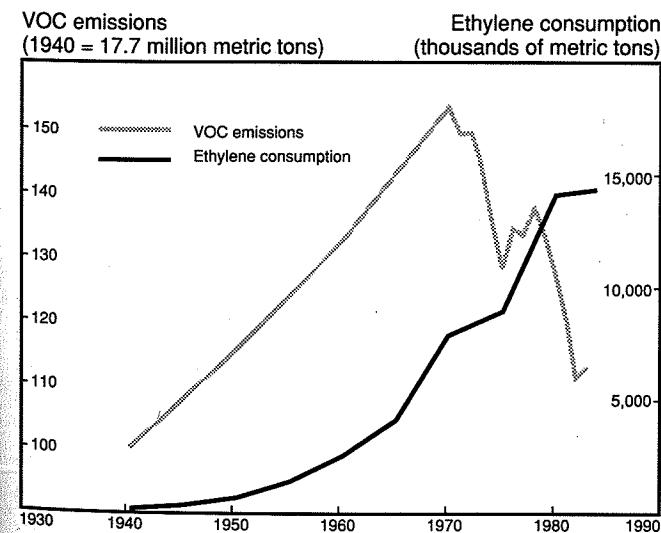
<sup>a</sup> 1976; <sup>b</sup> 1975.

Figure 26.10 Trends in emissions of volatile organic compounds in the United States during the post-World War II years. Data from Waddams 1980 and WRI 1986.

pounds on the health of a local population are largely unknown. The documented higher incidence of lung cancer in urban and industrial centers in relation to rural areas has been attributed by some to air pollution. The contribution, if any, of volatile organic trace pollutants from chemical industry to that effect, however, is speculative at best. In fact, it is quite likely that the observed effect is due to the combined and possibly synergistic effect of a mixture of agents. If so, the volatile organic compounds, some of them known to cause cancer in animals or humans, may ultimately contribute to adverse health effects. That contribution is probably quite small, however, in comparison with other contaminants such as trace metals or inhalable particulates.

The principal indirect local effects of volatile organic emissions are ozone and smog generation, through photochemical reactions with nitrogen oxides and other oxidants. Hydrocarbons with unsaturated bonds, such as ethylene or propylene, are the most reactive of the volatile organic compounds, and, along with hydrocarbon emissions from energy generation (heat production and transportation), contribute significantly to the formation of photochemical smog in highly industrial areas.

The atmospheric fate of volatile organic compounds with

Table 26-9 Production of volatile organic compounds in the United States and their atmospheric residence times

Compound	Annual production (calendar year) ( $\times 10^3$ mT)	Atmospheric residence time <sup>1</sup>
Ethylene	15,210 (87)	hours
Propylene	8,190 (87)	hours
Benzene	4,385 (84)	days
1,2 Dichloroethane	3,455 (82)	3–12 mos <sup>2</sup>
Vinyl Chloride	3,271 (86)	
Styrene	3,690 (87)	hours
Methanol	3,352 (87)	hours
Toluene	2,386 (84)	hours
Xylenes	2,812 (87)	hours
Butadiene	1,215 (87)	hours
Acrylonitrile	1,080 (87)	hours
Cyclohexane	1,012 (87)	hours
Tetrachloroethylene	347 (78)	
Carbon tetrachloride	332 (81)	60–100 yr
Dichloromethane	320 (84)	1–2 yr
Trichloroethane	315 (80)	
Chloroform	169 (82)	
111-Trichloroethane	612 (85)	6.5 yr
Chlorobenzenes	70 (78)	up to 4 mos
Vinylidene chloride	90 (78)	days

Source: U.S. EPA Health Assessment Documents.

<sup>1</sup> Residence times vary with atmospheric conditions. Different values are therefore reported among sources. The following ranges are used here: hours, from less than 1 to approximately 24 hours; days, from 1 to approximately 30 days.

<sup>2</sup> Calculated from a half-life reported in the literature, assuming that residence time equals five half-lives.

long atmospheric residence times is particularly interesting because of their ability to be transported over long distances and to pose, therefore, potentially adverse effects on a global scale. Among these, the halocarbons (chloromethanes, chlorofluorocarbons, bromofluorocarbons, bromochlorocarbons, bromochlorofluorocarbons, and bromocarbons) have been extensively studied in recent years because of their tendency to accumulate in the upper stratosphere and their capacity for depleting the ozone layer. Global production, atmospheric concentrations, and estimated residence times of selected halocarbons are listed in Table 26-10. Of these, CFC-11, CFC-12, and carbon tetrachloride are the most troublesome environmentally because of their combined high atmospheric concentrations, large production volumes, and very long atmospheric lifetimes (>50 years).

The cumulative amounts of carbon tetrachloride and combined CFC-11 and CFC-12 lost to the atmosphere worldwide between 1930 and 1985 are shown in Fig. 26.11. Approximately 65% of the total carbon tetrachloride was emitted before 1960, whereas 96% of the CFCs was released after 1965. Based on the data shown in Table 26-10, CFC-22 and CFC-113 are also of concern, not only because of their long lifetimes and large production volumes, but also because of their apparent rapid increase in atmospheric concentrations.

Thousand metric tons

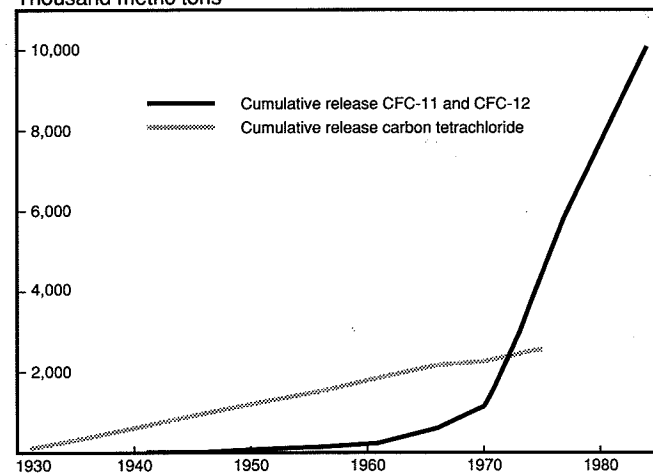


Figure 26.11 Worldwide cumulative releases of chlorofluorocarbons CFC-11 and CFC-12 and of carbon tetrachloride. Data from NAS 1978 and WRI 1986.

