NOAA Technical Memorandum NOS OMA 43

An Historical Reconstruction of Major Pollutant Levels in the Hudson-Raritan Basin: 1880-1980

VOLUME III
Chemicals and Other Wastes

Rockville, Maryland
October 1988

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National Ocean Service

Office of Oceanography and Marine Assessment
National Ocean Service
National Oceanic and Atmospheric Administration
U.S. Department of Commerce

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Robert U. Ayers (Principal Investigator)
Leslie W. Ayers
Joel A. Tarr (Consultant)
Rolande C. Widgery (Consultant)

Variflex Corporation
Prepared for Martin-Marietta Environmental Systems (MMES)
Grant #NA 83AA-D-00059
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National Oceanic and Atmospheric Administration (NOAA)

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UNITED STATES DEPARTMENT OF COMMERCE

C. William Verity, Jr.
Secretary

National Oceanic and Atmospheric Administration

William E. Evans
Assistant Secretary and Administrator

National Ocean Service

Thomas Maginnis
Assistant Administrator for Ocean Services and Coastal Zone Management

Coastal and Estuarine Assessment Branch
Ocean Assessments Division
Office of Oceanography and Marine Assessment
National Ocean Service
National Oceanic and Atmospheric Administration
U.S. Department of Commerce
Rockville, Maryland

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Robert U. Ayres (Principal Investigator)
Leslie W. Ayres
Joel A. Tarr (Consultant)
Rolande C. Widgery (Consultant)

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1. Introduction to Volume III

Chapters 2-5 deal with chlorinated aromatic hydrocarbon-based biocides (insecticides, acaricides, fungicides, herbicides and germicides) that have been introduced since World War II. These have become major environmental pollutants due to their persistence (non-biodegradability), tendency to accumulate in the food chain, or because of toxic contaminants and/or breakdown products such as the dioxins. [Carson 62; HEW 69; Hindin 70; OECD 70; Rudd 70; USDA 71a; NAS 75; EPA 76; NJDA 79; OECD 80; Perkins 82] Figure 1-1 shows the major interrelationships among these products.

Chapter 6 is concerned with PCB's, another class of chlorinated aromatic hydrocarbons, manufactured since 1930, that were utilized not for their biocidal properties but because of their physical properties and extraordinary chemical stability. However this, combined with an extreme tendency toward bioconcentration in the fatty tissue of marine organisms and birds, has also created a severe environmental threat in some locations [OECD 73; NRC 80].

Chapter 7 is concerned with a class of non-chlorinated polynuclear aromatic hydrocarbons (PAH's) that occurs naturally in crude oil, coal tar, pitch and asphalt and is created artificially by most combustion processes. These chemicals tend to be both toxic and carcinogenetic. Chapter 8 deals with another subclass of waste hydrocarbons; oils and greases. Chapter 9 deals with the broader category of organic carbon, which is a measure of the tendency of organic material in polluted water to oxidize, measured by Biological Oxygen Demand or BOD, and thus to deprive fish and other higher organisms in the water of oxygen needed to sustain life.

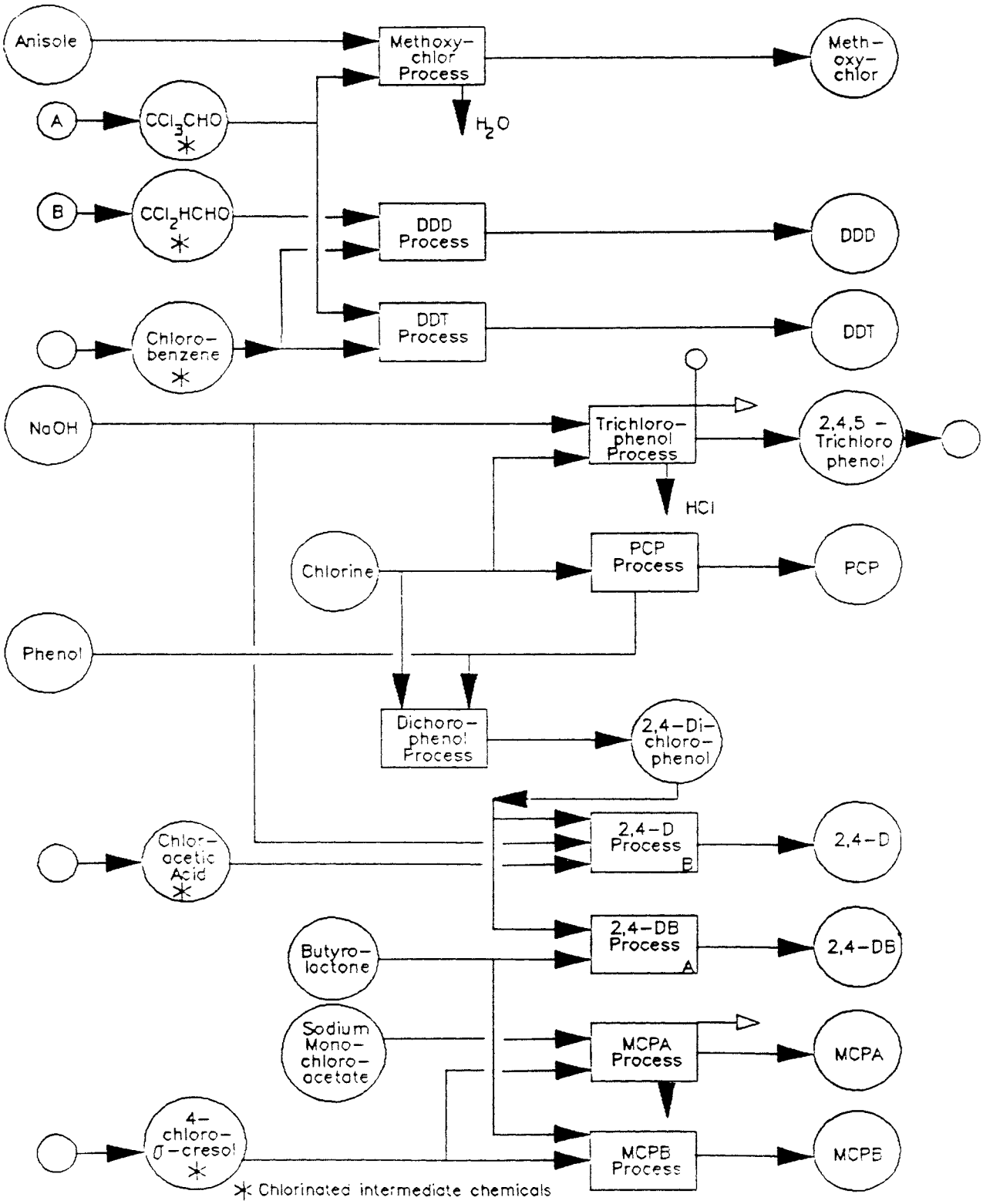
Chapters 10 and 11 deal with other essential components of organic material (called 'nutrients' for this reason) namely, nitrogen (N) and phosphorus (P). Again N and P are not toxic as such, but their presence may encourage the growth of algae and plankton in profusion. The danger is that excessive nutrient availability can lead to over-fertilization of the water (or "eutrophication") and this, in turn, can lead to oxygen depletion and a sudden collapse of the population of living organisms [OECD 70, 74, 77, 80; NRC 78].

Finally, chapter 12 deals with water withdrawals *per se*. It has become clear in recent decades that the turbulence and de-oxygenation associated with most large-scale uses of water for cooling, waste

dilution or other purposes, is physically harmful to spawning fish and some other ecologically important biota.

It should be pointed out here that the pesticide consumption tables presented in chapters 2-4 are all constructed by combining data from a variety of different, incomplete sources. Total domestic pesticide chemical consumption was taken -- where possible -- from the annual report of the US Tariff Commission [USTC annual], or its successor, the International Trade Commission (ITC). Supplementary data is found in [SRI 84]. Agricultural pesticide consumption by crop for certain years (1964, 1971, 1976) comes from the Census of Agriculture [Census 68, 75, 80] and surveys by the US Department of Agriculture [USDA 54, 56,58, 60, 63, 68, 68a, 71, 73] where otherwise noted. More recent surveys have been conducted by EPA's Office of Pesticide Programs [EPA 77a; Carey, Gowen & Wiersman 78; Reese & Kempter 79]. However direct data on non-agricultural usage is almost non-existent. In some cases we can arrive at a total by subtracting USDA agricultural consumption figures from USTC data on domestic sales of a chemical. In other cases, we only have firm data on sales for a whole group of chemicals and this must be allocated among chemicals as well as use categories. Obviously much detective work and not a little guesswork is involved.

FIGURE 1-1: Flow Sheet for DDT & Some Aromatic Chlorinated Hydrocarbon Pesticides



Source: [*Honea & Parsons 77, p. 17*]

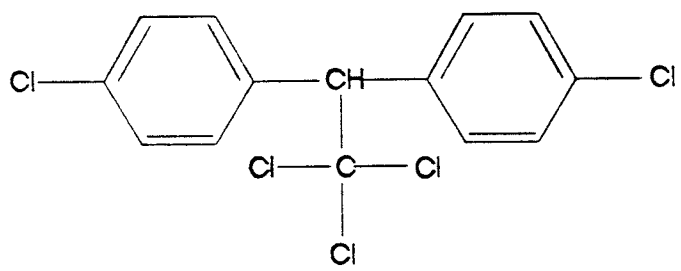
2. Chlorinated Pesticides: DDT and Its Analogs

2.1 DDT

DDT was first synthesized in 1874 by Zeidler, but no great effort was made to find a use for it. It was not until 1939 that it was proven to be a highly effective insecticide by Muller et al at Ciba-Geigy AG in Switzerland. It was licensed by Geigy for production to a number of British and American firms in 1942 and played an important role in WWII.

Physically it is a white amorphous powder, made by reacting monochlorobenzene with chloral in the presence of sulfuric acid. Chemically technical DDT consists of up to 14 separate chemicals. The principal one is the active p,p DDT (Figure 2-1) which usually constitutes from 65-80% of the total; others include ortho, para DDT, 15-21%, DDD 1,1,dichloro 2,2, bis (p-chlorophenyl) ethane which may range up to 4% and small amounts of ortho-ortho DDT and bis (p-chlorophenyl) sulfone [Kirk & Othmar 78]. DDT is not soluble in water, has small solubility in petroleum fractions, but is highly soluble in acetone, lipids, and many chlorinated hydrocarbons. Its formal chemical name and structure are shown in Figure 2-1.

Figure 2-1: DDT Structure



1,1,1-Trichloro-2,2-bis-(p-chlorophenyl) ethane
(DDT)

DDT's low vapor pressure, insolubility in water and resistance to degradation make it very long lasting in use. This was regarded as a favorable characteristic when it was first marketed. Over 10^9 pounds were used in the U.S. alone during the period 1945-1972. Its popularity, persistence, and tendency to accumulate in the body-fat of living organisms from plankton and worms to birds, animals, and humans has led to its being widely distributed throughout the environment. These characteristics also resulted in serious environmental concerns leading, ultimately, to its ban [Carson 62; Graham 70; Dunlap 81]

The acute oral toxicity (LD_{50}) for rats is 113 to 150 mg/kg (ppm) of body weight and the hazardous chronic level is at levels ranging from 113 ppm to 150 ppm (body weight). Comparisons with other chlorinated hydrocarbons are shown in Table 2-1. Although DDT is not immediately toxic in humans, there has been great concern as to the possible long term effects when the average level in human tissues rose to more than 7 ppm. Serious damage to fish and bird populations resulted from concentration from lower to higher trophic levels in the food chain. Since 1972 its use has been prohibited in the U.S. except for essential public health requirements. DDT is produced by the reaction of chloral with monochlorobenzene by the reaction

$$Cl_3CHO + 2C_6H_5Cl \qquad (C_6H_4Cl)_2Cl + CCl_3 + H_20$$

using strong sulfuric acid or oleum as a catalyst. (Chloral is made by chlorination of acetaldehyde or oxychlorination of ethanol). Subsequently the spent acid is drawn off and the organic product is water washed and neutralized. DDT is finally separated from unreacted chlorobenzene by distillation of the latter. A typical process flow chart is shown in Figure 2-2. At least one plant was located in New Jersey.

2.1.1 Production, Exports, Sales 1945-82

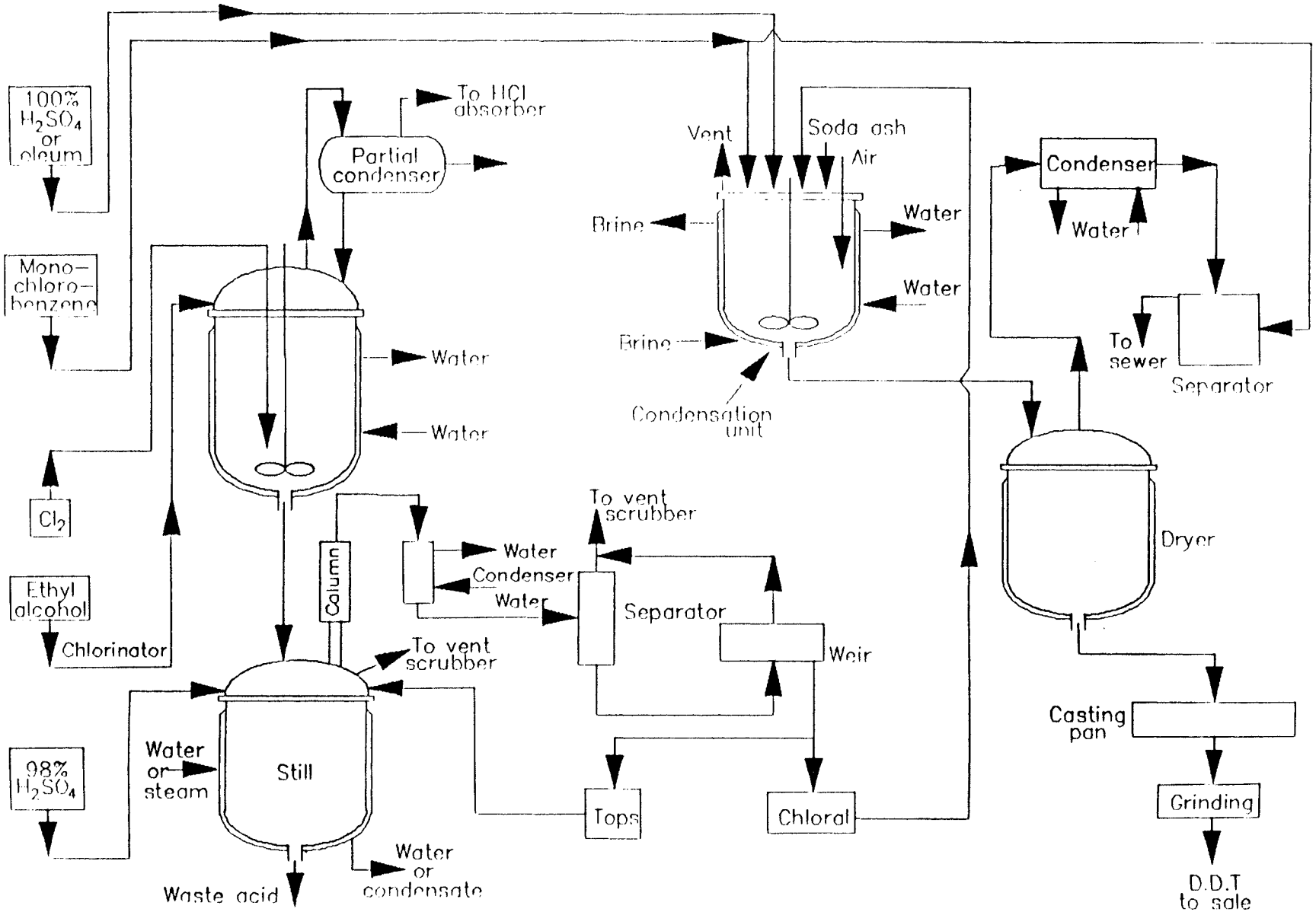
The U.S. Tariff Commission and its successor the U.S. International Trade Commission, have published production and sales data since the chemical began to be produced by more than three U.S. firms. This data is shown in Table 2-2. The series was discontinued in 1972, as some producers ceased operations. As many as 15 chemical companies manufactured DDT under licence at one time or another. Table 2-3 lists major producers. The peak year for output was 1963, when 188 million lbs were produced in the U.S., almost two thirds for export. Production and use declined thereafter, as public awareness of the adverse effects of DDT on the environment grew. The last producer in the U.S., Montrose Chemical Co., closed in 1983. Domestic sales (i.e. consumption) topped out at 78 million lbs in 1959 and declined rather steadily thereafter.

Table 2-1: Toxicity and Health Effects of Chlorinated Hydrocarbon Insecticides

	Acute Oral Rat LD_{50}	Acute Oral Rat LD_{10}	Safe level in diet Rat	Safe level in diet Dog	Comments
		(units=mg/kg)			
Aldrin-Toxaphene Group					
Aldrin	38-67	98-200	0.5	1	Carcinogen in mice & rats
Chlordane	367-515	>200	2.5	na	Carcinogen in mice
Dieldrin	10-46	10-102	0.5	1	Carcinogen; 2 mg/kg is hazard to humans
Endrin	7-45	15			
Heptachlor	147-220	119-320	0.5	4	Carcinogen in mice
Heptachlor Epoxide			0.5	0.5	Carcinogen in mice
Toxaphene	69-91		10	400	Carcinogen in mice
DDT Related					
Chlorobenzilate	729		<50	2564	
DDD (Rhothane)	3400		100	4000	
DDT	113-150		5	400	250 mg/kg is hazard to humans
Dicofol (Kelthane)	809		20-100	300	Under EPA review
Dimite	500				
Methoxychlor	5000-6000				
Ovex	2000		25	200	
Perthane	8170		500	100	
Polychloro					
BHC	125		10	n1	
Lindane	88-125	1000	50	715	

SOURCES: [Rosen & Kraybill 66; Thomson 67; Kirk & Othmer 78; Meister 81]

FIGURE 2-2: Flowchart for DDT Manufacture



Source: Pao & Sittig 73

Table 2-2: U.S. Domestic DDT Production, Consumption and Exports (million lbs)

Year	Production	Domestic Sales	Exports
1945	33.243	31.595	1.648
1946	45.651	43.499	2.152
1947	49.600	36.073	13.527
1948	20.260	30.000	NA
1949	37.904	37.389	NA
1950	67.320	57.638	7.898
1951	97.875	72.686	NA
1952	115.717	70.074	32.288
1953	72.802	62.400	31.410
1954	90.712	45.117	42.743
1955	110.550	61.800	50.968
1956	137.747	75.000	54.821
1957	129.730	71.000	61.069
1958	131.862	66.700	69.523
1959	156.150	78.682	76.369
1960	160.007	70.146	86.611
1961	175.657	64.068	103.696
1962	162.633	67.265	106.940
1963	187.782	61.165	113.757
1964	135.749	50.542	77.178
1965	140.785	52.986	90.414
1966	141.349	46.672	90.914
1967	103.411	40.257	81.828
1968	139.401	32.753	109.148
1969	123.103	30.256	82.078
1970	59.316	25.657	69.550
1971	63.134	18.000	45.134
1972	57.427	22.000	35.424
1973			73.766
1974			58.172
1975			47.278
1976			25.433
1977			NA
1978			20.379
1979			20.000
1980			20.000
1981			12.000
1982			5.000
TOTAL (Million Lbs)	2946.877	1421.420	1537.088

SOURCES: [USTC annual; EPA 75]

2.1.2 Uses

DDT was spectacularly successful at first and was rushed into use for an extremely wide variety of applications. By the year of maximum consumption (1959) it was registered for more than 334 applications. Large amounts were used initially by the U.S. Army in foreign countries for control of

Table 2-3: Major Producers of DDT, 1966-67

	Production (1966)	Capacity (1967)
	millions of lbs.	
Allied Chemical, Marcus Hook, PA[1]	9.1	20
Diamond Shamrock, Houston, TX	15.9	35
Geigy Corporation[2]	20.0	?
Lebanon Chemical, Lebanon, Pa[3]	6.8	15
Montrose Chemical, Torrance, CA[4]	38.6	80
Olin Mathieson, Huntsville, Al	13.6	30
	---	---
	103.9	180

(1) last year of operation 1967
(2) last year of operation 1966 (not reported in 1967)
(3) last year of operation 1978
(4) last year of operation 1982

malaria-carrying mosquitos, body lice, and other carriers of disease. This made the product familiar around the world and export demand increased. As it became available domestically there was substantial use on cotton and tobacco and many other crops, and for home and garden and industrial uses ranging from moth prevention to termite control. A breakdown of DDT use nationally in 1964 and 1971 is shown in Table 2-4.

In the Hudson-Raritan basin the major use of DDT appears to have been on apple orchards. In 1964 DDT was applied at ~50 lbs/acre to orchards in the Hudson-Raritan basin. use on apples was recommended for a wide diversity of pests, including apple flea weevil, apple and thorn skeletonizer, apple maggot, apple red bug, shothole borer, cankerworm, coddling moth, several different cutworms, fall webworm, Japanese beetle, leafhoppers, leaf rollers and tent caterpillars. Because of the variety of pests which infest orchards frequent sprays were required. Almost all of the insecticide accumulated on the soil, either during spraying *per se*, or later as the leaves fell and rain washed the surfaces of the trees.

Other farm use in the Hudson-Raritan basin included that on corn for cutworms, wireworms, corn ear borer and corn root borer. These uses were largely replaced by chlordane and aldrin-dieldrin when those materials became available in the 1950's and the danger of DDT use on forage (due to meat and milk contamination) was realized. On vegetables it was used against thrips, leaf miners, and spittle bugs. In its early years of use livestock and agricultural premises were liberally sprayed -- again, until increasing appreciation of the tendency of DDT to accumulate in the fat of living creatures led to a search for other pesticides.

Table 2-4: U.S. Consumption of DDT in 1964 & 1971

	1964	1971	1964	1971
	1000 lbs.		Percent	
FARM Use	33543	14569	66.37%	80.74%
Crop Use	31835	14324	62.99%	79.38%
Corn	105	4	0.21%	0.02%
Other Grain		147		0.81%
Soybeans	483	197	0.96%	1.09%
Hay(incl. Alfalfa)		1		0.01%
Cotton	23558	13158	46.61%	72.92%
Peanuts		62		0.34%
Tobacco	1187	7	2.35%	0.04%
Citrus		5		0.03%
Potatoes(White)	373	77	0.74%	0.43%
Other Vegetables	1340	330	2.65%	1.83%
Apples	1641		3.25%	
Other Fruits&Nuts	864	16	1.71%	0.09%
Other Field Crops	2284	320	4.52%	1.77%
Livestock	646	245	1.76%	1.36%
Beef Cattle	575	158	1.14%	0.88%
Dairy	26	55	0.05%	0.30%
Other	45	32	0.09%	0.18%
Other Farm Use	1062	0	2.10%	0.00%
FOREST Use	1000	180	1.98%	1.00%
NON-AGRICULTURAL Use	7000	1696	13.85%	9.40%
Nursery	1000	296	1.98%	1.64%
Turf	1000	200	1.98%	1.11%
Home&Garden	5000	1200	9.89%	6.65%
PEST CONTROL	6000	1300	11.87%	7.20%
GOVERNMENTAL Use	3000	300	5.94%	1.66%
GRAND TOTAL	50543	18045	100.00%	100.00%
Northeast % of U.S.	3.14%	2.23%		

A major non-agricultural use of DDT in the Hudson-Raritan region was in the control of gypsy moth infestation. DDT became available for use against the gypsy moth in 1945. Each year following that saw generally an increased use of DDT until it reached a peak of 2,774,417 pounds in 1957 -- almost 4% of all DDT consumed in the U.S. Spraying for this purpose ceased in 1965. Annual levels of use are shown in

Table 2-5: Use of DDT to Curb Gypsy Moth in New York State, 1945-1965

Year	Pounds
1945	335
1946	26234
1947	64914
1948	73320
1949	134370
1950	146200
1951	121648
1952	149750
1953	122652
1954	87742
1955	194376
1956	446302
1957	2774417
1958	2040
1959	894
1960	11262
1961	55112
1962	146008
1963	144058
1964	31500
1965	13486
TOTAL	4746620

Source [Reese et al 72]

Table 2-5 [Reese et al 72]. In Table 2-6 are shown the principal ecosystems in New York and New Jersey. Table 2-7 lists some of the specific pests that have infested northeastern forests in recent years, and recommended treatments. It can be seen that DDT was the standard treatment for several of the major pests at that time (1954).

Table 2-6: New York and New Jersey Forest Land Area by Ecosystem

Type	New York	New Jersey	Total
	Thousand Acres		
All	17,218	1,924	19,142
Maple - Birch	6,659	100	6,759
Elm - Ash Cottonwood	3,147	245	3,392
White/Red Jack Pine	1,764	12	1,776
Fir - Spruce	1,543	0	1,543
Oak - Hickory	1,329	0	1,329
Aspen - Birch	1,176	0	1,176
Oak - Pine	299	184	483
Loblolly Shortleaf	0	482	482
Non stocked	1,301	61	1,362

Source: [USDA 81]

Table 2-7: Recommended Use of Insecticides in Forests (1954)

Pest	Recommended Application Per Acre		
Juniper Webworm	2 lb	50%	DDT
Aphids	1 lb	25%	Lindane
		100%	BHC
Early leaf feeders	2 lb	50%	DDT
Pine sawflies	2 lb	50%	DDT
Birch leaf miner	1 lb	25%	Lindane
Elm leaf miner	1 lb	25%	Lindane
Lace bugs	2 lb	50%	DDT
	1 lb	25%	Lindane

Source: [Cornell 67]

While other programs have not been on the scale of the attempts to fight the gypsy moth, Forest Service information suggests that in the period 1945-1966 a total of about 2.0 million pounds was applied to forest areas in the Hudson-Raritan basin. Most of this was ultimately deposited on the forest floor. Losses by processes of weathering, wind erosion and runoff have been very slow. At some locations, high proportions of the amount originally sprayed have been found years afterwards. While some research indicates that there is an inverse ratio of persistence to humus in the soil, this appears to correlate better for open fields than it does for northern forests.

In addition to pests which themselves damage trees, other insects host tree-damaging diseases such as the Dutch elm disease, the alternate host of which is the elm bark beetle. Heavy use of DDT for control of these beetles, particularly on ornamental shade trees, occurred in the Hudson-Raritan basin, much of it within towns. Since not all of this was not coordinated by the forest service or the Department of Agriculture, it is difficult to obtain specific data on the extent of use.

In August 1969 DDT usage was substantially reduced in the USDA cooperative Federal-State pest control program. In December of that year the Secretary of Agriculture cancelled all DDT use permits for house and garden pests, shade tree pests, pests in aquatic areas and tobacco pests. These prohibited uses accounted for about 14 million pounds (35%) of all DDT used annually in the U.S. at that time. All remaining uses found to be unessential were to be terminated by December 30, 1970. use in NY state was banned by the state after December 30, 1970.

A major change in regulatory authority occurred on December 2, 1970 when the federal regulation of pesticides was transferred to the Environmental Protection Agency. In January 1971 the EPA issued notices of intent to cancel all remaining Federal registrations of products containing DDT -- principally affecting its use on cotton, citrus and certain vegetables. On June 14 of 1972 the Administrator announced the final cancellation of all uses (except public health emergencies). The ban went into effect January 1, 1973.

Since the outright ban, only two exceptions have been granted; one for the control of the pea weevil and the other for the control of the Douglas fir tussock moth. Since both of these were in the far West they did not affect the Hudson-Raritan basin.

2.1.3 Non-Agricultural Uses

When DDT became generally available in the 1940's because of its broad effectiveness, low price and apparent safety to humans and warm blooded animals it was used in a great many non-agricultural applications. DDT was included in household sprays for flies and mosquitos, in sprays for mothproofing of clothing, for cockroaches, ants, carpet beetles, silverfish and other pests found in the home. For garden use it was recommended and made available in a variety of dusts and sprays for use in the control of crickets, beetles, caterpillars, leaf miners, mosquitos, millipedes, powderpost beetles, silverfish and firebrats, weevils such as the strawberry root weevil, wasps and hornets. For control of lawn pests DDT was found to be less effective than chlordane. By the late 1960's DDT was only recommended for lawn and garden use to control sod webworms and cutworms.

Because of the great variety of uses by households, no meaningful data can be derived from USDA recommendations as could be done for farm related uses. We must therefore rely on the findings of household surveys. Total pesticide usage by household (excluding warfarin, a rat poison) was estimated by EPA to be about .838 pounds per household in 1976-77 [EPA 80]. DDT constituted at least half that used in the period 1947 to 1960, declining to about 1/4 of the total by the time DDT was cancelled in 1972. Since the Hudson-Raritan basin is in a temperate zone, per capita pesticide use is well below the national average. That average is distorted by the very high use in the south and southwest where major infestations are more frequent and insect activity is experienced for a much longer portion of the year.

An important factor in the non agricultural use of insecticides and rodenticides are the commercial pest control operations (hereafter abbreviated as PCO'S). In the study on household use cited above [EPA 80] PCO'S were used by 23.8% of the households in the EPA Region 2 (NY, NJ and PA) and, of these, 14.2% required termite control. This was probably the largest PCO use for DDT in the 1950's. If we assume the typical house treated in the area has a 1,050 square foot first floor or basement the perimeter would be about 130 feet. A standard formulation of DDT as a soil poison called for an application of 4 gallons per 10 foot section of a 5% DDT solution. Such a solution requires 1/3 lb DDT per gallon [Snyder 35] or approximately 17 pounds per average house treated. Since chlordane was also in widespread use throughout the period we can assume that DDT was used on the average in no more than half the cases treated.

Another large demand for termite protection comes from commercial and industrial customers whose premises are on the average much larger. While in newer buildings steel, concrete, brick and other inorganic materials are used to the virtual exclusion of wood, the Hudson-Raritan basin still has large numbers of stores, warehouses, restaurants etc. that are subject to termite attack.

PCO's are also called on to control cockroaches, ants, flies, clothes moths, carpet beetles and other pests. DDT was often used to combat these pests, either in sprays of 5% DDT or dusts of 10%, applied to closets, drawers and carpets. Alternatives included 2% chlordane, 0.5% lindane or 0.5% dieldrin in spray, or dust of twice these concentrations.

PCO's and the professional maintenance staffs at parks, golf clubs and other institutions in country locations such as office headquarters, college campuses, hospitals and sanitaria take care of considerable acreages of turf. As in the case of home lawns there was some application of DDT for control of grubs, ants, etc. However, the advantages of chlordane (more effective) and later products such as carbaryl meant that this use of DDT was phased out in the late 1950's and early 1960's.

The non-agricultural category of useage is one in which few data are available and for which the outer magnitudes must be obtained by subtracting agricultural use from total domestic disappearance. Within this framework a total US figure may be obtained and the use rate for the Hudson-Raritan basin can be related to it on terms of population. Correction of these percentages by figures representing the

adjustment for the cooler summers and longer winters provides a probable total for the basin. Within this framework estimated household and PCO use patterns make it possible to estimate amounts used in each category.

2.2 DDT Analogs

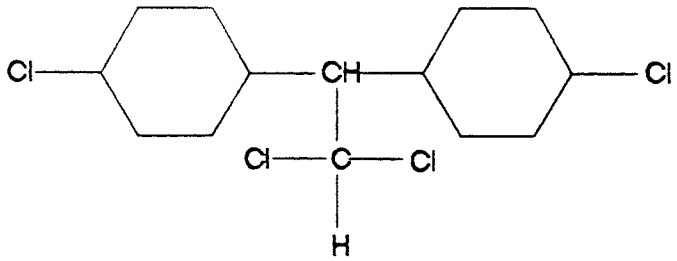
While the "technical" DDT described above was the primary commercial form some other analogs have been important. The use of these, (a few of which are chemically identical to degradation products of DDT) has led to their being found with DDT and other degradation products in residues in mammals, birds, fish etc. and in soil and similar sediments. We therefore briefly review the major analogs below so that the part they play in contributing to DDT-type residues can be understood.

While earlier studies simply measured the DDT found in the environment, recent efforts attempt to measure DDT, DDE and TDE -- and in some cases to differentiate between the para-para and ortho-para isomers of each. The reason for this last concern is that the ortho-para isomer is said to be 5 to 9 times less toxic, in tests with rats, than the pp isomers [Dale et al 66].

2.2.1 TDE

Trade names of TDE included DDD and Rhothane. The chemical structure is shown in Figure 2-3.

Figure 2-3: TDE Structure



1,1-Dichloro-2,2-bis-(p-chlorophenyl) ethane
(TDE)

This product was developed in 1944 and made thereafter by Rohm and Haas (Bristol PA). It is reported to have been only 1/5 to 1/10 as toxic to mammals as DDT with an oral LD_{50} in rats of 3400 mg/kg. Like DDT it was both a stomach poison and a contact insecticide with relatively long-lasting residual effects.

In the 1950's it appears to have been used primarily on orchards (apples, pears, cherries etc.) and vegetables (cabbage, cauliflower etc.). While generally less effective than DDT, it is superior for black fly larvae, leaf rollers and tomato hornworms [Chisholm, Koblitsky & Westlake 62]. Because there was only one producer, no production data are available. In the early 1960's the volume of TDE consumed was about 10% that of DDT used. The largest use was to control tobacco hornworms. Lesser amounts were applied on vegetables and fruits. It appears insect resistance to TDE developed in similar proportions as it did to DDT. As other insecticides became available production and use ceased in the U.S. in the early 1970's. National consumption of TDE in 1964 and 1971 is shown in Table 2-8.

2.2.2 Perthane (Ethylan)

Perthane is known as the diethyl analog of DDT. Among the chief advantages of Perthane was its low oral toxicity and biodegradability which led to its use where very low acute and chronic toxicities were essential. Perthane was also produced by Rohm and Haas. The chemical structure is shown in Figure 2-4.

DDE was specifically used for vegetable pest (e.g. cabbage looper) control and for control of pear psylla. Another use was in formulations for the control of moths and carpet beetles by the dry cleaning and textile industries, as a substitute for DDT. DDE does not seem to have been found in residues because of its biodegradability, nor is it a degradation product of DDT.

2.2.3 Methoxychlor

Trade names included Methoxcide, Orthotox, Chemform, Marlate and Moxie. The chemical structure is shown in Figure 2-5.

