

*"Materials-Cycle Optimisation in the  
Production of Major Finished Materials"*  
**CHAPTER 9: THE CHLOR-ALKALI SECTOR**

by

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This chapter is part of a report made for the EC DGXII on a project entitled "*Materials-Cycle Optimisation in the Production of Major Finished Materials*". This project aims at facilitating the identification of longer-term R&D needs for materials-cycle optimisation, especially by using wastes, co-products, or by-products from one process as inputs to other processes. Book publication is envisaged. Following is the list of chapters:

- Chapter 1: Summary and Overview (*Insead ref N°: 95/05/EPS*)
- Chapter 2: Alumina, Aluminium and Gallium (*Insead ref N°: 95/06/EPS*)
- Chapter 3: Copper, Cobalt, Silver & Arsenic (*Insead ref N°: 95/07/EPS*)
- Chapter 4: Chromium Sources, Uses and Losses (*Insead ref N°: 95/08/EPS*)
- Chapter 5: Zinc and Cadmium (*Insead ref N°: 95/09/EPS*)
- Chapter 6: Sulfur and Sulfuric Acid (*Insead ref N°: 95/10/EPS*)
- Chapter 7: Phosphorus, Fluorine and Gypsum (*Insead ref N°: 95/11/EPS*)
- Chapter 8: Nitrogen-based Chemicals (*Insead ref N°: 95/12/EPS*)
- Chapter 9: The Chlor-Alkali Sector (*Insead ref: N°: 95/13/EPS*)
- Chapter 10: Electronic Grade Silicon (EGS) for Semiconductors (*Insead ref N°: 95/14/EPS*)
- Chapter 11: Packaging Wastes (*Insead ref N°: 95/15/EPS*)
- Chapter 12: Scrap Tires (*Insead ref N°: 95/16/EPS*)
- Chapter 13: Coal Ash: Sources and Possible Uses (*Insead ref N° 95/17/EPS*)

All chapters are individually available as INSEAD Working Papers.

# CHAPTER 9. THE CHLOR-ALKALI SECTOR<sup>1</sup>

## 9.1. Summary

Chlorine is a chemically active element that is invariably combined with other elements, usually sodium, but occasionally with potassium, magnesium or ammonium. Its major compound is sodium chloride (NaCl) or ordinary salt, which constitutes roughly 3.7%, by weight, of seawater. There are large underground deposits of evaporite salt left over from earlier seas that have since dried up. However, apart from this one mineral, chlorine is comparatively rare in the earth's crust, although it is apparently released in significant quantities by volcanos as hydrochloric acid, HCl.<sup>2</sup> Its role in biochemistry is equally limited. While salt is a necessary component of every diet, its role appears to be mainly that of maintaining the internal osmotic pressure of cells at an equilibrium level. It is also, of course, the source of hydrochloric acid released in the stomach to assist with digestion. Until recently it was thought that chlorine is rarely, if ever, found in organic molecules of natural origin.<sup>3</sup>

Perhaps it is for this reason that decay bacteria tend to metabolize chlorinated organics very slowly, and higher organisms metabolize them scarcely at all. Yet, a number of organo-chlorines are biologically active in the sense that they are capable of interfering with certain normal biochemical functions, especially in the endocrine systems of animals and humans. In other words, organo-chlorines may be toxic, carcinogenic, teratogenic or even mutagenic. In some cases these characteristics were deliberately exploited, as in the development of a whole family of chlorinated pesticides and herbicides during the 1950's and 60's. In other cases, the toxic or carcinogenic effects turned up be accident, as in the case of the widely used solvents such as trichloroethylene (TCE) and 1-1-1-trichloroethane, or the chemicals ethylene dichloride (highly toxic to aquatic systems), and the monomer vinyl chloride (a potent carcinogen).

The exact mechanisms whereby these biological effects occur are not yet understood, for the most part. (If they were, it would be much easier to design both chemical agents for particular purposes, and also to design effective antidotes or therapies). All that can be said at present, with some confidence, is that the biological activity of organo-chlorine molecules is probably related to their physical structures (i.e. shapes). This follows with a high degree of probability from the fact that organo-chlorines differing only by the exact placement of a chlorine atom on (say) a benzene ring can have totally different biological effects. Evidence has been accumulating of malign biological consequences of long-term low-level exposures to chemicals that mimic the effects of the hormone estrogen on cells. Among the possible effects are birth defects (such as those associated with use of the drug diethylstilbestrol or DES, now banned), breast, prostate and testicular cancers, and a range of male reproductive problems, including a widely observed decrease in male sperm counts [Scientific American, Sept 1993, p.16].

Moreover, since organo-chlorines are not actively metabolized, but simply stored (mainly in fatty tissue) and passed on, many of them are bio-accumulated through the food chain. Thus, what would be an insignificant concentration in a simple organism (such as a mosquito larva), may become a lethal concentration in a top predator three steps up the chain. This is why eagles, ospreys, falcons and game fish were the main victims of dichloro-diphenyl-

trichloroethane (DDT) and other chlorinated pesticides, even though they were never its targets. Much the same sort of problem has been identified for other classes of organo-chlorines, notable the polychlorinated biphenyls (PCB's).

It is not only the organo-chlorines that are manufactured for specific biocidal (or other) purposes that have been implicated in undesirable side-effects. On the contrary, it may be the unexpected by-products of reactions that occur in incineration furnaces (and accidental fires) that cause the greatest public concern — justified or not. Here we refer to the poly-chlorinated dioxins (PCDD's) and poly-chlorinated dibenzyl furans (PCDF's) that may be the most carcinogenic compounds yet discovered, at least based on animal tests [Gough 1988]. The U.S. Environmental Protection Agency (EPA) has been working on a new report on dioxin that is expected to say that dioxin is a serious potential threat to human health [Time, Sept 19, 1994].

Apart from its biological activity, chlorine has been implicated in the destruction of stratospheric ozone. The details of the chemical mechanism involved need not detail us here. It is only of interest that chlorine is mainly transported into the stratosphere in the first place by virtue of the great stability (i.e. persistence) of chlorofluorocarbons (CFC's) in the presence of atmospheric oxygen and OH radicals. Whereas most organic chemicals are rapidly oxidized in the lower atmosphere (or washed out by rain), this is not true of the CFC's.<sup>4</sup> These are compounds used widely as refrigerants, foam blowing agents and solvents (and formerly as aerosol propellants) precisely because of this stability.