Among the halocarbons listed in Table 26-10, trichloroethane, chloroform, iodoform, and dibromoethane have shorter lifetimes than others and are removed from the atmosphere by reactions with stratospheric hydroxyl radicals. They are therefore not considered to pose a threat to the stratospheric ozone and have not been subject to the international activities aimed at reducing halocarbon production. Among these, trichloroethane (whose worldwide production has been growing steadily since the early 1950s, reaching approximately 612,000 t in 1985) is of particular interest. Because of its considerably lower toxicity than that of other chlorinated ethanes and ethylenes, its presumed very small contribution to ozone formation in the stratosphere, and its apparent lack of threat to the stratospheric ozone, this air contaminant has been consistently excluded from regulatory activities in the United States under the provisions of the Clean Air Act. As a result, its use has been steadily growing as it replaced other chlorinated ethanes and ethylenes (trichloroethylene and tetrachloroethylene, for example) whose toxicity or photochemical reactivity became of concern. As shown in Table 26-10, the worldwide production and the atmospheric concentration of trichloroethane has been increasing steadily. It is also a commonly found groundwater pollutant (Table 26-11). With no apparent adverse effects on humans or the environment at the current atmospheric levels, trichloroethane seems to be an ideal industrial and commercial solvent. While this may indeed be the case, the growing reliance on this solvent and the accompanying atmospheric releases merit attention and ongoing monitoring, especially in the stratosphere, which may be receiving some fraction of the considerable emissions into the ambient air.

In addition to the ambient air, groundwater and surface water are targets of environmental partitioning of volatile organic compounds. Contrary to the ambient emissions, which originate primarily from industrial and commercial processes, the pollution of soil and water by volatile organic solvents is largely the result of improper disposal of industrial

Table 26-10 Global production, atmospheric concentrations, and atmospheric lifetimes of selected halocarbons

Compound	Atmospheric concentration		Annual global production $\times 10^3$ tons (in years)	Atmospheric lifetime
	ppt (year)	Increase %/year (year)		
CFC-11 (C <sub>1</sub> F <sub>3</sub> )	200 (83)	5.7 (81)	310 (82)	65
CFC-12 (C <sub>1</sub> F <sub>2</sub> )	320 (83)	6 (81)	444 (82)	120
CFC-13 (CF <sub>3</sub> Cl)	~3.4 (80)		—	400
CFC-22 (CHClF <sub>2</sub> )	~52 (80)	11.7	206 (84)	20
CFC-113	~32 (85)	10.0	140 (84)	90
CFC-114	—		13 (84)	180
CFC-115	4 (80)		—	380
CFC-116	~4 (80)		—	>500
CCl <sub>4</sub>	~140 (79)	1.8 (81)	~830 (83)	50
CH <sub>3</sub> Cl	630 (80)		~500 (84)	~1.5
CH <sub>3</sub> I	~1 (81)			0.02
CBrClF <sub>2</sub>	~1 (84)		(~5?)	0.02
CBrF <sub>3</sub>	~1 (84)		8 (84)	25
C <sub>2</sub> H <sub>4</sub> Br <sub>2</sub>	~1 (84)		—	110
CH <sub>3</sub> CCl <sub>3</sub>	~120 (83)	9–40 (81)	0.1 (51)	~1
			7.9 (55)	6.5
			37 (60)	
			178 (70)	
			371 (75)	
			580 (80)	
			570 (81)	
			540 (82)	
			545 (83)	
			~579 (84)	
			~612 (85)	

Source: World Meteorological Organization 1985; Prinn, et al. 1987.

and commercial waste and of the underground storage of gasoline and industrial stocks. Incidents of contamination have been extensively documented in the United States. The frequency and extent of contamination suggest that surface waters are more frequently contaminated than groundwater (Table 26-11). Both groundwater and surface-water contamination have localized effects, although for different reasons. For contaminants in surface water, dilution, evaporation, and biological and chemical degradation lead to a steeply declining concentration gradient around the source. Thus the area affected by the contamination tends to be limited in extent. For groundwater contaminants, the physical boundaries of the aquifer, rather than the physicochemical and biological attrition processes, confine the problem area. These differences in confinement also explain the differences in persistence of the contamination problem. Whereas the concentration of volatile contaminants in surface water drops rapidly over time and may become negligible within days or weeks, the groundwater contaminants usually persist for decades and may become a serious water-supply problem for a local population.

Industrial countries have allocated substantial efforts over the past decade toward preventing groundwater contamination. The focus has been on all stages of the process that may lead ultimately to groundwater pollution, including:

1. severe restrictions on land disposal of domestic, commercial, and industrial liquid waste;
2. incentives for waste reduction through changes in technology;
3. strict penalties for illegal land disposal and underground storage of volatile solvents;
4. setting water-quality standards for chemicals;
5. public acquisition of lands surrounding important sources of water;
6. intense monitoring of groundwater;
7. public education.