Like the other analogs Methoxychlor is a chlorinated hydrocarbon insecticide of long residual activity. Unfortunately resistance to DDT developed by insects carries over to methoxychlor. Advantages are much lower toxicity to mammals (rat oral LD_{50} is 6000mg/kg), as well as a rapid knockdown of many

Table 2-8: U.S. Consumption of TDE in 1964 and 1971

	1964	1971	1964	1971
	Thousand Pounds		Percent	
FARM Use	3386	244	100.00%	100.00%
Crop Use	3374	244	99.65%	95.54%
Corn	5		0.15%	0.11%
	Other Grain			
Soybeans		1		3.55%
	Hay(incl. Alfalfa)			
Cotton	191		5.64%	3.78%
	Sorghum			
	Peanuts			
Tobacco	2331	162	68.84%	71.28%
	Citrus			
Potatoes(White)				1.83%
Other Vegetables	552	77	16.30%	8.47%
Apples	148	1	4.37%	3.20%
Other Fruits&Nuts	147	3	4.34%	3.32%
Livestock	3		0.09%	4.46%
Other Farm Use	9		0.27%	
GRAND TOTAL	3386	844		

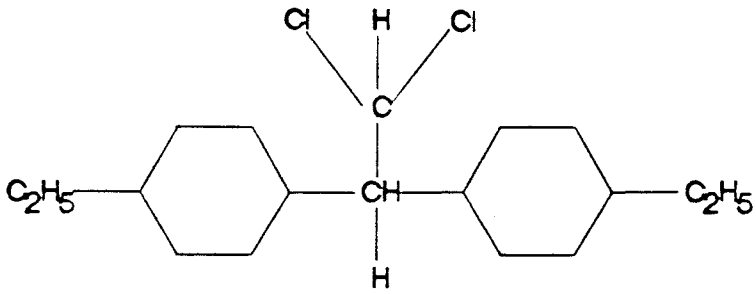
SOURCE: [USDA 71]

insects. In the bodies of mammals the molecule is degraded to phenols which can be eliminated, thus it does not bioaccumulate as do DDT or TDE. For this reason it has continued to be used in small quantities on alfalfa, citrus, vegetables, and dairy and beef cattle.

2.2.4 Dicofol

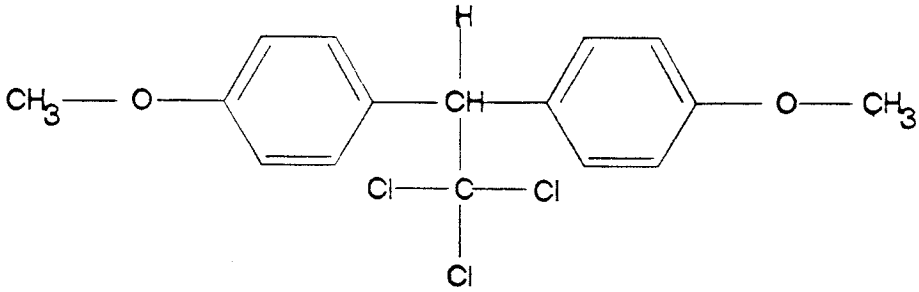
Dicofol (also known as Kelthane) is an important analog of DDT and is manufactured from it. Unlike the insecticidal analogs previously reviewed it is an acaricide (i.e. effective against arachnids) and not toxic to insects. Acaricides are used in the control of mites and ticks. These pests increased in importance as the use of DDT reduced the natural predators that had previously controlled mites on apple and other fruit crops. In addition to its production and use as an acaricide Dicofol is released into the environment as a DDT metabolite, e.g. in excretions from Drosophila flies and German cockroaches. Its structure is shown in Figure 2-6.

Figure 2-4: Perthane Structure



1,1-Dichloro-2,2-bis-(p-ethyl phenyl) ethane
(Perthane)

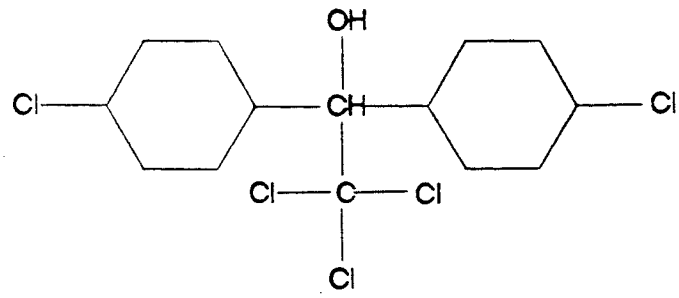
Figure 2-5: Methoxychlor Structure



2,2-bis-(Methoxyphenyl)-1,1,1-trichlorethane
(Methoxychlor)

Currently the EPA is investigating Dicofol because, since it is made from DDT, it is said to contain

Figure 2-6: Dicofol Structure



4,4'-Dichloro-alpha-(trichloromethyl) benzhydrol
(Dicofol)

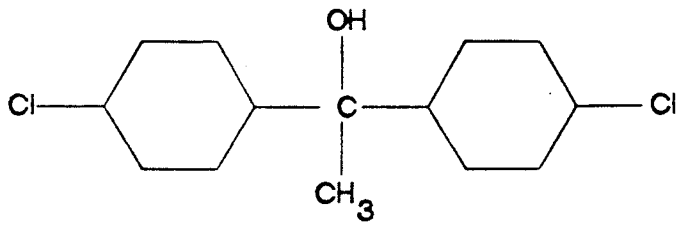
about 10% DDT in the commercial product. While it does not appear to degrade directly to DDT (which would be an endothermic reaction) there is concern because it can degrade to 4,4-dichlorodibenzophenone (DPC), a pathway in common with that of DDT [Walsh & Hites 79].

2.2.5 Other DDT Analogs

Two other DDT analogs that are also acaricides but not insecticides are DMC (sold under the trade name Dimite) and Chlorobenzilate. Chemical structures are shown in Figures 2-7 and 2-8.

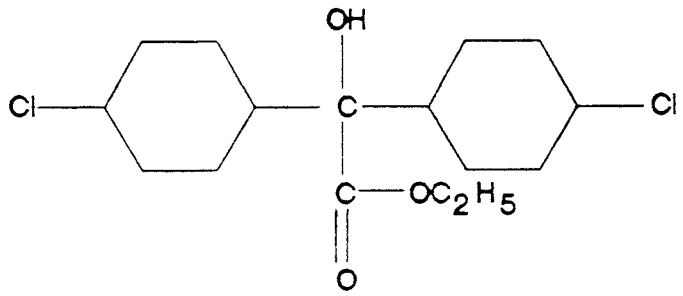
Dimite has the advantage of being effective against both eggs and active stages of mites. It was also used to reduce resistance of houseflies to DDT. The oral toxicity of DMC and chlorobenzilate to rats is low: respectively 926-1391 mg/kg and 3100-4850 mg/kg. There is some evidence that chlorobenzilate is persistant in the field. Because of the relatively small quantities of acaricides used (compared to insecticides) they are statistically less well reported. There have not been many studies of the impact of acaricides on wild life or the food chain. It is probably only in apple orchards, where they have been used regularly for years, that they may have affected readings of DDT residues.

Figure 2-7: DMC Structure



4,4'-Dichloro-alpha-methylbenzhydrol
(DMC)

Figure 2-8: Chlorobenzilate Structure



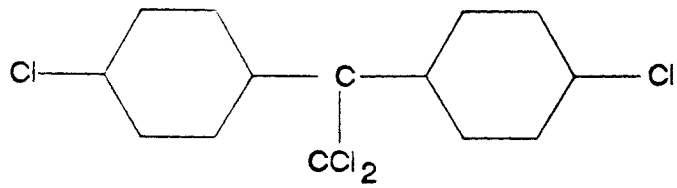
Ethyl-4,4'-dichlorobenzilate
(Chlorobenzilate)

2.3 Degradation Products of DDT

Although, as will be discussed later, varying amounts of DDT may be lost by drift, volatility, wind erosion and removal with crop, a large proportion lands on the soil and becomes mixed with the top layers down to about 6". Because of microbial action in most soils there is a slow degradation of the DDT molecule to a variety of metabolites. Among the more important products so formed is DDE. Its structure

is shown in Figure 2-9. It can be produced chemically from DDT by reaction with an alcoholic alkali, catalyzed by iron, aluminum or chromium salts, in which dehydrochlorination takes place.

Figure 2-9: DDE Structure



Dichlorodiphenyldichloroethane
(DDE)

2.3.1 TDE

Another degradation product is TDE (DDD) the same as the commercial product discussed earlier. It is produced *in vivo* by reductive dechlorination of DDT -- and may in turn be further dechlorinated to DDA, 4,4'dichlorodiphenylacetic acid. In humans and animals total DDT, DDD and DDE were found to have reached an average of 12 ppm in 1970 but have since fallen below 7 ppm. A result of anerobic degradation, under either flooded or *in vivo* conditions, is DDCN (4,4'dichloro diphenylacetonitrile).

2.4 Persistence in Soil

The persistance of DDT in soil has been proven in many studies. The rate of disappearance is difficult to predict, however, since many factors can affect the nature, rate and extent of its degradation [Spencer 67]. Such factors include:

Rate of application
rates varied from 1 to 50 pounds/acre.

Mode of application
surface spray or mixtures with soil.

Soil type sand, gravelly loam, mulch etc.

Soil fertility
percent organic matter.

Type of formulation
wettable powders, dusts.

Topography
well drained slopes or poorly drained level areas.

Climate conditions
average temperature, rainfall etc.

Cropping practices
removal of entire crop or only fruit.

Soil ph

As a result of variation among these factors the half-life may vary from a few years to decades .

Since DDT and its major metabolites DDD (which is also highly persistent), and DDE are strongly absorbed by and adhere to soil particles they tend to remain in place in the soil. The insolubility of these chemicals in water means that very little is dissolved in the water that passes through the soil. But where soil surfaces are disturbed and surface run-off carries off soil particles, these particles carry the attached metabolites with them into the lakes and river systems where they continue to degrade slowly, or are taken up in the food chain [Faust 71]. Hence, the less disturbed the soil surface the greater the apparent persistence of the DDT and its degradation products.

A study of a Maine forest treated for spruce budworm control is reported to have shown no significant decline of DDT after a nine year period [EPA 71] and an Oregon orchard still had 40% of the original amount applied after twenty years (ref?). A rough average of various measurements in turf suggests the following survival percentages: 92% after 2 years; 43% afters 4 years; 36% after 6 years and 29% after 7 years. Kuhr, Davis and Taschenberg found that even after twenty four years some 22% of DDT and its metabolites (27% present as DDE) could be recovered [Kuhr, Davis & Taschenberg 72]. Evidently there is some slowing of the disappearance rate as time goes on. Another study, by Fleming and Maines [Terriere et al 65] is also of interest. Briefly stated, the study showed that in two thirds of 84 mineral soils tested in the northeast about half of the DDT remained after eight years and in more than nine tenths a 25% or greater residue remained. While there was some tendency to show greater residues in areas of less organic matter, the main differences were between types of soil, with the highest persistence being in sandy soil.

In a study made in 1973 Kuhr, this time collaborating with David and Bourke, specifically studied the DDT residues of New York apple orchards. They estimated that the 72,000 acres of apple orchards in New York State had been typically sprayed with 250-400 lbs/acre over the 1947-1960 period [Kuhr, Davis & Bourke 74]. They found in surveys made in 1972 that all samples contained measurable amounts of DDT and DDE and many also contained DDD. The total load of DDT, DDE and DDD varied from a high of 258.8 lbs/acre to a low of 21.8 lbs/acre under the trees and a high of 78.5 lbs/acre to a low of 7.3 lbs/acre between the rows of trees.

Since no accurate record of the spray programs had been made, there was no way in which the percent surviving could be determined. We estimate that, assuming twice the area under the trees as between the rows, all tests would give an average of 110 lbs/acre remaining in the soil in 1972, or 34% of the estimated average 325 lbs/acre applied originally. Assuming 325 lbs/acre and 72,000 acres implies about 23.4 million pounds applied since 1947. Assuming further that loss by drift, volatilization, removal with crop and weathering and wind erosion reduced the actual amount reaching the soil by 25 lbs/acre, we have a reduction from 300 to 110 lbs/acre by 1972. Since the average time this had been on the ground would have been 16 years it is possible to derive a decay curve from this data, showing a half life of approximately 12 years. On this basis we find the average loading/acre to be

Year	1956	1968	1980	1992
Pounds	300	150	75	37.5

Note that the implied disappearance rate for orchards is slower than that for plowed fields or turf.

Soil monitoring programs since the end of DDT application tend to find much lower levels in croplands than in orchards or forests [e.g. Fleming & Maines 53; Gau & Petrie 79]. Part of this is due to wind and rain erosion carrying off soil particles from freshly plowed fields and part is also due to the more rapid and complete weathering as soil is exposed to the sun's heat and light each time the field is plowed or harrowed.

DDT tends to vaporize very slowly. The rate increases with temperature and exposure. However, pp-DDE volatilizes more rapidly. Volatility varies with temperature, type of application, surface exposed and extent of absorption on substrate[Ware, Cahill & Estesen 75]. It appears that volatilization from the soil does not account for more than 5%-10% on the average, though as much as 40% has been lost in some cases due to high soil temperatures.

DDT in runoff may arise from drift due to aerial spraying. A greater amount is washed from plants (and non-absorbent surfaces like city streets) by rain. But the major source of DDT in runoff is the adsorption of DDT on soil particles which are loosened and carried off by surface erosion. This is the principal route by which lakes and streams can become contaminated [EPA 75]. [Bradley, Sheets & Jackson 72] found that over a six month period some 2.83% of the DDT applied to an experimental plot (cotton) was carried away in runoff waters and that 96% of this was in association with the sediment fraction [Dale et al 66]. The amount eroded undoubtedly varies widely with the extent to which the soil is disturbed, the type of soil, the slope of the land, land cover such as leaves or grass and the rate of rainfall. Since the major application in the Hudson-Raritan basin appear to have been in orchards and forests (in which the soil is relatively undisturbed) it seems more likely that the runoff component of loss would not be more than about 2%-4% on the average of the total DDT applied.

3. Chlorinated Pesticides: Benzene Hexachloride (BHC), Lindane, & Hexachlorobenzene (HCB)

3.1 BHC

Benzene hexachloride has been used as a pesticide since 1942 when production was started in both France and England. BHC ($C_6H_6Cl_6$) is made by a direct chlorination of benzene, catalyzed by UV light. It consists of several isomers, of which by far the most important is the active gamma isomer, and four almost completely inactive isomers. In addition to these there is usually about 4% of heptachlorocyclohexane and a trace of octachlorocyclohexane, neither of which show insecticidal activity.

Physically BHC is a greyish or brownish solid, amorphous in character, with a melting point of 65°C. It has a characterisic odor and a phytotoxicity that results in an off-flavor in many fruits and vegetables. In higher concentrations it can retard germination of seeds.

Initially the active crude product was widely used. However, it later became apparent that the gamma-isomer was actually the only toxic component. Oronite (later Ortho) Division of Standard Oil of California (later Chevron) began in 1942 to separate this isomer and gave it the name lindane. Later Hooker Chemical Company (Now a division of Occidental Petroleum) built a plant at Niagara Falls, NY. The process consists of contacting the crude BHC with acetic acid or methyl alcohol. The alpha and beta isomers are nearly insoluble in these liquids; thus the gamma concentration is more than doubled. A fractional crystallization step is used to remove the remaining alpha and beta isomers. Lindane became the preferred form of BHC in the U.S. because of its higher concentration and the fact that it contributed less undesirable flavor to the crops on which it was used, but BHC continued to be used on cotton and for other crops not affected by 'off flavor'.

During periods when there were as many as six companies producing BHC, production data was available (See Table 3-1). Lindane, which was only produced by two companies (Chevron and Hooker), was included with BHC to avoid disclosure of individual company operations. However, as other companies dropped out of BHC production leaving only Hooker, the ITC stopped reporting data for either product. Sales data were reported until 1967 by which time the other producers presumably had sold their inventories and withdrawn from the market. No production took place in the Hudson-Raritan basin.

Table 3-1: Production of Benzene Hexachloride and Lindane (1000 lbs.)

Year	Production	Sales	Exports
1947	8197	5042	
1948	15554	11991	
1949	27937	20651	
1950	76698	67773	
1951	116988	71223	
1952	85090	65045	
1953	57363	60934	
1954	76934	57339	
1955	56051	69491	
1956	84599	70988	2286
1957	39559	41316	4234
1958	30797	32602	3411
1959	27574	30036	1918
1960	37444	30664	1538
1961	25080	23221	2427
1962	23033	12400	
1963	6778	9819	
1964		11765	
1965		6948	
1966		8522	
1967		6042	

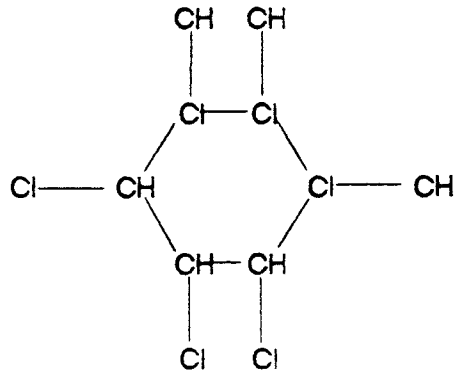
3.2 Lindane

Lindane, also called by several trade names such as Isoto, Gamma, BHC, Lindust, etc. is a potent chlorinated insecticide. Its structure is shown in Figure.3-1.

The commercial product must contain at least 99% of the gamma isomer of Benzene Hexachloride. Physically it is prepared in clear crystalline form. It is sold in a variety of formulations including 100% crystalline, wettable powders at 25%-90%, spray liquids of 1.7 pounds per gallon, dusts of 1-3%, smears at around 3% and aerosols. Lindane is compatible with a variety of other insecticides and is sold in mixtures with malathion, toxaphene, pyrethrins and others.

Since there was no known production in the Hudson-Raritan basin, no waste products from lindane manufacture as such entered the basin directly. However many chemical processes include the chlorination of benzene and it is possible that benzene hexachlorides, including the gamma isomer, sometimes occur in their waste streams. [JRB 79]

Figure 3-1: Lindane Structure



gamma-1,2,3,4,5,6-Hexachlorocyclohexane
(Lindane)

3.3 Uses of BHC Lindane

As both a stomach and contact poison, BHC-lindane has been used to combat a wide variety of pests of many different plants. One major crop, cotton, has been particularly subject to heavy amounts of BHC spray (since the problem of off-flavor was not of concern). Other crops on which BHC-lindane were widely used of little significance to the area under study were tobacco, citrus and peanuts. (See Table 3-2). BHC has also been a potent weapon against grasshoppers, which have been a major pest in the Midwest and Plains States.

BHC-lindane was used for control of aphids, thrips, lygus bugs, spittlebugs, ants wireworms, and many other pests affecting vegetables at rates from 1/4 lb to 4 lbs/acre depending on the type of infestation and the resistance of the pests. However, BHC often caused an 'off flavor' which particularly affected root crops and so the pure gamma isomer (lindane) was preferred for vegetable crops. Its use on corn and other grains was limited by the desire not to contaminate forage usually made from grain plants.

Table 3-2: U.S. Consumption of BHC (Benzene Hexachloride) in 1964 and 1966

	1964 1000 lbs	1966 1000 lbs	1964 Percent	1966 Percent
FARM Use	1315	576	64.91%	44.72%
Crop Use	955	283	47.14%	21.97%
Corn	6		0.30%	
Other Grain	21	44	1.04%	3.42%
Cotton	540	163	26.65%	12.66%
Tobacco	75	2	3.70%	0.16%
Citrus		38		2.95%
Other Vegetables	133	17	6.56%	1.32%
Apples	137		6.76%	
Other Fruits&Nuts	43		2.12%	
Other Field Crops		19		1.48%
Livestock	360	293	17.77%	22.75%
Beef Cattle	186	130	9.18%	10.09%
Dairy	19	24	0.94%	1.86%
Other	155	139	7.65%	10.79%
NON-AGRICULTURAL Use	711	712	35.09%	55.28%
Nursery	11	12	0.54%	0.93%
Home&Garden	200	200	9.87%	15.53%
Pest Control	500	500	24.68%	38.82%
GRAND TOTAL	2026	1288		
U.S. SALES	11765	8522		

In orchards BHC and Lindane were used primarily against aphids. USDA recommendations 1961 set their use at 1/4 pound per 100 gallons of spray for apple, apple grain, rosy apple, and wooly apple aphids. It was also used on the trunks of fruit trees to combat bark beetles.

Lacking the persistence of DDT, BHC -- and more particularly lindane -- became an important pesticide in the care of livestock, particularly beef cattle and other non dairy animals. A smaller amount was used around dairy barns for fly and mosquito control, particularly where resistance to DDT had developed.

There were a number of applications of lindane in forestry. One use for lindane in New York State in 1959 was its application at a rate of 0.5 lb/tree for the control of white pine weevil. Other occasional forest uses include the control of leaf miners and lace bugs and other sucking and chewing insects.

3.3.1 Non Agricultural Uses

The higher volatility and the lower persistence of BHC-lindane than DDT, dieldrin, chlordane etc. have led to its different use pattern. In some cases, however, it was recommended as a possible alternate to traditional materials. In termite control, for example, it was promoted by some companies but appears to have been relatively little used. Both BHC and Lindane were included as acceptable soil poisons to use for termite protection in the FHA Minimum Property Standards for termite protection -- with a specification of 0.8% active gamma-BHC in oil solution or water emulsion [Eichers, Andrilenas & Anderson 78].

A somewhat controversial aspect of lindane use was its formulation in a variety of household products in the 1950's to provide insect protection. Typical of these were floor wax, dog shampoos etc., to protect against flies, fleas, etc., particularly as these developed resistance to DDT. It was not long, however, before they in turn became resistant to BHC-lindane.

3.3.2 Degradation

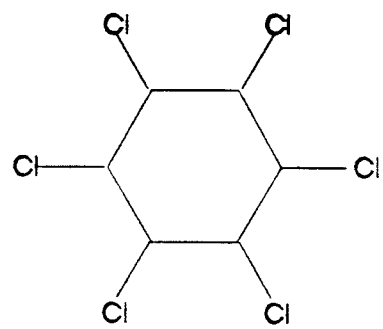
Yule et al [Yule, Chiga & Morley 67] reported that lindane decomposed in soil to PCCH (gamma 1,3,4,5,6,pentachlorocyclohexane). The vapor pressure for PCCH is much higher than that of lindane -- ranging from 10 times at 20°C to 22 times at 40°C. In the field with variable temperature conditions probably two thirds to three fourths of the applied lindane was volatilized and lost as PCCH [Cliath & Spencer 72].

This route for the volatilization of lindane and its principal metabolite probably account for the fact that residues in the soil in crop areas are minimal and found in only a few test sites. In a soils monitoring study in 1970 [EPA 75] a summary table of chlorinated hydrocarbon residues in cropland soils at all sites shows that of 1,506 analyses in 35 states lindane was detected at only 6 sites or 0.4% of sites tested and residues detected ranged from <0.01 to 0.15 ppm, with an arithmetic mean of <0.01 [Tashiro, Bourke & Gibbs 80]. A similar study for 1971 appears to have found no trace of lindane [Carey et al 78].

3.4 Hexachlorobenzene

Hexachlorobenzene (HCB) is chemically perchlorobenzene. The chemical formula is C_6Cl_6, differing from BHC (which has been manufactured in much larger quantities) in having no hydrogen. Its structure is shown in Figure 3-2.

Figure 3-2: HCB Structure



Physically it is a clear crystalline material with a melting point of 227°C and boiling point 326°C. It sublimes readily. It is chemically stable. It is nearly insoluble in water but soluble in alcohol and lipids. For this reason it tends to accumulate in fatty tissues of animals that ingest the material [EPA 73].

During the 1950's HCB was produced as a fungicide by Montrose Chemical Co. but low demand and the general suspicion of the polychlorinated benzenes led to a decision by the manufacturer to terminate production in the U.S. In recent years it is or has also been produced by several other firms, notably Dover Chemical Co., ICC Industries, Dow Chemical Co., Stauffer Chemical Co., Rhodia, Inc. and Hummel Chemical Co. The latter is located in South Plainfield, NJ. (Raritan R. basin). The product was also manufactured overseas by BP: Compania Quimica S.A. in Argentina.

In the U.S. HCB (Trade names: No Bunt, HCB, Antiaru) has been used as a fungicide to protect seed of wheat, oats, barley and rye against seed borne diseases such as bunt, smuts, seed decay and seedling blight. It was sold in combination with Maneb under the trade name "GRANOX Flowable" by the Chipman Chemical Co. for similar purposes. HCB was found to be a major impurity in at least two widely used pesticides, dimethyl tetrachloroterephthalate (dacthal) and pentachloronitrobenzene (PCNB). At one time, HCB was also used as an intermediate in the manufacture of the widely used wood preserver, pentachlorophenol.

Although there have been several producers at times, volumes were not published by the U.S. Tariff Commission and (if imported) it was not imported in large enough quantities to be reported separately in the import statistics. Two production estimates exist: the largest is 2700 metric tons for 1977 (See Table 3-3).

Since HCB does not 'surface' in any of the reports of farm chemical use since 1964 it must be presumed to have been used in very small volume. use as a seed treatment is known to have been concentrated in Washington, Oregon and California in the early 1970's. It was probably not been used to a significant degree in the Hudson-Raritan basin. This would tend to be confirmed by the fact that it is not identified as a soil residue problem in the soil monitoring studies covering that area.

HCB is also produced inadvertently as a major contaminant in the manufacture of chlorine and certain chlorinated chemicals, notably carbon tetrachloride, perchloroethylene, trichloroethylene, and dacthal. As such, it is a constituent of some process waste streams. A summary of 1977 HCB production is given in Table 3-3. This is the most likely source of its presence in the Hudson River.

Table 3-3: Estimated Production of HCB, 1972 & Implied Emission Coefficients

	Production (1000 metric tons)		Emission Coefficent (ppm)	
	High	Low	High	Low
Production for Use	2700 (1977)	1500 (1975)		
Contaminant of Perchlorethylene	1590	794	5000 -	2500
Contaminant of Trichlorethylene	204	104	1000 -	500
Contaminant of Carbon Tetrachloride	182	90	400 -	200
Contaminant of Chlorine	177	73	18 -	8.4
Contaminant of Dacthal	45	36	50000 -	40000
Contaminant of Vinyl Chloride	12	0	6 -	0
Contaminant of PCNB	3	1	2100 -	700
Contaminant of Mirex	0.9	0.4	2250 -	1000
TOTAL	4900	2600		

4. Chlorinated Pesticides: Aldrin, Chlordane, Dieldrin, Endrin, Heptachlor, & Toxaphene

The "Aldrin group" of cyclic chlorinated hydrocarbon insecticides included chlordane, aldrin, dieldrin, endrin, heptachlor, and toxaphene. The group is related in that, with the exception of toxaphene, production of all of them is based on dicyclo-pentadiene.

Chlordane was developed in 1944 by Julius Hyman and others at Velsicol Corp. in the course of a search for uses of cyclopentadiene, a by-product of synthetic rubber manufacture. Endrin, also developed and produced by Velsicol, was put into production in 1947. Hyman left Velsicol about that time to set up his own company, Julius Hyman and Company. Aldrin and dieldrin were developed by Hyman et al in 1948 and found to have very strong insecticidal properties. Because all of the work on chlordane and much of the work on aldrin and dieldrin had been done at Velsicol the rights to the patent applications for all three products were claimed by Velsicol and were so awarded by the courts. Velsicol was the sole manufacturer of chlordane, endrin and heptachlor. Subsequently Shell Development bought the Julius Hyman Co. and purchased exclusive rights to aldrin and dieldrin from Velsicol.

Shell Chemical Co. commenced production of aldrin and dieldrin in 1948 in Denver, Colorado [Jewkes, Sawers & Stillerman 71] and operated the plant until April 1975, after the banning of most uses in 1974. Most U.S. uses for chlordane and heptachlor were initially suspended in 1975 with the remaining applications phased out during the years 1978-1983 [Pest 78].

Toxaphene was produced principally in the U.S. by Hercules Corp. at a plant in Georgia. Later Tenneco operated a plant at Fords NJ for a number of years. Although toxaphene was the subject of an RPAR in 1978, many applications have been permitted and it is only now being phased out as alternate materials become available. Unlike the other materials it was produced from the chlorination of terpenes such as alpha-pinene or camphene derived from pine oils, but it is included in the aldrin group because of its chemical similarity to the other members. Statistics on production, exports and sales for the aldrin-toxaphene group as a whole and production of aldrin and dieldrin are given in Table 4-1. Statistics for the other members of the group are not published due to the fact that each was produced by only one company. However domestic U.S. sales of aldrin and dieldrin were published in the Federal Register at the time of proposed withdrawal of registration in 1974. These are shown, and have been used in the

construction of Tables 4-2 and 4-5. Unfortunately, the sum total of all consumption accounted for by the USDA falls considerably short (by 35%) of total U.S. sales data in Table 4-1. We cannot account for this discrepancy in terms of non-farm uses alone. There may have been under-reporting in the USDA surveys, or major stock adjustments, or under-reported exports, or all three.

Table 4-1: Production, Exports & Sales of the Aldrin-Toxaphene Group (million pounds)

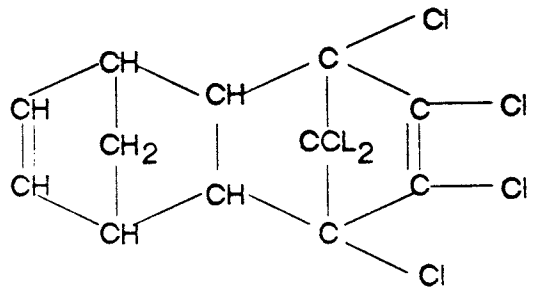
	------Aldrin-Toxaphene Group Total-------			Aldrin	Dieldrin
	Production	Exports	Sales	Sales	Sales
1950				1.455	0.000
1951				3.288	0.185
1952	49.0			0.814	0.756
1953	29.0			1.234	1.135
1954	45.2	na	na	2.993	1.777
1955	77.0	prior	prior	4.372	2.585
1956	86.7	to	to	6.495	3.635
1957	75.4	1970	1962	2.431	2.673
1958	98.3			4.971	3.074
1959	86.9			5.566	3.008
1960	90.0 (e)			8.109	2.650
1961	95.0 (e)			9.926	2.764
1962	100.0 (e)		42.0	10.886	2.990
1963	106.0		101.1	12.152	2.685
1964	105.3		105.6	12.693	2.052
1965	118.8		110.8	14.278	1.814
1966	130.5		128.1	19.327	1.998
1967	120.8		134.3	18.092	1.473
1968	116.0		122.0	13.690	1.322
1969	104.0 (e)		110.4	9.902	1.266
1970	88.6	22.6	84.2	8.909	0.749
1971	116.3	30.5	112.7	11.615	0.705
1972	141.9	30.4	140.2	11.868	0.740
1973	145.6	62.8	142.0	10.000 (e)	0.565
1974	141.7	63.9	40.0	9.790 (e)	na
1975	59.3	20.3	47.9	na	na
1976	42.2	21.3	na	na	na
1977	39.8	30.1	40.4	na	na
1978	40.4	21.1	na	na	na
1979	na	14.0	na	na	na
1980	na	11.9	na	na	na
1981	na	8.8	na	na	na
1982	na	9.5	na	na	na

Source for Aldrin/Dieldrin Sales:
Federal Register, Vol. 39, # 203, p. 37251, 1974 (From Velsicol Corp.)

4.1 Aldrin

Aldrin has also been given the trade names HHDN, Octalene, Aldrec, Algran, Mersect, and Soildrin. The structure of Aldrin is shown is Figure 4-1. It is produced by the Diels-Alder reaction of hexachlorocyclopentadiene and bicycloheptadiene [Thomson 67].

Figure 4-1: Aldrin Structure



1,2,3,4,10,10-Hexachloro-1,4,4a-5,8,8a-hexahydro-endo-1,
4,endo-exo-5,8-dimethanonaphthalene

Physically it is a brown to white crystalline solid that is insoluble in water but soluble in most organic solvents. It was considered compatible with most fertilizers, herbicides, fungicides, and other insecticides, and often sold mixed with them. Mixtures sold often included DDT, dieldrin, chlordane, malathion, parathion, sulfur, lindane, and fertilizers. A major (in plant) use for aldrin is the production of dieldrin, by oxidation. Dieldrin is also a major degradation product of aldrin [Hauley 77].

Formulations of aldrin included wettable powders, dusts and granules in the 20% to 50% concentration and seed treatments up to 75%. Reported data are in terms of 100% active ingredient [Thomson 67].

4.1.1 Aldrin Use

Uses for which aldrin was recommended include a vast range of field garden and orchard plants including apples, barley, corn, potatoes, rye, soybeans, vegetables, and other crops important to the Hudson-Raritan Basin. The major pests it was claimed to control included ants, cutworms, army worms, boll weevils, crickets, Diabrotica, wireworms, flea hoppers, grasshoppers, Japanese beetles, chinch bugs, leaf miners, slugs, snails, sowbugs, spittlebugs, thrips, and many others. It was said to be the most suitable pesticide available for grasshopper control. Recommended applications ranged from 1/2 to 5 pounds of active ingredient/acre, but it was most often applied at about one pound/acre.

By far the largest use of aldrin until its registration for agricultural uses was cancelled (1974) was as a soil poison for the control of corn rootworms, cutworms and wireworms. In fact, the percentage of all farm use of aldrin allocated to corn was 96.6% in 1966 and 88% in 1971 [USDA 73], [USDA 71].

The growth of Aldrin use in the 1960's was in part due to the shift to a more continuous use of land for corn production which led to the increase in corn rootworm populations. Use reached a peak in 1967. The subsequent decline may in part be explained by the fact that some corn rootworms, seed corn beetles and seed corn maggots had become resistant to aldrin, prompting a shift to other means of control [USDA 74].

Aldrin use was heaviest in the cornbelt states. Farmers in just two states, Illinois and Iowa, accounted for 59% of the total acres treated in 1971. In fact, states outside the midwest used only 2.7% of the aldrin consumed on corn in 1966 and only 0.5% in 1971 [USDA 71]. The northeastern states used 1% of the aldrin or 13,400 kg in 1966 on 16,000,000 acres of corn, of which the Hudson-Raritan Basin includes about 192,000 acres. Thus it would appear that, at the rate of 1.875 lb/acre on 1% of this land, only 1600 kg of aldrin were applied in the basin in a year of near maximum national use. Other years for which estimates have been made confirm this general pattern.

Other crop uses of aldrin were all minor. They include other grains, soyabeans, deciduous fruit trees, vegetables, cotton, tobacco, and citrus. Obviously the last three are of no importance in the northeast. Non-agricultural uses of Aldrin primarily were as use as soil poison for termites and in a wide variety of lawn and garden preparations: both as 'general purpose' pesticides and mixed with fertilizers to control grubs while feeding the roots.

The somewhat higher toxicity of aldrin and the dieldrin (to which much of it is converted) made it possible to use fewer pounds than are used with chlordane. Three to four pounds suffice for the average termite treatment. A breakdown of aldrin uses in 1964 and 1971 is given in Table 4-2[1].

Table 4-2: U.S. Consumption of Aldrin in 1964 & 1971

	1964 1000 lbs	1971 1000 lbs
FARM USE	11146	7928
Crop Use	11119	7907
Corn	10172	7759
Other Grain	144	98
Soybeans	37	11
Hay(incl. Alfalfa)		1
Cotton	17	
Tobacco	135	
Citrus		4
Other Vegetables	68	
Apples	6	
Other Crops	540	34
Livestock	0	14
Beef Cattle		14
Other Farm Use	27	7
NON-AGRICULTURAL USE	1547	3687
Home&Garden	47	87
Pest Control	1500	3600
GRAND TOTAL	12693	11615

4.1.2 Degradation of Aldrin

Rates of degradation of aldrin have been studied by several researchers. Bollen, Roberts and Morrison [Bollen, Roberts & Morrison 58] found that 623 days (1.7 years) after aldrin had been applied to a silty loam soil the amount detectable had declined to 25% of that applied. However, more than 56% of the original weight of the aldrin had been converted to dieldrin. They could not account for the remaining 19%. They concluded that the conversion of aldrin to dieldrin is not dependent on microbial action, but possibly with cation exchange capacities and Ca and Mg content.