Because of all of these problems, the industrial use of chlorine itself is being increasingly questioned by some environmental organizations, notably Greenpeace. The chlorine industry, feeling threatened, is mounting an active defense. This chapter is not intended as an intervention in that debate, either for the unrestricted use of chlorine, or for a total ban. Because of the debate, there has already been a rather intensive examination of potential technological alternatives to the use of chlorine. It is indisputable that alternatives can be found to most of them. What is much less clear is how costly the substitutes would be and whether the costs would be justified by the presumed benefits.

We acknowledge the validity of some of the environmental/health arguments against the use of chlorine for bleaching paper pulp, and against the dissipative use of chlorinated pesticides, chlorocarbon solvents and chlorofluorocarbons. We also believe that a total ban on chlorine use would be extremely disruptive and probably excessively costly in relation to the benefits achieved. In effect, we argue for a much more complete and sophisticated life-cycle analysis of the chlorine industry than anything yet attempted along these lines. Thus we see some on both sides). We wish to focus attention here on the need for the industry to release accurate quantitative information on the production, consumption, trade and stockpiling of individual chemicals. Without such data the requisite analysis cannot be carried out and intelligent public policy cannot be made

**Goals of Public Policy:** Reduce mercury emissions and electricity consumption; reduce dissipative uses of chlorine, chlorinated hydrocarbons, especially solvents, pesticides and other organics; increase recycling of PVC to minimize potential for combustion of PVC-containing

wastes (see also *Chapter 11, Packaging*); increase public understanding of the costs and benefits associated with pending proposals such as the proposed ban on all chlorine use.

## 9.2. Sources & Uses of Chlorine

Chlorine and caustic soda (sodium hydroxide) are co-products of the electrolysis of sodium chloride (salt), mainly in the form of brine made by solution mining of underground salt (halite) deposits. World production and consumption of chlorine in 1990 was 37.433 MMT, of which the U.S. accounted for 29% and Western Europe 25%. The output of caustic soda is essentially proportional to that of chlorine, in the ratio of their respective molecular weights (40:35.5 = 1.12). Thus 1.12 tonnes of (100%) caustic soda are produced by electrolysis per tonne of chlorine, or 42.1 MMT for the world. However, the situation is slightly confused by the existence of several alternative minor routes to chlorine (mainly, electrolysis of HCl and MgCl). In Europe, these routes altogether account for only 3.4% of 1988 chlorine capacity.

There are three important variants of the basic electrolytic process for chlor-alkali production, viz. the de Nora mercury cell (63.1% of 1988 European capacity; 17 % of 1989 U.S. capacity), the diaphragm cell (28% of European capacity) and the membrane cell (5.3%). The mercury cell is a significant source of environmental pollution, since some mercury is lost in the process. Historical data on the use of mercury for this process is shown in *Table 9.1*.

The diaphragm cell is also a source of pollution, namely asbestos fiber. The membrane cell is the most efficient and least polluting, but the chlor-alkali industry has been surprisingly slow to adopt it, due to the fact that there has been little growth in demand since the early 1970's and because existing facilities are fully depreciated but still functional. The three processes are summarized in *Table 9.2(a,b,c)*.

**Table 9.1. Mercury consumption in chlorine production**

Year	Hg used for Cl <sub>2</sub> mfg, U.S. tonnes	Cl made by Hg cell, U.S. %	Cl production, U.S. kMT	Cl production, W. Europe kMT	Cl made by Hg cell, W. Europe %
1970		25% <sup>(b)</sup>	8858	5008	
1973	450.6		9437		
1974	582.5		9755		
1975	524.8		8316	6734	
1976	553.4		9415		
1977	370.4		9592		
1978	384.9		10026		
1979	419.9		11150		
1980	326.5		10361	8272	
1981	252.4		9764	8050	
1982	215.2		8324	7881	62%
1983	277.6		8948	8715	
1984	253.0	20% <sup>(c)</sup>	9707	9421	
1985	235.0		9437	9564	
1986	259.0		9473	9422	
1987	311.0		10050	9807	
1988	445.0		10212	9800	63%
1989	381.0	17% <sup>(c)</sup>	10354	9750	
1990	247.0	16.25% <sup>(c)</sup>	10713	9250	
1991	184.0		10361	8800	
1992			10107	8560	
	(a)		(d)	(e)	(e)

a) [USBuMines *Minerals Yearbooks*, various years]

b) [Tellus Institute 1993]

c) [US Bureau of Mines preliminary estimates]

d) [US Department of Commerce, *Business Statistics, 1961-1991 & Current Industrial Reports: Inorganic Chemicals*, 4th quarter 1992]

e) [SRI, various years]