It is interesting that a concern over potential rather than observed adverse health effects has driven these initiatives. The actual adverse health effects of drinking water polluted with small amounts of volatile organic solvents remain unknown. Attempts to document those effects through epidemiologic studies have generated mostly inconclusive results, due both to the methodological difficulties in conducting such studies and the general insensitivity of epidemiology in detecting small changes in health status of a diverse human population. Far from demonstrating the absence of adverse effects, these studies have shown that:

1. the groundwater contamination most commonly found is unlikely to produce acute illness;

Table 26-11 (a) Occurrence of selected volatile organic compounds in finished groundwater in the United States

Compound	Number of sites sampled	Number of positive samples	Mean* ( $\mu\text{g/l.}$ )	Maximum concentration ( $\mu\text{g/l.}$ )
Trichloroethylene	402	4.0	24.8	210
Carbon tetrachloride	432	3.0	1.7	13
Tetrachloroethylene	413	5.6	2.8	30
1,2-Dichloroethane	418	1.9	0.6	1.2
1,1,1-Trichloroethane	399	4.5	30.0	650
cis-, trans-, and 1,1-Dichloroethylene	390	3.3	10.4	82
Methylene chloride	38	2.8	7.0	7.0
Vinyl chloride	25	4.00	76	76

\* Of the positive samples.

Table 26-11 (b) Occurrence of selected volatile organic compounds of finished surface water (EPA Surveys)

Compound	Number of sites sampled	Number of positive samples	Mean* ( $\mu\text{g/l.}$ )	Maximum concentration ( $\mu\text{g/l.}$ )
Trichloroethylene	133	32.3	0.47	3.2
Carbon tetrachloride	144	35.7	3.46	30
Tetrachloroethylene	180	12.8	1.49	21
1,2-Dichloroethane	196	13.8	0.93	4.8
1,1,1-Trichloroethane	133	16.5	0.56	3.3
cis-, trans-, and 1,1-Dichloroethylene	103	4.9	0.66	2.2
Methylene chloride	178	18.0	1.8	13
Vinyl chloride	133	2.3	3.43	9.8

Source: Council on Environmental Quality 1981.

\* Of the positive samples.

2. the magnitude of chronic illness, such as cancer or subtle neurological disorders, often associated with many of these compounds in laboratory studies on animals, is probably not very large in any one individual.

That is not to say, however, that the aggregate effect on a large population, through increased incidence of chronic disease over a long period of time, may not occur or may not be substantial.

Our observations of the recent growth of centers of organic synthetic chemical industry in newly industrializing countries leads us to expect that the magnitude of water contamination has most likely increased in those countries and will continue to rise during the next decades. In Poland, an industrialized society, the magnitude of surface water and groundwater containing industrial waste has risen so sharply as to render them unusable even for agriculture (UNDP 1979). In the developing countries, the increase in water contamination is likely to grow faster than the rate of growth of the industry, due to the lag in investment in pollution control and chemical-waste-disposal technology and to their less stringent environmental regulations. Although cases of contamination are likely to be localized geographically, the aggregate impact of the overall trend may become significant over time.

Polychlorinated biphenyls (PCBs) are another class of unintentionally released organic synthetic chemicals that, like halocarbons, are highly persistent, but whose main environmental sinks are sediments, oceans, and biota. As shown in

Fig. 26.12, the production of PCBs in the United States has declined rapidly since the peak years of the late 1960s. Concerns over the global accumulation of these persistent compounds, as well as their potential adverse health effects, have stimulated these reductions. Evidence now exists to suggest that sediments are not the final sink of PCBs, as previously thought, but are a reservoir from which PCBs may be redistributed to biota, waters, and the atmosphere (Larsson 1985). The net flux, however, is from the atmosphere to lakes, and thence to sediments. Environmental levels of PCBs in the air have declined, following reduced production rates (Figs. 26.12 and 26.15), and should continue to decline worldwide. The reduction will be slow, however, due to the persistence of PCBs, their ability to recycle among environmental compartments, and the large environmental reservoir (estimated in 1975 at 82,000t). Meanwhile, PCBs still in service and in landfills, dumps, and impoundments will continue to produce local instances of high PCB levels, pending destructive disposal of these reservoirs.

Overall, the adverse health effects to humans and biota from prolonged exposures to low levels of PCBs are probably not very significant, although this class of compounds has been implicated in cancer and reproductive effects in some species. The phenomenal environmental spread of PCBs and their virtual omnipresence in all environmental compartments and in living organisms is therefore probably more important as a symbol than as an actual threat to the ecosystem. It symbolizes the irreversibility and globality of