[1]Note that total non-agricultural uses in Table 4-2, is estimated by subtracting farm use from total "disappearance", i.e. domestic sales (Table 4-1). The allocation among sub-categories is estimated by the authors (RUA,RW)

Lichtenstein and Schulz found that there was a considerable difference in the rate at which aldrin was degraded to dieldrin depending on the type of soil in which the product was applied [Lichtenstein & Schulz 58]. At normal applications (2 lbs/acre) little if any aldrin could be found after the end of a 4 year test. But at 20 lbs/acre the dieldrin to aldrin ratio was 1.69 for muck, 6.00 for a silt loam and 12.6 for a sandy loam. It was also found that conversion to dieldrin was sensitive to temperature, with a maximum being reached at about two months, and then an equilibrium seemed to be established. Other work by Lichtenstein and Schulz confirmed these findings and estimated that half life for aldrin after 3 years was 13.0 months for muck and 9.7 months for loam, with still shorter times in sandy soils [Lichtenstein & Schulz 59].

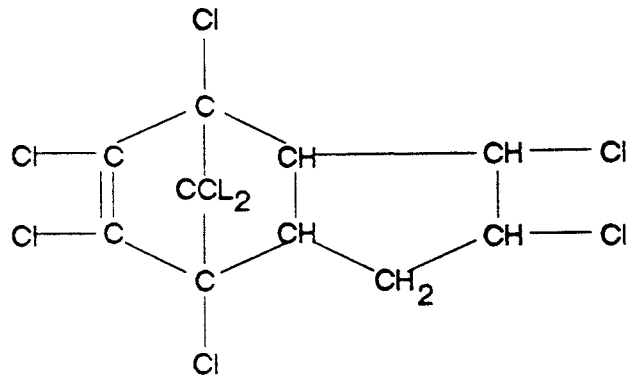
Given that use of aldrin in the Hudson-Raritan region was minimal -- mostly low rates of application on the relatively few acres to which it was applied -- and with half life estimated in months, it seems unlikely that measurable amounts of aldrin still remain in the soils of the Hudson-Raritan Basin. This tends to be confirmed by the results of soil monitoring studies. Although the National Soils Monitoring program FY1969 [Wiersman, Tai & Sand 75] and FY1970 [Crockett et al 74] both found aldrin and dieldrin residues in states in which aldrin had been used in larger quantities, neither found reportable quantities of aldrin in New York or New Jersey.

4.2 Chlordane

Chlordane is a chlorinated organic insecticide having both stomach poison and fumigant properties. Sold under a variety of trade names such as Chlordan, Oktachlor, Prentox, Synklor, its structure is shown in Figure 4-2.

Physically chlordane is an amber liquid with a boiling point of 175°C at 25mm Hg. Chemically chlordane is a mixture of isomers of which about 60% consists of alpha-trans (mp 106.5°C) and beta-cis (mp 104.5°). Of these it is the beta isomer which has the greater insecticidal activity. The remaining portion includes heptachlor (1,4,5,6,7,8,8 heptachloro 3_a 4.77_a tetrahydro 4,7 methanoindene) (mp 95°C) and unreacted chlordene. Heptachlor is itself a powerful insecticide (3-5 times as strong as chlordane). It is discussed in a separate section as it is produced commercially by a different process. Velsicol Corporation was the only producer of chlordane. The plant was located at Marshal, IL. Although the product was developed by 1946, significant use was begun in the late 1940's and phased out in the early 1980's. Some of the product was exported.

Figure 4-2: Chlordane Structure



1,2,4,5,6,7,8,8-Octachloro-2,3,3a,4,7,7a-
hexahydro-4,7-methanoindene

Formulations included sprays at 1.45-8.00lbs./gallon, wettable powders at 40%-50%, dusts and granules at.2-20%, oil solutions at 2-3%, aerosols at .5-2% and mixtures with fertilizers. Its acute toxicity compares favorably with most other chlorinated hydrocarbons. Like DDT it has a high degree of persistence and a tendency to be concentrated in the food chain. Because of these factors the government ordered a phaseout of chlordane production in the period 1978-1983.

Chlordane was recommended for use on more than fifty crops. The principal use was on corn, tobacco, and to a much less extent on alfalfa. It was used on corn to control such pests as cutworms and wireworms. Other crops treated include potatoes, tomatoes and strawberries. The average application was about 1.1 pounds per acre treated, except that concentrations used on alfalfa have been considerably lower.

Chlordane has been widely used in commercial and retail pest control formulations for roaches and termites, and other applications around buildings, and in the treatment of lawns, gardens, golf courses and city parks. This last market amounted to more than 70% of total chlordane use in 1974. Principal pests for which it is used around buildings include ants, cockroaches, crickets, flies, fleas, spiders and termites, while the lawn and garden market is mainly concerned with ants, chinch bugs, cutworms, crickets, earwigs, grasshoppers, Japanese beetles, wasps, and mosquitos. But by 1975 many of chlordane's uses had been curtailed and it was only recommended for use against termites and for the dipping of nursery stock.

The fact that much of the lawn and garden use was in the form of sprays and dusts led to some loss of chlordane to the air. Airborne droplets (and some on the surface of plants, paths, etc.) may have been carried by rains into the water system by way of streets, storm drains or natural drainage to streams. However, much of it remains buried in the soil where bio-degradation is very slow.

4.2.1 Agricultural Uses

The most accurate data we have for chlordane was that presented by its manufacturer, Velsicol, at hearings held by the EPA to determine whether many of its uses should be suspended [EPA/OPP 76]. This information is summarized in Table 4-3. Agriculture accounted for only 28.3% of the total in 1974 although use on corn grew between 1973 and 1974 because of the cancellation of aldrin/dieldrin. Still corn accounted for by far the largest fraction (73%) of agricultural use. Cutworms, especially the black cutworm, are the primary corn pests for which chlordane was used as a control. Earlier chlordane was also used for rootworms, but these apparently developed significant resistance to chlordane and it was phased out as alternative materials became available.

Because of the variation in cutworm infestations from year to year and location to location, chlordane use on corn varied. But acreage treated remained at relatively low levels. Chlordane was applied to 1.3% of U.S. corn acreage in 1974, increasing to 1.6% in 1975. By the end of 1975 other pesticides had been developed and registered for use on corn that provided an alternative for pests which had begun to develop a resistance to chlordane.

Table 4-3: U.S. Consumption of Chlordane in 1964 and 1971

	1964 1000 lbs	1971 1000 lbs
FARM USE	526	5470
Crop Use	452	5470
Corn		4320
Other Grain	159	
Hay(incl. Alfalfa)	47	
Sorghum	3	
Tobacco	26	
Citrus	15	
Potatoes(White)	155	1110
Other Vegetables	18	
Apples	3	
Other Fruits&Nuts	24	40
Other Field Crops	2	
Livestock	71	0
Other Farm Use	3	
NON-AGRICULTURAL USE	9710	13165
Nursery	10	25
Turf	200	200
Home&Garden	4500	5600
Pest Control	5000	7340
GRAND TOTAL	10236	18635

The most serious infestations of cutworm have been in the relatively flat bottomlands along the Missouri and Mississippi rivers. use in these areas was most intense, with up to 30% of the farms reporting the use of chlorinated pesticides for corn. States with cooler climates and better drained soils required considerably less. In fact, in 1971 the whole Northeast accounted for only ,6% of total U.S. insecticide use on corn. Thus, although chlordane use on corn nationally has been significant, it was mostly confined to the "cornbelt" states. The amounts used on corn in the Hudson-Raritan Basin are relatively small. The use of chlordane on corn was officially suspended August 1, 1976.

For several years New York and New Jersey each recommended chlordane for use on strawberries though the New York recommendation was limited to only those strawberry areas which had previously been in sod. It was incorporated in the top 3-4 inches as a soil poison. New York growers produce 4

million pounds of strawberries on an estimated 4,000 acres. The principal insect pests attacking these include white grubs, strawberry rootworms, strawberry root weevil (or crown girdler) and strawberry crown borer.

The New York strawberry crop is about 1% of the national total. The final settlement order of the EPA granted a 50,000 lb allowance for the industry, of which 500 lb might have been used in the Hudson-Raritan Basin.

Other crops on which chlordane was used include other grains (wheat, oats, barley, rye etc.), hay and alfalfa. These accounted for less than 200,000 lbs of chlordane on a national basis. The amount used in the Hudson-Raritan Basin on these is estimated to be less than 1,000 lbs per year, based on local production share and lower relative susceptibility to pests in the northeastern region of the country.

Irish potatoes apparently have been another consistent user, accounting for an estimated 1,110,000 pounds in 1974. use on other crops, including 'other vegetables', has been minor, with U.S. use of 90,000 lbs indicated in 1974. The proportional share of the Hudson-Raritan Basin in potato production is estimated to be 4%, implying a use of 120 lb of chlordane in 1966.

Some 40,000 pounds of chlordane per year were used across the country on fruit trees in 1974. This apparently increased to 100,000 lbs per year in 1976-1978. Since New York state is the second largest producer of apples, this is of greater than proportional importance for the Hudson-Raritan Basin. The proportional share of apple production in the Hudson-Raritan Basin is 31.1% of the northeast, implying a use of 311 lb of chlordane in 1966. Chlordane was used on some crops not grown in the Hudson-Raritan Basin, including tobacco, peanuts (mainly for control of white fringed beetles prevalent in the South) and citrus (ants, root weevil larvae and Fuller's rose beetle larvae in California, Florida and Texas). It was also used against the fire ant in the South and Southwest.

Prior to 1973 there was a moderate use of chlordane against pests of livestock. While this reached a level of 366,000 pounds in 1971, it was apparently mainly used against ticks and other pests of beef cattle. The livestock in the Hudson-Raritan Basin are mainly dairy herds, for which chlordane use was not recommended.

4.2.2 Non Agricultural Uses

Large amounts of chlordane have been used to control wood-destroying insect pests, including subterranean termites, carpenter ants, powder post beetles, and old house borers. With increasing resistance to DDT becoming evident, (and later the cancellation of its registration), large numbers of pest control operators turned to the use of chlordane to combat pests threatening damage to wooden structures.

In these uses the affected wood and/or the soil under and/or surrounding the structure was treated. In some cases the use was for pretreatment of soil beneath the slabs of new construction. U.S. consumption for this application was reported by the manufacturer at some 7.5 million pounds in 1974. Because of the importance of this use an exception was made in the EPA's proceedings against chlordane and heptachlor which covered the use of these materials in [EPA/OPP 76a] "subsurface ground application for termite control", (34 FR - 41256 Nov. 1974).

This exception meant that use in termite control could continue without interference, subject to the requirement that the material could only be handled by trained pest control operators (PCO's). use of chlordane by PCO's grew rapidly in the early 1950's and has continued until the present time. However in the early days chlordane shared this market with DDT and later with aldrin - dieldrin.

In an EPA study of usage of pesticides [EPA 80] it was found that in EPA region II (New York and New Jersey) 23.8% of the population surveyed had used pest control operators and 14.2% had used them for termite control in that year. Since the lower part of the Hudson-Raritan Basin where the largest proportion of the population lives is in the 'moderate to heavy' range of termite infestation there is a large amount of activity in termite control.

Because of its location under slabs or around buildings, where it is covered by several inches of topsoil, the pesticides used in termite control tend to be locked into its position in the ground and become adsorbed on the soil particles. In most cases there is negligible loss from volatility, runoff or the other factors. Therefore, the survival of the material in situ depends only on microbial degradation. This, in turn, is affected by the soil moisture and temperature.

In studies of the effectiveness of soil poisons it has been found that the duration of the protection increases with concentration. Concentrations of up to 3% have been used where an extra margin of protection is required.

Soil poisons such as chlordane used in termite protection are normally not a source of pollution. However, in some cases they can be brought to the surface in construction projects where old buildings are cleared away and the land used for parks, etc. The rate of release by this mechanism is difficult to project, but small [Dorough & Pass 72]. At most it might amount to a few percent of the amount used at any one location, from runoff carrying silt into waterways. Another source of chlordane in water would have been in the cleaning of equipment and the disposal of containers. While in recent years there has been pressure for controls on disposal, apparently few restrictions were observed on the disposal of containers and unused pesticides in New York State up until 1977 [EPA 77].

In the case of structural pests other than termites, chlordane solutions (typically 2.0%) are sprayed on or injected into the affected timbers. The amount used varies greatly with the application, but probably accounts for no more than 25% of the amount used in termite control.

4.2.3 Lawn, Garden and Household Use

Control of lawn pests and crabgrass was another important use of chlordane. Application recommendations for this use range up to 60 lbs/ acre, to eliminate the white grubs of the Japanese beetle, June bug, Asiatic garden beetle and European chafer, among others. There are many affluent suburban areas with large areas devoted to landscaping (as distinct from the home garden and lawn category). These areas include golf courses, parks, parkways, landscaping around "garden" apartments, airports and their surrounding areas, company headquarters and research installations, schools and colleges, hospitals and nursing homes. Because no specific reports on such uses are made, there are no data on its extent. Since the use of many of the facilities is related to the disposable income of those utilizing them an approximation can be based on population and personal income.

The importance of lawn and garden uses is confirmed by measurements of soil residues in cities. The Urban Soils Monitoring Program (covering both urban and suburban areas), found that residues of chlordane in soil samples of each of the 37 cities included in the survey. In these cities, from 20% to 40%

of the samples contained chlordane, and in those cases in which it was present it exceeded the levels in the surrounding cropland areas [EPA/OPP 76].

Chlordane was also recommended for many uses around the house and has been used in many household sprays. Specifically in advice prepared in 1967 at Cornell University it was recommended for ants (including carpenter ants) chiggers, cutworms, carpenter bees, grubs, spiders, sod worms and termites [Cornell 67]. In years prior to the development of carbamate and phosphate insecticides it was probably recommended for a still wider variety of pests.

A study made of national use of household pesticides in 1976-1977 concluded that nine out of ten households used some pesticides in the house, garden or yard during the year prior to the interview. Chlordane was used in 674 of the 8254 households in the study and was fourth in number of those reported by those interviewed [EPA 80]. Regional data showed that households in Region II (including New York and New Jersey) had used an estimated 215,000 pounds in the previous year and had 252,000 pounds on hand. These amounted to 2.55% of national use as determined in the study and 4.78% of that still in inventory. There seem to be several reasons for the smaller than average use per capita in Region 2 (which has 11.0% of the U.S. population). One reason is the less frequent and aggressive insect infestations in these states *vis a vis* other areas. (In particular, southern states have a much longer season during which pests are active outdoors.) Low use probably is also due to the higher proportion of the population living in multi-family dwellings without individual lawns or gardens (19). Also many of these dwellings are of concrete and steel and are thus relatively immune to infestations of some types of pests.

Adjusting the 3.8 million pound figure extrapolated from this survey to the 5.6 million pound figure from Velsicol implies a consumption of 206,000 pounds of chlordane in the Hudson-Raritan Basin in 1976-1977. Using the average population of the Hudson-Raritan Basin over the period 1950-1976, and assuming a constant per capita consumption, this would have led to the cumulative use of some 5.2 million pounds of chlordane over the period.

Most of the chlordane used outdoors soon finds its way to the soil. However when used on gardens and lawns there is some loss to surrounding walks and streets. Runoff in the period immediately following an application is probably quite significant. This is confirmed by surveys covering other cities that have

found significant levels in air and storm sewer water. For instance, chlordane levels in storm sewer water samples from a Baltimore residential area ranged up to 97 parts per trillion [EPA/OPP 76]. Pesticides used indoors are more likely to enter the sanitary sewer system as sprayed surfaces are mopped or cleaned and cleaning cloths washed. Examination of bottom sediments in the Hudson by their location also confirm the belief that much of the chlordane reaching the river is carried by storm sewers.

Some chlordane also gets into the air and is washed out via rainwater [EPA/OPP 76]. In the above study chlordane levels in rainwater were reported to range from undetectable (<1pp trillion) to 660 parts per trillion (ibid).

4.2.4 Nursery Use (Ornamentals)

USDA plant protection and quarantine programs require treatment of plants imported into or transported within the U.S. to prevent the spread of certain pests. In areas where infestations are located, the USDA requires the use of specific insecticides to treat the stock prior to its removal from a quarantined area. For many years treatment with chlordane by dipping roots and tops was the required treatment to prevent the spread of Japanese beetles, fire ants and several other pests. Because of the lack of suitable alternatives, the use was initially excepted from the prohibition on the use of chlordane (39 FR 41256) [EPA/OPP 76]. On March 6, 1978, the EPA released an order permitting 500,000 pounds of chlordane to be used for nursery quarantine purposes, with the proviso that no more than half the amount should be used in either calendar year 1978 or 79.

Nationally the use of chlordane on nursery stock has been one of the smaller ones from the volume standpoint. However, the New York and New Jersey areas in the Hudson Valley include many affluent residential districts that are good markets for ornamentals. Undoubtedly there is a net inflow of treated stock. There are also counties (Monmouth, Middlesex, Hunterdon, Bergen and Somerset) in the New Jersey portion of the basin in which the nursery industry is significant. In a survey of pesticide usage in the New Jersey part of the basin it was found that some 34.4% of the insecticides used in agricultural production were used in treating nursery stock [NJCRS 78]. Though chlordane was not specifically mentioned, its use for quarantine purposes means that it was introduced into the soil of the basin indirectly via imported stock, probably in proportion to the population of the basin adjusted to represent those not living in highrise buildings.

4.2.5 Degradation of Chlordane

Residues of chlordane have been found to be more persistent than those of aldrin and heptachlor but less so than DDT and dieldrin [Edwards 66]. The measurement of chlordane residues is complicated by the variety of compounds (including heptachlor and as many as 18 unidentified compounds) that make up technical chlordane. Apparently all other constituents degrade more quickly than the pure isomers. To determine the rates of degradation of pure chlordane isomers, Wilson and Oloffs tested Velsicol HCS 3260 (95% alpha and gamma chlordane) in a variety of soils [Wilson & Oloffs 73]. There was a rapid loss during the first month (possibly from volatization), followed by a loss proportional to time. This confirms the observation by Edwards [Edwards 66] that 55% remained at the end of one year, and agrees well with the half-life of 14.3 months reported by Onsager et al [Onsager, Rusk & Bulten 70].

It is significant that there was a noticeably higher recovery of the chlordane in the plots tested at higher rates of application [e.g. Gutenmann et al 72]. This tends to explain the relatively minor findings of chlordane residues in agricultural soils where the applications have been on the order of 2 pounds/acre. On the other hand, where applications in concentrations up to 60 pounds per acre have occurred (e.g. for crabgrass, lawn grubs or termite treatment) the degradation rate has been lower.

In the National Soils Monitoring program for 1971 only 2 (5.3%) of 38 soil sites tested in New York State showed positive evidence of chlordane [Carey et al 78] These residues had an arithmetic mean concentration of 0.01 ppm of chlordane dry weight of the soil sample. In the 'mid-Atlantic states' there was only one (5.6%) positive detection among the 18 samples taken in the survey. Given that the half life of chlordane is about 14 months under field conditions, and that so little residue was evident in the 1971 survey, it seems safe to say that most agricultural chlordane residues have been degraded by now to negligible levels (unlike DDT or dieldrin).

Bopp et al found that residues of chlordane were not easily detectable in sediments taken from the Hudson river above New York harbor [Bopp et al 82]. These were only about 8 parts in 10^9, but degradation products were not discernable. Analysis showed both alpha-and gamma at about 5 parts in 10^9. In the harbor itself, however, chlordane levels were much higher, confirming the urban source for these pesticides.

Harbor samples also exhibited a peak corresponding to oxychlordane a persistent chlordane derivative- with oxychlordane amounting to 8 to 15% of the alpha- and gamma- chlordane. These residues appear to have dated from the early to mid 1960's as they were concoincident in the deposits with fallout from that period. While trans-nonachlor, (a minor component of chlordane) was not identified separately it was suspected of being present and adding to the peak of alpha-chlordane on the chromatograph (Ref 39765-80-5). The presence of trans-nonachlor in the core samples from the Hudson some 10 years or more after it was adsorbed by silt and trapped in river bottom sediment would indicate that it is quite persistent [Bopp et al 82].

Trans-nonachlor is of specific concern because of its tendency to be accumulated by fish. In a study to determine the amount of technical chlordane that would affect fish it was found the component accumulated to the greatest extent was trans-nonachlor for which whole body residues were up to 145,000 times higher than those in the water [Cardwell, Payne & Wilbur 77].

In summary, then, we estimate total non-agricultural uses of chlordane in the Hudson-Raritan Basin as follows:

Table 4-4: Non-Agricultural Use of Chlordane, Hudson-Raritan Basin, 1945-1982 (1000 lbs.)

PCO's	16,400
Turf	552
Nurseries	312
Home lawn and garden	5,200

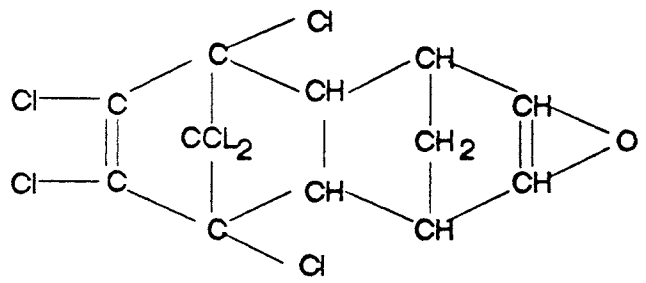
Total	22,464

4.3 Dieldrin

Dieldrin, (also called Octalox, Heod, Alvit, and Quintox) is chemically very similar to aldrin and in fact is manufactured from it. It also results from the degradation of aldrin in the environment. The structure of dieldrin is shown in Figure 4-3.

It can be seen that the addition of the epoxy group to the right of the structure and addition of two hydrogens complete the change from aldrin to dieldrin. This is accomplished commercially by reaction of aldrin with peracids.

Figure 4-3: Dieldrin Structure



1,2,3,4,10,10-Hexachloro-exo-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo,exo-5,6-dimethanonaphthalene

Formulations in which dieldrin has been made available include sprays of 1.5 to 2 lbs. active ingredient per gallon . Wettable powders ranging from 50 to 25% dusts of 1.5 and 2% granules containig 10% and mixtures. Mixtures were produced both with other chlorinated pesticides such as lindane and toxaphene, and with phosphatic types such as malathion and copper, maneb and zineb. Recommended rates of application usually ranged from one half to four and one half pounds actual per hundred gallons of water, or one half to five pounds actual per acre.

Although production starting in 1948 was reported to the U.S. Tariff Commission, production volumes could not be published to avoid revealing company proprietary data because aldrin and dieldrin were produced only by Shell Chemical and later also by AMVAC. In fact, it was not until 1968 that an "Aldrin" group was included in the annual Synthetic Organic Chemicals Manufacture and Sales. (This group included aldrin, chlordane, dieldrin, heptachlor, terpene polychlorinates, and toxaphene.) While estimates of production of aldrin and dieldrin vary, it is probable that combined production rose to a peak of about 20 million pounds in the mid-1960's and then declined. From domestic use data, production was about 90% aldrin and 10% dieldrin. The Shell producing facility was closed in 1975, followed by the AMVAC

plant in 1978, after the use of the product in the U.S. was banned for most applications. Because no production occurred in the Hudson-Raritan Basin, none of the residues in the area can be blamed on the waste or emissions from manufacture.

Dieldrin, like aldrin, was recommended for use on a vast list of crops (about 90). Like aldrin, the principal use is as a soil poison and for this use it is either sprayed on the ground, applied in a band, and promptly tilled into the soil, or placed in the furrow at time of planting.

Principal uses appear to have been on corn, hay, small grains (wheat, rye, barley and oats) fruit orchards and vegetables. Outside the Northeast there was also use on tobacco, cotton, and citrus pests. Control of harvester ant, a problem in the south, was a farm application unrelated to any specific crop. Dieldrin was occasionally used on alfalfa to combat the alfalfa snout beetle and such treatment has been made in New York state.

Typical of its use in orchards was in 'petal fall' spray of dieldrin at .25 lb/acre to combat the European apple sawfly. Similarly it was used to control curculio on peaches. Its irregular use to treat infestations of insects which, for one reason or another were no longer controllable by DDT etc., makes it somewhat difficult to generalize about its use than it is for more routinely used products.

Strangely, the Northeastern States seem to have had a greater propensity to use dieldrin than the rest of the country, at least in 1966. The northeast only used 0.2% of the aldrin used on crops, but used 6.1% of the dieldrin used on crops. Possibly this was due to some special combination of pest infestations.

Dieldrin was promoted for use in termite control. It was also recommended for other 'structural' pests. However, its higher price and small production capacity served to limit its markets to a minor portion of the total, probably not exceeding 1 million kg for all non-agricultual pest control uses. Because of its admittedly higher toxicity, dieldrin was not used as indiscriminately in formulating proprietary products as were aldrin, DDT or chlordane. National consumption of Dieldrin in 1964 and 1971 is shown in Table 4-5.

Table 4-5: U.S. Consumption of Dieldrin in 1964 and 1971

	1964 1000 lbs	1971 1000 lbs
FARM USE	938	332
Crop Use	927	321
Corn	67	
Other Grain	285	118
Soybeans		28
Cotton		65
Tobacco	93	1
Citrus	12	1
Potatoes (White)	41	
Other Vegetables	45	64
Apples	102	
Other Fruits & Nuts	254	
Other Crops		72
Livestock	0	4
Other Farm Use	11	7
NON-AGRICULTURAL USE	1114	373
Pest Control	1114	373
GRAND TOTAL	2052	705

4.3.1 Degradation of Dieldrin

There appear to be few studies that reveal the degradation rate of dieldrin apart from its existence in equilibrium with aldrin. There appears to be ample evidence, however, that dieldrin is more persistent than aldrin and this can be attributed to its physical and chemical properties.

Its low volatility, (vapor pressure of only 1.78×10^{7} mm Hg at 20°C), prevents loss to the air from volatility. Its low solubility in water (186 microgram/liter at 25°C to 29°C) means that it is not dissolved by water passing through the soil.

It is also highly apolar which reduces its solubility in polar fluids but makes it soluble in fats and oils. This lipid solubility leads it to become dissolved in plant and animal fats and waxes with which it comes into contact. Like DDT it is concentrated in the food chain -- showing up in meat and milk -- sometimes at levels possibly dangerous to consumers.

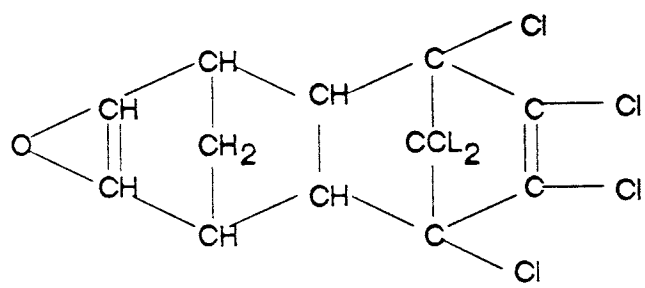
Dieldrin degradation appears to be a function of the concentration of dieldrin in the soil. Beyer and Gish [Beyer & Gish 80] determined that at 0.6 kg/ha the half time (the time it took to degrade half the material) was an average of 2.6 years, at 2.2 kg/ha half time averaged 4.1 years and at 9.0 kg/ha the half time was 12.5 years.

It is undoubtedly for this reason that persistent levels of dieldrin are found where there has been a high concentration, either from a single application (such as might be made for termite control) or repeated sprayings.

4.4 Endrin

Endrin, also called Mendrin, has a structure shown in Figure 4-4. It is the endo-endo isomer of dieldrin, the difference being the spatial arrangement of the rings.

Figure 4-4: Endrin Structure



1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo-endo-5,8-dimethanonaphthalene

Endrin is somewhat less stable than dieldrin, but it is extremely insoluble in water (0.000023 gm/liter at 25°C) and more soluble in acetone (17) and aromatic hydrocarbons (benzene 13.8 gm/liter). Physically it is a white crystalline solid. It can be formulated into sprays ranging from 1.6 to 2 lbs. active/gallon

wettable powders (25% and 75% active), dusts (1-2%) active or granules (1-2% active). It can also be formulated as poison baits of various compositions. It is compatible with other insecticides and has been sold in many mixtures with them.

Endrin has been recommended for use on a wide variety of field crops vegetables and fruits. The major uses have been on cotton and tobacco with lesser amounts on potatoes and apples.National use of endrin in 1964 and 1971 is shown in Table 4-6.

Table 4-6: U.S. Consumption of Endrin in 1964 and 1971

	1964 1000 lbs	1971 1000 lbs
FARM USE	2169	1418
Crop Use	2151	1418
Corn		30
Other Grain	12	30
Soybeans	9	23
Cotton	1865	1068
Peanuts		85
Tobacco	150	
Potatoes (White)	61	5
Other Vegetables	20	1
Apples	30	2
Other Fruits & Nuts		33
Other Crops	4	141
Other Farm Use	18	
GRAND TOTAL	2169	1418

The major use of endrin in the Hudson-Raritan Basin has probably been on vegetables. It has been used against the usual list of pests, from ants and aphids, cutworms, grasshoppers, and loopers, to thrips. There was some use of endrin in soil treatment of seed to protect the seedlings from damage by birds. Another important use was on specific pests in orchards; namely, fall and spring cankerworms (1/2 pound per acre) and redbanded leafrollers (1/4 pound per acre). Endrin was also used occasionally as a rodenticide in orchards to control mice -- particularly the pine mouse.

Since endrin tended to enter the plants in treated soil by transport through the roots, and to some extent by vaporization and redeposit on the leaves, it became necessary to prohibit its use too close to

harvesting [Nash & Beall 70]. The specific number of days of prohibition varied by crop. However, the heavier amounts transported into the stems of corn and other grains used as forage led to concern that it would be further concentrated in the food chain. It was therefore not recommended for forage crops in most cases. USDA did suggest its use against the fall armyworm and southwest cornborer (each at 1/2 lb/acre), with the precaution that crop residues not be fed to dairy or meat animals. No non-farm uses have been identified.

4.4.1 Degradation of Endrin

As mentioned above, endrin is quite volatile at higher temperatures. It also appears to be unstable and susceptible to breakdown from heat and sunlight. These factors lead to loss from surface applications. While endrin is stable in alkalis, it breaks down in strong acids and, over time, from microbial attack. The resulting metabolites appear to have only slight insecticidal activity and possibly are not as persistent as endrin itself.

The two principal residues of endrin for which soil samples are tested are endrin aldehyde and endrin ketone. Because of its sparse use in the Hudson-Raritan Basin, no significant residues have been found in the soil monitoring test program in New York and New Jersey. A 1969 FY survey showed no positive tests in NJ and one positive in NY (and that only 0.56 ppm in 38 samples), while 1970 FY reported none in NY [Wiersman, Tai & Sand 75], [Crockett et al 74].

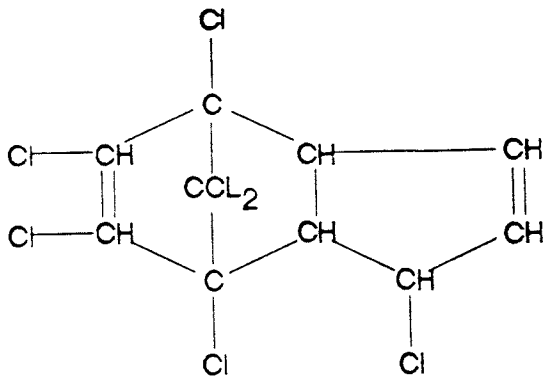
Among the factors tending to minimize endrin use was its acknowledged toxicity, which led to the recommendation that it only be applied by trained operators and than one should not enter treated fields for five days after treatment without protective clothing.

While only moderately toxic to mammals (oral LD_{50} to rats at 10 Mg/kg and dermal LD_{50} of 15 Mg/kg), it is extremely toxic to fish. It accumulates in their tissues to a concentration of as much as a thousand times that of the water in which they swim. Levels of .5ppb in water have been reported as hazardous to fish. A very large fish kill below the Velsicol plant at Memphis, TN aroused popular concern about endrin. Its use was challenged by EPA in 1976 and banned shortly thereafter.

4.5 Heptachlor

As mentioned in the section on chlordane, a portion of that product (about 7%) is heptachlor. Technical heptachlor is about 3-5 times more effective as an insecticide than chlordane. Its structure is shown is Figure 4-5.

Figure 4-5: Heptachlor Structure



1,4,5,6,7,8,8–Heptachloro–3a,4,7,7,7a–
tetra–hydro–4,7–Methanonindene

The technical product contains several related materials, including about 20% chlordane. Since each product contains the other there are difficulties in separating the effects and residues, particularly in soils on which both have been used. Heptachlor is highly soluble in a variety of organic chemicals, but it is almost soluble in water (0.0000056 at 27°C). Vapor pressure is moderate at 0.04 Pa (0.3 mHg at 25°C), which accounts for some loss to the air, particularly during application at high temperatures.

4.5.1 Manufacture

Commercially heptachlor was produced by Velsicol Chemical Co. starting in 1946 (subsidiary of Northwest Industries, Inc.) at Memphis, TN. The plant is believed to have had a capacity of 10 million pounds per year. The process involved chlorinating chlordene (hexachloro cyclopentadiene) with SO_2Cl_2.

Since domestic use in recent years is believed not to have much exceeded 2,000,000 pounds per year there have been large amounts for export. Since only aggregate production statistics are available from government sources, neither specific production nor export data have been available on a regular basis. One available production estimate is that of Matsumura, who reported 1971 production at 6 million lbs [Matsumura 75].

However, information in a House Subcommittee Report [US Congress 78] indicated a production level in 1976 of 1,511,640 pounds and exports of 1,347,592 pounds. With domestic consumption at 1,829,000 lbs in 1976 these figures indicate a rundown of inventory, anticipating possible cancellation of registration for agricultural uses. The same report, projected a resurgence in production in the following year, 1977, to 2,474,000 pounds.

Since the production has been at Memphis, Tennessee since 1946 there has been no pollution of the Hudson-Raritan Basin from heptachlor manufacture.

4.5.2 Agricultural Use

Heptachlor has been primarily an agricultural insecticide through most of its commercial life. Again, the most authoritative figures on its use are those presented by Velsicol at the hearings on suspension of its registration. These are shown in Table 4-7. Both the data shown and those published by the USDA, indicate that its use was about 70% agricultural (of which 95% was on corn). The other 30% was used against fire ants, for seed dressing, and for minor uses such as the dipping of narcissus bulbs.

Heptachlor was registered, and no doubt used, in earlier years against grasshoppers, onion thrips, cotton weevils and plum curculio. Amounts used tended to be small because of its high insecticidal effectiveness. Recommended application for grasshoppers were as low as 2.0 oz. per acre. In seed treatment 1.0 to 1.503 ounces were used to treat 100 lb of sorghum seed -- sufficient for 10 to 25 acres

Table 4-7: Heptachlor Use Pattern 1973-1974

Use	Millions of Pounds		Percent	
	1973	1974	1973	1974
Corn	1.13	1.19	57.4	58.0
Seed Dressing	.19	.27	9.6	13.2
Fire Ants, Misc	.032	.04	1.6	2.0
Other	.62	.55	31.4	26.8
	---	---	---	---
TOTAL	1.97	2.05	100.0	100.0

Source: [EPA/OPP 76]

[EPA/OPP 76]. Apparently use on some vegetable crops was also relatively heavy because, in the literature, some of the highest residues of heptachlor (and chlordane) have been found in certain onion and other vegetable growing areas.