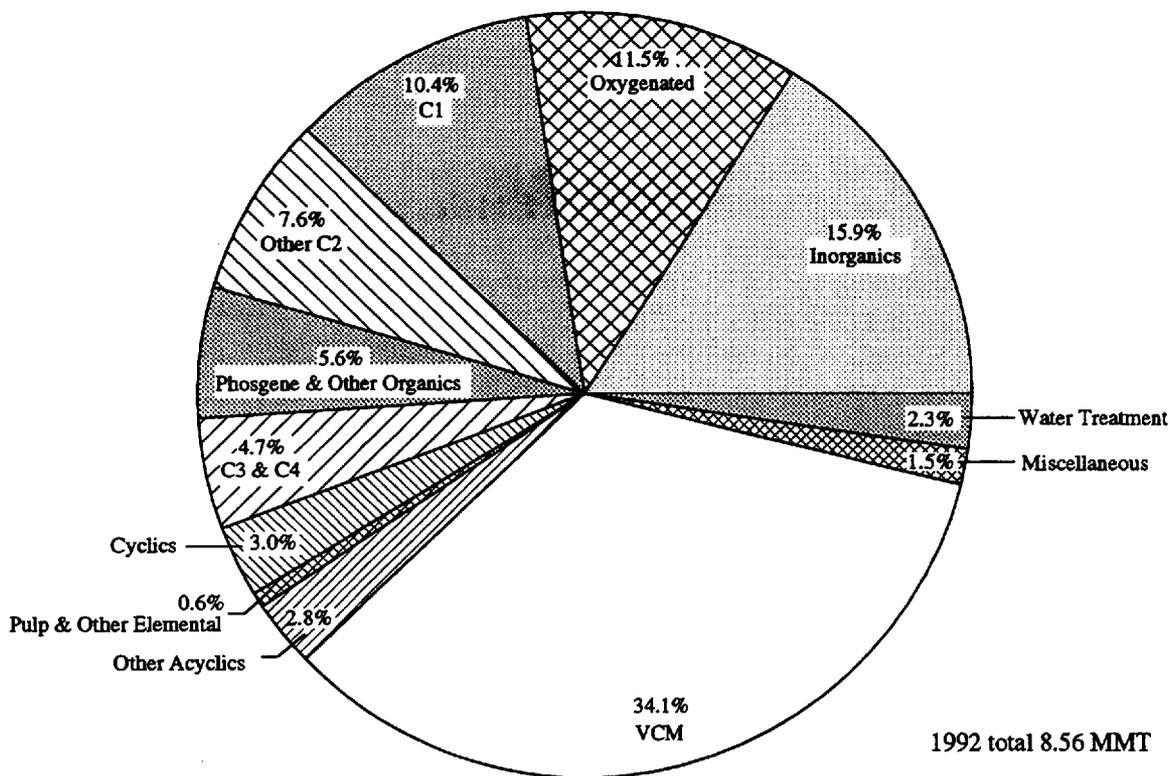


Figure 9.1. Western European consumption of chlorine 1992. Source: [Detournay 1993]

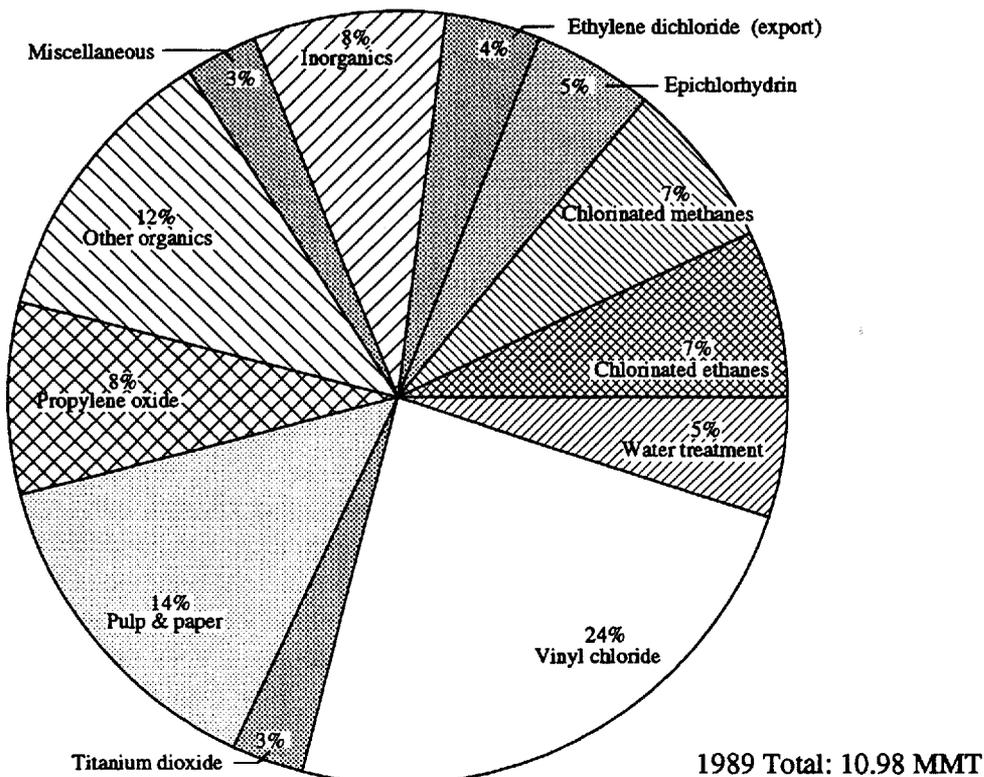


Figure 9.2. U.S. consumption of chlorine 1989. Source: [MIT 1993]

Table 9.2. Processes for the production of chlorine

A. CHLORINE: BY ELECTROLYSIS OF NA CL IN DIAPHRAGM CELLS				
Utility inputs & outputs			Other uncounted	
Water (cooling) (input)	69	tonnes	Hydrogen (as fuel) (T-Cal)	906
Steam (input)	2.4	tonnes		
Electricity (input)	2811	kWh		
INPUTS (metric tonnes)			OUTPUTS (metric tonnes)	
Sodium chloride	1.712		Caustic soda	1.128
Sulfuric acid	0.0087		Sulfuric acid (65%)	0.008686
Calcium Chloride	0.0129		CHLORINE	1
Hydrochloric acid (20BE)	0.0564		(caustic soda byproduct)	
Carbon tetrachloride	0.000011			
Water (process)	0.01			
INPUTS ACCOUNTED FOR	1.800011		OUTPUTS ACCOUNTED FOR	2.136686
Source: [SRI #110]		-0.336675	= Difference = -18.70% of input	
B. CHLORINE: BY ELECTROLYSIS OF NA CL IN MEMBRANE CELLS				
Utility inputs & outputs			Other uncounted	
Water (cooling) (input)	152	tonnes	Membrane (Sq. cm)	166.9
Steam (input)	0.89	tonnes	Hydrogen (as fuel) (T-Cal)	916
Electricity (input)	2798	kWh		
INPUTS (metric tonnes)			OUTPUTS (metric tonnes)	
Sodium chloride	2.43		Caustic soda	1.143
sodium carbonate	0.0345		Sulfuric acid (65%)	0.00934
Sulfuric acid	0.00934		CHLORINE	1
Hydrochloric acid (20BE)	0.0114		(caustic soda byproduct)	
Water (process)	3.7			
INPUTS ACCOUNTED FOR	6.18524		OUTPUTS ACCOUNTED FOR	2.15234
Source: [SRI #111]		4.0329	= Difference = 65.20% of inputs	
C. CHLORINE: BY ELECTROLYSIS OF NA CL IN MERCURY CELLS				
Utility inputs & outputs			Other uncounted	
Water (cooling) (input)	208	tonnes	Hydrogen (as fuel) (T-Cal)	898
Steam (input)	2	tonnes		
Electricity (input)	3575	kWh		
INPUTS (metric tonnes)			OUTPUTS (metric tonnes)	
Sodium chloride	1.711		Caustic soda	1.118
Sulfuric acid	0.008624		Sulfuric acid (dilute)	0.00883
Calcium chloride	0.0144		CHLORINE	1
Sodium carbonate	0.0386			
Hydrochloric acid	0.0399			
Sodium sulfide (flake)	0.000112			
Mercury	0.000003			
Water (process)	0.03			
INPUTS ACCOUNTED FOR	1.842639		OUTPUTS ACCOUNTED FOR	2.12683
Source: [SRI #112]		-0.284191	= Difference = -15.42% of inputs	
Note: The inputs and outputs do not balance exactly because only about 98% of the sodium chloride in the brine is consumed, and because some of the chlorine is lost in the process. Based on Toxic Release Inventory data for the U.S. (1990), air emissions of chlorine amounted to 45 KMT (fugitive) and 290 KMT (stack), or 0.42% and 2.7% of output respectively [Kostick 1994].				