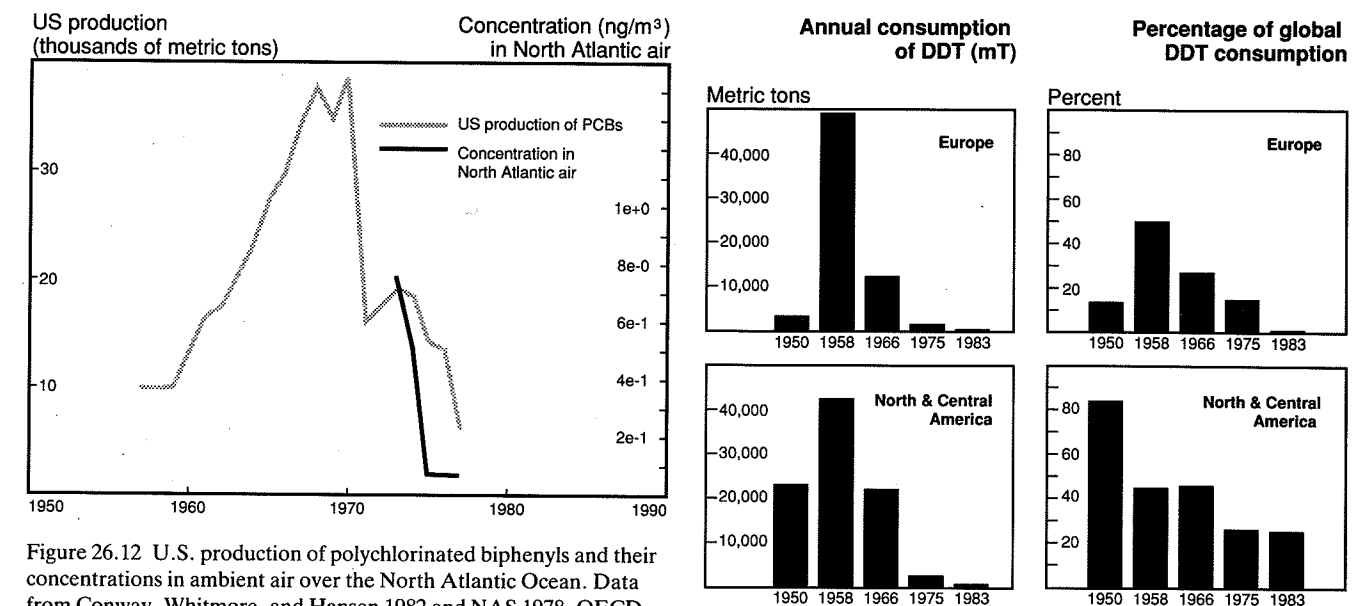


Figure 26.12 U.S. production of polychlorinated biphenyls and their concentrations in ambient air over the North Atlantic Ocean. Data from Conway, Whitmore, and Hansen 1982 and NAS 1978, OECD 1979.

the effects of the release of large quantities of persistent chemicals and of short-sighted societal behavior toward the environment.

In contrast to most other organic chemicals of anthropogenic origin, pesticides are intended for release into the environment. Therefore, production and consumption figures closely parallel total releases. DDT is a prototype pesticide with a high persistence in the environment and an extensive, global distribution.

Developed by Swiss chemists at Geigy laboratories in 1939, DDT won rapid acceptance due to wartime pressures for increased agricultural production, the need for a delousing agent for refugees and military personnel, and the need for protection against insect-borne diseases prevalent in the diverse climates of the war theaters. By 1945, DDT had also been released for civilian use in the United States, and it gained a quick acceptance due to its low mammalian acute toxicity, its persistence, its broad-range activity, and its relatively low cost (Perkins 1982). In 1955, the United Nations World Health Organization launched a campaign to control malaria using DDT, and by 1972 it claimed eradication of the disease in 36 countries, which would have affected 710 million people (Plimmer 1982).

While the benefits of DDT to public health programs were becoming manifest, awareness of its serious environmental hazards was growing. As early as 1950, DDT's interference with pest control by natural predators was noted (Perkins 1982). By the 1960s, DDT's persistence in the environment, due to physicochemical properties similar to those of PCBs, and its bioaccumulation and biomagnification along the food chain of various species were evident. Birds seemed especially sensitive, with eggshell thinning and bone abnormalities the most obvious effects, even with exposures in the parts-per-billion range (Garrels, MacKenzie, and Hunt 1973).

Total world consumption of DDT peaked in the late 1950s and early 1960s, and has declined continuously since (Fig. 26.13). In 1984, global consumption reached only approximately 1.5% of the previous peak value. The decline started

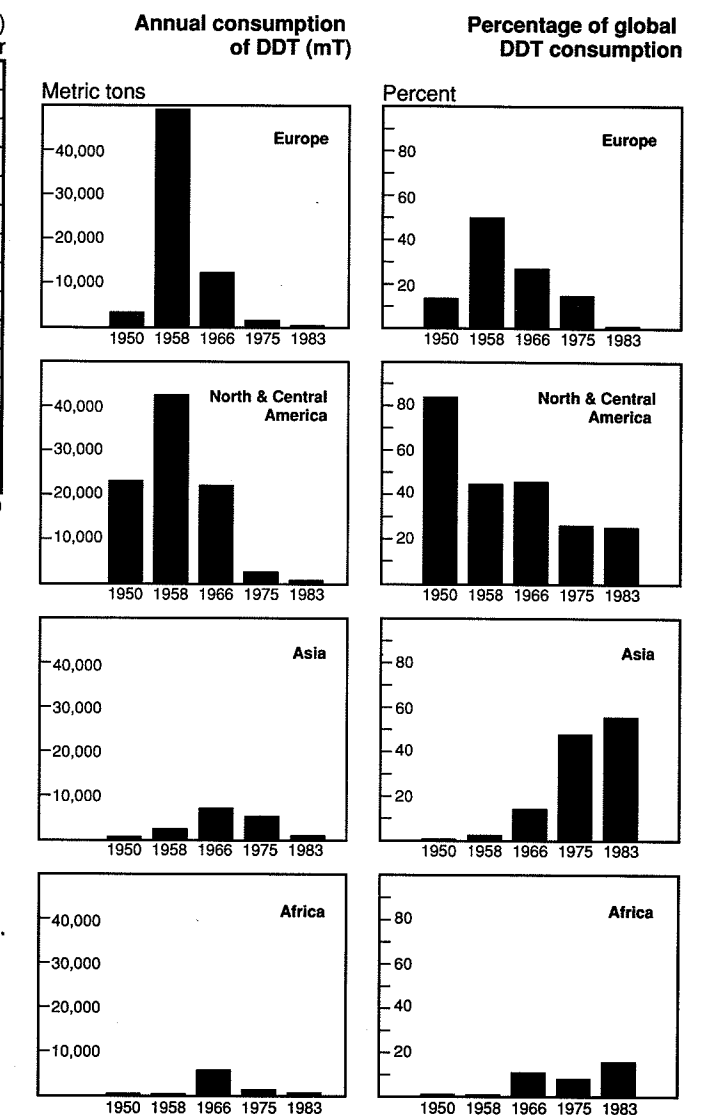


Figure 26.13 Trends in global consumption of DDT by region for selected years, expressed in metric tons and as a percentage of total annual consumption. Data from U.N. FAO Production Yearbooks.

in Europe and North America, followed by Africa and Asia about eight years later. Since the rate of decrease has been lower in Asia and Africa than in Europe and North and Central America, a dramatic geographic shift in the pattern of world consumption has occurred. Thus, Europe and North and Central America combined went from 96% of world consumption in 1958 to 26% in 1983, whereas Asia and Africa went from 3% to 74% during the same period.