While corn is a major crop use for many pesticides, the proportion of corn acreage treated with insecticides has never been high. Throughout the period during which the chlorinated organic pesticides were being used, more than 70% of the total acreage received no treatment at all. Infestations of rootworms, cutworms and wireworms tended to vary from year to year, but typically they were much heavier in the "corn belt" and some of the lower Mississippi valley states than in the northeast.

End use studies by USDA indicate very slight use of heptachlor on corn in the northeastern U.S. In fact, in 1964 only 50,000 pounds of all chlorinated organic pesticides were used on corn in that region. This was a mere 0.32% of the total amount used on corn in the U.S. that same year. The impact in the Hudson-Raritan Basin was evidently very small indeed.

The area of the Hudson-Raritan Basin devoted to corn is about 2.9% of the corn growing land in the northeast. Assuming rates of application are comparable in the whole area, and 84% of the heptachlor was used on corn [USDA 68], we estimate .029x0.842x17,000 or 422.2 lbs used on corn in 1964.

Table 4-8: Heptachlor Use on Corn: 1964

Region	Quantity Used on Corn (lb)
US	1,301,000
Northeast	17,000
Hudson-Raritan	422.2

The same source [USDA 68] indicates that altogether 16,000 acres in the northeast states were treated with heptachlor. This implies an average application rate of 1.0625 lbs/acre.

The other agricultural uses for heptachlor specifically mentioned -- seed treatment and dipping of narcissus bulbs -- have not been of much significance for the Hudson-Raritan Basin. The former has been primarily of interest in the Southwest and the latter in Washington-Oregon.

4.5.3 Non Agricultural Use

Non agricultural use of heptachlor has been almost entirely for the control of subterranean termites. Agreement was reached March 6, 1978 to allow continued use of heptachlor and chlordane for six years with a maximum combined production of 7.2 million pounds per year. This was justified because the chemicals do not come into direct human contact after they are injected into the subsoil [EPA/OPP 76]. The official data released by Velsicol for 1973-1974 indicated PCO use of 610 thousand lbs and 550 thousand lbs respectively for those years. These figures are 8.2% and 7.4% respectively of the quantity of chlordane used for the same purpose in those years. We assume heptachlor was used in the same proportion to chlordane in the Hudson-Raritan basin as in the nation as a whole.

Heptachlor was used to a small extent in general purpose home and garden pesticide formulations. It was also used in specific preparations for the control of the fire ant. Other products subsequently became available for most of these applications. These uses can be assumed to be distributed essentially in proportion to population -- after subtraction of 10,000 lbs that was used for the fire ant eradication program. An additional 8,000 pounds used in 1974 may have mostly been used on citrus groves in Florida, as a replacement for aldrin formerly used in that application. National use of Heptachlor in 1964 and 1971 is shown in Table 4-9.

4.5.4 Loss and Degradation

In many studies there appears to be evidence of rapid initial loss of heptachlor by volatilization or co-distillation. The extent of this and its relation to ambient temperatures is revealed by the data presented by Lichtenstein and Schulz in 1959 [Lichtenstein & Schulz 59]. In testing the effect of temperature of heptachlor loss from a Miami silt loam treated at 20 lb/acre there was a disappearance of 26.8% at 6°C, 49% at 26°C and 98.2% at 46°C. Since the temperature of the soil on a hot summer day approaches the highest level it is clear that there can be substantial losses to the air by evaporation

Table 4-9: U.S. Consumption of Heptachlor in 1964 and 1971

	1964 1000 Lbs	1971 1000 Lbs
FARM USE	1305	1460
Crop Use	1301	1460
Corn	1099	1190
Other Grain	69	
Hay(incl. Alfalfa)	100	
Tobacco	24	
Other Crops	9	270
Other Farm Use	4	
NON-AGRICULTURAL USE	528	590
Home&Garden	28	40
Pest Control	500	550
GRAND TOTAL	1833	2050

immediately after spraying. Heptachlor that is adsorbed onto soil particles apparently becomes much less volatile, so the rate of loss drops off in a few days at lower temperatures (but appeared to continue for the full 56 days of the test at the 46°C level). It may well be this evaporative loss and subsequent deposition of evaporated endrin, along with its intentional use on corn grown as forage, that accounts for the wide distribution of heptachlor thoughout the environment.

Many researchers studying the degradation of heptachlor in the 1950's and the early 1960's found that heptachlor degraded to heptachlor epoxide in animals, in plants, and in soil [Ginsberg & Reed 54]. Miles, Tu and Harris reviewed this work and proceeded to determine the mechanisms by which heptachlor was converted to its epoxide, and other pathways to degradation [Miles, Tu & Harris 69]. Briefly, they found microbial action resulted in conversion to heptachlor epoxide, thence to chlordene, and finally to chlordene epoxide. Hydrolysis in the presence of water to 1-hydroxychlordene, was followed in its turn by microbial conversion to 1-hydroxy 2,3 epoxychlordene and other unidentifiable degradation products. Miles et al believe this may be an important route whereby residues enter water systems.

In a review of the subject an EPA team listed reports of degradation studies, mostly based on the work of C.A.Edwards, concerning the maximum and mean of the concentrations of total heptachlor and heptachlor epoxides at some 4,323 sampling sites [EPA/OPP 76a]. The mean of the means of the

residues for those showing more than a trace was 0.065 ppm. Another report on the chlorinated hydrocarbon residues in cropland soils by state for FY 1970 [Crockett et al 74] found traces of heptachlor use in only 1 out of 38 sites and that site had residues of <0.01 ppm. Work by Beyer and Gish determined a half-life (50% degraded) of 3.2 years for heptachlor [Beyer & Gish 80]. Analysis of the graphs in this study indicates that the heptachlor epoxide, in turn, had a half-life of about 7.5 years.

It is not surprising, then, that in many soil samples researchers find significant residues of heptachlor expoxide but no heptachlor. With agricultural applications of heptachlor continuing until 1976, there may yet be some traces of heptachlor epoxide to be found; but it seems likely that they will be relatively slight.

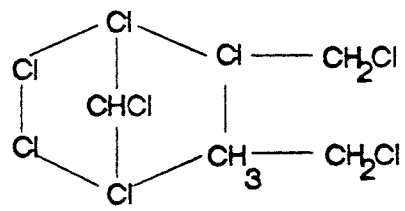
Because of some use in lawn and garden preparations and its continued use in termite applications, reported levels in urban studies have recently been higher than those in farming areas. While monitoring of urban soil by the EPA from 1971 to 1977 seemed to show no particular trend in the proportion of samples indicating heptachlor or heptachlor epoxide, it is significant that there was a decline in the ratio of heptachlor to heptachlor epoxide starting at 25% in 1972 and declining to 3.33% in 1977. The evidence that there are other pathways to the degradation of heptachlor may explain in part why residues are not as predictable as expected.

4.6 Toxaphene

Toxaphene is one of a group of chlorinated terpenes. The terpenes used are of natural origin, derived mainly from turpentine or pine oil. Toxaphene, also sold under several trade names such as Aletox and Toxakil is specifically from a bi-cyclic terpene, camphene, which when chlorinated has the empirical formula $C_{10}H_{10}Cl_{18}$ and contains 67-69% chlorine. The technical product is reported to contain some 175 polychloro derivatives. The most insecticidally active of these are 2,2,5-endo-6-exo-8,9,10-heptachlorobornane and 2,2,5-endo-exo-8,9,9,10-octachlorbornane, each of which forms some 2-6% of the technical product.

Physically toxaphene is a yellow semi-crystalline gum, having a melting point range of 65-90°C and a density of 1.64 gms/cc. In formulation it was sold in sprays of 4,6, and 8 pounds, wettable powders containing 40%, dusts of 5, 10 and 20%, granulars of 5, 10 and 20% and baits of 1%. It has also been made available in mixtures with DDT. The structure of toxaphene is shown in Figure 4-6.

Figure 4-6: Toxaphene Structure



2,2,5-endo-6-exo-8,9,10-Heptachlorobornane
2,2,5-endo-exo-8,9,9,10-octachlorobornane

4.6.1 Manufacture

The Hercules Powder Company developed toxaphene in 1946 as a means of finding an additional market for alpha-pinene from pine oil operations. It produced toxaphene at Brunswick, Georgia, to take advantage of raw materials in the area. Alpha-pinene is recovered from turpentine and reacted with alkali to produce camphene. This in turn is reacted with chlorine in a combined thermal-photolytic process.

While Hercules remained the principal manufacturer from 1947-1982, it was joined in 1970 by Tenneco, which had been producing chlorinated terpenes since 1963. The Tenneco plant was at Fords, NJ, in the watershed of the Raritan River. In 1967 Sonford Chemicals began production. Vertac Inc., initially a subsidiary of Vicksburg Chemical Company entered the business with a plant in Vicksburg, Mississippi. In January 1984, this was the sole plant remaining in operation.

Under normal operating conditions the amount of product in waste (at 200 ppb) would only result in a contamination of 96 pounds per year - but there were undoubtedly times when operations were not normal and somewhat larger amounts were released.

4.6.2 Uses

Toxaphene has been used as a pesticide since 1947 and was the most heavily used insecticide from the early 1960's to the mid 1970's. While toxaphene has been recommended for a long list of crops and pests, by far its largest application has been on cotton (38.4 million lbs in 1974) with a mere 4.8 million pounds being applied to other field crops (1.5 millions lbs of which was on soybeans) in that year.

In the Hudson-Raritan Basin toxaphene has been recommended for use on corn for control of army worm, cinch bug and corn borer, and on soybeans and vegetables, but apparently has not been used on a large scale. Insecticidal treatment of livestock and poultry, which used some 3 million pounds nationwide in 1974, was the only significant market for toxaphene in non-crop applications. In recent years much of its use on soybeans has been as an herbicide to control sicklepod under a special local need label, SLN, in several southern states. Some estimates of national use are shown in Table 4-10 [Vlier & Zygadlo 82]

Table 4-10: U.S. Consumption of Toxaphene in 1964 and 1971

	1964 1000 lbs	1971 1000 lbs
FARM USE	39564	36572
Crop Use	34861	32840
Corn	1099	182
Other Grain	3305	488
Soybeans	1319	1524
Hay(incl. Alfalfa)	1000	50
Cotton	26915	28112
Peanuts		1356
Tobacco		206
Citrus		9
Potatoes(White)		142
Other Vegetables	1223	628
Other Fruits & Nuts		58
Other Field Crops		85
Livestock	4703	3732
Beef Cattle	4075	3483
Dairy	177	200
Other	451	49
NON-AGRICULTURAL Use - No data		

For a number of reasons the production and use of toxaphene has been mainly concentrated in the South. Table 4-11 reveals that while 87.12% of toxaphene was used in Southeastern, South Central and West South Central States, only 1.18% was used the the Northeastern States, comprising New Jersey, New York, Pennsylvania and all of New England. Note that the totals in Tables 4-10 and 4-11 do not agree. We cannot explain the discrepancy. However, for other reasons it appears likely that the larger numbers are more accurate. The regional breakdown in percentage terms is probably realistic.

Table 4-11: Regional Distribution of Toxaphene Use in U.S.

	1964		1971	
	1000 lbs	Percent	1000 lbs	Percent
Northeast	3	.0%	0	0.0%
Lake States	53	0.2%	40	0.1%
Corn Belt	1298	3.8%	189	0.6%
Northern Plains	1	.0%	87	0.3%
Appalachia	4179	12.2%	2196	6.7%
Southeast	11502	33.6%	15369	46.8%
Delta States	10256	30.0%	10754	32.7%
Southern Plains	5065	14.8%	2694	8.2%
Mountain	1040	3.0%	1238	3.8%
Pacific (1)	792	2.3%	300	0.9%
TOTAL	34189		32867	

(1) Does not include Alaska

Sources: [USDA 68; USDA 71]

Because of the very minimal use in the Northeast, it is not surprising to find that the soil testing FY69 and FY70 programs found no trace of toxaphene residues at the sites tested [Wiersman, Tai & Sand 75]. However, research has indicated that toxaphene is transported from the soil into the stems and leaves of plants [Clare et al ??]. This does not appear to have affected fruits and grains, but is of some significance for vegetables. In a study of residues in food, it was found that in some years more than 7% of the leaf and stem vegetables tested had more than a trace of toxaphene and in 1964, 1965 and 1967 there were more than 2% having residues of more than 2 ppm [FDA 68]. In view of the importation of products from areas in which more toxaphene is used, there may have been some entering the area both on the surface of and contained in these products.

4.6.3 Toxicology of Toxaphene

Toxaphene is one of the more toxic of the chlorinated hydrocarbon pesticides, as shown in Table 2-1, and the use of protective clothing and eye wear has been stressed in its handling. Aside from its toxicity to mammals, it is also hazardous to aquatic life and has 'never to exceed' limits of 1.6 g/l for fresh water and 0.07 g/l for salt water. It is a suspected carcinogen. The International Agency for Research on Cancer and the National Cancer Institute have researched the subject and have issued reports [Shepard 51], [Reid & Streebin 72].

In view of the evident hazards of the material, an RPAR was issued against toxaphene on May 25, 1977 on the basis of oncogenicity and reductions in nontarget species [Sittig 81]. After several years of legal process the EPA revoked the registration of toxaphene in 1982 and thereby prohibited all uses except for minor quantities for control of scabies on cattle and sheep.

5. Chlorinated Herbicides (2-4-5-T, Silvex) and Chlorinated Phenols: Sources of Dioxins

5.1 2,4,5-T, Silvex, and Associated Dioxins

Dioxins are a sub-class of poly-chlorinated compounds (see Figure 1-1 in Chapter 1) consisting of two chlorinated benzene rings linked in two places by oxygen atoms. There are 75 isomers (depending on the number and position of the chlorines), of which the most toxic by far is known as 2,3,7,8 - tetrachloro-dibenzene-paradioxin or 2,3,7,8 TCDD. It is toxic to rats at 5 parts per trillion in food, causing cancer anf other disabilities.

It is recognized that the herbicide 2,4,5-trichlorophenoxyacetic acid known as (2,4,5-T), and as a component of"agent orange" in Vietnam, contains some of the chlorinated dibenzo p-dioxins, especially 2,3,7,8 TCDD, as a contaminant. The 2,4,5-T used in Vietnam was reported to contain 8.36 ppm TCDD [Imhoff & Fair ??, table 2]. A related product (2,4,5-trichlorophenoxy) propionic acid commonly called silvex also has the same contaminant, as does the germicide hexachlorophene. In all three cases, the contaminant probably arises from the production of a common intermediate, 2,4,5 trichlorophenol. The controversy rages as to the effects that exposure might have had in industrial plants producing the material and to sprays encountered by military personnel in Vietnam. However, in the Hudson-Raritan basin, production of chlorinated phenols is the most likely source of dioxin in the environment -- though contamination from herbicide usage cannot be ruled out.

5.1.1 Manufacture of Chlorophenols & Derivatives

Phenol is usually chlorinated stepwise to a mixture of (ortho- and para-) mono, di, tri, and tetra chlorophenols. These are separated from the unreacted phenol by reacting with potassium carbonate to form water soluble salts. Polychlorophenols are then separated from each other by fractional distillation. Pentachlorophenol is usually made in a subsequent reaction from polychlorinated feeds, with the help of a catalyst ($FeCl_3$ or $AlCl_3$). The 2,4,5-Trichlorophenol isomer is reacted with chloroacetic acid and sodium hydroxide to produce 2,4,5-T. Another route to 2,4,5-trichlorophenol is from 1,2,4,5-tetrachlorobenzene at high temperatures and pressures in the presence of NaOH (See Figure 1-1 in Chapter 1).

The manufacturing of 2,4,5-T began in 1948 and production levels were reported to the U.S. Tariff Commission beginning in 1951. Production levels rose erratically to 6.3 million pounds annually in 1960 (Table 5-1). Production jumped during the period 1961 - 1968 to accomodate heavy military -use in Vietnam (mainly during 1964 - 1968), which consumed 44 million pounds of the chemical in "agent orange". Military sales slowed sharply in 1969 and output in that year dropped to 5 million pounds and some producers dropped out. Production statistics are unavailable after 1969. Production data for Silvex and hexachlorophene are not available at all, although consumption data for 2,4,5-T and Silvex have been given for 1978 (Table 5-4). No data on production of the intermediate 2,4,5-trichlorophenol is available. Sylvex was produced by replacing the chloroacetic acid with chloropropionic acid. Alcohols were then reacted to provide the esters where these were desired. Since the various reactions are similar to those in other chemical processing some companies may have actually produced 2,4,5-T compounds over a relatively short period and have converted to the processing of other products. This is true of Berkeley Chemicals (1955) which reappears later as the Berkeley Chemical Dept. of Millmaster Onyx, which reported the production of silvex in 1967. Similarly, Chemical Insecticide Corp. made a number of different derivatives during the 1960's including 2,4,5-T in some years but not others. In Tables 5-2 and 5-3 are shown some of the companies which manufactured 2,4,5-Trichlorophenoxy acetic acid and derivatives in 1955, 1965 and 1969.

Table 5-1: Production of 2,4,5-T Acid(1000 lbs)

1948	NA	1960	6337
1949	NA	1961	6909
1950	NA	1962	8369
1951	2454	1963	9090
1952	3490	1964	11434
1953	5281	1965	11601
1954	2697	1966	15489
1955	2925	1967	15067
1956	5169	1968	17530
1957	5334	1969	4999
1958	3678		
1959	5547		

It is of particular significance that three of these -- Berkeley Chemical Co., Chemical Insecticide Corp. and Biochemicals Division of Diamond Shamrock were located in northern New Jersey. Each of these locations drain into the Hudson-Raritan basin -- Metuchen into the Raritan and the other two into Newark Bay and thence into the upper New York Harbor and Arthur Kill. Depending on the capacities of these plants they may have had product loss in cooling water of a few hundred pounds per year of 2,4,5-T.

Table 5-2: Producers of 2,4,5-T and/or derivatives in 1955 & 1965

Berkeley Chemical Dept. (Millmaster Onyx Corp), Berkeley Heights, NJ
Diamond Alkali, Newark, NJ
Dow Chemical Company, Midland, Mich
Ethyl Corp., Richmond, VA
Monsanto Chemical-Nitro, WV
Pittsburgh Coke & Chemical, Pittsburgh, PA
Thompson Chemicals Corp.-St. Louis (1955)

Table 5-3: Producers of 2,4,5-T and/or Derivatives in 1969

Berkeley Chemical Dept. (Millmaster Onyx Corp.), Berkeley Heights, NJ
Chemical Insecticide Company, Metuchen, NJ
Diamond Shamrock (Biochemicals Division), NJ
Dow Chemical Company, Midland, Mich
Hooker Chemical Div.(Occidental Petroleum Co), Niagara Falls, NY

5.1.2 Use pattern, for 2,4,5-T and Silvex

The use patterns for,4,5-T and Silvex are shown for the year 1978 in Table 5-4. Obviously the industrial and commercial use at 66.2% of the total is of most significance. Pasture and rangeland at 28% account for almost all of the remainder. While there may have been some spot use of 2,4,5-T to remove woody growth from pasture in the eastern U.S. most of this category was used in the "improvement" of western rangeland (e.g. to control mesquite). Lawn and turf use (1.4%) is low because almost all such applications utilized straight 2,4-D. The 4.2% used on rice was entirely outside the Hudson-Raritan basin. The use pattern for 1978 has probably been fairly typical of use over the past three decades, averaging 9.3 million lbs./yr. sprayed on 2 million acres.

Data for 1978 are shown because this is the last year of unrestricted use. Both 2,4,5-T and silvex were restricted in February 1979 by a suspension of their registration for use on rights-of-way and pastures [EPA 79]. Uses not suspended at that time included permanent rangeland, airports, fences, hedgerows, lumber yards, refineries, non-food crop areas, storage areas, tank farms, industrial sites, and all other areas not previously suspended were suspended by the final order banning all uses which was issued in 1980.

The principal uses of 2,4,5-T (as compared to 2,4 D) have been for the control of broad-leafed woody growths and weeds, while leaving grass unaffected [e.g. Schreiber & Fertig 56]. In the private sector, railway, electric power and pipeline companies use it as a way of keeping clear rights-of-way and other

Table 5-4: Use Pattern 1978 for 2,4,5-T and Silvex

	2,4,5-T Millions/lbs	Silvex active
Non Agricultural		
Industrial & Commercial	4.7	1.1
Pasture & Rangeland	2.0	0.7
Lawns & Turf	0.1	0.2
Aquatic	0	0.6
	---	---
Total	6.8	2.6
Agricultural		
Other crops outside Hudson-Raritan	0.3	
	---	---
Grand Total	7.1	2.6

areas that were likely to become overgrown. In the government sector highway departments, forestry and parks departments use it for clearing shoulders,fire lanes and access roads all with considerably less manual labor than was previously needed. It has also been used in forest management to remove undesirable deciduous trees and prepare land for planting. This application, using helicopters for aerial spray coverage, is blamed for having caused a high frequency of miscarriages among the women in one area in Oregon (this episode led to the product being suspended for most uses March 1, 1979).

It is known, incidentally, that the most toxic dioxin (2,3,7,8-TCDD) is generated when 2,4,5-T is burned (as in a brush or forest fire) at low or moderate temperatures. About 1 mg of dioxin would be formed by combustion of 1 kg of 2,4,5-T (1 ppm). See Stehl and Lamparski and Ahling et al [cited in Imhoff & Fair].

5.2 Pentachlorophenol(PCP) and Associated Dioxins

Over the years 1955-1981 some 668 million pounds of pentachlorophenol(PCP) was consumed in the U.S. in preserving wood. Production in 1977 was 45 million pounds. Eventually part of this wood -- whether in the disposal of sawdust and scraps left over from construction or in the accidental or intentional disposal of wooden structures -- has been burned.It has been found that representative samples of wood preservatives with technical grade pentachlorophenol have been high in impurities -- particularly chlorodioxins and benzofurans. Table 5-5 shows the composition of a commercial PCP, Dowicide, produced by Dow Chemical Company.

Table 5-5: Composition of a Commercial Pentachlorophenol (Dowicide 7. Sample 9522A)

Component	Analytical Results
Pentachlorophenol	88.4%
Tetrachlorophenol	4.4%
Trichlorophenol	<0.1%
Chlorinated phenoxyphenols	6.2%
Octachlorodioxin	2,500 ppm
Heptachlorodioxins	125 ppm
Hexachlorodioxins	4 ppm
Octachlorodibenzofurans	80 ppm
Heptachlorodibenzofurans	80 ppm
Hexachlorodibenzofurans	30 ppm

Source: [Wagner 83]

5.2.1 Manufacturing of Pentachlorophenol

Table 5-6 shows the reported pentachlorophenol plants as of May 1969. At that time only one plant was in the Hudson-Raritan basin -- that of Merck & Co. at Hawthorne, NJ, near the Passaic River which drains into Newark Bay. Unfortunately, its capacity was not given.

Table 5-6: PCP Producers in 1969

Company	Location	Capacity million lbs
Dow Chemical Company	Midland, Mich	15
Merck & Company, Inc (Chem. Mfg. Div.)	Hawthorne, NJ	N.A.
Monsanto Company (Organic Chems. Div.)	Sauget, Ill	26
Reichhold Chemicals, Inc.	Tacoma, Wash	7
Sanford Chemical Company	Port Neches, Tex	10
Vulcan Materials Company (Chems. Div.)	Wichita, Kans	7

Source: Oil, Paint & Drug Reporter, 5/26/69

While a reputable company such as Merck may have been particularly conscientious in cleaning up its cooling water and properly disposing of other wastes some small amounts of PCP and its impurities could have come from this operation.

5.2.2 Dioxins from Incineration of PCP-Treated Wood

The concern about the burning of PCP treated material is that the burning of chlorinated phenoxyphenols will, under conditions of combustion, yield polychlorinated dioxins --and that these may be carried into the atmosphere. This concern appears to be supported by a number of reports that dioxins have been found in incinerator effluent in Canada, France [Karasek, Clement & Viam 82] and the Netherlands [Olie, Lustenhouwer & Hutzinger 78].

It is an open question whether the dioxins found near incinerators were produced by the incineration process or whether they were present in the materials being burned. Dow has attempted [NRC 75] to prove that dioxins were produced only by incineration and energy production, but this study itself has been challenged [Imhoff & Fair ??].

While it is impossible to conclude that dioxin contaminants are universally present in incinerator fly ash and /or stack gasses, it appears quite possible that dioxins from such sources may by now constitute a greater problem than those associated with that 2,4,5-T and silvex when they were widely used. However not nearly enough is known, as yet, to trace the likely sources of dioxins with any degree of confidence.

5.3 Degradation of Dioxins(TCDD)

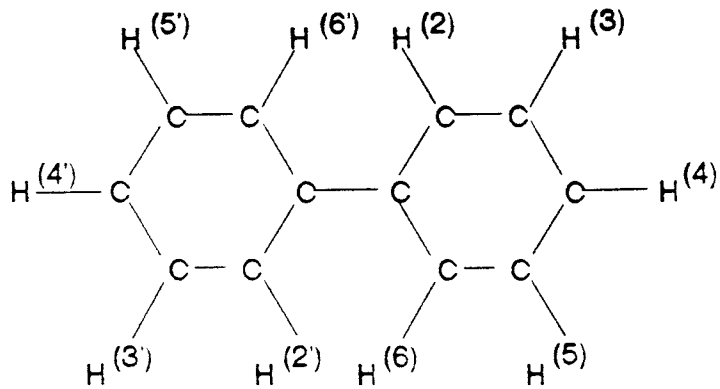
It is reported that TCDD in an organic solvent may have a half-life as short as one hour on leaves in sunlight. When deposited on the soil surface it has a half life of about 50-55 hours [Wagner 83]. Under the soil, however, degradation depends on bacterial action which is much slower. In this case the half life is believed to be about one year [Kearny et al 73]. In a case of known excessive application (accumlulating 1000 lb/acre of 2,4,5-T at Eglin Air Force base) TCDD persisted for more than ten years [Wagner 83]. In a similar case in Seveso, Italy half life has been estimated at ten years [DiDomenico et al 80].

Because most of the 2,4,5-T spray used to control brush will eventually be subject to photodegradation it is probably only where excessive amounts have penetrated the soil that significant TCDD residues remain. However, the concentrated amounts of PCDD, and polychlorodibenzofurans in treated wood appear to present a longer term problem.

6. Other Chlorinated Chemicals: Polychlorinated Biphenyls (PCB's)

The class of polychlorinated biphenyls consists of compounds formed by chlorination of a biphenyl with the general formula ($C_{12}H_{10}$). Biphenyls are double ring hydrocarbons having the structure shown in Figure 6-1. There are 10 possible forms, depending on the number of chlorine substitutions in the biphenyl molecule as viz. monochloro-, dichloro-, trichloro-etc.

Figure 6-1: Biphenyl Structure



Chlorine content ranges from 18% to 79% by weight. There are several isomers of each form, as shown in Table 6-1 depending on the available hydrogen substitution sites (2-6, 2'-6'). The major U.S. producer was Monsanto, which designated its PCB products by the trade name Arochlor (R). Other trade names used in the U.S. include Chloretol, Dykanol, Inerteen, Noflamol and Pyranol [NRC 80].

Arochlors were sold in a number of formulations, distinguished mainly by chlorine percentage [Versar 76]. The bulk (~60%) of Monsanto's total output was Arochlor 1242 (42%Cl), followed in importance by Arochlor 1254 (54%Cl) and Arochlor 1248 (48%Cl), accounting for roughly 15% and 10% respectively. The other 15% was mostly highly chlorinated forms (>60%Cl). Rather small quantities of the less chlorinated forms were produced, mostly after 1970.

Table 6-1: Composition of Chlorinated Biphenyls

Formula Chlorobiphenyls	Empirical Molecular Weight[a]	Percent Chlorine[a]	No. of Isomers
$C_{12}H_{10}$	154	0	1
$C_{12}H_9Cl$	188	18	3
$C_{12}H_8Cl_2$	222	31	12
$C_{12}H_7Cl_3$	256	41	24
$C_{12}H_6Cl_4$	290	48	42
$C_{12}H_5Cl_5$	324	54	46
$C_{12}H_4Cl_6$	358	58	42
$C_{12}H_3Cl_7$	392	62	24
$C_{12}H_2Cl_8$	426	65	12
$C_{12}HCl_9$	460	68	3
$C_{12}Cl_{10}$	494	79	1

[a]Based on Cl_{35}

Source: [FHA 59]

PCB's are very stable compounds. Their industrial uses were based on this chemical stability. They are heavy liquids, ranging from mobile oils (less chlorinated) to sticky resins (most chlorinated). Boiling points range from 275°C to 400°C [Hutzinger, Safe & Zitko ??].

Apart from resistance to degradation, PCB's are almost insoluble in water, but are soluble in fats (lipids). This accounts for the fact that they tend to be accumulated via food chains and build up in the tissues of higher animals and fish. For example, a concentration factor of 230,000 has been reported in fathead minnows. Cod and pike have been found with up to 10 mg/kg of fat. Further concentration occurs in fish-eating birds, where levels as high as 400 mg/kg have been found in the fat of cormorants and 600-700 mg/kg in the fat of herring gulls [EPA 79a; NRC 80].

6.1 Production & Use

The manufacturing process used by Monsanto was a straightforward (iron-based) catalytic batch chlorination, at elevated temperatures, followed by alkaline washing and distillation. The general scheme is shown in Figure [NRC 80, Figure D1]. Small quantities of chlorodibenzofurans (CDF's) were apparently produced in some batches, at the wash or distillation stage, reflecting variations in the process details [NRC 80, p147]. Production began in 1930. Monsanto Chemical Company manufactured PCB's in two plants: Anniston, Ala. (closed 1970) and Sauget, Ill. (closed 1977).

Total cumulative U.S. production from 1930 through 1975 totalled an estimated 625,000 tonnes, (in addition to exports of 65,000 tonnes and imports of 1400 tonnes). Of U.S. consumption of 570,000 tonnes an estimated 340,000 tonnes were still in service, in that year [Versar 76, p7]. Annual domestic sales by Monsanto have been released for the eighteen years 1957-1974 accounting for about 300,000 tonnes [Versar 76, pp199-200]. Sales by type of arochlor are shown in Figure 6-3. Sales by use category are given in Figure

From 1930 to 1975, 76% of total PCB's consumed in the U.S. were used as dielectrics in electrical equipment, mainly transformers (26%) and capacitors (50%). About 8% was used in relatively long-lived applications: hydraulic systems, heat transfer fluids and lubricants. The remainder (16%) was divided up between several short-lived dissipative uses, mainly plasticizers -- e.g. for "baggies" -- (9.2%), carbonless copy paper (3.6%) and miscellaneous industrial uses such as adhesives, ink and dye carriers, pesticide extenders, etc. [Versar 76, Table 1.2-1, p7]. In 1971 Monsanto voluntarily eliminated sales for non-electrical uses. All production ceased in 1977. Table 6-2 shows production, sales and use breakdown for PCB's.

6.2 Emissions to the Environment

Substantially all the PCB's used in non-electrical equipment or for other purposes are by now out of service. Lubricants have a short life and are either lost *in situ* (e.g. by leakage) or collected and discarded later. Ditto for hydraulic fluids. Most of these ended in landfills, with a fraction leaked onto factory floors or paved areas where they could be washed into sewers. Plasticizers for packaging materials and carbonless copy paper rapidly become refuse and go to landfills (85%) or to incinerators (15%). The incineration of paper and packaging products containing PCB's probably accounted for most of the airborne PCB's observed in the early 1970's.