**Table 9.3. Production/consumption of chlorine, caustic soda & hydrochloric acid (kMT)**

Country	Chlorine 1988		Caustic Soda 1988		HCl <sup>(a)</sup>	
	Prod	Cons	Prod	Cons	Prod	Year
Austria	87	40	82	205		
Belgium	685	693	685	130		
Denmark	25	30	28	149	8	1987
Finland	240	240	269	480	14.4	1987
France	1418.5	1415	1480.5	1427	237.8	1989
Germany	3452	3496	3625	2228	957.6	1989
Greece	20	20	22	77	53.4	1985
Ireland	3	5	3	111		
Italy	1050	994	1176	993	500	1986
Netherlands	550	504	616	914	81.2	1989
Norway	230	237	258	112		
Portugal	70	70	78	100	53.6	1986
Spain	578	563	625	466	147.3	1988
Sweden	360	318	403	508	82.4	1987
Switzerland	70	67	78	57		
United Kingdom	1050	1055	1176	1367	166.5	1989
W. Europe	9888.5	9747	10604.5	9324	2302.2	

Source: *Ecoplan*

(a) Consumption of HCl is almost entirely captive

Production and consumption of chlorine and caustic soda need not be (and are not) proportional in any given country. See *Table 9.3* for 1988, which is the last year for which we have a breakdown by country. Major uses of chlorine and hydrochloric acid in Western Europe are summarized for 1992 and for the U.S. in 1989 in *Figures 9.1 & 9.2*. A less detailed breakdown for 1994 is shown in *Table 9.4*. The biggest single use of chlorine in all countries is in the manufacture

**Table 9.4. World demand for chlorine by end-use, 1994**

Use Category	Europe	United States	Japan	Rest of World
Organic Chemicals	37%	32%	26%	38%
EDC/VCM	35%	34%	29%	20%
Pulp & Paper	1%	9%	5%	8%
Inorganic Chemicals	13%	12%	10%	14%
Water Treatment	4%	5%	5%	11%
Miscellaneous	10%	8%	25%	9%

Source: Consulting Resources Corporation (for the US Bureau of Mines)

of vinyl chloride, the monomer for the plastic polyvinyl chloride or PVC. A few major regional differences are worthy of comment. For one thing, 25% of Japanese chlorine consumption is used for inorganic chemicals, as compared to only 8-10% for Europe, the U.S. and the rest of the world. Another difference is that pulp and paper bleaching accounted for only 1% of European chlorine consumption in 1994 (5.8% in 1987) vs 9% in the U.S. (14% in 1989) and 5% in Japan. On the other hand, water treatment accounted for 4% in Europe, 5% in the U.S. and Japan, but 11% in the rest of the world. Ethylene dichloride

(EDC) is the most important intermediate in tonnage terms, as shown in *Table 9.5*. Almost all EDC in Europe, (97.2% in 1991) is consumed in the production of vinyl chloride monomer (VCM).

Most HCl (about 91%) is recovered as a by-product of one of the chlorination processes. This is an important form of recycling. This happens because chlorination is often an intermediate step in a complex process, often followed by a subsequent step in which (some or all of) the chlorine is released as HCl. The best known example is probably the production of vinyl chloride (VCM) via direct chlorination of ethylene to ethylene dichloride (EDC), which is then catalytically split to yield VCM and HCl. The HCl is normally used in a complementary process in which HCl reacts with ethylene and oxygen to yield more EDC (and water). These two processes are normally balanced to consume all the HCl that is produced. In Europe, some VCM is also produced by reacting HCl with acetylene — an older process that has been phased out in the U.S. because of the much lower cost of ethylene.

Other important examples of the use of chlorine (and HCl) as an intermediate in the production of chemicals that do not themselves contain chlorine are as follows [Fonds Chem 1992]:

*toluene diisocyanate*, a basic feedstock for polyurethanes is made by reacting toluene diamine with a chlorine-containing intermediate (phosgene,  $\text{CCl}_2\text{O}$ ), with HCl as a by-product. (In this case the HCl is recycled to hydrogen and chlorine by electrolysis)

*propylene oxide (epoxipropane)*, is itself an intermediate feedstock for polyesters and polyurethane, is made by two processes. The older "chlorhydrin" process proceeds via dichloropropane (DCP). HCl is a by-product, of the second stage. It can be recycled. The newer process (Oxirane) does not require chlorine, but it is used primarily to produce tert-butyl alcohol (TBA), from i-butane and/or ethylbenzene en route to the gasoline octane additive methyl-tert-butyl ether (MTBE). Propylene oxide is only a minor by-product, whence the Oxirane process only accounts for about 4% of worldwide capacity as of 1989-90 [Fonds Chem. 1992]

*silicones* are polymers based on a chain of molecules with the composition  $(\text{CH}_3)_2\text{SiO}$ , containing no chlorine. However, the starting point is a reaction between silicon metal Si and methyl chloride ( $\text{CH}_3\text{Cl}$ ) which produces methylchlorosilane  $(\text{CH}_3)_2\text{SiCl}_2$ . The latter reacts with water yielding the silicone monomer plus by-product HCl [Fonds Chem. 1992]

*tetrafluoroethylene (TFE)* is  $\text{C}_2\text{F}_4$ , the monomer for the polymer best known is "Teflon®". It contains no chlorine, but is made by high temperature pyrolysis of the solvent monochlorodifluoromethane ( $\text{CClF}_2\text{H}$ ), releasing chlorine for recycling.