The environmental effects of DDT are initially most evident in the areas of its release. For instance, in agricultural areas, DDT concentrations in the soil are as much as 10,000 times higher than in nonagricultural areas (Woodwell et al. 1975). Its physicochemical properties (moderate volatility, chemical stability, and ability to accumulate in sediments, soils, and biota), however, favor long-range environmental cycling and worldwide diffusion. Indeed, DDT residues have been detected in all environmental media and in biota. A model of the global flux of DDT residues, based on an

assumed annual average consumption of 8,000 t/yr, suggests environmental fluxes of: land, 5,000 t (62%); oceans, 2,000 t (25%); atmosphere, 1,000 t (12%); and sediments, 80 t (1%) (Garrels et al. 1973; Woodwell et al. 1975). As with PCBs, one would expect a slow decline in levels of DDT and its decomposition product DDD in the environment and biota, due to recycling. There is, for example, a 20- to 25-year lag period in the reduction of DDT residues in eastern Canadian seals (Fig. 26.14). Based on the DDT data, one would expect that the concentrations of PCBs in the seals, having continuously risen between 1975 and 1982, should now be reaching their peak, to be followed by a slow decline similar to that of DDT residues (Fig. 26.15). The overall worldwide decline in

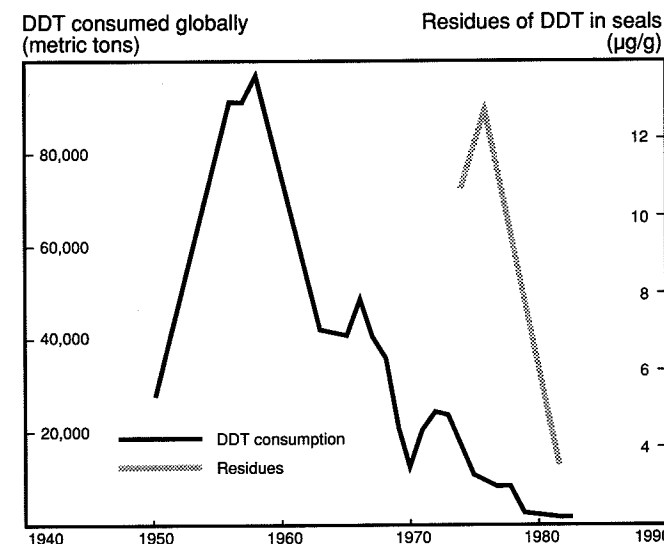


Figure 26.14 Relationship between DDT consumption and its residues in the flesh of eastern Canadian seals. Data from Addison, Brodie, and Zink 1984; U.N. FAO Production Yearbooks.

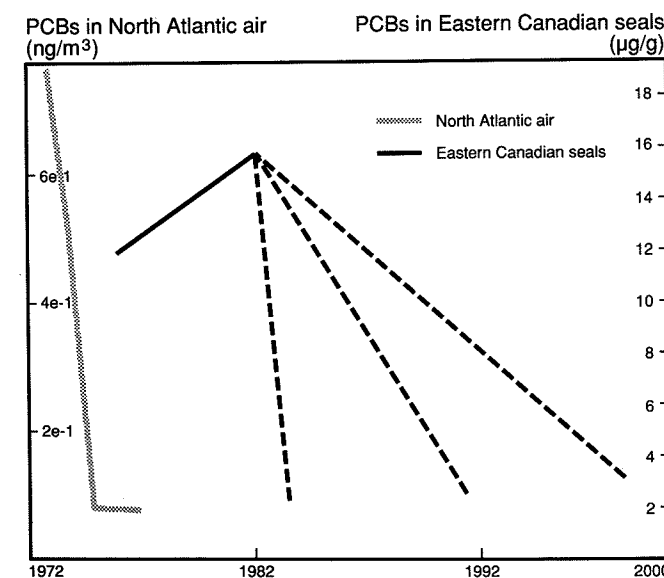


Figure 26.15 Concentration of polychlorinated biphenyls in North Atlantic air compared with actual and anticipated trends in biota. Dashed lines represent anticipated decline in PCB concentration in biota. Three hypothetical lines signify that the rate of decline is not known. Data from Addison et al. 1984; Conway et al. 1982.

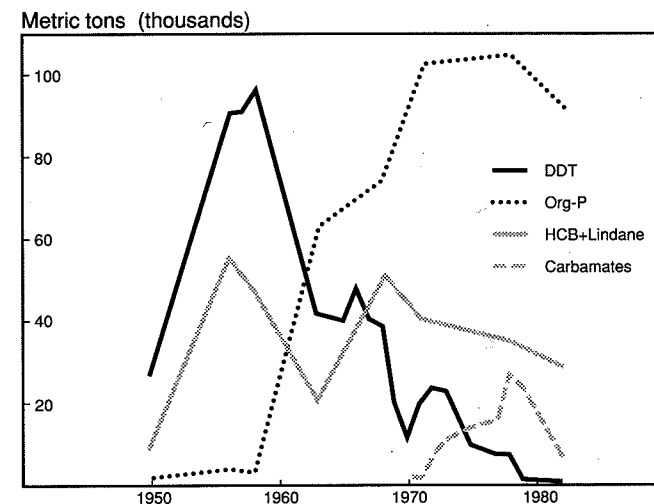


Figure 26.16 Trends in global consumption of pesticides by class, 1950-1982. Data from U.N. FAO Production Yearbooks.