FIGURE 6-2: Monsanto Manufacturing Process

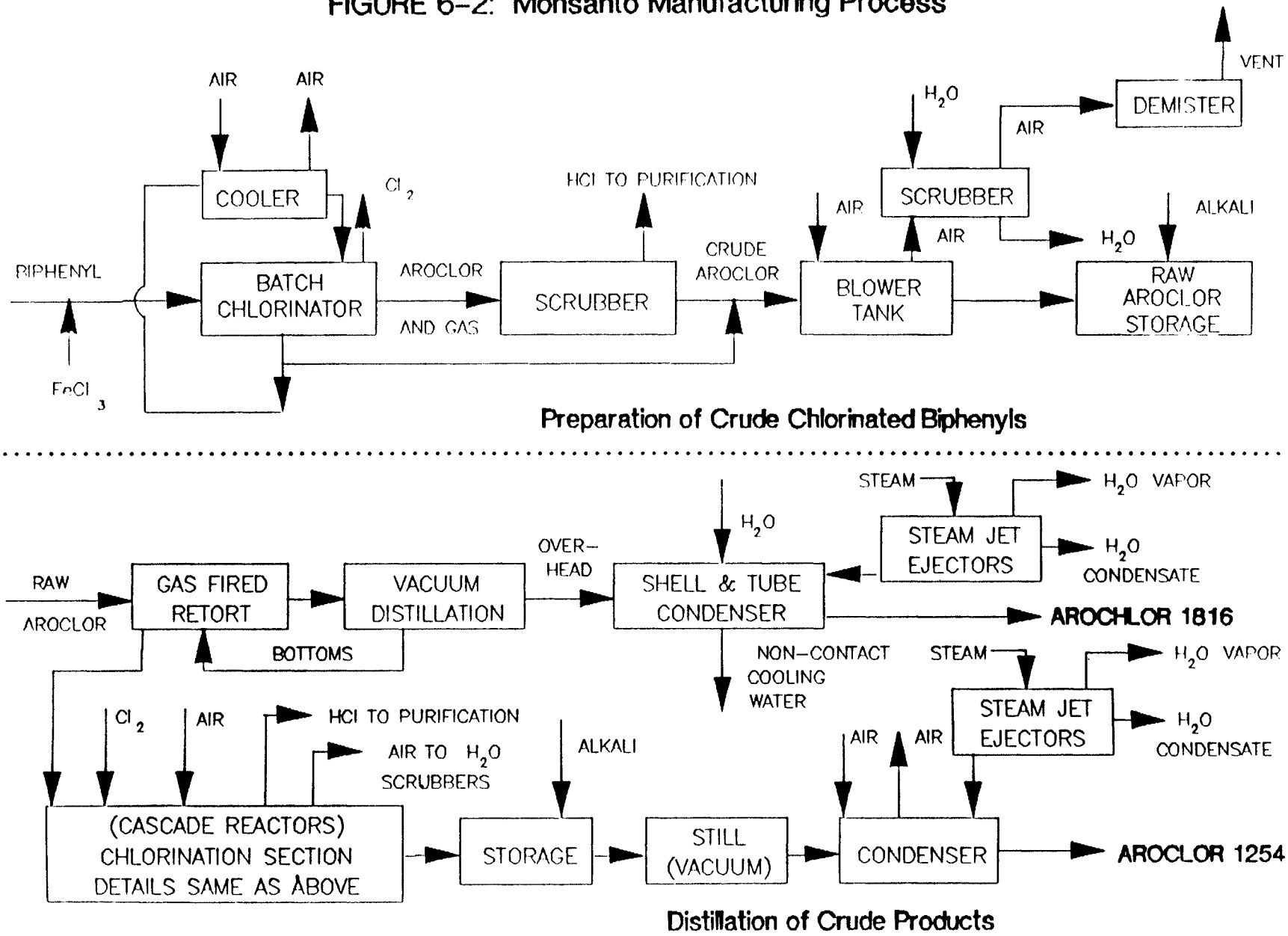


FIGURE 6-3: U.S. Sales of Monsanto's PCB's by Use

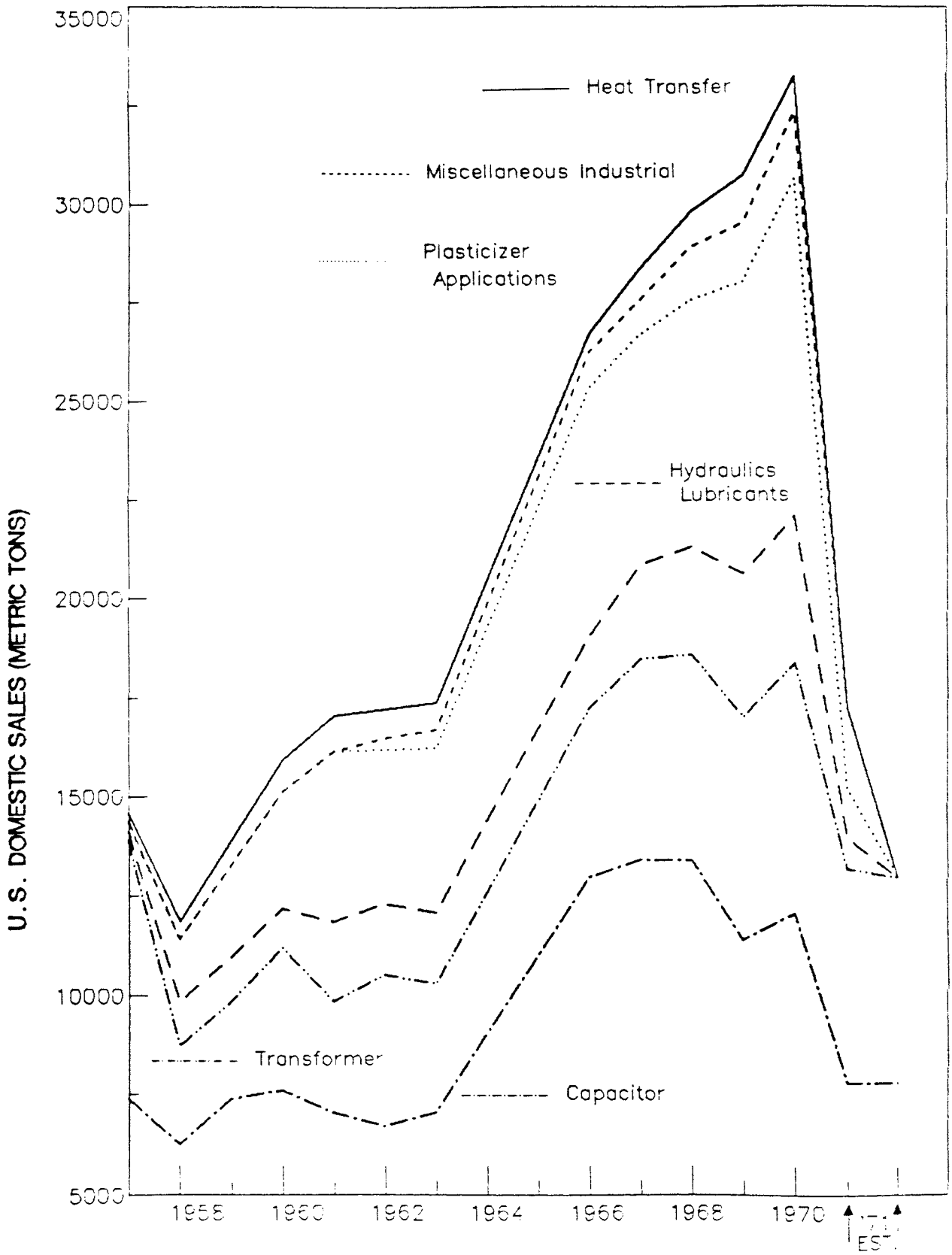


FIGURE 6-4: U.S. Sales of Monsanto's PCB's
Specific Arochlors

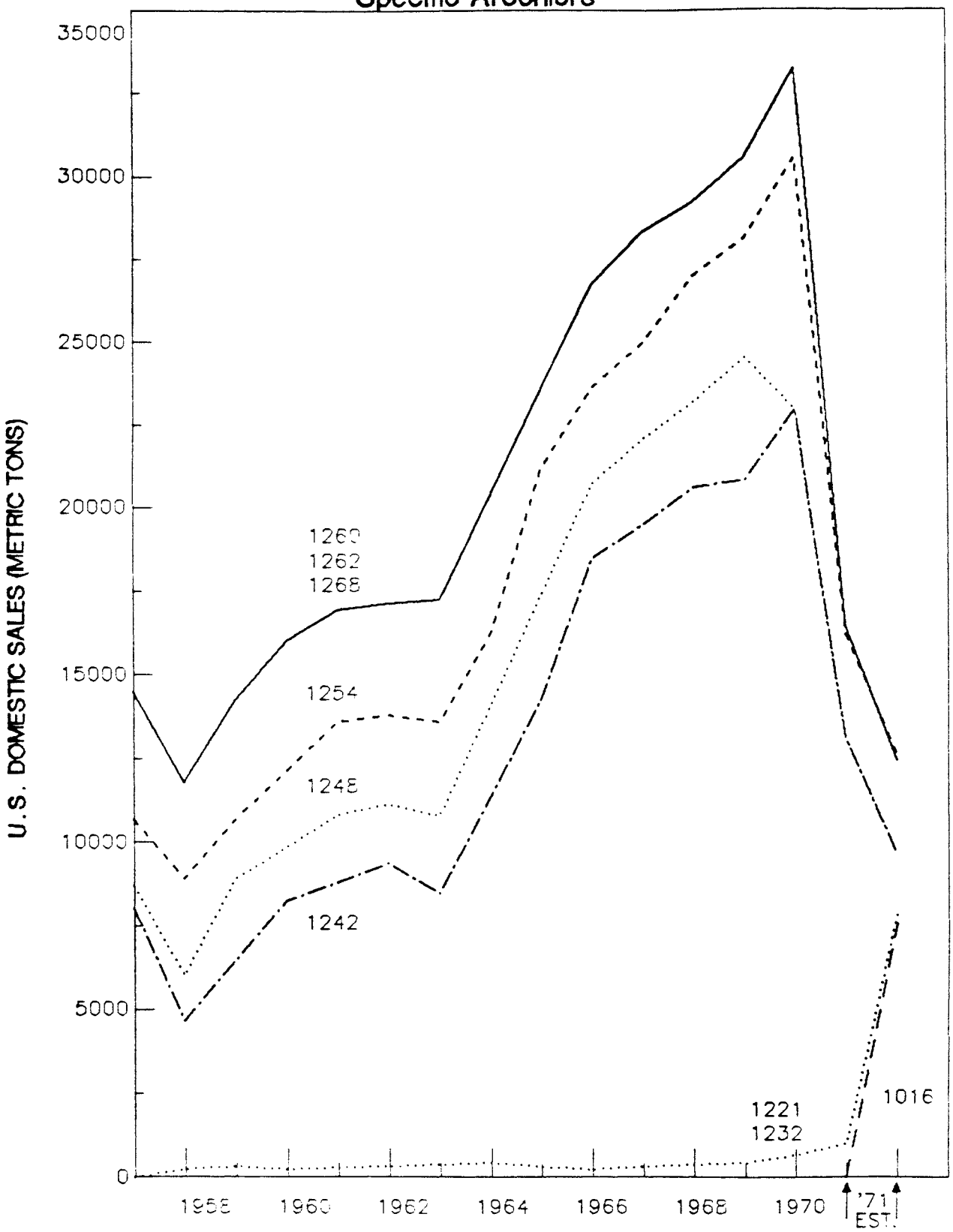


Table 6-2: PCB Manufacture & Sales (1000 tonnes)

	US Production of PCBs	Exports of PCBs	Total US Sales of PCBs	Use Breakdown by Category: Heat Transfer	Lubricants/ Hydraul.	Misc. Industrial	Transformers	Capacitors	Plasticizers
1957	NA	NA	14.651		0.731	0.319	5.876	7.724	0.000
1958	NA	NA	11.821		0.703	0.356	2.594	6.395	1.787
1959	NA	NA	14.202		1.218	0.712	2.714	7.484	2.074
1960	17.200	NA	15.973		1.144	0.707	3.593	7.696	2.832
1961	16.563	NA	17.027		1.864	0.959	2.849	7.228	4.127
1962	17.397	NA	17.256	0.071	1.776	0.762	3.621	6.977	4.048
1963	20.291	1.654	17.296	0.264	1.789	0.693	3.307	7.079	4.164
1964	23.057	2.399	20.352	0.421	1.984	0.767	3.627	8.863	4.689
1965	27.433	1.921	23.494	0.561	2.094	0.835	3.927	10.772	5.305
1966	29.873	3.108	26.797	0.801	1.931	0.807	4.042	13.102	6.115
1967	34.160	3.685	28.334	1.026	2.106	0.647	5.022	13.473	6.060
1968	37.582	5.094	29.536	1.147	2.615	0.582	5.255	13.404	6.534
1969	34.649	4.819	30.479	1.383	3.646	1.142	5.491	11.350	7.466
1970	38.580	6.192	33.140	1.795	3.358	0.738	6.272	12.115	8.862
1971	15.873	0.000	15.559	1.388	0.704	0.524	5.050	6.414	1.478
1972	17.509	2.898	11.978	0.341	0	0	11.637		0.000
1973	19.132	3.786	17.119				17.119		
1974	18.355	2.447	15.606				15.606		

Source: [Versar 76, Tables 1.1-1 and 1.1-2]

Misc. Category for 1969 contains 1439 pounds (.653 tonnes) of petroleum additives

As of 1975 223,000 tonnes of PCB's were estimated [NRC 80] to have been disposed of in various ways, viz

Table 6-3: Disposal of PCB's(1000 tonnes)

Production[2] wastes to landfill	50	
Obsolete equipment in landfill	36	
Other	36	
Total landfill		122
Equipment dumps, other	8	
Mobile Environmental Reservoir (MER) in soil, water[3]	68	
Degraded or incinerated	25	
Total accounted for		223

The estimated rate of PCB entry into landfills in 1975 was estimated to be 5500 tonnes/yr. However the ending of PCB production has substantially reduced the contribution from manufacturing processes.

[2]Refers to wastes from manufacturing electrical equipment.

[3]Primarily from non-electrical uses.

From 1980 onward, the major contribution to landfills will be from obsolete electrical equipment, specifically liquid filled capacitors and large transformers.

Based on sample data in the late 1970's, 240 tonnes of PCB's would have ended up in sewage sludge. Of this, about 15% was incinerated while the rest was sent to landfills.[4] Of the incinerated fraction (36 tonnes), 85% to 90% was probably destroyed, the remainder being also returned to landfills in ash. Most of the PCB's passing through municipal treatment systems are believed to originate in the mobile environmental reservoir (MER) of PCB's already released, not from "new" sources [NRC 80].

The MER consists of PCB's that have escaped into the environment by various routes but that have not been permanently immobilized. Most of the MER is still in river bottom sediments -- much of it in the Great Lakes and the Hudson River -- which are mobile to the extent of the potential for disturbance by dredging and floods, with attendant risks of evaporative loss or biological uptake.

The MER is gradually being reduced by three routes: the largest fraction is attached to soil particles or finds its way to lake or river bottom sediments that move very slowly to the ocean. The second largest fraction is apparently being 'recycled' to landfills by way of sewage sludges and incinerator ashes. A small amount is degraded each year to simple chemicals. Unfortunately PCB's in water bodies can escape to the atmosphere by evaporation from saturated waters. They are also incorporated into biota.

A pertinent example of remobilization occurred in the upper Hudson River, where GE manufactured capacitors at Fort Edward and Hudson Falls (beginning in 1947 and 1952 respectively). These two facilities purchased 35,000 tonnes of PCB's between 1966 and 1974 alone, roughly 15% of total U.S. consumption. PCB losses from the facility of 0.14% (13-14 kg per day or ~5.8 tonnes/yr) were acknowledged by GE [Hetling, Horn & Tofflemire 78]. Essentially all of this lost material accumulated initially behind the Fort Edward dam. Extrapolating to the period prior to 1966, of the order of 75,000 tonnes of PCB's was used at Ft. Edward and (it now appears) nearly 600 tonnes were released into the river. It is now fairly obvious that GE's discharges were actually far greater than 5 tonnes/yr.

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[4] In the case of New York City, however, sewage sludge is barged about 20 miles out into the New York bight and dumped in deep water due to lack of landfill sites

In October 1973 the aging Ft. Edwards dam was removed and large quantities of contaminated sediments from behind the dam were inadvertently released. Most of the released material was later trapped by other dams and locks on the river, and on the order of 240 tonnes has subsequently been dredged out of the river and dumped on land sites. However, substantial remnant deposits remain in the upper basin as "hot spots". Loss rates from dump sites by seepage to groundwater or erosion back into the river are apparently minor (though not zero). Interestingly, the quantity of PCB's now estimated to be in dredge spoil dump sites in the upper basin alone is over 2.5 times the amount implied by GE's original estimated rate of discharge into the river. Estimates of the disposition of PCB's in the river and estuary as of 1978 are given in Table 6-4, based on a large number (~1300) of sediment core samples.

Table 6-4: Summary Distribution of Residual PCB's in the Hudson River Basin (1978)

Area	Estimated total PCB's tonnes	Estimated scourable PCB's tonnes	Calculated loss rate* tonnes/yr)
River sediments			
Remnant deposits	62.5	20	3.8
Upper Hudson riverbed (Ft. Edward Dam Site to Troy)	134	44	2.5
Lower Hudson riverbed (Estuary-Troy to New York Harbor)	90	?	?
Dredge spoil areas (Upper Hudson)	71.5	?	.075
Landfills and dumps (Upper Hudson)	236.5		.36
Biota	10-100		?
Total	595.	> 64	

* Does not include volatilization.
Source [Tofflemire et al, Table 19, p46]

Though most of the PCB's dumped in the upper basin have either been dredged and removed, or still remain in the sediments, there has been a marked increase in downstream contamination. Recent sediments in the (tidal) Hudson estuary are contaminated to an average level of ~10 ppm, which is about two to three orders of magnitude higher than most other large rivers and estuaries [Bopp et al 81]. Measurements by the U.S. Geological Survey in 1976 recorded about 3.6 tonnes/yr moving downstream across the last dam at Troy, NY. This rate of discharge declined by about half in 1979 and dropped to less than 0.4 tonnes/yr in 1981 [Bopp et al 81].

Downstream from Troy, it is estimated by Bopp [op. cit.] on the basis of over 150 analyses and 80 core samples that at least 76 tonnes of PCB's are associated with river sediments. The figure given by Tofflemire et al (Table 6-4) is 90 tonnes. Of this amount, it appears that 10% is actually in the channel and subtidal banks (65% of the area). Coves and shallows account for 25% of the area and an equal fraction of the contamination. The other 10% of the area, with 65% of the PCB's is in the regions of exceptionally high deposition (that are normally dredged for shipping). This is mostly in NY Harbor, and a few other locations.

The PCB's that are deposited in dredged areas are fairly rapidly removed by the dredging itself. Dredging in NY Harbor removes about 0.62 million tonnes of fine-grained sediment from shipping channels annually and up to one million additional tonnes from slip dredging [Bopp et al 81]. Disregarding the latter entirely, and assuming 3 ppm PCB's for the former, in agreement with recent measurements in the Harbor, implies a recent annual removal rate of 1.86 tonnes to the NY Bight (where dredged material is taken for disposal). A more realistic estimate of the removal rate would have to take into account slip dredging. In addition the disposal of sewage sludge from New York city (3.5 ppm, dry weight) removes about 0.7 tonnes per year.

A comparison of this removal rate with the 1981 input rate at Troy dam (0.4 tonnes/yr) suggests that input at the upper end of the tidal river in the late 1970's had fallen well below the rate of removal from the lower end of the river. Recent inflows from the upper Hudson obviously cannot account for the PCB levels being found in the lower river. Probably the major source of PCB's in the lower river in the 1970's was the waste material that was discharged by GE at Ft. Edward prior to 1977. The transport and disposition of PCB's is, in fact, a fairly complex phenomenon. Two different transport mechanisms are evidently at work [Schroeder & Barnes 83, p 10 et seq].

1. A simple diffusion mechanism in which the rate of PCB mobilization is essentially proportional to the concentration of PCB's in the bottom sediments. This mechanism results in a concentration of dissolved PCB's in the river water that is highest at low river flow rates[5], and falls off at higher flow rates, due simply to greater dilution. This mechanism presumably releases PCB's in proportion to the *surface area* of contaminated material in contact with the water.
2. At high (turbulent) flow rates a non-linear "scouring" mechanism takes over. The onset of scouring occurs at a threshold rate that varies from place to place, depending on river bed

[5]except that at *very* low flow rates PCB concentration appears to decrease for reasons not fully understood.

morphology. The critical flow level was exceeded in the upper basin on 28 days in 1977, 13 days in 1978, 28 days in 1979, 6 days in 1980 and 7 days in 1981. These represent extreme for the Husdon River. Sediments that have settled on the bottom are resuspended and carried along by the water -- taking the PCB's along with the particulates.

Several kinds of evidence can be cited to confirm this interpretation. One significant confirming observation is that the PCB concentration in water is indeed lowest at intermediate flow rates. As would be expected, the empirical relationship between concentration and flow appears to be inverse. Another piece of supporting evidence is that at low river flow rates the dissolved PCB's constitute up to 80% of total load, whereas at high flow rates the dissolved fraction becomes insignificant.

6.2.1 Degradation of PCB's

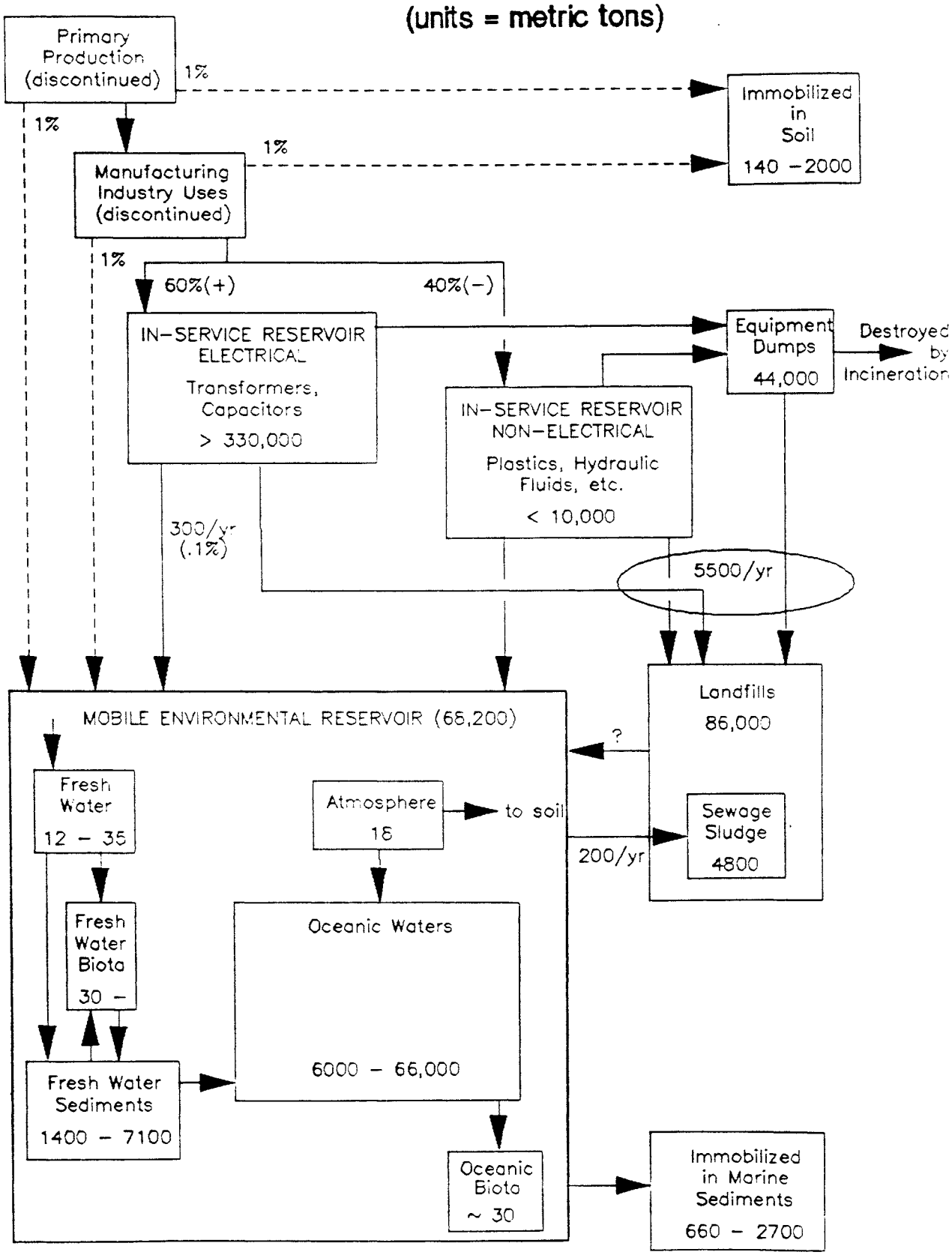
As noted previously, PCB's are very stable and unreactive under ambient environmental conditions. In particular, oxidation, reduction, nitration, isomerization and nucleoplectic reactions with alkalis alkoxides or amines take place only under conditions of temperature and pressure not likely to be encountered in the natural chemical environment. The only significant chemical breakdown process identified so far occurs when BCB's are heated to 500-600°C, when some chlorinated dibenzofurans (CDF's) are formed. This occasionally happens in electrical fires, though the quantities affected are small.

Irradiation by sunlight (especially uv) can cause a variety of reactions, including the replacement of some (ortho) chlorines by hydroxy groups. This permits an oxygen atom to bind in the corresponding position on the other ring to form CDF's. However PCB's in soil or in the aquatic environment, are very unlikely to be exposed to sunlight. Microbes can degrade the less chlorinated PCB's fairly readily in sewage plants but the more highly chlorinated forms (constituting the bulk of all production) are biodegraded very slowly by microbial action.

PCB's in existing landfills do not appear to lead to significant groundwater contamination although the potential for disturbance and accidental release always exists for any dump site.

A summary of the national sources and reservoirs of PCB's is given in Figure 6-5. As of 1975, the total of all reservoirs was estimated by the NRC [NRC 80] to be about 545,000 tonnes, of which 340,000 tonnes were still in service and 68,200 were in potentially mobile environmental reservoirs (excluding soils, equipment dumps, landfills, and marine sediments). The quantity being added to landfills each year

FIGURE 6-5: Sources & Reservoirs of PCB's, 1975
(units = metric tons)



at that time was roughly 5700 tonnes. However the quantity removed from service each year via various routes is very difficult to estimate. Transformers and power capacitors tend to have very long useful lives, while plastics and hydraulic fluids have intermediate periods of useful life. Estimates of 40 years and 6 years, respectively, were made in the NRC report [NRC 80, p63]. Based on this assumption, it can be assumed that the annual removal from the electrical equipment in service reservoir in 1975 would be roughly equal to consumption for that purpose 40 years earlier (i.e. in 1935) By the same argument, the reservoir of non-electrical equipment in service must have been largely depleted by 1975 since production for this purpose was discontinued after 1969. The annual rate of removal in the early 1970's would have been roughly equal to peak annual consumption for these purposes in the late 1960's (~4500 tonnes/yr) and would have begun to decline sharply as the reservoir itself was emptied.

7. Anthropogenic Sources of Polynuclear Aromatic Hydrocarbons (PAH)

The term PAH comprises a group of organic polycyclic hydrocarbon compounds such as anthracenes, fluorenes, fluoranthenes, pyrenes and their nitrogen analogs aza and imino arenes. Crude oil averages 1% to 3% PAH by weight [Pucknat 81]. In the refining process they are concentrated in the heavier fractions,especially pitch, tar, coke and residual oil. Airborne emissions from refineries arise mainly from the regeneration of cracking catalysts. These compounds also are formed during hydrocarbon combustion processes, primarily of coal,especially under pyrolysis (reducing) conditions at temperatures in the range 500°- 800°C [Hine et al 80]. A list of the PAH compounds that have been detected in air is attached (Table 7-1). These compounds are generally associated with particulates in the atmosphere. They decompose rapidly in sunlight, particularly in contact with ozone. However, the details of their atmospheric chemistry are complex and not fully understood [SRI 76].

As noted, PAH in the air is almost entirely created in combustion processes. Other minor sources include asphalt manufacturing and coal-tar processing [Cincinnati 78]. The best documented of the strongly carcinogenetic members of the PAH family of organic chemicals is Benzo(a)pyrene,[6] or BaP. BaP emissions are closely correlated with PAH emissions and are often taken as an indicator of the latter. Formation of BaP per BTU is highest for coal, followed by oil and natural gas in that order. Emissions are inversely proportional to combustion temperature and equipment size. (See Figure 7-1). Several estimates of aggregate emissions for the U.S. have been prepared (Table 7-2). As a benchmark, one study reported 840 mg of BaP per tonne of coal consumed by a modern coal fired plant.

Emission rates for smaller and less efficient coal burning operations range up to 4 orders of magnitude higher, as shown in Figure 7-1. The largest contributors by far are residential heating using coal as a fuel, coke manufacturing and uncontrolled coal refuse fires. The next most important sources appear to be agricultural waste burning and wood burning for residential heating. Refuse burning is also a significant source. All of these, except coke manufacturing and enclosed waste incineration have declined dramatically from earlier levels, since the use of coal (and wood) for residential heating has dropped sharply, and coke manufacturing has become much more efficient with a far lower level of emissions than was once the case.

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[6]This isomer has been called "3 4 benzpyrene" in the U.S. by some American scientists and "1,2-benzpyrene" in Europe while the non-carcinogentic isomer benzo(e)pyrene has been called "1,2 benzpyrene" in the U.S. and "4.5 benzpyrene" in Europe. [See Pucknat 81, chapter 1]

TABLE 7-1: PAH COMPOUNDS

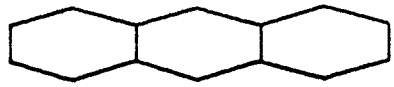
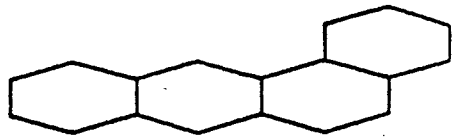
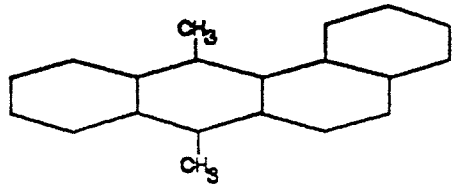
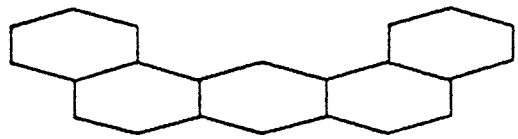
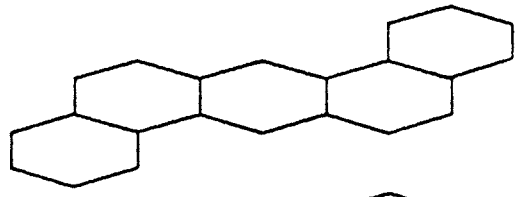
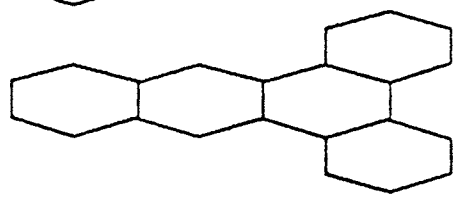
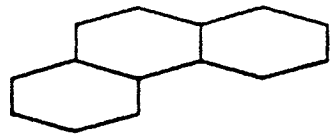
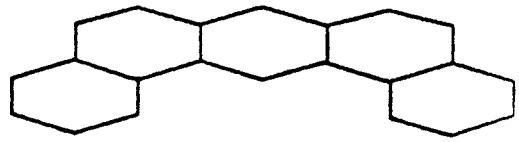
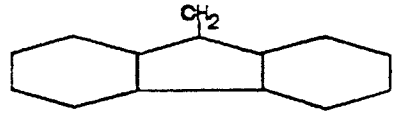
Compound Name	Acronym (carcinogenicity)	Formula	Structure
Anthracene	A (−)	$C_{14}H_{10}$	
Benz [a] anthracene	BaA (+)	$C_{18}H_{12}$	
7,12 Dimethylbenz [a] anthracene	DMBA (++++)	$C_{20}H_{16}$	
Dibenz [a,j] anthracene	(+)	$C_{22}H_{14}$	
Dibenz [a,h] anthracene	DBahA (+++)	$C_{22}H_{14}$	
Dibenz [a,c] anthracene	(+)	$C_{22}H_{14}$	
Phenanthrene	PA (−)	$C_{14}H_{10}$	
Benzo [c] phenanthrene	BcP (+++)	$C_{18}H_{12}$	
Fluorene	F (−)	$C_{13}H_{10}$	

TABLE 7-1: PAH COMPOUNDS - continued

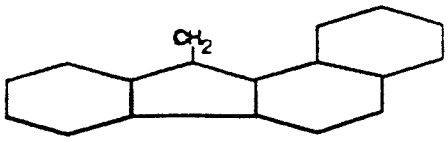
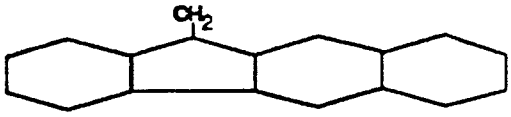
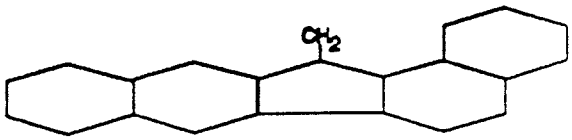
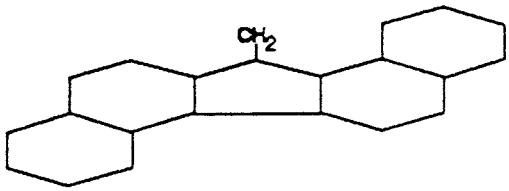
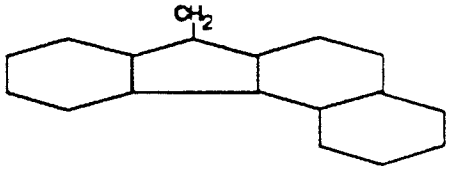
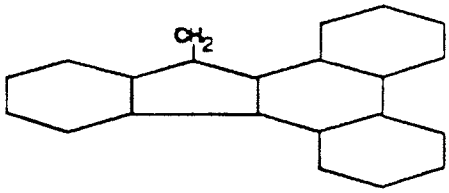
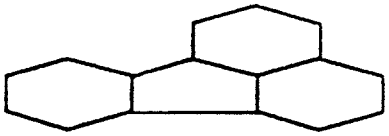
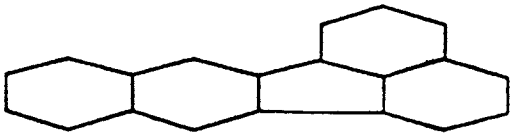
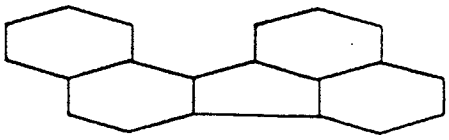
Compound Name	Acronym (carcinogenicity)	Formula	Structure
Benzo [a] fluorene	(−)	$C_{17}H_{12}$	
Benzo [b] fluorene	(−)	$C_{17}H_{12}$	
Dibenzo [a,h] fluorene	(±)	$C_{21}H_{14}$	
Dibenzo [a,g] fluorene	(+)	$C_{21}H_{14}$	
Benzo [c] fluorene	(−)	$C_{17}H_{12}$	
Dibenzo [a,c] fluorene	(±)	$C_{21}H_{14}$	
Fluoranthene	Fluor (−)	$C_{16}H_{10}$	
Benzo [b] fluoranthene	BbF (++)	$C_{20}H_{12}$	
Benzo [j] fluoranthene	BjF (++)	$C_{20}H_{12}$	

TABLE 7-1: PAH COMPOUNDS - continued

Compound Name	Acronym (carcinogenicity)	Formula	Structure
Benzo [k] fluoranthene	BkF (−)	$C_{20}H_{12}$	
Benzo [ghi] fluoranthene	(−)	$C_{18}H_{10}$	
Acenthrylene	(−)	$C_{16}H_{12}$	
Benzo[j] acenthrylene	(++)	$C_{20}H_{14}$	
Methylcholanthrene	(++++)	$C_{21}H_{16}$	
Nathphacene	(−)	$C_{18}H_{12}$	
Naphtho[2,1,8-gra]naphthacene	(−)	$C_{24}H_{14}$	
Pyrene	(−)	$C_{16}H_{10}$	
1-Methylpyrene		$C_{17}H_{12}$	