**Table 9.5. Production & consumption of EDC 1990 (kMT)**

Country	Production	Consumption
Benelux	2200 (22%)	2307 (24%)
France	1630 (16%)	1650 (17%)
Germany	2592 (26%)	2598 (27%)
Other	3472 (36%)	3127 (32%)
Total	9894 MMT	9682 MMT

*ultra-pure electronic grade silicon (EGS)*, the starting point for virtually all semiconductor products ("chips"), is produced by a process in which impure metallurgical grade silicon (MGS) is chlorinated to trichlorosilane ( $\text{SiHCl}_3$ ), which is subsequently reduced again (by reaction with hydrogen) to silicon and hydrochloric acid. The latter reacts with trichlorosilane to yield silicon tetrachloride ( $\text{SiCl}_4$ ) and hydrogen gas. In principle the hydrogen can also be recycled. The by-product  $\text{SiCl}_4$  is an intermediate for virtually all silicon chemicals. This complex system is described in more detail under Semiconductors in *Chapter 10*.

*titanium dioxide* is by far the most important white pigment for paint, paper, and other products. It contains no chlorine. Titanium is obtained from two ores, ilmenite and rutile. The process for extracting titanium dioxide from rutile involves chlorination as an intermediate step. In this case HCl is not recycled, but is neutralized; the waste product is sodium chloride (salt).

Sources of HCl in Europe are summarized for 1989 in *Figure 9.3*. As stated above, most HCl is essentially recycled. Also, we suspect that as much as a third of the total flux of HCl is dissipated within the chemical industry itself, in the sense that the chlorine is not exported from the sector embodied in any product. This would account for about 10% of all chlorine, or 1 MMT, more or less. HCl uses in Europe for 1989 are shown in *Figure 9.4*. The complexity of the chlorine "system" is not fully captured by the pie charts, of course. We have attempted to reconstruct more detailed chlorine flow charts for Europe and the U.S. in *Figures 9.5 & 9.6*.

### 9.3. Uses of Caustic Soda

Major uses of caustic soda in Western Europe (1992) are summarized in *Figure 9.7*. World data is given on an aggregated end-use basis, for 1994 in *Table 9.6*. The "misc" category includes neutralization of acid chemical wastes, manufacture of cellulose (rayon and cellophane); soaps and detergents; textiles; gasoline refining; water treatment; household products; tertiary oil recovery (in the U.S.) and exports.

**Table 9.6. World demand for NaOH by end-use, 1994**

<i>Use Category</i>	<i>Europe</i>	<i>United States</i>	<i>Japan</i>	<i>Rest of World</i>
Organic Chemicals	29%	36%	35%	34%
Pulp & Paper	13%	21%	13%	15%
Inorganic Chemicals	27%	16%	15%	13%
Miscellaneous	31%	27%	37%	38%

*Source: Consulting Resources Corporation (for US Bureau of Mines)*

Taking into account neutralization of acid wastes, soap/detergent manufacturing and some miscellaneous chemical products 56%-60% of caustic soda in Europe is consumed within the chemical manufacturing sector. Except for detergents, virtually all sodium chemicals based on caustic soda (or, for that matter, on sodium carbonate) are dissipative, either within the chemical sector or in other manufacturing processes. Virtually none, except detergents, is actually embodied in products.

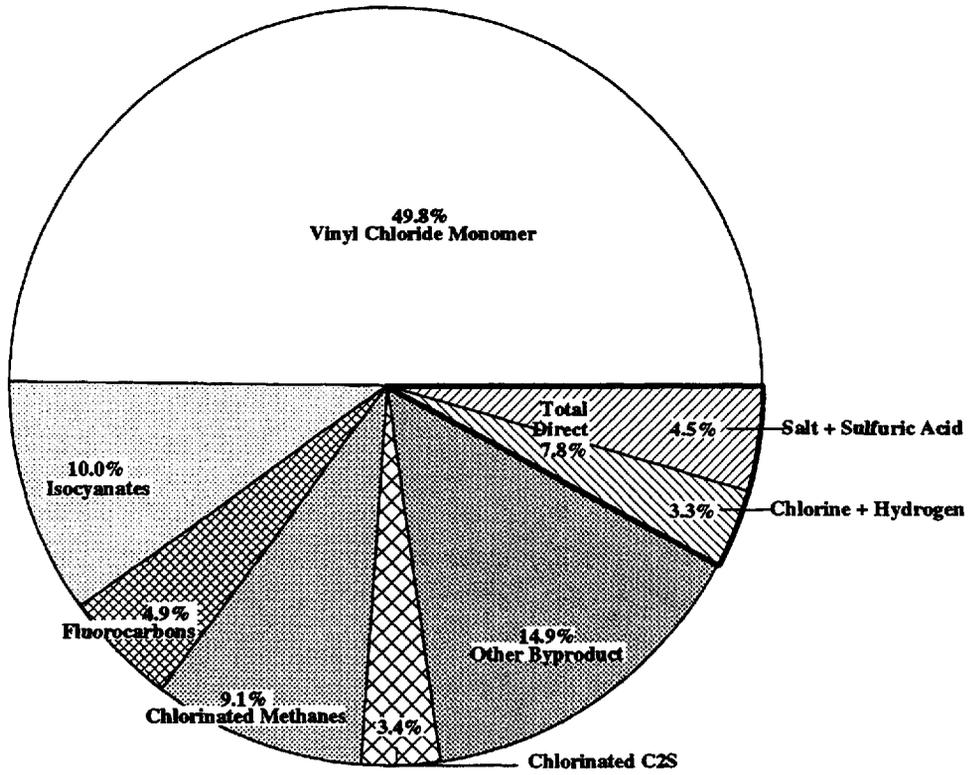


Figure 9.3. Western European production of hydrochloric acid 1989. Source: ECOPLAN