PCB residues will likely be slower than that of DDT because of their large environmental reservoirs, greater volatility and therefore aerial transport, slower degradation rate, and greater bioaccumulation.

On a smaller scale, the rate of decline depends on the proximity of vapor reservoirs and routes of transport. Thus, whereas the levels of DDT in arctic ringed seals in the eastern arctic have declined faster than those of PCBs during the period 1972 to 1981 (Addison et al. 1986), the opposite is true for the western arctic, most likely due to a continuing supply of DDT to the western arctic via air or water from the Far East, where its use continued throughout the 1970s (see Fig. 26.16). Ultimately, the decline in PCB and DDT residues in the seals of the western arctic should approximate the pattern seen in the eastern arctic if DDT consumption in the Far East continues to decline.

The recognition of the environmental persistence of DDT and other chlorinated pesticides has led to a recent shift toward the use of chemically less stable compounds. This new generation of pesticides, exemplified by carbamates and organophosphates, are water-soluble, biodegradable, and chemically much more reactive than past agents. The time course of the rise and decline in the worldwide consumption of four major classes of pesticides is shown in Fig. 26.16. The decline in the consumption of the highly persistent hexachlorocyclohexane, lindane, and DDT that took place during the late 1950s and early 1960s coincided with a rapid growth in the consumption of organophosphates and, later, carbamates. The consumption of carbamates, never matching the other classes in volume, declined during the 1980s, possibly due to the competition from other products and the awareness of the potential environmental build-up under special local conditions (UNEP 1986).

The physicochemical properties of carbamates and other similar pesticides allow for an environmental partitioning pattern similar to that of land-disposed volatile organic compounds. Their principal sinks are soils, surface water, and groundwater. Incidents of groundwater contamination have been well documented throughout the United States, with

concentrations of various agents ranging from less than one to hundreds of parts per million (Holden 1986). As with VOCs, the environmental effects of these contaminants are mostly localized, with significantly longer residence times in groundwater than in surface waters. Recent monitoring of groundwater in 30 states in the United States has shown that about 50 to 60 pesticides have been detected.

Unlike the volatile organic compounds, carbamates, organophosphates, and other pesticides that have been introduced recently into agriculture have a fairly high acute toxicity and, when inappropriately handled or applied, can cause illness among applicators and other agricultural workers. Judging by the rapid growth of the organic chemical industry in the industrializing countries, their strong reliance on synthetic agricultural pesticides, and probably limited knowledge among users of toxicologic and chemical properties of these substances, increasing incidence of accidental poisoning should be expected. Judging by the U.S. experience, we would also expect an increasing incidence of groundwater contamination by pesticides in these countries.

#### Discussion

A great variety of trace pollutants has been introduced into the terrestrial environment during the past three centuries as a result of human activities. To understand their impacts, we considered quantitative and qualitative aspects of these changes; the rate of growth or decline in the releases over time, and total quantities of materials involved, as well as the types of pollutant, the spatial distribution of their key sources of release, environmental partitioning and persistence of the agents, and their effects on ecosystems, humans, and the physical environment.

Figure 26.17 shows the relative annual growth of metal mining and utilization and organic-chemical manufacturing over the past three centuries. For comparison, the relative growth in energy generation is also shown. The choice of a reference year for energy generation and metal production was driven primarily by the availability of historical data and the scope of our research questions. For chemical manufacturing, the reference year represents the actual birth of large-

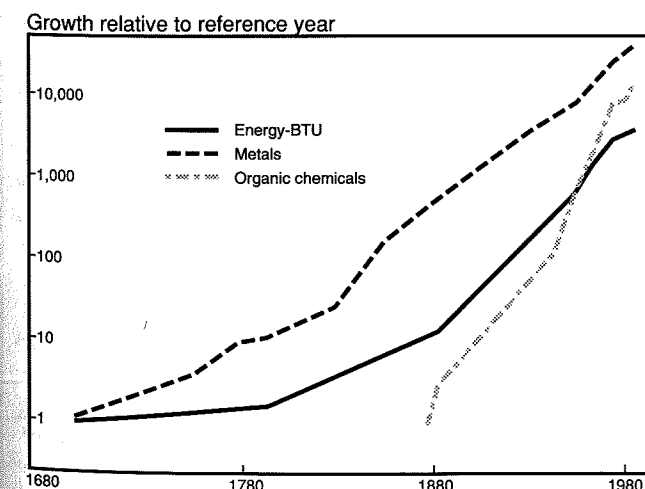


Figure 26.17 Growth trends for major human activities.

scale chemical manufacturing. The logarithmic scale allows us to cover a large range of changes in some activities and to get initial insights into the changes in rates of growth. The graph shows striking differences in the rates of growth of these human activities. Total energy production, measured in units of energy produced, has shown a steady growth before reaching a plateau in the past decade. The chemical industry, the most recent of the activities, has grown exponentially during the postwar years, at a rate greater than that for energy consumption, with some reduction in the rate of growth sometime around 1975. In contrast to energy generation, however, worldwide chemical production continues to increase. Metal mining and processing has exhibited the most striking increase over the past three centuries. This growth rate shows no signs of decline as of 1982.

A more detailed look at the specific pollutants generated by each of the two activities under study shows great diversity within each category. In the case of metals, the list of traditionally mined and fairly well-studied elements such as arsenic, lead, or iron has been supplemented during the past century by a large number of new ones, such as cadmium, manganese, and tungsten, whose rapid growth rate has not diminished the growth rate in the traditional elements. This increased diversity not only contributed to the rapid increase in the total volume of metals processed industrially, but also introduced a host of new questions with regard to the environmental fate and biological effects. To some of these questions no answers are readily available, as the pace of development of new materials and their uses exceeds that of research on environmental partitioning and chemistry of these new elements, as well as their interactions with organisms. Therefore, the assessment of the impacts of this activity is, to a large degree, an extrapolative process. Because of the paucity of specific knowledge about many of the metals, and the size of the task of evaluating them individually, we treat metals as a group. This treatment is justified partly on the grounds of certain common properties of metals such as indestructibility; affinity for organic particles in air, soil, and sediments; solubility in acids; and general toxicity to biological systems.