TABLE 7-1: PAH COMPOUNDS - continued

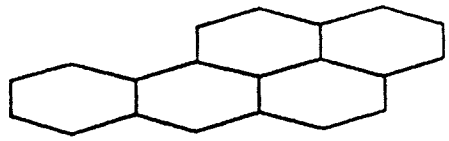
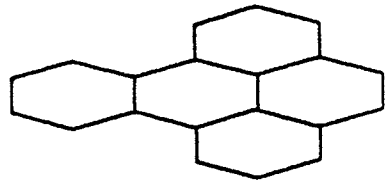
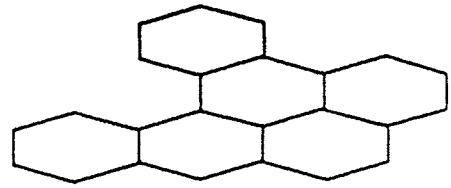
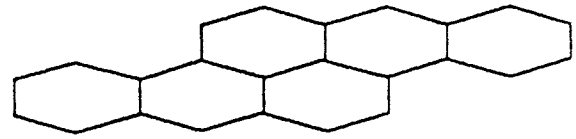
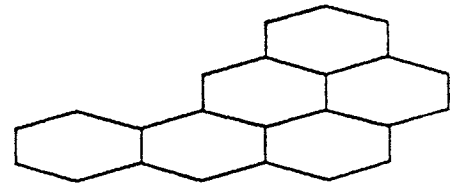
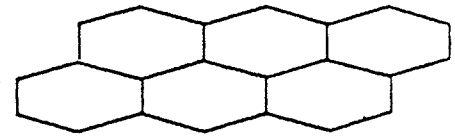
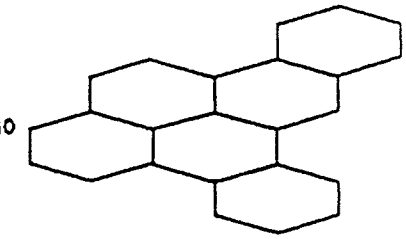
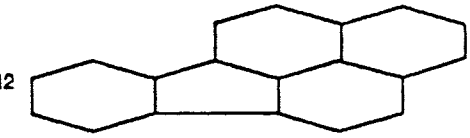
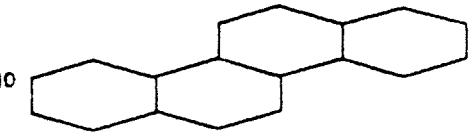
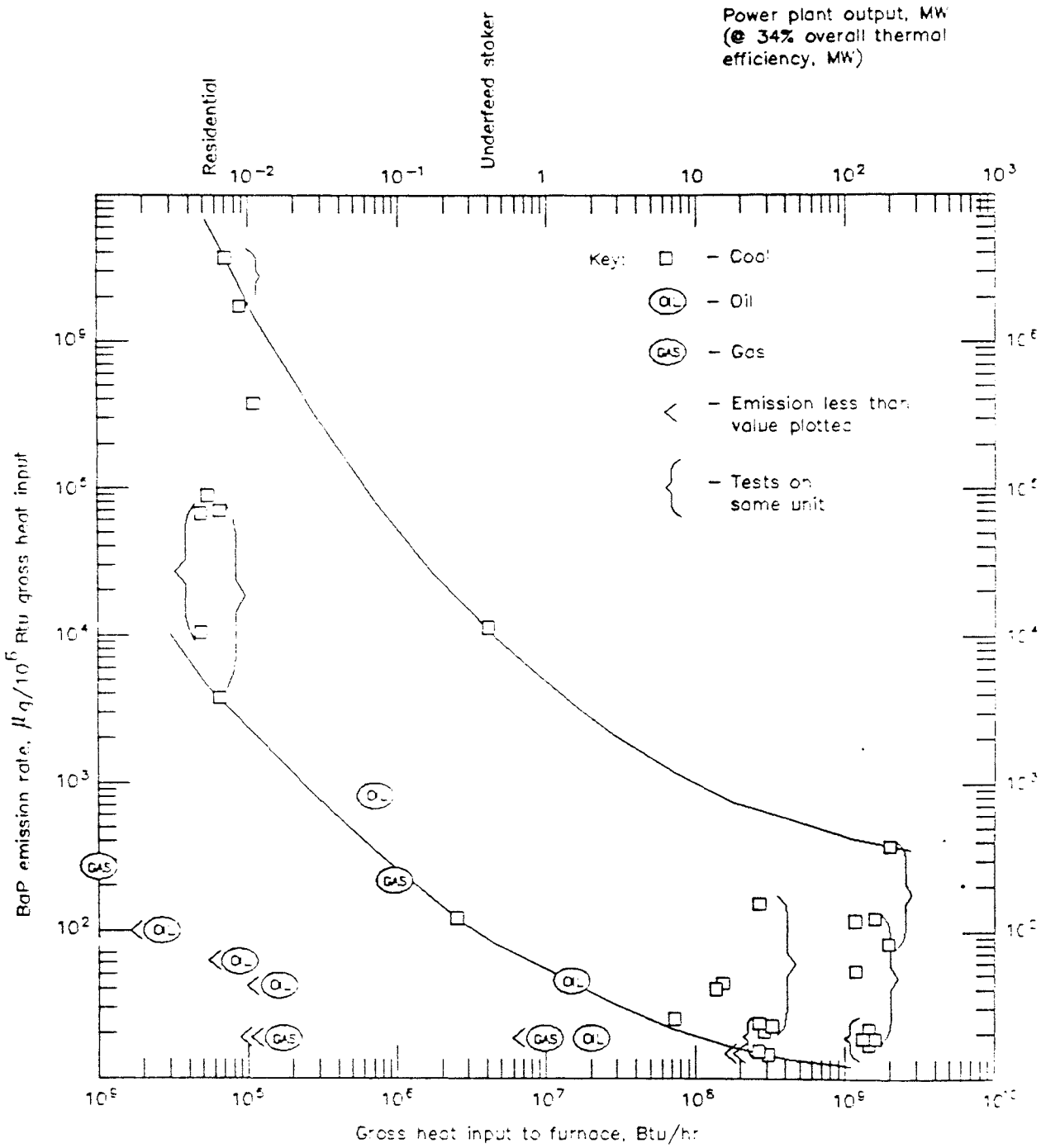
Compound Name	Acronym (carcinogenicity)	Formula	Structure
Benzo [a] pyrene	BaP (+++)	$C_{14}H_{10}$	
Benzo [e] pyrene	BeP (−)	$C_{18}H_{12}$	
Dibenzo [a,l] pyrene	(±)	$C_{20}H_{16}$	
Dibenzo [a,h] pyrene	DBahP (+++)	$C_{22}H_{14}$	
Dibenzo [a,i] pyrene	DBaiP (+++)	$C_{22}H_{14}$	
Dibenzo [cd,jk] pyrene	ANT (−)	$C_{22}H_{14}$	
Dibenzo [a,e] pyrene	(++ (24))	$C_{14}H_{10}$	
Indeno [1,2,3 cd] pyrene	IP (+)	$C_{18}H_{12}$	
Chrysene	CH (+ (25))	$C_{13}H_{10}$	

TABLE 7-1: PAH COMPOUNDS - continued

Compound Name	Acronym (carcinogenicity)	Formula	Structure
Perylene	Per (−)	$C_{20}H_{12}$	
Acridine	(−)	$C_{13}H_9N$	N
Benz [a] acridine		$C_{17}H_{11}N$	N
Benz [c] acridine		$C_{17}H_{11}N$	N
Dibenz [a,j] acridine	(++)	$C_{21}H_{13}N$	N
Dibenz [a,h] acridine	(++)	$C_{21}H_{13}N$	N
Dibenz [c,h] acridine	(±)	$C_{21}H_{13}N$	N
Benzo [ghi] perylene	BghiP (−)	$C_{22}H_{12}$	
Coronene	Cor (−)	$C_{24}H_{12}$	

FIGURE 7-1: Range of Benzo(a)pyrene Emissions from Coal, Oil and Natural Gas Heat Generation Processes



Source: NTIS EPRI EA-787-SY

Evidently, generation of airborne PAH from combustion of petroleum and petroleum products is of minor importance, although perhaps not quite negligible. However the washing of tanker oil tanks, spills and disposal of waste oils are significant contributors to surface waters, and these can contain significant amounts of PAH. As noted crude oils are very high in PAH, as are residual oils, tar, pitch and coke. Used motor oils may be underrated contributors. Motor oils have been found to accumulate up to 6 mg/g of PAH after only 1400 miles of use [Pucknat 81, p.51] or about 5.1 mg/g per 1000 miles of vehicle travel. Assuming bi-annual oil changes, and 10,000 vehicle-miles per year it would follow that used motor oil may contain as much as 25.5 mg/g PAH.[7] If 1 to 1.5 million tonnes of used motor oils are lost annually into waterways (see oil and grease) this would imply a loading of 25 to 37.5 tonnes of PAH directly into waterways. A similar amount may enter the air when used motor oils are incinerated in an uncontrolled manner.

Table 7-2: Estimated BaP Emissions to Air in the U.S. in tonnes/yr.

	1968	1972
Residential & commercial heating(coal)	380	270
Coal refuse fires, uncontrolled	308	281
Coke production	up to 150	
Forest & agricultural waste burning	127	10
Open refuse burning,	67	5
Enclosed refuse burning (incineration)	31	3
Motor vehicle exhaust & tires	30	30
Wood burning in fireplaces & stoves	36	23
Petroleum refining (catalytic cracking)	5	6
Industrial heating (80% from coal)	9	6
Commercial/industrial heating (oil & gas)	2	2
Electric power generation (95% from coal)	4	4

Source: [Pucknat 81, pp. 62-63]

Given above facts, two conclusions emerge. As regards emissions to the air (and thence to waters by way of runoff) it would appear that PAH outputs in the past must have been orders of magnitude higher than today, especially in northern cities where coal was burned for domestic heating. This conjecture is confirmed by observed declines in ambient BaP concentrations over the short period 1966-1970, as shown in Table 7-3. There is some year-to-year fluctuation, but for 5 stations in the NY metropolitan area the overall trend appears to have declined by 21% over the 5-year period 1966-1970 inclusive.

[7]Admittedly, this is a worst-case estimate. No convincing average figure has been published, unfortunately.

Table 7-3: Annual Average Ambient BaP Concentration at National Air Sampling Network Urban Stations (mg/cubic meter)

	1966	1967	1968	1969	1970
New York City, NY	4.1	3.9	(3.8)i	3.6	3.0
Jersey City, NJ	4.2	3.5	2.3	2.7	4.7
Newark, NJ	2.1	3.3	2.1	1.8	1.5
Patterson, NJ	(2.0)e	1.9	2.0	1.2	1.2
Perth Amboy, NJ	2.1	2.1	1.2	1.2	1.0
Average, NY area	3.125(4) (2.9)e	2.94(5)	(4) (2.28)i	2.1(5)	2.28(5)

e = extrapolation, i = interpolation
Numbers in parentheses after average indicate number of stations included

Given the relative dominance of coal-burning as a source of atmospheric PAH, and the absence of coke manufacturing activity in the area, past emissions to the air in the Hudson-Raritan basin must have been essentially proportional to uses of coal at low to moderate temperatures. This means, especially, coal used for residential heating purposes. PAH finds its way to the river waters themselves by direct deposition and (more important) via urban runoff carrying road dust and soot particles.

The second key point is that PAH loading in the Hudson-Raritan basin in recent years has certainly been predominantly associated with oil spills, inadvertent losses of crude oil in tanker operations (e.g. due to the practice of rinsing tanks with seawater prior to the early 1970's), and uncontrolled disposition of waste lubricating oils, especially motor oil. PAH loading can therefore be assumed to be closely proportional to oil/grease loading.

The major sources of combustion related atmospheric PAH's currently in the Hudson-Raritan basin (1980) are a coal-burning steam electric power plant (Hudson City, NJ) burning 620,000 tonnes of fuel/yr, and the New York city municipal incinerators. Other sources include a number of steam-electric plants burning residual oil, several municipal incinerators in New York City, and the large oil refineries. None of these point sources is quantitatively significant at present in comparison with oil-related sources, i.e. crude oil spills or waste oils. The latter are discussed in a separate section (oil and grease). Since thousands of tons of oil reaches surface waters annually (mostly from consumption-related wastes) and PAH constitutes up to 3.5% of crude oil and is a significant component of residual oil and waste used lubricating oils, it is easy to see that this is by far the dominant route to surface waters at the present time. In fact, in recent years the PAH loading can be assumed to be essentially proportional to the "oil and grease" loading.

In the decades before World War II, when petroleum was less important as a fuel than coal, the use of coal as a fuel for domestic heating was probably the major source of PAH. Unfortunately, because the route of entry to surface waters was so different (e.g. combustion, washout and runoff) and the mix of compounds was different, the two cannot readily be compared. Thus, "oil PAH's" and "coal PAH's" should probably be regarded as two different pollutant categories, especially since they may differ chemically and toxicologically.

8. Anthropogenic Sources of Oil and Grease

Petroleum and its products are the source of nearly all oil and grease that ends up in surface waters [Petrakis & Weiss 80].[8] One source of oil in water is from spills of crude petroleum that occur as tankers are loaded or unloaded in harbors. The quantity lost by this route can be assumed to be a small but constant fraction of the total quantity handled. Historically, tankers normally washed tanks after each voyage with seawater and dumped the oily wash water overboard. On average, this loss ranged from 0.1% for light refined products to 1.5% for residual oils, averaging about 0.35% of the tanker's capacity [NRC 75a, p.8]. Since the early 1970's a new procedure called LOT (load on top) has largely eliminated this practice, although losses are still estimated to be about 10% of the old rate or .03% of shipments [ibid p.9]. Shore terminal operations typically lose .0001% to .0002% of throughput as spillage [ibid p.9].

Refinery losses of oil to wastewater have been estimated at 0.07 lb per bbl (200 ppm) by Beychok [Beychok 67] and 0.025 lb per bbl (75 ppm) by an American Petroleum Institute study [API 68], assuming primary treatment (gravity oil separation), based on data from 23 refineries. See also [Hobson 75; ADLittle 76-iv]

The "benchmark" solution of Russell's residuals management model [Russell 73] was set at 0.047 lb/bbl. Another source [Cardwell, Payne & Wilbur 77] gave a total national estimate of 200,000 tonnes of waste oils from refineries. This corresponds to a loss rate of .09 lb/bbl or 265 ppm. However a more recent study for EPA [Hutzinger, Safe & Zitko ??] gives a raw waste load rate of .0096 lb/bbl or 29 ppm. This appears to be the most authorative.

Production and consumption of lubricating oils is given in Table 8-1. There is no published source of data to provide an accurate accounting for the disposition of used lubricating oils. The following attempt is based on information from a variety of sources of unknown reliability. In 1980 domestic production of lubricants was $2.8*10^9$ gallons, of which 10% was exported, leaving $2.52*10^9$ gallons (or 8.44 million tonnes) for domestic purposes. Of this, 45% was used by motor vehicles and aircraft, 33% for various other industrial lubricating purposes (e.g. machine oils) and 22% (1.85 million tonnes) was used as working fluids for pumps and hydraulic equipment [SRI 81]. The latter is mostly makeup for leakage.

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[8]Animal fats or vegetable oils would be the other possible sources, but except in the immediate vicinity of a meatpacking plant the quantities released to the environment are comparatively small compared to mineral oils.

Table 8-1: U.S. Production & Consumption of Lubricating Oils (1000 tonnes)

	Demand	Production	Production/ Runs	Runs to Stills
1880		91	3.55%	2,568
1885		152	0.63%	3,383
1890		302	0.87%	4,906
1895		489	1.01%	6,854
1900		704	1.26%	7,895
1905		1,260	1.59%	11,296
1910		1,800	1.35%	19,309
1915		2,045	0.90%	32,793
1920	1,987	3,078	0.75%	59,339
1925	2,854	4,236	0.58%	104,654
1930	2,992	4,340	0.46%	134,720
1935	2,875	4,109	0.40%	146,202
1940	3,673	5,150	0.39%	189,826
1945	4,859	6,269	0.36%	248,878
1950	5,370	7,567	0.33%	323,559
1955	5,885	7,878	0.28%	406,225
1960	5,988	8,190	0.26%	442,259
1965	6,538	9,114	0.26%	507,460
1970	7,096	9,337	0.22%	609,022
1975	7,979	9,171	0.19%	707,648
1980	8,358	9,052	0.19%	742,891

Source: [BEA biennial]

All values are five year averages centered on year shown except 1880=actual

Large users of lubricating oils usually collect the used oils for reclamation and re-refining. Maugh has estimated that 36% of all used oils are reclaimed as fuel oil [NRC 72], based on Massachusetts data, although this may be an over-estimate in view of the small size of the industry. See also [Fennelly & Spawn 76]. However, if true, it accounts for 3.04 million tonnes.

It is also estimated by one study that 35% of the motor lubricants, in particular, are consumed (i.e. carbonized) in place, lost by leakage, or discarded via oil filters [Travers & Luney 76]. We assume that 20% is carbonized and 15% is lost by leakage or via filters, etc. A similar percentage of industrial machine oils must also be carbonized in use (we assume 20%). Altogether, this accounts for another 22% or 1.85 million tonnes of the annual consumption. When motor oil is changed periodically it is disposed of differently depending on whether the oil is changed in service stations or by "do-it-yourselfers". Maugh estimated the national do-it-yourself share at 50% in 1976 [Maugh 76]. However Hoffman et al found a smaller percentage (35%) in Providence, RI, due -- they believe -- to the greater difficulty of privately

disposing of the old oil in a densely populated urban area [Hoffman, Falke & Quinn 80]. Hoffman et al also determined by survey that about 11% of the urban do-it-yourselfers admitted to dumping their waste oil on roadsides or directly into sewers.(This is almost certainly an underestimate, since some people are reluctant to admit anti-social behavior, even anonymously). A 15% figure seems to us more likely.

Rural do-it-yourselfers would have little problem finding a land disposal site, of course. Thus, while the so-it-yourself percentage declines with population density, the probability of disposal into sewers increases.

As noted, service stations and garages account for about 50% of used oil from individually owned vehicles (not including the 7% or so that is returned to service stations by do-it-yourselfers). To this one must add the contributions from fleet owners, including taxis, rental cars, company cars and trucks. This accounts for over 20% of motor vehicle mileage, so service stations and garages still dispose of over 60% of used motor oil nationally (and probably over 75% in the New York metropolitan area). Of this, 50% may be reclaimed, and the remainder is mostly disposed of in landfills or by incineration. However some incidental loss (~5%) to streets and sewers can reasonably be presumed. Our overall estimated allocation of loss routes is shown in Table 8-2. It must be noted that the above estimate of direct dumping of lubricants to sewers (3.2%) is far lower than the 1972 estimate of 350 million gallons (1.14 million tonnes), or 13.5% of all consumption [Reid & Streebin 72]. However the ultimate fate of hydrocarbons lost by way of "leakage" deserves further consideration. Clearly, most of this category of waste material is actually lost to factory floors, to garage floors, or to paved areas. From there it is either deliberately washed into drains (and thence to sewers) or it is carried off by surface runoff. Either way, much of it ends up in sewers.

Confirmation for this conclusion can be found in the studies of Hoffman et al, [Hoffman, Falke & Quinn 80; Hoffman & Quinn 84] which point out that direct disposition of used motor oils by do-it-yourselfers in Providence RI would (only) account for 19% of the oil discharged by local sewage plants, taking them at their word as to the percentage dumped [Hoffman, Falke & Quinn 80]. (We assume a somewhat higher percentage of waste oil disposed by individuals via this route than do Hoffman et al, but they mistakenly assume that all motor vehicles are operated by individuals.) In any case, it is probably rasonable to assume that the indirect losses to sewers are at least 4 times as great as the direct losses.

Table 8-2: Loss Routes for Lube Oils (%)

Motor Vehicle Lubricants			
Carbonized	(.2x45)	9.0	
Lost via leakage, oil filters, etc.	(.15x45)	6.8	
Disposal by service stations & garages	(.6x.65x45)	17.5	
to reclamation	(0.55.6x.65x45)	9.6	
to land	(.40x.6x.65x45)	7.0	
to sewers	(.05x.6x.65x45)	0.9	
Disposal by individuals	(.4x.65.45)	11.7	
to land	(.4x.65x45)	9.4	
to sewers	(.2x.4x.65x45)	2.3	
Total, Motor Vehicles			45.0
Industrial Lubricants			
Carbonized	(.2x33)	6.6	
Disposal by reclamation	(.8x33)	26.4	
Total, Industrial			33.0
Non-lube use (Hydraulic), leakage			22.0
Total of all Uses			100.0

Summing by loss/disposal route we arrive at the following

Reclamation	36.0
Carbonization	15.6
"Leakage"	28.8
Disposal to Land	16.4
Disposal to Sewers	3.2

On this basis, about one third of the "leakage" category probably ends up in sewers, which seems a fairly conservative estimate. In summary, we conclude that about 12% of all lubricants enter the sewers. Another 5% or so probably reaches surface waters by other routes. These figures are clearly uncertain (probably no better than plus or minus 25%).

9. Anthropogenic Sources of Total Carbon

Carbon in nature is mainly inorganic. Organic carbon occurs in nature in two predominant forms: carbohydrates (the form of fixed carbon in biomass) and hydrocarbons, derived from the former by natural geological processes. Excluded from the class are carbon dioxide, mineral carbonates amd elemental carbon (including graphite, coke and most of the substance of coal).

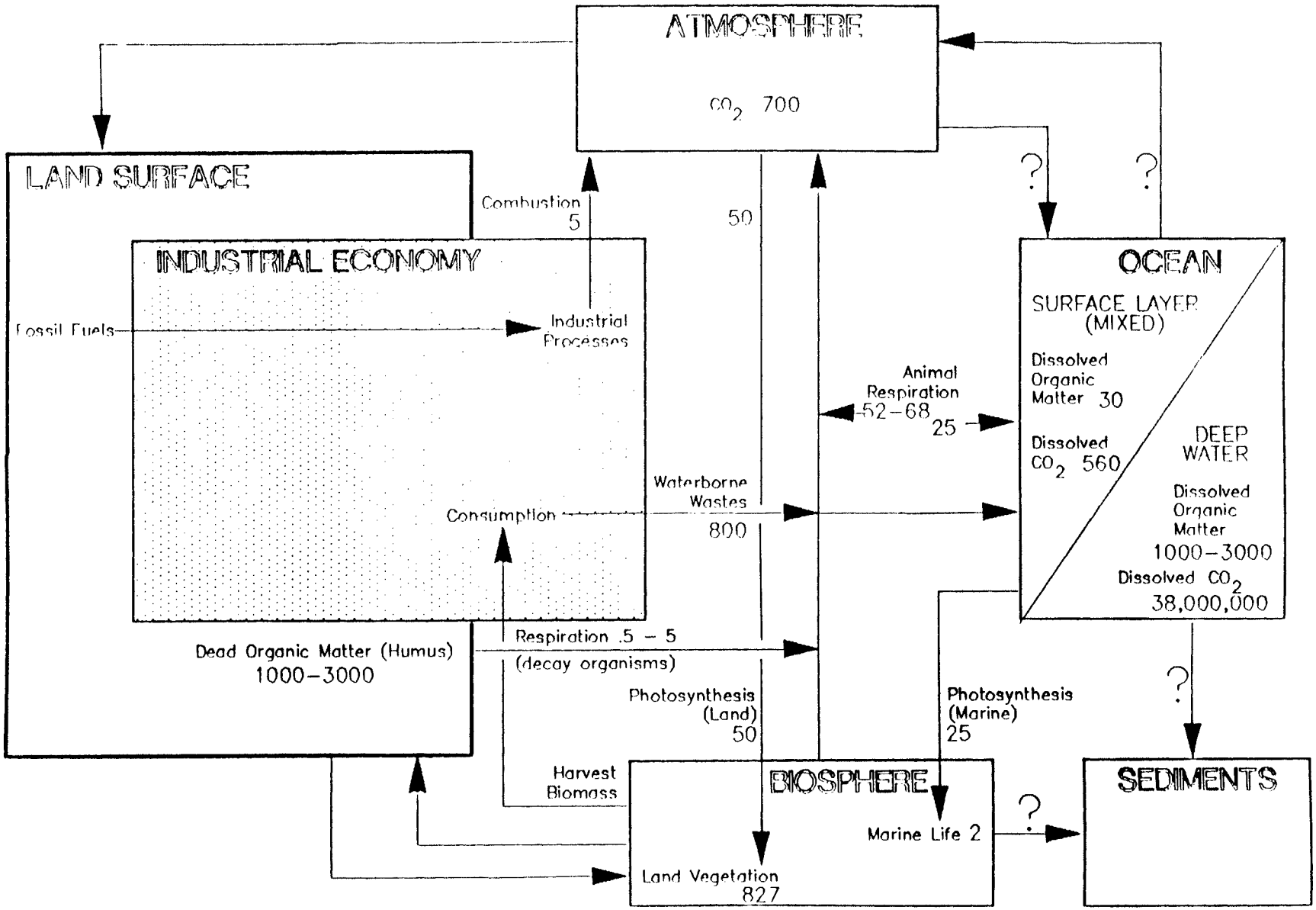
Environmental mobilization of TOC occurs via many processes. Combustion vaporizes some hydrocarbons which later condense on the surface of particulates and return to earth as dry or wet fallout. Airborne HCs are of considerable importance from the perspective of environmental health, but not of quantitative importance as a contribution to TOC in water. Hydrocarbons also find their way to bodies of water more directly and in vastly larger amounts by spillage and from disposal of waste oils. (This source has been discussed in the previous chapter and will not be considered further here.) Thus we focus in the section on carbohydrates derived from plant and animal biomass. Almost all land biomass is embodied in plants on a global basis (See Figure 9-1). Animal biomass is smaller at any given time by at least two orders of magnitude[9].

However, environmental mobilization of TOC is associated only with plant and animal waste products, mostly the former. In the case of land plants, there are two subcategories: annuals (e.g. crop plants) and perennials (mainly trees). The former die at the end of each season, leaving only their seeds. All of their photosynthetic product during the year eventually returns to the soil as humus. Some perennials also die back on the surface and regenerate the following season from roots or bulbs. However, woody broad-leafed plants and trees -- accounting for the largest share of land biomass -- lose only their leaves in the fall. Conifers (evergreens) also shed material but on a more continuous rather than a seasonal basis.

A rough indication of the magnitudes involved can be obtained from forestry statistics for New York State [USDA 81, 82]. In a typical recent year (1976) the gross product of photosynthesis in forests in the state was $1.035 \cdot 10^9$ cubic feet (bcf) of wood, from which must be subtracted .735 bcf that was physically removed (i.e. harvested) and .282 bcf which became unavailable due to "mortality" -- presumably dead branches and windfalls. There was a net increase of .017 bcf in the stock of wood during the year. The

[9]This is mainly due to the large mass of material embodied in trees -- about $827 \cdot 10^9$ tonnes of carbon (as cellulose)

FIGURE 9-1: Global Carbon Cycle (units = 10^9 metric tons C)



total mass of foliage cannot be estimated from the above data, but the mass of unharvested dead wood alone, each year, is of the order of 2.8 million tonnes for the whole state. About 20% of the land area of NY State is in the Hudson-Raritan Basin, and much of it is wooded. Cultivated areas may generate as much or more in waste plant material as wooded areas do. *Conservatively*, a million tonnes of dead organic matter is generated each year in the Hudson-Raritan Basin. While most of it remains on the land, even the small amount that is carried away by streams can easily overwhelm the animal waste contribution.

Since animals depend entirely on the *surplus* annual photsynthetic production of plants, of which they actually consume only a fraction, it is clear that plant wastes considerably exceed animal wastes in mass on a global basis. In a very densely poulated area such as the Hudson-Raritan Basin, however, large quantities of biomass are imported as food from other regions, and much of this is converted into human waste (i.e. sewage). Biomass is also imported as wood and paper products, cotton and wool textiles, leathergoods and so forth. However, the latter are disposed of either in landfills or by incineration -- which reduces almost all of the organic material to inarganic CO_2.

The processing of carbohydrate biomass into useful products is a major source of waterborne TOC (as BOD) in locations where such activities are the major sources of anthropogenic BOD, apart from untreated sewage.

In the Hudson-Raritan Basin, however, none of these primary biomass processing activities appear to have been carried out on a very large scale. On the other hand, the region is heavily forested, except where it is farmed, and the annual production of plant litter is large. Apart from untreated sewage, most of the BOD in the river can be attributed to non-anthropogenic ("background") sources reaching the river via runoff that change little from year to year.

10. Anthropogenic Nitrogen Sources and Flows

Inorganic Nitrogen (N_2) is a colorless, odorless, tasteless gas which constitutes almost 80% of the atmosphere. In this form it is chemically rather inert and inaccessible to living organisms, as well as other key chemicals in living cells. However, nitrogen is an essential element for protein production. It can only be ingested (by plants) as soluble ammonium (NH_4-) ions, nitrate (NO_3+) ions, or soluble organic molecules such as amino acids. There are many routes by which soluble nitrogen finds its way into the soil.

Nitrogen oxides are created in the air either by electric storms or fuel combustion. These oxides then react with water vapor and create nitrous or nitric acid (HNO_3) which falls as a component of acid rain. Nitric acid subsequently reacts with metallic salts to form nitrates. Ammonia is also emitted by volcanoes.

Rhizobia bacteria in the root nodules of legumes (such as soybeans) are able to fix nitrogen from the air. Some other varieties of bacteria can also fix nitrogen. A third source - from a practical point of view - is the recycling of plant and animal matter. Some of this nitrogen from decaying organic matter is released in the form of ammonia (NH_3), and, along with ammonia from anthropogenic sources, is returned to the soil in rain.

For centuries nitrogen fixation by atmospheric electrical discharges, from legumes and from decayed matter (manure) were the only means of restoring lost fertility to soil. Gradually, the recycling process was accelerated through composting and distribution. Organic matter in the soil may contain about 5-6% nitrogen, but this is not available to plants until it has been released by bacteria or fungi in the form of ammonia or nitrates. Soils with plentiful organic matter can retain much of this for future use by plants.

With continuing pressure on farmers to increase crop yields the available nitrogen in the soil was used more rapidly than it could be replaced by the available plant and animal materials. In 1930 the annual nitrogen deficit for the U.S. was estimated at 3.4 million tonnes, despite some use of nitrogen fertilizers [Shreve 56, p397]. These came from imported natural materials such as guano and sodium nitrate from the west coast of South America, and from ammoniac compounds derived from coal as a by-product of coke ovens and manufacturing illuminating gas. In fact, about 0.86 kg of NH_3 can be extracted from a ton of bituminous coking coal [Russell & Vaughan 76, Table 3.2], along with 178 kg of high-BTU gas (8800

cubic feet). Thus, production of 1 mcf of gas also yielded up to 98 kg of NH3. Later ammonia was produced in larger quantities from the coking of coal for the steel industry, but still as a byproduct. Its output could not be expanded above the limited amounts available from coal usage.

The first practical process for direct nitrogen fixation, around 1905, was the cyanamid process, yielding calcium cyanamide ($CaCN_2$) from limestone, coke and atmospheric nitrogen. It was quickly overtaken in importance by the Haber-Bosch ammonia synthesis process devloped by BASF in Germany in 1913. During World War II many ammonia plants were constructed to produce the nitrogenous materials for explosives (almost all of which were nitrogen-based) as well as fertilizers.The availability of substantial capacity for synthesizing ammonia gave rise to a growing nitrogen fertilizer industry in the U.S. after WWII. The standard process used in the U.S. today is based on the passage of a mixture of air and natural gas over a catalyst at very high pressure. Under the required conditions the methane in the gas is cracked and the carbon reacts with oxygen to form CO_2 while the hydrogen and nitrogen combine in the presence of a catalyst to form ammonia (NH_3). See Figure 10-1.

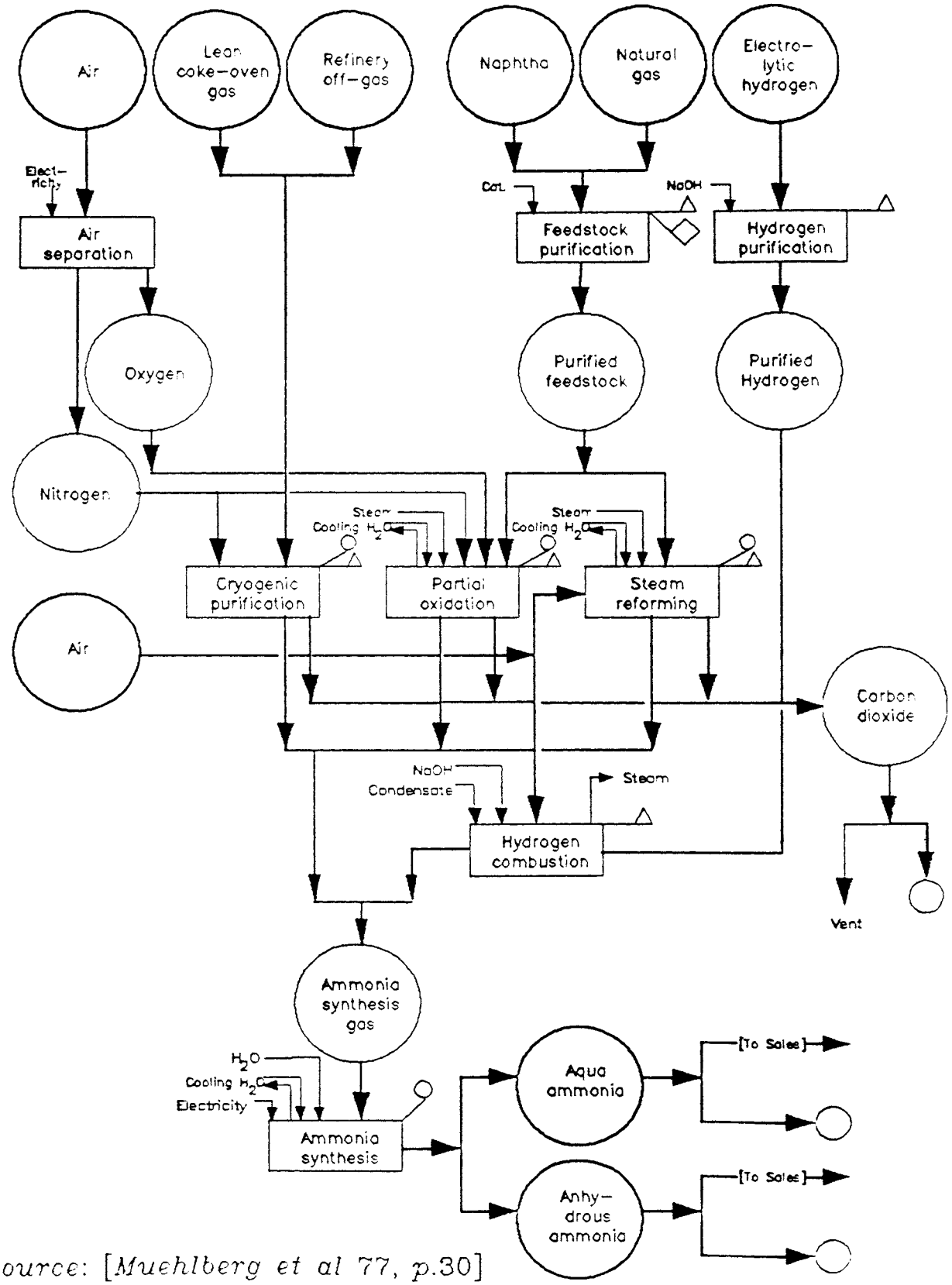
There are several variations of the basic process depending on (1) the separation of air to produce nitrogen or (2) the removal of the oxygen by combustion to leave a nitrogen CO_2 material that can then be separated. While the wartime plants were mainly in the 200-300 tonne/day range, in the 1960's the introduction of efficient single-stage centrifugal compressors made possible a new industry standard of 1,000 tonnes per day. The new technology increased capacity and cut costs sharply and further expanded the market (See Table 10-1).

Except possibly for some early ammonium sulfate plants from coal byproduct sources there have been no major synthetic nitrogen material plants in the Hudson - Raritan basin. Ammonia plants are generally co-located with sources of natural gas or, in some cases, in major consuming markets. Virtually all nitrogenous chemicals are now manufactured from ammonia. A list of these chemicals follows and materials process relationships for ammonia based chemicals are shown in Figures 10-2 and 10-3.

Acrylonitrile CH_2CHCN or vinyl cyanide made by reacting propylene with ammonia and air, is the major intermediate for manufacturing acrylic fibers, ABS and SAN plastics and nitrile rubber.

Ammonium Chloride NH_4Cl, made by reacting ammonia and hydrochloric acid or ammonium sulfate and sodium chloride, is used in dry cells, soldering flux, tanning and a number of other uses.