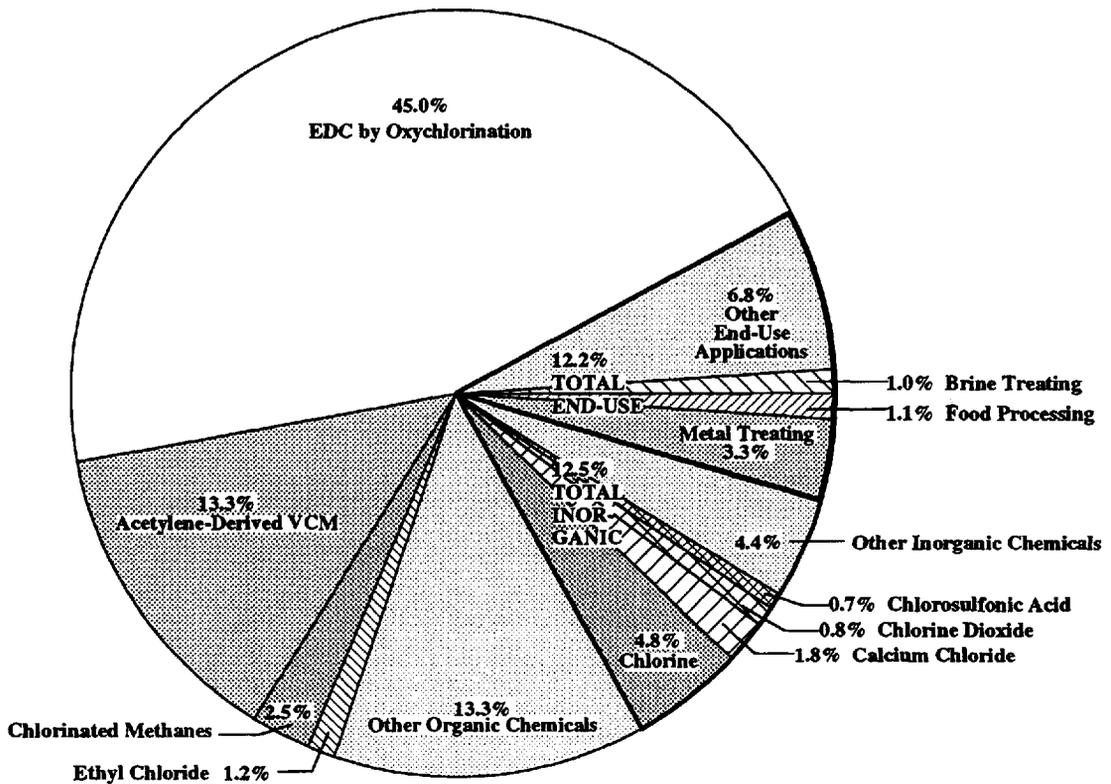


Figure 9.4. Western European consumption of hydrochloric acid by end use, 1989. Source: ECOPLAN

xx% = percent of Cl production

yy = Cl-content (MMT)

Data sources: [ECOPLAN]

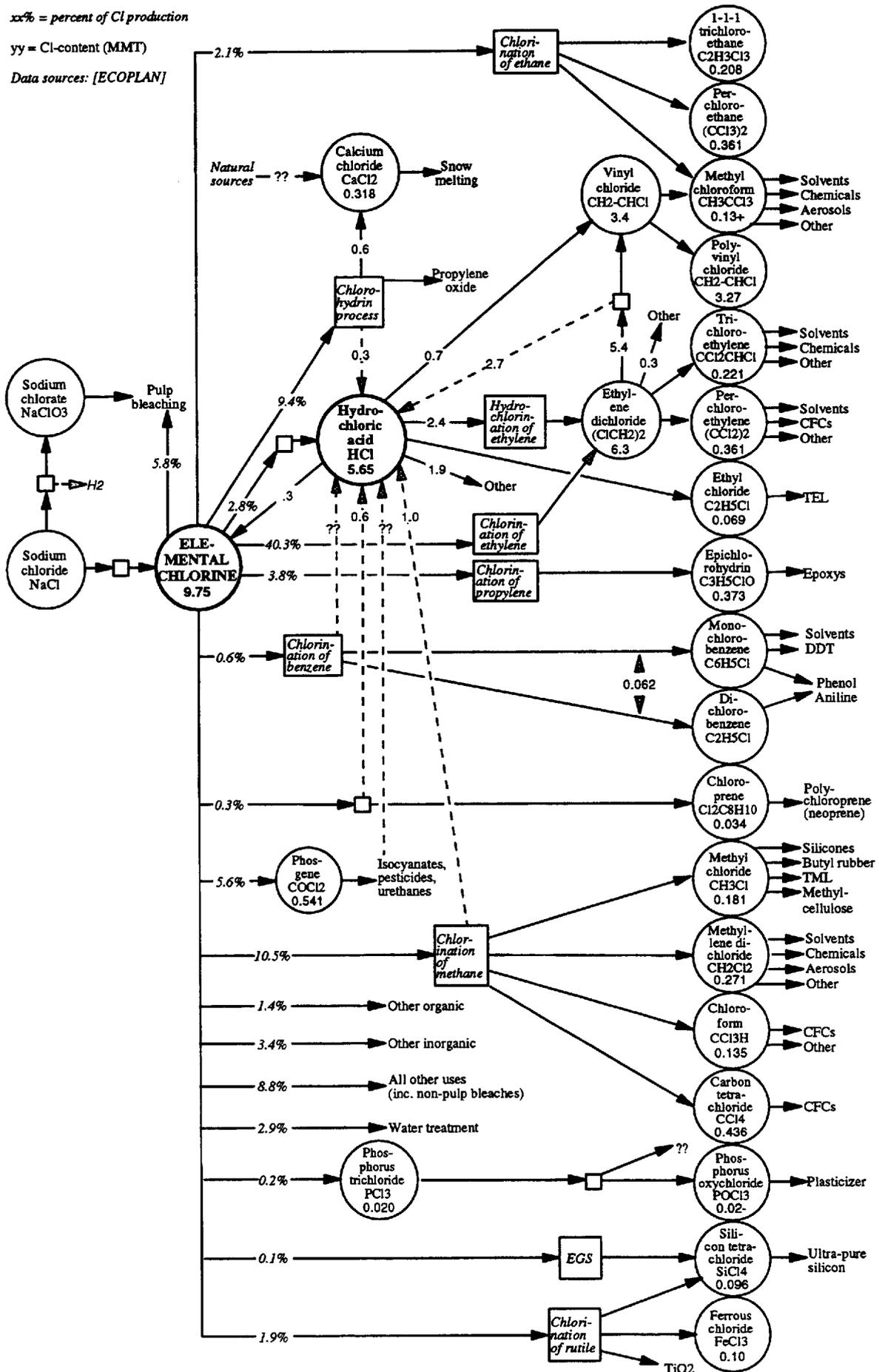


Figure 9.5. Chlorine process-product flows: Western Europe 1987

yy =  
Cl-content (MMT)  
xx% =  
percent of Cl production  
Name (nn %) =  
percent of precursor  
Data sources:  
[USITC 1992, IEI 1991]