The variety of pollutants, in terms of physical, biological, and environmental properties, that has been introduced by the organic chemical industry far surpasses that from metal mining and utilization. It is also the most rapidly changing group of agents, with commercial lives of some members only in the order of years. Analogously to the metals, the properties of many of these compounds are poorly understood, so that assessment of their impacts is largely judgmental in nature. Therefore, for the purpose of our analysis, we focused on the classes of organics that we considered important, either because of their large volumes introduced into the environment (volatile organic compounds, pesticides), or their unique environmental properties (persistence, for example, of DDT or PCBs), or both. Our choice was not driven by the degree of inherent toxicity or other harmful properties of the agents, although the magnitude of the releases or the persistence of the agents are clearly related to their cumulative adverse impacts.



Despite the many variables and even more unknowns, the emerging picture of the past, present, and future is a surprisingly coherent one. Overall, we found that each human activity contributes to each of the four combinations of effects described in our initial two-by-two matrix. As expected, the clustering of effects into persistent/global and short-lived/local occurs, but not to an extreme extent. Thus, in addition to the global/persistent effects of DDT, metals, and some halocarbons, and the local/short-lived effects of gaseous air emissions from chemical manufacturing, we also found local/persistent effects of pesticides and solvents on groundwater and metals on soils, as well as global/short-lived effects of ubiquitous gaseous air pollutants. Finally, we found that both activities have multiple types of effects, as vividly illustrated by airborne trace metals and persistent pesticides in soils.

The story for each human activity is different and must be told separately. Our studies of the chemical industry show geographic spread in the distribution of the centers of production from the technologically advanced to the newly industrializing countries, as measured by the production of ethylene. Among the undesirable major by-products of the chemical industry are environmental releases of volatile organic compounds. Ambient air is by far the most affected by these releases, followed by surface waters, soil, and groundwater. Contamination of air with volatile compounds has local as well as global effects. For many short-lived organic compounds, the effect on the local population is that of increased exposure to toxic chemicals and the secondary effects caused by urban smog generated through photochemical reactions with airborne oxidants. Recent trends in growth of both the chemical industry and energy consumption in newly industrializing countries indicate that growing emissions of photoreactive hydrocarbons and oxides may become concentrated in the same geographic locations, thus increasing the likelihood and severity of local air-pollution problems. For the governments, environmental community, and industries in those countries, prevention of these events may be among the most important challenges in the future years.

The experience of industrial countries shows that increased chemical production and the need associated with it for proper disposal of liquid chemical waste carry a high risk of groundwater contamination. Although localized, these effects are highly persistent and become severe in the areas in which reliance on groundwater is high. The incidence of these episodes is declining in the United States, but we expect it to increase in other parts of the world.

The most persistent among the volatile organic compounds, chlorofluorocarbons, have attracted widespread attention because of their threat to the stratospheric ozone. The focus has been on CFC-11 and CFC-12, which contribute the largest fraction of the worldwide production of chlorofluorocarbons. CFC-13 and CFC-22, whose volumes are smaller, are also of concern because of the clear upward trend in their atmospheric concentrations, as is carbon tetrachloride, because of its contribution to the stratospheric ozone depletion. Our research on volatile organic compounds shows that 1,1,1-trichloroethane has a unique place among the members of that class. One of the largest-volume commercial solvents, it

has replaced several chlorinated solvents judged to be environmentally unsafe. With low toxicity, low photochemical reactivity, and a shorter atmospheric life than the fully halogenated ethanes, 1,1,1-trichloroethane appears to present little direct threat to human health or to the ozone layer and is therefore a commercially attractive and versatile agent. Not surprisingly, its increasing production and use have also been accompanied by higher ambient air concentrations and frequent presence in contaminated groundwater, as is well documented in the United States. Given the incomplete state of knowledge of its toxic properties (for example, carcinogenicity) and its environmental fate (for example, its vertical mixing into the stratosphere), 1,1,1-trichloroethane thus stands out among the high-volume volatile organic compounds as an agent whose environmental behavior should be closely monitored in the future.

Among other persistent organics, DDT and PCBs tell a story of ignorance and lack of vision. Highly persistent, both were introduced into the environment in large quantities in the 1950s and 1960s and have since become distributed throughout the globe, being present in virtually all environmental compartments and biota. DDT levels are declining, with a similar trend predicted for PCBs, but the process will take decades. Although the biological effects of DDT are most severe only to some biologic species and those of PCBs are probably generally small, the realization of their uncontrolled environmental distribution following a release has shifted the emphasis to less persistent chemical agents, especially among pesticides. Currently used pesticides indeed have much lower persistence, but their acute toxicity and threat to groundwater are much higher than those of DDT. We therefore expect that groundwater contamination and acute accidental toxicity episodes will increase — once again mostly among rapidly developing countries, in which the growth in their use is high and the knowledge of their properties among the users is low.

The picture we have generated for metal pollution is dramatic but less clear. The extraordinary growth in the volume and variety of metals that have been mined and processed during the past 300 years, combined with direct emissions into ambient air from burning of wood, coal, and petroleum, suggest both local and global environmental impacts; on a local scale, human and nonhuman exposure through ambient air and the locally produced food chain have been fairly well documented; on a global scale, the recycling of metals between environmental compartments and their long residence times in soils and surface waters increase the likelihood of incorporation into crops and aquatic organisms. High levels of numerous metals in the flesh of fish and other seafood along the U.S. coastal and inland waters have been observed during past years. We anticipate that this trend will continue and possibly increase in the future. It is not clear what, if any, fraction of the metal residues in seafood can be attributed to the global cycling phenomenon, and what fraction to local deposition and discharges. Comparison of metal concentrations in seafood from coastal and remote locations would be helpful in addressing the question when such data become available. It will also be instructive to

estimate the total amounts of metals that are released into the ambient air and waters from various production processes and from dissipative consumption. So far, reliable emission figures exist mostly for metals released through combustion of wood and fossil fuels.