FIGURE 10-1: Materials Process Relationships for Ammonia Synthesis



Source: [Muehlberg et al 77, p.30]

Table 10-1: U.S. Nitrogen Production & Consumption (1000 tonnes)

	Production	Consumption			Production	Consumption		
			Nitric Acid	Acrylonitrile			Nitric Acid	Acrylonitrile
	NH3	NH3	HNO3	ACN	NH3	NH3	HNO3	ACN
	Gross Weight				Nitrogen Content			
1904	3				1			
1909	15				3			
1914	24				5			
1919	34				7			
1925	61				13			
1929	93				21			
1935	73				16			
1940	297				66			
1945	498		450	5	111		94	1
1950	1421		1250	12	315		260	3
1955	2950		2400	55	655		499	16
1960	4371		3000	105	970		624	30
1965	8046		4500	350	1786		936	100
1970	12310		7000	470	2733		1456	134
1976	12353	12001	7791	759	2742	2664	1621	217
1980	14736	16025	8933	915	3271	3557	1858	262

Ammonium Nitrate NH_4NO_3, made by reacting ammonia and nitric acid, is the most important nitrogen fertilizer and also an important ingredient in explosives.

Ammonium Phosphates are major forms of fertilizer and feed additives. diammonium = $(NH_4)_2HPO_4$ and monoammonium = $(NH_4)H_2PO_4$

Ammonium Sulfate $(NH_4)_2SO_4$ was largely recovered from by-product (aqueous) ammonia by sulfuric acid scrubbing. It is a major fertilizer.

Aniline $C_6H_5NH_2$, made from nitrobenzene, is an important intermediate in the manufacture of isocyanates (urethanes), rubber chemicals (nitriles), aniline dyes, hydroquinone, drugs and miscellaneous chemicals.

Ethanolamines known as MEA, DEA, TEA, (mono-$CH_2OH.CH_2NH_2$; di-$(CH_2OH.CH_2)_2NH$; tri-$(CH_2OH.CH_2)_3N$), are made from ethylene oxide and ammonia. They are used in detergents (DEA), gas conditioning (MEA) and petroleum products, emulsion polishes, herbicides, etc.

Ethylenediamine $NH_2CH_2CH_2NH_2$ is the basis of carbamate fungicides.

Hexamethylenetetramine $(CH_2)_6N_4$ is used as a phenolic thermosetting catalyst and an explosive (in RDX).

Hydrazine N_2H_4 is used as a rocket fuel

Melamine $C_3N_3(NH_2)_3$, made from urea, is an important thermosetting plastic (used with formaldehyde), in laminates, textiles, adhesives, etc.

Nitric Acid HNO_3, made by oxidation of ammonia, is a strong acid used in many processes, especially in the manufacture of ammonium nitrates, adipic acid, nitrobenzene, isocyanates and numerous other products.

Nitrobenzene $C_6H_5NO_2$, made from the reaction of nitric acid with benzene, is used in explosives and to manufacture aniline.

Urea NH_2CONH_2 NH_2CONH_2 is a fertilizer made from ammonia and carbon dioxide. It is also used in manufacturing melamine plastics.

10.1 Uses of Ammonia

About 70% of all ammonia is used for fertilizer (see Figure 10-4).

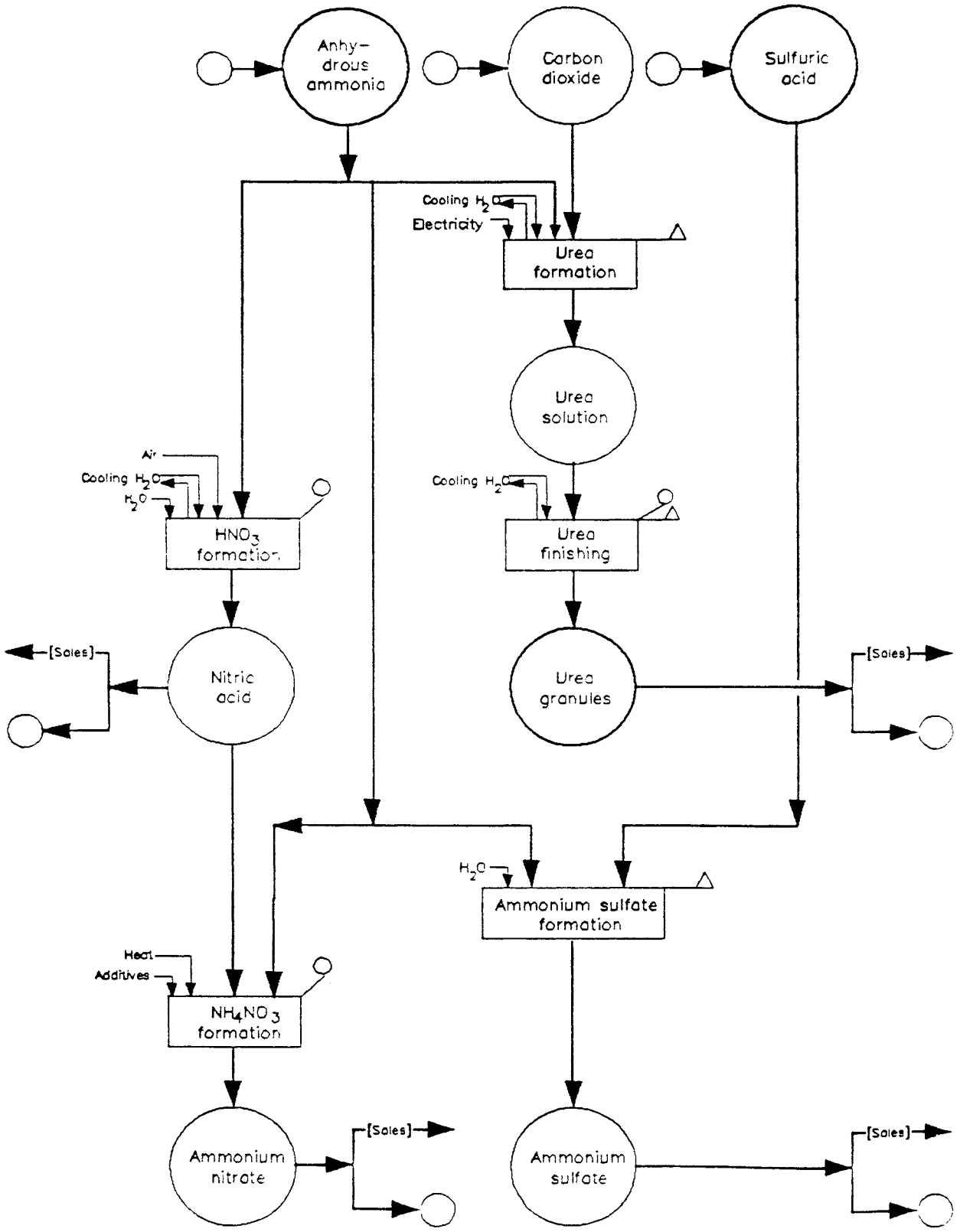
In recent years a growing proportion of nitrogen has been applied by direct injection of anhydrous ammonia into the soil, particularly in the large farms of the Mississippi valley. However, the major portion is still applied either in solid or liquid form that can be handled more easily and applied in combination with other plant nutrient materials. The principal primary nitrogenous fertilizer materials are shown in Table 10-2 which also shows the percentage nitrogen contained in the product.

These products may be applied either as straight materials or in various combinations known as mixtures which are made up to a standard set of specifications. By custom and law these are always reported as percentage of nitrogen - phosphate - potash. Because of the growth in the direct application of high nitrogen materials there has been a tendency for mixtures to stabilize nationally in the 21-24 million ton/year range while total application continues to grow (See Table 10-3).

Because of the more varied nature of the farming and smaller acreage of the farms in the New Jersey - New York region there has been a somewhat greater reliance on mixtures to convey fertilizer nitrogen and other nutrients. In Table 10-4 are shown data for New Jersey for the calender year 1968. This reveals that in that year 17214 tonnes of nitrogen were applied in mixtures while 11905 tonnes were applied as straight materials. Aside from the fact that some of the products (particularly ureaformaldehyde) may give up their nitrogen more slowly, all fertilizers can be considered equivalent on the basis of N content; i.e. "primary nutrient" value.

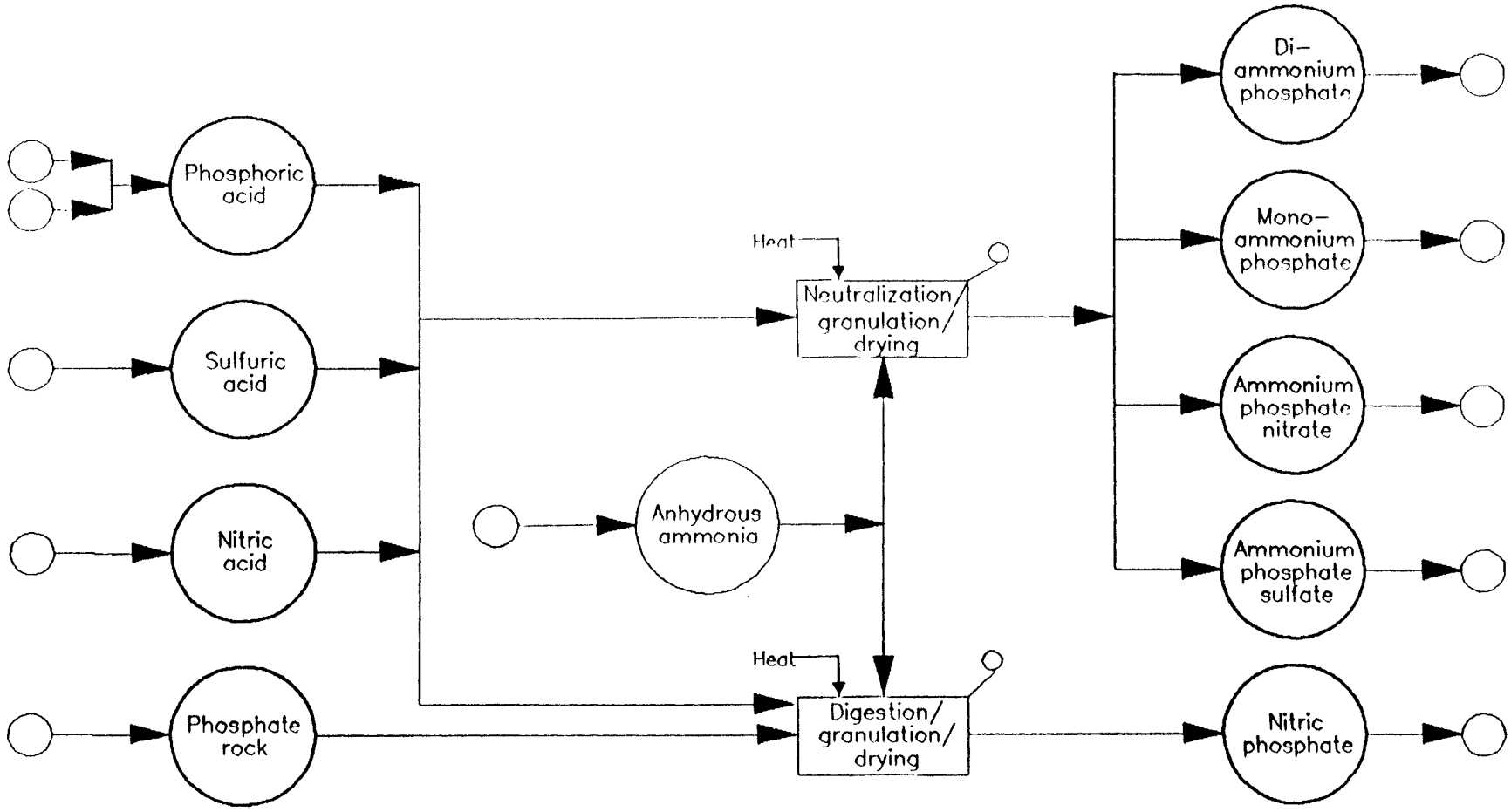
In Table 10-5 are shown the data for consumption of primary plant food nutrients in the U.S. for 1950-1980. It can be seen that the rate of increase in nitrogen consumption has far exceeded growth in the other two primary materials - phosporus and potash. Phosphorous is discussed in detail in the next chapter.

FIGURE 10-2: Materials Process Relationships for Ammonium Sulfate, Ammonium Nitrate and Urea



Source: Muehlberg et al 77, p.48]

FIGURE 10-3: Materials Process Relationships for Ammonium Phosphates and Nitric Phosphate



Source: [*Muehlberg et al* 77, *p.* 72]

FIGURE 10-4: U.S. Ammonia Flows 1980 (million metric tons)

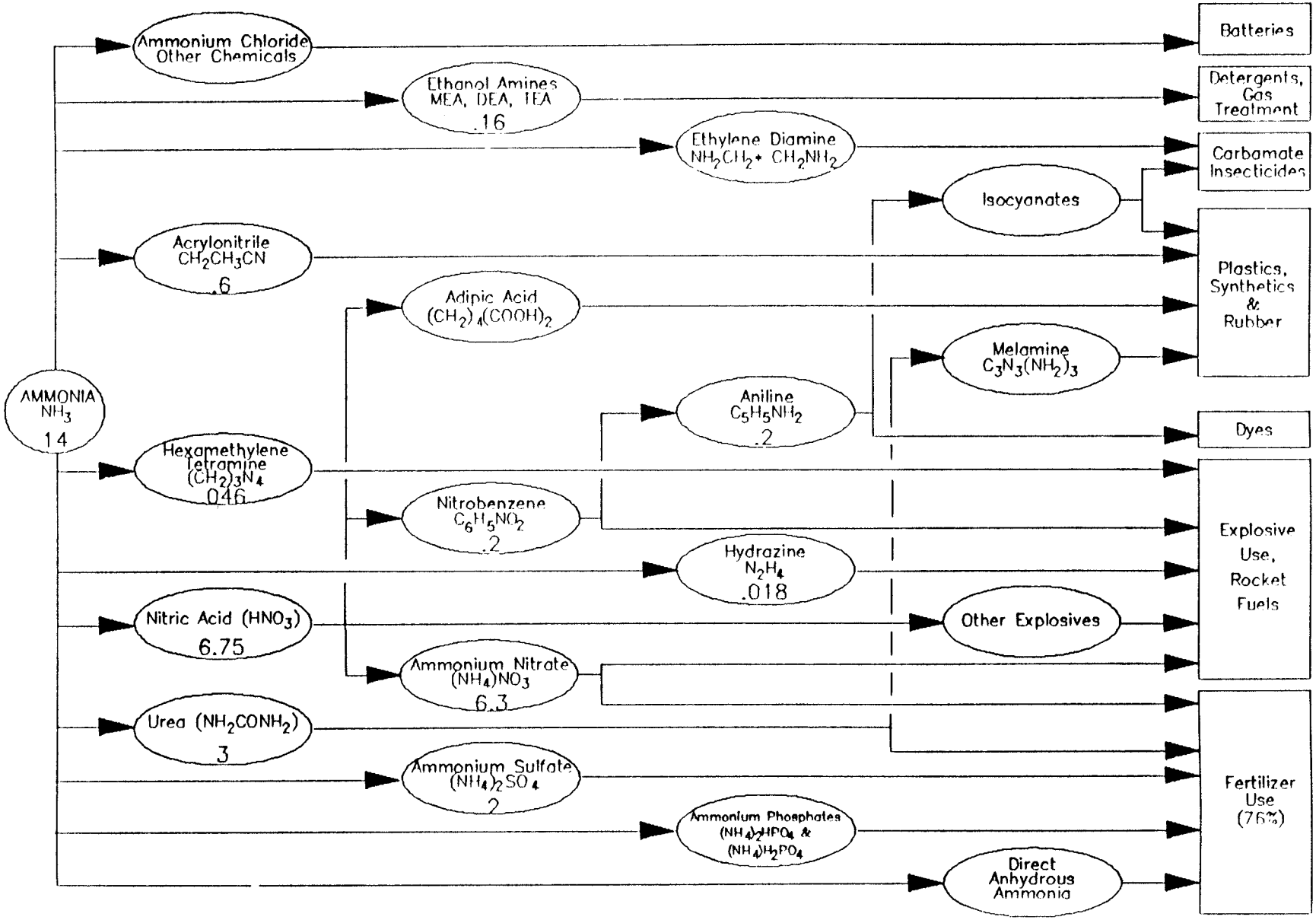


Table 10-2: Principal Nitrogenous Fertilizer Materials

Material	% Nitrogen
Ammonia NH_3	82.24
Ammonium nitrate $NH_4.NO_3$	36.65
Ammonium sulfate $(NH_4)_2SO_4$	21.20
Diammonium phosphate $NH_4H_2PO_4$	21.14
Monoammonium phosphate $(NH_4)_2HPO_4$	12.18
Calcium nitrate $Ca(NO_3)_2.4H_2O$	17.07
Calcium cyanamide $CaCN_2$	34.97
Potassium nitrate KNO_3	13.85
Sodium nitrate $NaNO_3$	16.48
Urea $CO(NH_2)_2$	47.0
Ureaformaldehyde $CO(NH_2)_2HCHO$	31.0

Table 10-3: Commercial Fertilizers Consumed & Their Average Primary Plant-Nutrient Content, 1968-82 (U.S.)

	Mixed Fertilizers				All Fertilizers w/ Primary Nutrients				
			Available Phosphoric				Available Phosphoric		Other Fertilizers
Year	1000 tonnes	Nitrogen N	Oxide P_2O_5	Potash K_2O	1000 tonnes	Nitrogen N	Oxide P_2O_5	Potash K_2O	1000 tonnes
1968	9659	8.77	16.81	12.67	16840	18.28	12.00	10.22	733
1969	9632	8.95	17.54	12.53	17061	18.50	12.41	10.34	605
1970	9508	9.25	17.69	12.70	17369	19.48	11.95	10.54	588
1971	9758	9.59	18.33	13.00	18099	20.38	12.04	10.60	552
1972	9757	9.91	18.58	12.93	17643	20.11	12.19	10.85	594
1973	10227	10.21	18.79	12.76	18970	19.83	12.16	11.12	665
1974	10917	10.10	17.75	12.66	20395	20.37	11.34	11.30	966
1975	9365	10.16	17.99	12.50	18419	21.18	11.10	10.97	852
1976	10414	10.53	19.29	12.52	21270	22.20	11.15	11.11	1041
1977	10931	10.58	19.87	12.78	22271	21.69	11.47	11.88	1145
1978	10029	10.74	19.63	12.79	20693	21.82	11.16	12.10	851
1979	10769	10.84	20.09	12.84	22381	21.72	11.36	12.66	970
1980	10555	10.79	19.61	13.06	22902	22.59	10.76	12.37	1041
1981	10671	10.99	20.13	12.75	23478	23.04	10.50	12.21	1010
1982	9442	11.23	20.39	12.38	21309	23.58	10.26	11.95	796

To determine the fertilizer nitrogen consumption in the Hudson - Raritan basin the available information has been reviewed. Unfortunately, while statistics are available for consumption of fertilizer

Table 10-4: New Jersey Fertilizer Tonnage Report, 1968 (tonnes)

CHEMICAL NITROGEN MATERIALS		
Anhydrous Ammonia - 82% N		283
Ammonium Nitrate		6505
Ammonium Nitrate - Limestone Mixture - 20.5% N		345
Ammonium Sulfate - 21% N		319
Cyanamid		711
Nitrate of Soda		974
Nitrogen Solutions		1470
Urea		999
Ureaform - 38% N		171
Other		128
Total Chemical Nitrogen Materials		11905
PHOSPHATE MATERIALS		
bonemeal		527
Superphosphate - grades 22% & under		1197
Other		642
Total Phosphate Materials		2367
POTASH MATERIALS		
Muriate of Potash - 60% K_2O		3600
Other		238
Total Potash Materials		3837
ORGANIC MATERIALS		
Dried Manure		4065
Sewage Sludge		1824
Other		1813
Total Organic Materials		7703
Total Secondary Nutrient Materials		455
Total Materials		26268
TOTAL MIXED FERTILIZERS		
Actual N	17214	
Actual P_2O_5	20145	
Actual K_2)	18733	
Total Mixed Fertilizers		189438
GRAND TOTAL - Mixed Fertilizers and Materials		215706

by each of the major crop groups (fruit and vegetables, Irish potatoes, and all others) for some census years, there is no consistency of coverage for all census years. It has therefore been necessary to utilize crop acreage data and estimate fertilizer use for particular years based on trends in amounts used and acreage cultivated. The total fertilizer figures can then be related to the total use pattern for primary materials in New York and New Jersey. Nitrogen consumption is estimated for each major crop category. These calculations are shown in Tables 10-6 and 10-7.

Table 10-5: Total U.S. Primary Nutrient Consumption In Agriculture (1000 tonnes)

Year	Gross Weight	N	P_2O_5	K_2O	Total Nutrients
1950	16227	912	1769	1001	3672
1951	18433	1122	1914	1252	4288
1952	19638	1290	1995	1434	4719
1953	20443	1485	2060	1577	5122
1954	19193	1676	2028	1646	5349
1955	19905	1779	2072	1701	5552
1956	19416	1754	2038	1701	5493
1957	19744	1937	2091	1757	5785
1958	19573	2072	2080	1755	5908
1959	21853	2424	2333	1988	6745
1960	23500	2738	2572	2153	7464
1961	24373	3031	2645	2169	7845
1962	25306	3370	2807	2271	8448
1963	27383	3929	3073	2503	9505
1964	29203	4353	3378	2730	10461
1965	30314	4639	3512	2835	10985
1966	33070	5326	3897	3221	12445
1967	35686	6027	4305	3642	13974
1968	37125	6788	4453	3792	15033
1969	37607	6958	4666	3892	15515
1970	38338	7459	4574	4036	16068
1971	40301	8134	4803	4231	17168
1972	39851	8022	4864	4327	17213
1973	41775	8295	5085	4649	18029
1974	44975	9157	5099	5083	19338
1975	39881	8601	4507	4453	17561
1976	46220	10412	5228	5210	20849
1977	48365	10647	5630	5834	22111
1978	44883	9965	5096	5526	20587
1979	49432	10715	5606	6244	22565
1980	50368	11400	5391	6161	22952

Table 10-6: Calculation of Fertilizer Use in the Hudson - Raritan Basin by Major Crops

	Fruits & Vegetables			Irish Potatoes			Others		
Year	Acres	Acres Treated	Short Tons	Acres	Acres Treated	Short Tons	Acres	Acres Treated	Short Tons
1954	-	60320	1456	-	33234	16000	950105	83886	17422
1959	113346	111203	32248	13354	13271	15183	902037	147226	40095
1964	122281	100457	31133	11092	10131	15150	764292	123477	35717
1969	76498	65789	21144	8222	7083	8093	648546	116738	35721
1974	64328	52749	17644	5312	5101	4565	667836	13357	42742
1978	83044	65874	21080	4635	4450	3916	674859	13497	41841

It can be seen that while fruit and vegetables were supplied with more nitrogen in the early 1960's than later,this was due to greater acreage in these crops in the earlier period. Consumption fell to lower levels in the late 1960's even though the nitrogen concentration of fertilizers continued to rise. A more important observation is that the Hudson-Raritan basin now accounts for less than 0.1% of U.S. nitrogen fertilizer use -- down from 0.2% in 1954. (Compare Table 10-5.)

Table 10-7: Nitrogen in the Hudson - Raritan Basin

Year	Fruits & Vegetables		Irish Potatoes		Other		Total
	%	Tons	%	Tons	%	Tons	Tons
1954	48.5	1839	24.6	933	26.9	1020	3972
1959	36.9	2253	17.3	1057	45.8	2797	6107
1964	38.0	2827	18.5	1376	43.5	3236	7440
1969	32.6	2279	12.4	867	55.0	3846	6992
1974	26.9	2392	7.8	694	65.3	5806	8892
1978	31.9	2901	4.8	437	63.5	5775	9095

It is evident that suburban and industrial development after World War II, together with trends towards larger farms and specialization of farms in the Hudson-Raritan basin in higher value crops and dairy products were responsible for the decline. Irish potato cultivation, in particular, declined throughout the period. The substantial increases in fertilizer use on "Other" crops including wheat and other small grains, hay, and other forage materials such as alfalfa, is mainly due to the fact that the very low rate of fertilizer use on these in the 1940's has risen. Nationally, the use of fertilizer on corn increased from 24.5% of nitrogen use in 1947 to 43.1% by 1964.

10.2 Nitrogen Removal

Obviously since fertilizers are supplied as 'plant foods' a significant fraction is taken up by plants and (unless the crop is 'plowed under) much of it is removed from the soil. Of course, the specific proportions removed vary from crop to crop and depend on the ratio between what is supplied and what is required. Analyses have been made as to total removal by crops in the U.S. and it is interesting to note that during the 1970's the average N removal was 72.4% of the fertilizer nitrogen applied. This figure varies somewhat with individual years, from a high of 78.5 in 1973 to a low of 64.0 in the following year.

The nitrogen removed by crops in the Hudson-Raritan basin is ultimately consumed in food, either directly, as in fresh vegetables, or after conversion to meat, eggs, etc. The average per capita food

consumption comes to about 1000 pounds retail weight per year (exclusive of water content of fresh milk and fruit juices). While mnay foods have above average protein (meat, milk and eggs) and other little or none (e.g. sugar), average nitrogen content is at least 2% (equal to the average of harvested crops), or 20 pounds per capita. Nationally, this amounts to 2.2 million tons (2,000,000 tonnes), which is less than 20% of the total nitrogen input as fertilizer. (Most of this eventually reappears in sewage effluent and sludge.) The remaining 80% of the input must be lost by other routes; e.g. volatilization, animal feed lots and food processing plants.

In well ventilated soils having low organic matter (with a carbon nitrogen ratio of less than 15) when the quantity of ammonium ions exceeds the absorption by plants and microbes the excess ammonia is oxidized to nitrates by a nitrification process. The first step (to nitrite) is brought about by bacteria such as nitrosomas. The second step (to nitrate) is carried out by other bacteria such as nitrobacter. These nitrates remain in the soil for plant use, up to certain limits depending on temperature, etc. Unlike the pesticidal residues discussed earlier in this study high concentrations of nitrogen in soil are desirable for plant growth, and reduction in nitrogen levels soon results in declining crop yields. Because of the desirable nature of soil nitrogen and the fact that it varies significantly as crops are grown, it is not a subject of soil monitoring studies as are pesticides.

Many nitrogen compounds are soluble and can be leached from the soil -- particularly in permeable soils having low organic matter and high rainfall. In clogged soils having insufficient air circulation, fertilizer nitrates may be reduced to gaseous nitrogen by microbes which break up the molecules to satisfy their demand for oxygen. However, in soils with high levels of decaying organic matter, air circulation, and a high microbial population, the microbes consume the nitrogen in the form of ammonia and effectively store it for future use by plants -- resulting in very little loss by leaching. Bacterial action also continuously removes nitrogen from soils altogether by converting organic nitrogen to volatile NH_3, some of which escapes into the atmosphere.

10.3 Nitrogen Emissions

While runoff from fertilizer use in agricultural areas is now the dominant source of aggregate nitrogen emissions to the water (and has been since the 1960's), it is clear that this was *not* the case previously. As noted previously, crop harvesting (and erosion) removed nitrogen from the soil considerably faster

than it was being replaced, probably until some time in the 1960's[10] That removal process resulted in a substantial net flow of nitrogen from rural to urban areas (embodied in food products) from whence much of it was returned to the environment in sewage and/or garbage. In addition, large-scale animal feed lots became major point sources of nitrogen by way of non-recycled excreta, especially urine[11]. Additional nitrogen is lost in primary food/feed processing operations such as beet sugar production, cheese-making, brewing, flour milling and meat packing. These operations are largely concentrated in the midwest and west near major sources of supply.

In the extreme case of a heavily urbanized region such as the Hudson-Raritan basin, where relatively little fertilizer is used on farms, and little food processing is done but urban population density is exceptionally high, most N-emissions can evidently be attributed to human consumption wastes, with some contribution from home garden use. These appear in water mainly as sewage or urban runoff.

Nitrogen content in sewage, and urban runoff in the Hudson-Raritan basin in turn, can be attributed almost entirely to human and animal food consumption with minor contributions from detergents, dyes, house and garden fertilizer and ammonia use, and acid rain. Human wastes alone amount to 10 gm (N) per capita per year, or 1.3 million tonnes on a national basis (1976). Of this, 7.2% or 55,000 tonnes (N) can be attributed to the Hudson-Raritan basin. We can assume that the rural population (about 1 million) and perhaps an equal number of exurbanites, use septic tanks. At least 80% of the Hudson-Raritan population is served by sewers. Primary and secondary sewage treatment remove, at most, 20% of the contained nitrogen, which resides in the sludge. The remainder, about 46,000 tonnes (N), contributes to the N-pollution of the river itself. Animal wastes, especially from pets, also contribute a further increment by way of urban runoff -- probably about 5% of the sewage contribution (based on San Francisco data [Junge 74, Table 6.9].

As a matter of interest, the maximum nitrate content of acid rain deposition in the Hudson-Raritan basin can be estimated as follows: Based on 1955-56 data collected by Junge [cited in Junge 74], The

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[10]When U.S. consumption of synthetic nitrogenous fertilizers presumably reached rough balance with annual removals by harvesting and erosion. It is interesting to note that the National Research Council estimates a net nitrogen buildup in soil and groundwater of the order of 1.5 million tonnes per year (1972) [NRC 76]

[11]Animal urine accounts for at least 50% of excreted nitrogen, in the form of urea. Under typical feedlot conditions urea is rapidly hydrolized to carbon dioxide and ammonia

Table 10-8: Nitrogen Balances 1930-1972 (million tonnes)

	1930(a)	1972(b)
Inputs to Soil(tilled & pasture)		
Bacterial fixation	2.70	4.8
Rainfall (NOx)	1.17	<5.6(c)
Fertilizers (all kinds)	0.36	7.5
Total	4.23	17.9
Removals from Soil		
Harvested crops	7.0	16.8
fiber		0.2
sugar	0.6	
plant protein to human		0.9
plant protein to animals		15.1
runoff from soil	1.4	(d)
Denitrification from soil (e)		8.9
less animal manure and other wastes returned to soil locally		<4.2(f)
Net Retention (Loss)	(3.7)(e)	1.5

(a) [Collings 34] cited in [Shreve 56]

(b) National Research Council (1972) cited in [NRC 78]

(c) Refers to all U.S.land, hence an overestimate for tilled land and pasture.

(d) Not specifically estimated by NRC. Probably similar in 1930 and 1972.

(e) Not estimated by Collings. Hence his estimate of the net loss was too low by a substantial margin.

(f) Not estimated specifically by NRC, but needed to compare the two tables. The NRC balance assumed 4,200,000 tonnes of N-content in excretions by animals (compared to 1.2 million for humans) plus 15.6 million tonnes of "other" nitrogenous wastes, some of which presumably remain in the soil.

Hudson-Raritan basin received between 2 and 2.5 kg/ha of total N in rainfall, or 6,500 tonnes for the 3.23 million hectares of the basin. According to other evidence, dry fallout contributes between 2 and 3 times as much as rainfall, yielding a probable 16,000 tonnes (N) and an upper limit of perhaps 20,000 tonnes (N). The atmospheric deposition of N in the Hudson-Raritan basin exceeds the sewage contribution it is deposited mostly on land. It contributes directly to water pollution by way of urban runoff -- a very small fraction of the total. However the runoff contribution is increasing. From 1955-56 to 1972-73 the nitric acid component of (acid) rainfall has increased by a factor of 340% [Nisbet 75] cited in [NRC 78, Table 6.17].

The deposition of total nitrates, as measured in Ithaca NY, doubled over the same period [Likens 72] cited in [Junge 74, Figure 6.20].

To summarize, before 1960 except for lightning only non-anthropogenic sources, sewage, food processing, and animal wastes need be considered in the Hudson-Raritan basin. (The population served by sewers is the relevant one). In the late 19th century and early 20th century wastes from horses and mules used for urban transport were an important contributor. Since 1960 some upward adjustment must be made for fertilizer use in the basin, atmospheric deposition, and some dissipative uses of nitrogenous industrial chemicals. These currently account for 25% of total synthetic ammonia consumption, but only insignificant amounts appear to end up as waterborne wastes. Only the few chemicals that are discharged directly to water after use (e.g. detergents) appear to be relevant in this context.[12]

The nitrogen released in the effluent of most sewage plants is measured and that of the sludge can be estimated on average. These totals for the sewage plants in the basin could be accumulated to obtain much more precise data.

[12]The major non-agricultural uses of nitrogenous chemicals are as explosives, sythetics (e.g. ABS rubber, nylon, melamine) and the use of HNO_3 as an oxidant in certain reactions. None of these results in significant waterborne wastes

11. Anthropogenic Phosphorus Sources and Flows

Phosphorus is an element, atomic weight 30.98, that has a valence of 3 or 5. Because of its high reactivity it is found only in combination in nature. There are about 200 minerals in which it is present in concentrations of 5% or more, but most of the phosphorus available for commercial use is that found in deposits of calcium phosphates of as the apatite family. Phosphate rock has the general formula ($Ca_{10}(PO_4)_6F_2$).

Although it is necessary to life, and is a part of every living cell, phosphorus is relatively scarce. It constitutes only about 0.12% of the soils and rocks in the earth's crust. In fact, it is classed as a trace element. Because of this scarcity, most soils farmed regularly soon become depleted of their phosphate content unless it is replaced by the addition of phosphorus compounds.

Early sources of phosphorus, as of nitrogen, were decaying plant and animal matter -- humus and manure. As more concentrated sources were sought it was found that ground bone -- containing 20-30% phosphorus -- provided a convenient fertilizer. Further processing by treatment with sulfuric acid or hydrochloric acid (in glue production) and steam improved its properties. Some bone meal is still used, mostly by home gardeners. Another natural product used was guano. Fresh deposits contain 10-12% phosphorus pentoxide (P_2O_5) and some nitrogen. Old leached material contains 20 to 30 percent P_2O_5, but little or no nitrogen. Other sources are relatively limited when compared to the mineral deposits of phosphate rock. Those of most commercial importance in the U.S. are in four areas: Florida (78%), N. Carolina (3%), Tennessee (5%) and Idaho, Montana, Utah and Wyoming (14%). Production in 1980 was 48.6 million tonnes of rock, containing 15.5 million tonnes of $P_2O_5$and 6.4 million tonnes of P. The U.S. is currently self-sufficient in phosphates and a substantial fraction of total production is exported (26% in 1980) (See Table 11-1).

Because of the tight chemical bonding of the phosphate in rock, it is insoluble and not readily available to plants. It is also combined with calcium and other inert (or toxic) constituents that would be expensive to ship and, in most cases, would not be desired by the farmer. Small amounts of phosphate rock are used for direct application at points not too distant from the source, but most is locally processed near the mine to separate the P_2O_5 from the matrix or gangue.