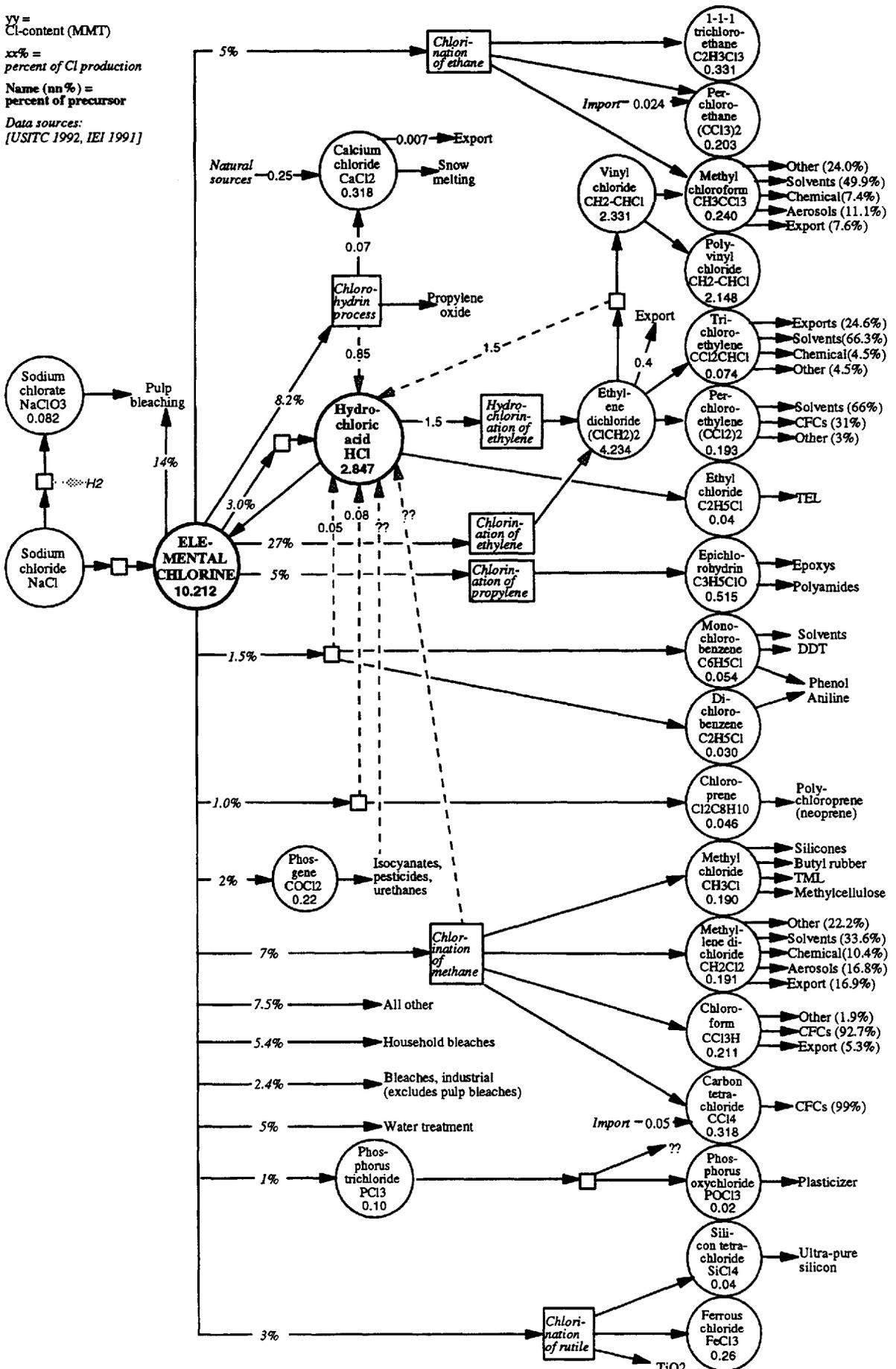


Figure 9.6. Chlorine process-product flows: US 1988

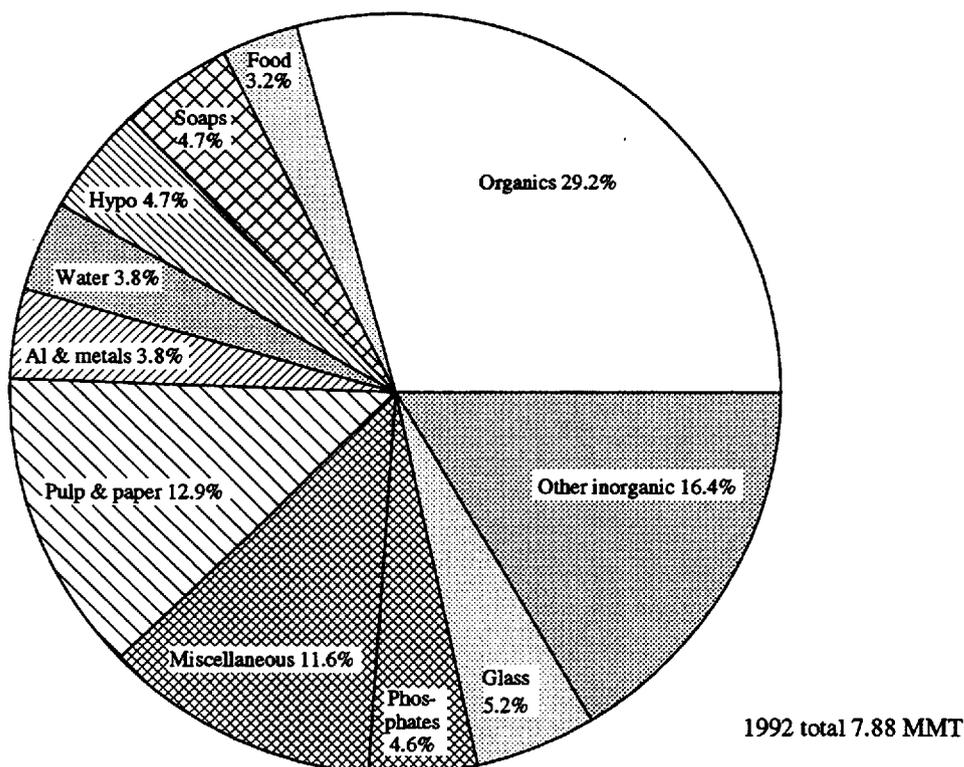


Figure 9.7. Western European consumption of caustic soda by end-use 1992. Source: [Detournay 1993]

The ultimate fate of most of the sodium hydroxide consumed in the chemical industry is to react with either sulfuric acid, yielding sodium sulfate, or with hydrochloric acid, yielding sodium chloride as a waste. Sodium sulfate has more uses (notably in the manufacture of pulp for paper), whence sulfuric acid is the preferable reagent where either acid could be used.