Lead is the only metal for which emission reduction has become the focus of intense national and international efforts, albeit mostly in technologically advanced countries. The effects of the phasing out of leaded gasoline in the United States have been gratifying; the average concentration of lead in the blood of the U.S. population has clearly decreased. The decline is slowing down, however, and will eventually reach a plateau, simply because other sources, mostly food, dissipation of consumer products, and existing environmental reservoirs will become the major sources of long-term human exposure to lead. For other metals, ambient air will continue to be a significant pathway of exposure to populations living in the vicinity of metal-processing and energy-generating industries. On a global scale and over long time periods, however, the food chain is likely to be an important pathway of exposure.

Indeed, continuing future exposures to trace metals, globally through food chains and locally through air, merit the serious attention of the international community. Along with ozone depletion due to photoreactive halocarbons and the possible global warming from accumulation of carbon dioxide and other gases, it has the characteristics of a global problem. This is not to say that serious adverse health effects necessarily will occur. The toxicology of metals is complex, unique for each element and for each route of exposure (ingestion versus inhalation, for instance). Adverse effects at low doses are known for only a handful of the 80 elements listed in the periodic table. Among these that are better known, cadmium, lead, and mercury have been shown to produce adverse effects in humans at very low levels of exposure, possibly without a meaningful threshold level. For many others, the paucity of data does not permit defensible conclusions. Complex mutual interactions of metals in organisms, with largely unpredictable combined effects on health, virtually preclude any meaningful assessment of risks from simultaneous exposure to multiple metals. These great uncertainties in the dose-response relationships suggest that, at least on a local scale, minimizing emissions may be the most effective approach to the problem. On a global scale, where the distribution is already wide and certain to persist for a long time, accelerated studies of the toxicity of recently introduced metals and their environmental partitioning are a pressing need.

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## 27

## The Ionizing Radiations

MERRIL EISENBUD

All forms of life have always been exposed to a broad spectrum of naturally occurring radiations, among which are visible light, infrared, ultraviolet, and the ionizing radiations. The latter are distinguished by their ability to disrupt molecular bonds when they interact with matter, and include X-rays, gamma radiation, alpha and beta particles, neutrons, protons, and the cosmic rays, which enter the earth's atmosphere from extraterrestrial sources. Until about one century ago, the only sources of exposure to the ionizing radiations were from the undisturbed natural state. A few exceptions existed, such as uranium oxide as a coloring agent for ceramic glazes, and thorium in gas mantles, but these sources exposed relatively few people, and to only a modest degree.

When radioactivity and X-rays were discovered toward the end of the last century, the situation began to change. Radium was extracted from the earth's crust in small quantities and was used in the practice of medicine. Unfortunately, among the uses for radium were also many misuses, and the first kilogram extracted prior to World War II resulted in death from cancer of more than 100 persons. The misuses of X-rays during the same period probably resulted in a much larger toll of injuries and deaths, mainly among physicians and physicists, but also among patients and technicians. The exact figure is not likely ever to be known.

Until after World War II, relatively few members of the general public were aware of the harmful effects of the ionizing radiations. Such knowledge became more general with the bombings of Hiroshima and Nagasaki in August 1945. The association of nuclear radiation with the bombings of the two cities has left an indelible impression on the people of many nations and has resulted in widespread apprehension of the effects of radioactivity not only in war, but also in peacetime as well.

It is now almost half a century since the discovery of nuclear fission. Uranium, which is a slightly radioactive metal, is extracted from the earth in great quantities to provide fuel for the 1,000 or so nuclear reactors of various kinds that exist today in the world. These reactors produce electricity, provide propulsion for naval vessels and ice breakers, produce plutonium for nuclear and thermonuclear weapons, serve the

research needs of physical and biological scientists, and produce radioactive pharmaceuticals. The infrastructure required for the operation of these reactors and the processing and use of the radioactive materials they produce results in the release of radioactive substances to the environment. The releases ordinarily occur in small quantities, but sometimes in much greater amounts as a result of accidents or abnormal occurrences, and in huge amounts when nuclear weapons are exploded (Eisenbud 1987).

## Effects of Exposure to Ionizing Radiation

As a result of the many decades of international collaboration, more is known about the effects of ionizing radiation than about any of the many other noxious agents that contaminate the environment. It is necessary to begin a discussion of the effects of ionizing radiation exposure with certain dichotomies that include in part the following:

1. whether the source of exposure is external to the body (as in the case of exposure to medical X-rays) or internal (as when radioactive iodine is inhaled or ingested and then deposits in the thyroid);
2. whether the dose is from a relatively massive exposure delivered in a short period of time (less than a few days) or in small bits over a long period of time, which may extend over many years;
3. whether the effects appear soon after exposure ("acute" or "prompt" effects) or are delayed for many months or years ("delayed" or "late" effects).

The effects also should be separated according to whether they are stochastic or nonstochastic. The stochastic effects include cancer and genetic damage, for which it is believed that there are no thresholds and that the probability of occurrence increases as the dose increases, but the severity of the effect is independent of the dose.

The nonstochastic effects are seen at doses above approximately 50 rem and include suppression of bone-marrow function, damage to the gastrointestinal tract, skin burns, cataracts, and temporary sterility in males. These effects occur at doses that are so high as to be experienced in peacetime only as the