Table 11-1: U.S. Phosphorus Production & Consumption (1000 tonnes)

	Phosphate Rock Production	Phosphate Rock Exports	Phosphate Rock Consumption	Phosphate Rock Use For Fertilizer	Phosphate Rock Use For Detergent	Phosphoric Acid (H_3PO_4) Use	Sodium Tripoly Phosphate (STPP)
1880	214						
1885	684						
1890	518						
1895	1056						
1900	1515						
1905	1979						
1910	2698	1554					
1915	1865	257					
1920	4169	1087					
1925	3538	884					
1930	3989	1246					
1935	3091	1121					
1940	4067	763					
1945	5900	499				250	-
1950	10418	1788				540	215
1955	13397	2218				1200	500
1960	17478	4058				1850	620
1965	26344	6643	19836	15868	1587	3600	840
1970	34403	10649	24642	19713	1970	5150	1240
1975	40167	10098	28143				
1980	49364	12951	37005				

Average P_2O_5 content .32 (.318 in 1980). P content .132

11.1 Phosphoric Acid

To make the phosphorus more available to plants requires chemical treatment using either an acid or heat. Over 90% of commercial phosphoric acid is produced by treatment of phosphate rock with sulfuric acid by what is known as the wet process. While several phosphoric acids are produced in the reaction, orthophosphoric (H_3PO_4) is the most common. In the wet process it is produced initially in a concentration of 53-54% P_2O_5 but can be further concentrated to the 68-70% level. About 80% of phosphate rock was converted by the wet process in 1975.

Phosphoric acid solutions are only used directly as fertilizer in some places in the west, where the soil is alkaline. The largest portion is further processed to make solid fertilizers, such as enriched, triple superphosphate, diammonium phosphate, or other compounds. Below are listed the principal phosphorus containing products and the P_2O_5 percentage they typically contain. Figure 11-1 charts the major uses. Figure 11-2 shows the major process-product relationships for phosphate rock.

FIGURE 11-1: U.S. Phosphorus Production & Domestic Consumption 1975
(units = 1000 metric tons of contained phosphorus)

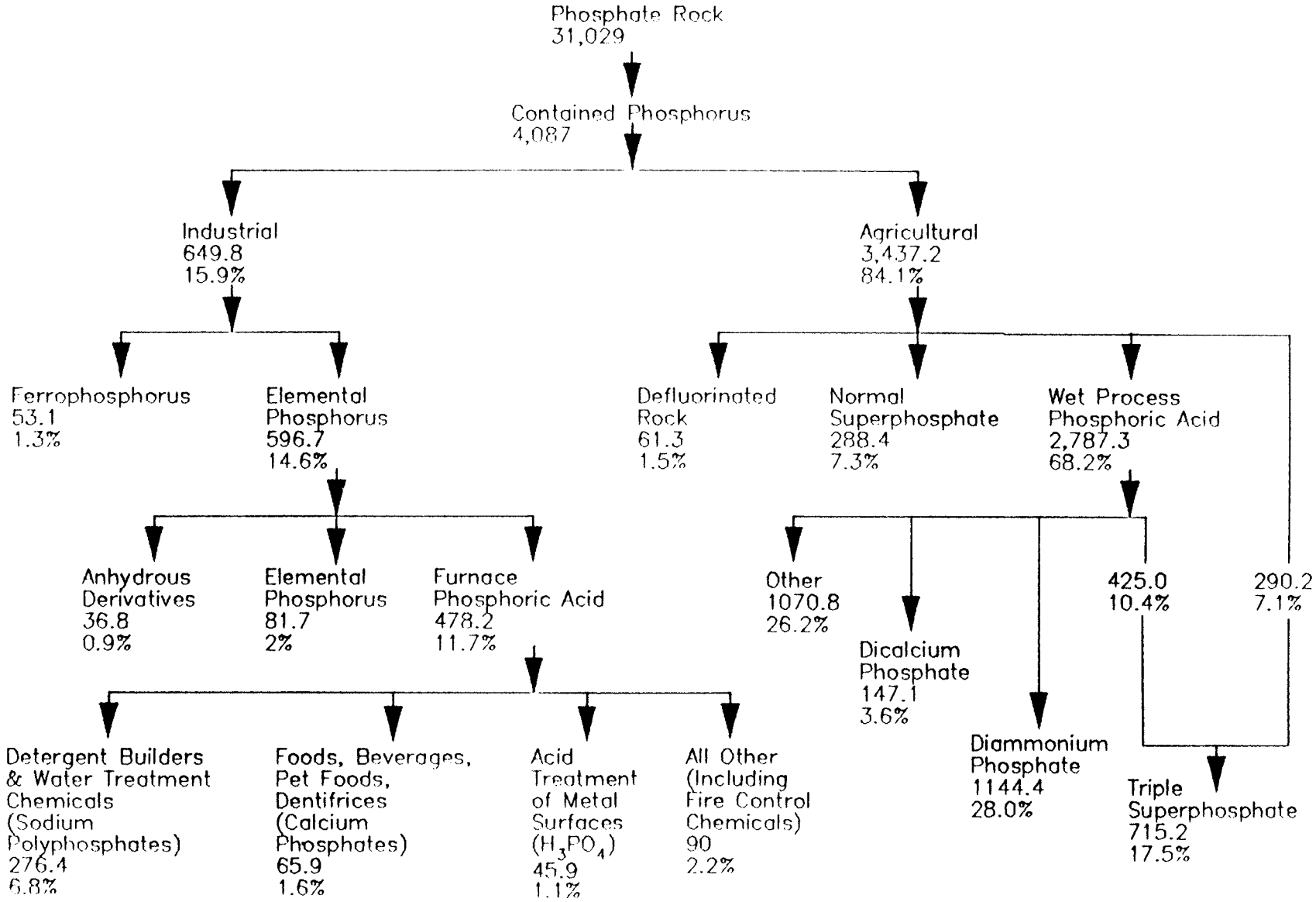
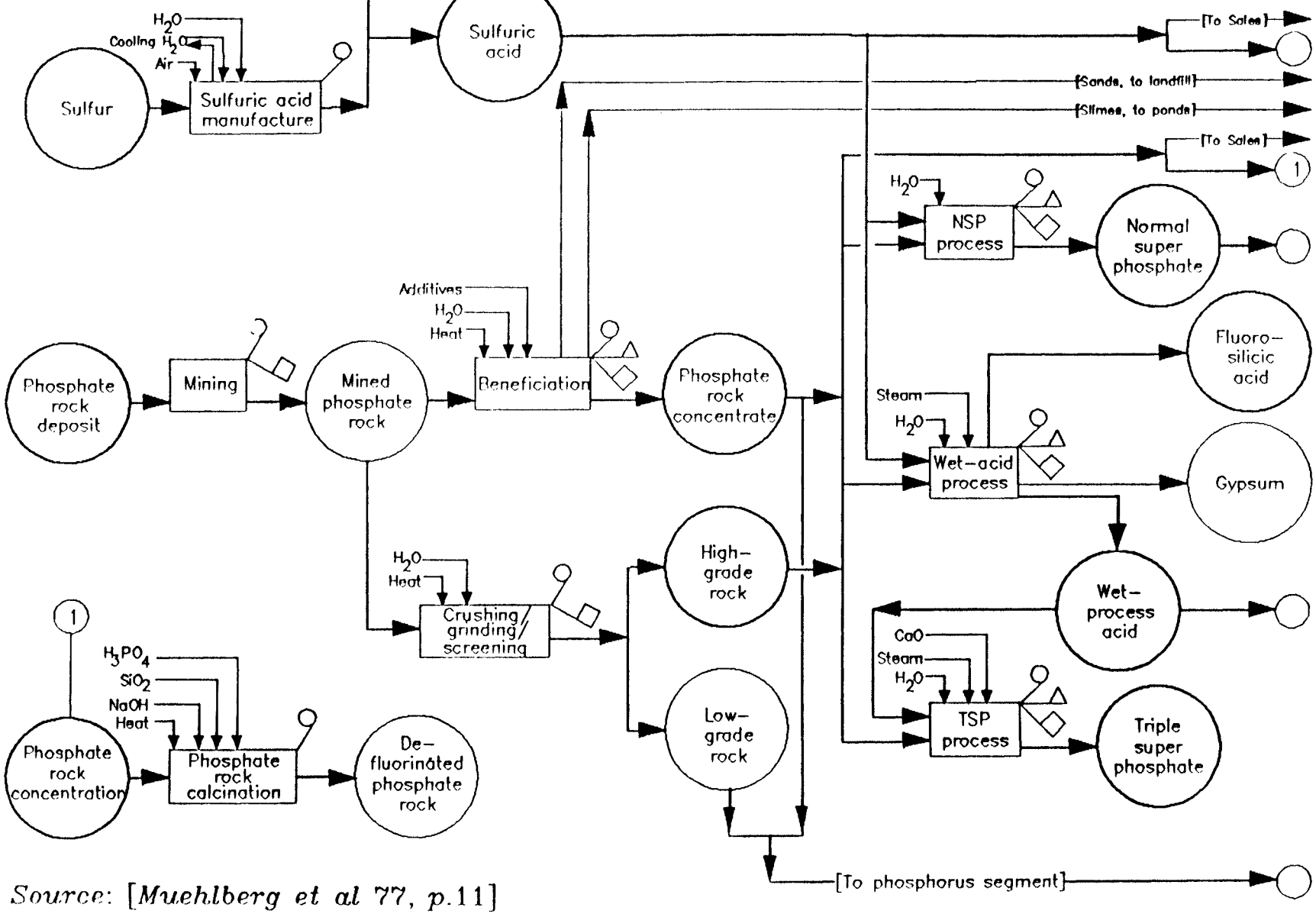
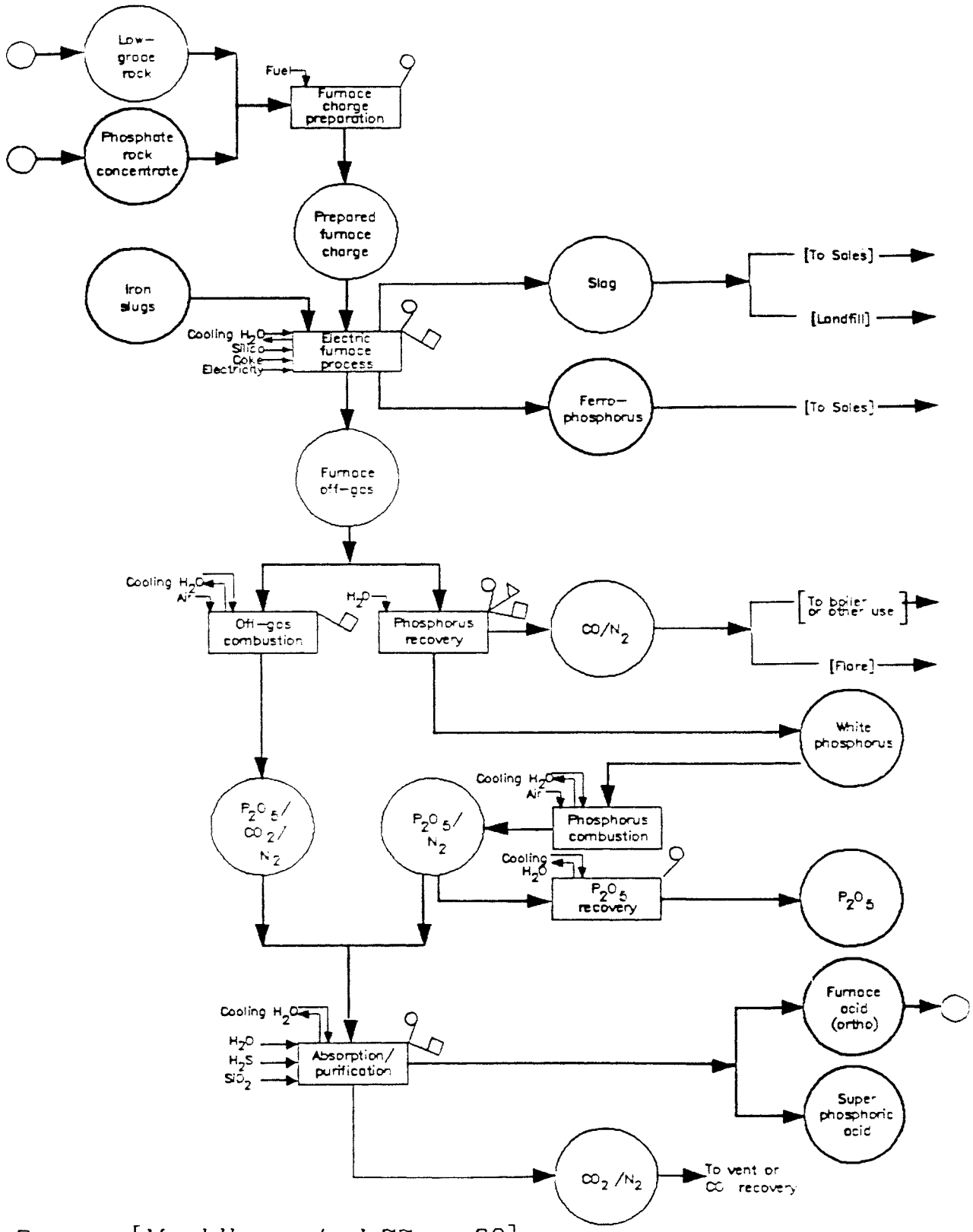


FIGURE 11-2: Phosphate Rock Processing



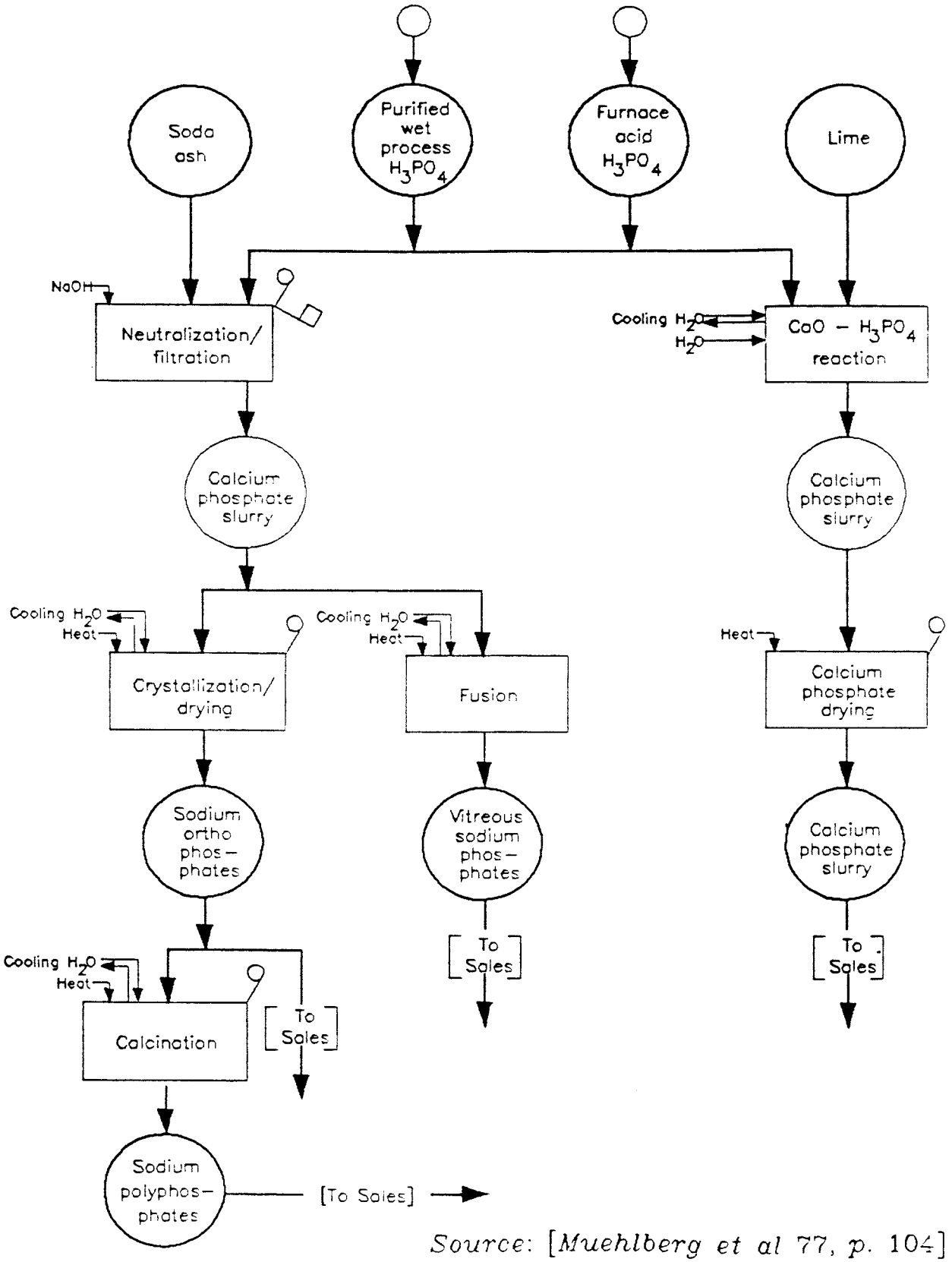
Source: [*Muehlberg et al 77, p.11*]

FIGURE 11-3: Elemental Phosphorus & Furnace Acid



Source: [*Muehlberg et al 77, p. 89*]

FIGURE 11-4: Sodium Phosphates & Calcium Phosphates



Source: [Muehlberg et al 77, p. 104]

Pure phosphorus pentoxide, known as "furnace acid" is made from elemental phosphorus, typically from western rock smelted in an electric furnace. This process accounted for 16% of 1975 domestic production. Major process-product relationships for elemental phosphorus are shown in Figure 11-3. When power costs were low it was used to make high quality liquid fertilizers. But as the cost of electricity has risen, furnace acid is primarily used in the preparation of chemical derivatives requiring higher purity, such as detergents and feed additives. Other major phosphorus products are as follows:

- **Phosphoric acids** are reaction products of P_2O_5 with H_2O
    - Metaphosphoric acid HPO_3 or $1/2(P_2O_5.H_2O)$
    - Tetrapolyphosphoric acid $H_6P_4O_{13}$ or $(2P_2O_5.3H_2O)$
    - Tripolyphosphoric acid $H_5P_3O_{10}$ or $1/2(3P_2O_5.5H_2O)$
    - Pyrophosphoric acid $H_4P_2O_7$ or$(P_2O_5.2H_2O)$
    - Orthophosphoric acid H_3PO_4 or $1/2(P_2O_5.3H_2O)$ is the major form
- b<Calcium phosphates> are made from phosphate rock (See Figure 11-4)
    - Monocalcium phosphate$(CaH_4(PO4)_2.H_2O)$ and
    - Dicalcium phosphate$(CaHPO_4.2H_2O)$ are the key ingredients of fertilizer
    - Tricalcium phosphate $Ca_3(PO_4)_2$is the principal component of phosphate rock
    - Calcium metaphosphate $Ca(PO_3)_2$
    - Calcium pyrophosphate $Ca_2P_2O_7$, is used in dentifrices
- **Monoammonium phosphate** $(NH_4)_2HPO_4$) and **Diammonium phosphate** $(NH_4H_2PO_4)$ are soluble fertilizers made by reacting phosphoric acid in the ammonia. These are the most common fertilizers.
- **Phosphate tetraurea** $Ca(H_2PO_4)_2.4CO(NH_2)_2$ is a fertilizer material produced by reacting a solution of phosphoric acid and monocalcium phosphate with urea.
- **Phosphorus metal** (yellow or white) is made by reducing phosphate rock with coke in an electric arc furnace. It is mostly used to make pure P_2O_5, "furnace acid".
- **Superphosphate** is a fertilizer product made by digesting phosphate rock with sulfuric acid. It contains approximately 20% P_2O_5. Declining in importance, except as a basis for manufacturing triple superphosphate.
- **Triple super phosphate** is made from normal superphosphate by addition of pure phosphoric acids to raise the P_2O_5 content to 46%.
- **Sodium phosphates** are reaction products of ortho phosphoric acid, sodium carbonate and sodium hydroxide. There are seven important sodium phosphates, below (See Figure 11-4)The dibasic form (disodium phosphate) is the ordinary commercial product. It is the intermediate in production of the tripoly form (STPP) that is an important component of detergents. Only STPP is crystalline.

•

- Monobasic (NaH_2PO_4)
- Dibasic (Na_2HPO_4)
- Tribasic (Na_3PO_4)
- Tetrabasic ($Na_4P_2O_7$)
- Acid ($Na_2H_2P_2O_7$)
- Meta $(NaPO_3)_6$
- Tripoly ($Na_5P_3O_{10}$)

- **Phosphorus Oxychloride** ($POCl_3$) is made by reacting phosphorus pentoxide and phosphorus trichloride. It is used in the manufacture of phosphate esters (e.g. tricresyl, cresyl diphenyl, and triphenyl phosphates)
- **Phosphorus Trichloride** (PCl_3) is made by reacting metallic phosphorus with chlorine. It is an intermediate in the manufacture of phosphorus oxychloride, surfactants, and phosphate esters
- **Phosphorus pentasulfide** (P_2S_5) is made by reacting metallic phosphorus and sulfur. It is used in the manufacture of zinc dithiophosphate, a lube additive, and some organophosphate pesticides including malathion
- **Phosphorus trichlorosulfide** ($PSCl_3$), or thiophosphoryl chloride, is manufactured by chlorination of phosphorus pentasulfide. It is the basis for organophosphate pesticides such as parathion, methyl parathion and diazinon
- **Tricresyl phosphate** (TCP), an organic ester of phosphoric acid is a plasticizer and petroleum additive
- **Triphenyl phosphate** (TPP), is a plasticizer and intermediate
- **Zinc dithiophosphate** is an anti-oxident additive to motor oil. It is made from phosphorus pentasulfide

11.2 Superphosphates

To make the "standard", "single", or "simple" superphosphate 93% sulfuric acid is reacted with phosphate rock. The phosphoric oxide content usually is about 20% and, if lower, it may be raised to this level with more concentrated acid or superphosphates. In the production of "enriched superphosphate" (by definition any superphosphate product having P_2O_5 content above 20% and less than 40%) phosphoric acid (H_3PO_4) is added to the sulfuric acid to raise the phosphoric oxide content to about 27%

Since 1964, production of 'concentrated' superphosphate -- frequently called 'triple' superphosphate -- has been expanded at the expense of 'normal' and 'enriched' forms. The term refers to a product made by treating phosphate rock with phosphoric acid -- and removing most of the calcium sulfate formed. (The resulting calcium sulfate hydrate is called phosphogypsum. While it is useful in the treatment of soil in arid

regions to release potassium, and in manufacture of wallboard, the amount produced so far greatly exceeds requirements).

Phosphatic fertilizer materials can either be blended into mixtures or applied undiluted. The use of unblended (straight) materials has grown most rapidly, particularly for use by larger farms. The northeast tends to lag this trend. It can be seen in Table 10-4 that in 1968 almost ten times as much phosphate was applied in mixtures as in straight materials.

Whatever the means by which it is made chemically available or transported, once it is in the soil it is the 'primary nutrient' P_2O_5 that counts. We will therefore always refer to P_2O_5 content in the discussion below.

11.3 Production

No phosphate rock is processed in the northeast. There are three ortho-phosphoric acid plants (furnace process) in the Hudson-Raritan basin: FMC Corp. (Carteret NJ), Mobil Oil Co. (Carteret NJ) and Monsanto (Kearney NJ). Together, these plants have a capacity of about 250,000 tonnes/year, which is 2.3% of the national total. The output is apparently entirely used for manufacturing sodium tripolyphosphate (STPP) for detergents.

11.4 Fertilizer Phosphorus Use

About 80% of all phosphorus (P_2O_5content) is used as fertilizer. The consumption of phosphorus in fertilizer (as P_2O_5) in the U.S. for the years 1950 to 1980 is shown in Table 10-5 (See Chapter 10, Nitrogen). There has obviously been an upward trend in phosphate use but at a very much slower pace than was the case for nitrogen. There was a 229% increase over the 1950-1980 period (as compared to tenfold increase for N). Interestingly, the N:P ratio in fertilizer shifted from 1:2 in 1954 to the reverse (2:1) in 1978.

In the data for NY and NJ we find that in 1954 the nitrogen-phosphorus ratio was slightly greater than the national average. However growth in nitrogen use was slower that the national average. By 1978 the N:P ratio in NJ-NY was 1.13. Using available estimates for phosphorus removal by crop we find that, on the average, 73.6% of the fertilizer phosphates applied were embodied in the harvest -- primarily in the edible component. It eventually returns to the environment in food processing wastes, garbage or sewage.

Fertilizer materials must be somewhat soluble in water to be accessible to plants. The soluble phosphatic content of high quality triple superphosphate is largely monocalcium phosphate (CaH_4PO_3) The solubility of calcium metaphosphate ($Ca(PO_3)_2$) is only 0.001 parts per 100 of water; for dicalcium phophosphate ($CaHPO_4.2H_2O$) it is .02 parts per 100. Compounds having both N and P_2O_5 values are highly soluble: for example diammonium phosphate at 25 parts per hundred of water and monoammonium phosphate ($NH_4H_2PO_4$) at 43 parts per hundred of water. There is more likely to be some loss of the more soluble materials to runoff if heavy rains fall before they are worked into the ground. After the materials have penetrated into the soil, been incorporated in organic material, and become part of the life cycle of soil microbes there is less danger of phosphate loss by leaching (though some decay organisms generate ammonia).

In Table 11-2 are shown data for estimated consumption of phosphorus on the major crop groups grown in the Hudson-Raritan basin. Mainly because of declines in the acreage planted, the use of phosphate actually declined in both 'fruit and vegetables' and 'Irish potatoes'. Growth in other crop use was stronger. But on the whole the consumption curve was relatively flat; declining acreage somewhat compensated for a somewhat higher rate of application.

Table 11-2: Phosphorus Use (as P_2O_5)in the Hudson Raritan Basin

	Fruit & Vegetable		Irish Potatoes		----- Other -----		Total
	%	tonnes	%	tonnes	%	tonnes	tonnes
1954	48.5%	3439	24.6%	1745	26.9%	1908	7091
1959	36.9%	3348	17.3%	1570	45.8%	4157	9075
1964	38.0%	3270	18.5%	1591	43.5%	3744	8606
1969	32.6%	2585	12.4%	983	55.0%	4361	7929
1974	26.9%	1836	7.8%	533	65.3%	4457	6826
1978	31.9%	2337	4.8%	352	63.3%	4637	7326

In summary we estimate that from 1950 to the present a total of 265,000 tonnes of P_2O_5 has been applied in the Hudson-Raritan valley and that roughly 73% of this has been removed by crops. Of the remaining 27% most remains in the soil, but in less soluble forms. A portion is recycled in plant material. Some has undoubtedly entered the streams and rivers draining the fields. The buildup in soil phosphate levels is quantitatively unknown, however. Because of the beneficial and non-hazardous nature of phosphate residues most soil monitoring programs have not tested for their presence.

It must be noted that the six middle Atlantic States collectively only consume about 4.75% of all phosphate fertilizers, and the Hudson-Raritan valley constitutes only about 5% of the arable area of these states. Thus only a quarter of 1% of the phosphate fertilizer is used in a basin with 8% of the nations population.

11.5 Chemical Uses

As noted above, about 16% of phosphate rock was converted (1974) to "furnace acid" via electric furnace, and thence to other chemical forms, mainly sodium and calcium phosphates. Sodium tripolyphosphate is a major component of commercial and industrial detergents and water softeners,[13] which together account for 85% of all *non-agricultural* consumption. The remainder is used in the manufacture of soft drinks and other food products (7%), textiles (2%), dentifrices (1%), animal feeds (1%), clay processing (1%), drilling muds (1%), matches, and pesticides, lube oil additives and other uses. All of these uses are quantitatively unimportant in comparison with the two major uses.

11.6 Phosphate Emissions

The phosphorus removed with crops is believed generally to amount to about 0.5% of the dry weight of harvested product. Department of Agriculture figures indicate that the average consumption of food in 1980 was about 450 kg per capita (retail weight, except for the water content of fruit juices and whole milk). Assuming that variations in the phosphorus content of individual foods balance out the phosphorus consumption per capita would have been 2.2 kg. The population of the Hudson-Raritan basin for 1980 was about 16 million. Thus the total phosphorus consumed in food in the Hudson-Raritan basin is on the order of 36,000 tonnes/yr -- mostly imported from other farming areas. To this must be added the phosphorus content of soft drinks consumed in the area (and excreted). In urban areas, most of this input ultimately finds its way into the sewage system. After treatment the bulk of the phosphorus is embodied in sludge that is disposed of in landfills, by incineration, or (in the case of New York City) by ocean dumping. However some of the soluble phosphorus content of sewage passes through the treatment plant and back into the stream.

[13]Soluble sodium phosphates readily combine with oxides of iron -- which give water its "hardness" -- and enable them to be removed by filtration

Annual national phosphorus emissions in 1978 have been estimated to be 2.93 million tonnes, of which over 99% went into waterways [Mumma et al 79, Table 6-18] and 87% was from non-point sources, mainly agricultural runoff. A breakdown of these sources is shown in Table 11-3. Obviously regions will differ significantly from these averages. In particular, it must be noted that the Hudson-Raritan basin utilizes an insignificant fraction of phosphate fertilizers, and contains no phosphate rock processing operations, whereas it includes sizeable fractions of other phosphorus emission generating activities -- notably population. Taking all factors into account, it appears that the Hudson-Raritan basin should account for approximately 1.5% of the national phosphorus emissions, or 44,800 tonnes in 1978, primarily from sewage and urban runoff. This figure can be expected to change over time in proportion to non-agricultural phosphate uses.

Table 11-3: Phosporus Emissions

Emission Source Category	Type of Source	Estimated % of National Discharge
Pasture & rangeland runoff	NP	33.6
Municipal sewage treatment effluent	P	10.6
Cropland runoff	NP	48.9
Phosphate rock mining beneficiation	P	0.2
Animal feed production (feed grade calcium phosphates & defluorinated phosphate rock)	P	1.0
Phosphate fertilizer & intermediate chemical production	P	0.2
Forestland runoff	NP	0.6
Inadvertent sources (total)	P + NP	1.1
Urban runoff	NP	0.6
Use of phosphorus-based water treatment chemicals	NP + P	0.8

Percent shown is for emission source category

12. Water Withdrawals

Water withdrawals cannot meaningfully be discussed on a national basis (although national estimates are available, as shown in Table 12-1). In the northeastern U.S. irrigation is not a factor and consumptive uses are minor. In the case of the Hudson-Raritan basin, less than 1% of the water of the upper basin were used consumptively for all purposes in 1975 even in periods of low flow (e.g. flow exceeded 90% of the time). In the lower basin withdrawals never exceed 4% on the same basis [USDA 81, Table 7.11, p298]. One reason is that municipal supplies for all population centers in the region are obtained from reservoirs in reserved watersheds. The only other significant use of water is for purposes of cooling the condensers of steam-electric power plants located in the basin. It may be noted that usage for this purpose is of the same magnitude as the river flow (in millions of gallons per day or mgd). The data for industrial withdrawals for 1980 is shown in Table 12-2 below. It may be assumed that most of the fresh water withdrawals in NY state are taken from Lake Erie, Lake Huron and the upper basin of the Hudson, since the lower Hudson is tidal (i.e. saline) as far north as Troy. In the case of NJ the fresh water withdrawals are taken largely from the Delaware north of Philadelphia. Saline withdrawals are only partly from the Hudson-Raritan estuary. For both NY and NJ many power plants use water from Long Island Sound, the Delaware estuary or the Atlantic Ocean. Nevertheless, in low flow conditions up to half of the water in the lower Hudson-Raritan basin -- 6000 mgd -- may have been withdrawn for power plant cooling (and subsequently returned) as of 1975 [Murray & Reeves 77]. The quantities withdrawn in earlier years can be assumed to be nearly proportional to electricity generation in the basin, adjusted for the somewhat lower generating efficiencies (i.e. greater cooling required) in earlier years.

Assuming 1980 technology, a 1000 MWE coal-fired power plant generates 1560 MW waste heat (to air and water) without the use of wet limestone scrubbers or 1860 MW if scrubbers are used. A light water nuclear reactor generates 1940 MW. A typical 1000 MWe operating at 70% average capacity and losing 20% of its waste heat to the air would require 1850 mgd of cooling water per day, assuming a temperature increase (for the water) of 10°F.

Table 12-1: Estimated National Water Use (10^9 gallons)

	TOTAL	Public Water Utilities			Steam Electric Utilities			--Industrial & Misc.---		
	Other *	Total	Ground	Other *	Total	Ground	Other *	Total	Ground	Other *
1900	14.54	3.00	1.05	1.95	5.00	0.01	4.99	10.00	2.40	7.60
1910	20.55	4.70	1.49	3.21	6.50	0.01	6.49	14.00	3.15	10.85
1920	27.53	6.00	1.79	4.21	9.20	0.01	9.19	18.00	3.87	14.13
1930	40.71	8.00	2.30	5.70	18.40	0.02	18.38	21.00	4.37	16.63
1940	53.60	10.10	2.82	7.28	23.20	0.02	23.18	29.00	5.86	23.14
1944	81.72	12.00	3.30	8.70	34.60	0.03	34.57	48.00	9.55	38.45
1945	72.77	12.00	3.28	8.72	31.20	0.03	31.17	41.00	8.12	32.88
1946	66.02	12.00	3.25	8.75	30.80	0.03	30.77	33.00	6.50	26.50
1950	86.80	14.10	3.78	10.32	45.90	0.05	45.85	38.10	7.47	30.63
1955	128.30	16.30	4.27	12.03	76.60	0.08	76.52	49.20	9.45	39.75
1958	150.15	19.72	5.12	14.60	89.96	0.09	89.87	56.40	10.72	45.68
1960	164.55	22.00	5.68	16.32	98.70	0.10	98.60	61.20	11.57	49.63
1961	171.90	22.71	5.88	16.83	103.13	0.14	102.99	64.22	12.14	52.08
1962	178.40	23.31	6.00	17.31	107.17	0.15	107.02	66.62	12.55	54.07
1963	184.07	23.80	6.04	17.76	110.82	0.11	110.71	68.40	12.80	55.60
1964	190.58	24.40	6.16	18.24	114.86	0.11	114.75	70.80	13.21	57.59
1965	140.02	23.74	5.96	17.78	84.54	0.08	84.46	46.41	8.63	37.78
1966	202.23	25.40	6.35	19.05	121.58	0.12	121.46	75.76	14.04	61.72
1967	207.37	25.80	6.42	19.38	124.26	0.12	124.14	78.32	14.47	63.85
1968	212.50	26.20	6.49	19.71	126.94	0.13	126.81	80.88	14.90	65.98
1969	217.65	26.60	6.56	20.04	129.62	0.13	129.49	83.44	15.32	68.12
1970	231.06	27.03	6.65	20.38	170.80	0.12	170.68	46.00	6.00	40.00
1975	167.55	29.14	9.40	19.74	92.60	1.47	91.13	65.68	9.00	56.68
1980	313.59	61.48	14.40	47.08	179.40	2.47	176.93	107.58	18.00	89.58

Sources: Statistical Abstract & Historical Statistics

Table 12-2: Industrial Water Withdrawals, Hudson-Raritan Basin 1980
(millions of gallons per day)

	Fresh	Saline	HR(low flow)
NY (Entire State)	4300 (EU) 980 (OI)	8500 (EU) 120 (OI)	11,886(combined)
NJ (Entire State)	910 (EU) 600 (OI)	6500 (EU) 1000 (OI)	

EU = Electric Utility
OI = Other Industrial

Source: [USGS 84, pp 173, 179]

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