#### 9.4. Factors Affecting Chlorine Supply/Demand

In both the U.S. and Western Europe the demand for chlorine has historically been stronger and less elastic than the demand for caustic soda. In effect, chlorine was the primary product and caustic the by-product. However, the situation has been changing. In 1984 nearly 18% of caustic soda produced in Europe was exported. This has declined rather steadily to 10.5% in 1991 [Detournay 1993]. Meanwhile, caustic soda spot prices have increased sharply, from a range of \$40-\$80 per tonne in the years 1984-86 to a peak of nearly \$500/tonne in 1987. Subsequently the spot price declined moderately, but by 1992 it still remained around \$300/tonne since 1987 [ibid].<sup>5</sup>

This peculiar price behavior is a consequence of both real and anticipated declines in the demand for chlorine in certain applications. The peak price for sodium hydroxide coincided with the signing of the Montreal Protocol (1987), which called for the gradual phasing out of chlorofluorocarbons, due to concern about the "ozone hole". Meanwhile, the use of chlorinated pesticides and herbicides, polychlorinated biphenyls (PCB's) and several major

chlorinated solvents had already been declining for a number of years. Demand for chlorinated solvents from 1986 through 1992 is shown in *Table 9.7*.

**Table 9.7. Western European production & sales of chlorinated solvents (kMT)**

	<i>Trichloro ethylene</i>		<i>Perchloro ethylene</i>		<i>Methyl chloride</i>		<i>1-1-1-tri chloroethane</i>	
	<i>Prod.</i>	<i>Sales</i>	<i>Prod.</i>	<i>Sales</i>	<i>Prod.</i>	<i>Sales</i>	<i>Prod.</i>	<i>Sales</i>
1986	182.7	138.7	340.6	161.6	331.5	197.0	204.6	137.8
1987	165.7	134.3	322.8	151.8	305.2	181.2	203.2	129.6
1988	168.9	133.9	342.9	144.1	309.8	182.4	218.1	128.5
1989	153.6	118.4	317.1	131.3	293.4	175.4	222.3	129.3
1990	130.9	107.8	279.8	122.6	293.3	169.6	228.5	122.4
1991	113.3	96.1	218.5	113.4	244.0	157.1	202.1	109.0
1992	125.2	83.0	210.6	88.6	234.1	153.9	198.3	92.7

Source: [ECSA undated]

Another factor depressing demand for chlorine has been the discovery of traces of highly carcinogenic dioxins in paper. This was traced to the chlorine pulp bleaching process. A major public outcry arose in Europe against chlorine-bleached paper (led by Greenpeace in Germany). The Scandinavian pulp and paper industry quickly responded to consumer demand for "chlorine-free" paper by publicly committing itself to eliminate the use of chlorine bleaching. The primary alternative to chlorine is some form of oxygen bleaching, initially using chlorine dioxide (from sodium chlorate),<sup>6</sup> but perhaps eventually using ozone or hydrogen peroxide. This trend has spread. As noted above, already by 1987, only 5.5% of chlorine produced in Europe was used for pulp bleaching, as compared to 14% in the U.S. By 1994 these figures were down to 1% and 9% respectively.

## 9.5. Environment, Health, Technology & Policies

The environmental dangers associated with chlorinated pesticides (such as DDT), PCB's, CFC's and so on are rather well-known by now and need not be reviewed here. They are relevant, however, insofar as they constitute the background for an increasingly determined effort by the environmental group Greenpeace (with support from others) for an across-the-board ban all production and use of chlorine, on the grounds that it is implicated in so many toxic, carcinogenic, mutagenic or ozone-destroying substances that its use — at least in organic form — should be eliminated altogether. The main focus of this effort is on the ubiquitous plastic PVC.

In support of the anti-PVC argument, it is true that both major intermediates in PVC production, ethylene dichloride (EDC) and vinyl chloride monomer (VCM) are classed as hazardous. VCM, however, is polymerized to make the durable and harmless plastic PVC.<sup>7</sup> PVC accounts for nearly 31 of European elemental chlorine output. On the other hand, PVC does not lock up the chlorine permanently. All PVC products have finite lifetimes, ranging

from a few weeks for bottles to more than 30 years (perhaps much more) for structural products such as pipes.

The only significant hazard associated with PVC, after it has been produced, is fire. This hazard applies largely to short-lived PVC products, primarily bottles and other containers that may be incinerated (see *Chapter 11, Packaging*). There is a lesser but not negligible hazard associated with PVC embodied in structures. Though it is not particularly combustible, PVC will burn. In a fire the chlorine in PVC is largely converted to hydrochloric acid (HCl), and plasticizers, stabilizers and other additives, if any, can be released.<sup>8</sup> This contributes slightly to environmental acidification. However the major environmental concern is the possibility of generating traces of toxic phosgene and carcinogenic dioxins.

To put this into perspective, a German study estimated the average annual intake of PCDD/PCDF (toxic equivalents) from various combustion sources as follows [Fonds Chem. 1992]:

Household refuse incineration	432
Non-ferrous metal refining	380
Household coal-burning (for heat)	164
Gasoline (leaded)	20.9
Medical wastes	5.4
Cable insulation smoldering	4.6
All other	4.4

It is probably fair to say that PVC is the major (but not the only) source of dioxins from household waste (mainly packaging products) incineration, medical wastes (also packaging) and electrical cable insulation. On the other hand there are other significant sources, especially coal-burning and non-ferrous metal refining.

There are also other threats that might lead to further regulation of chlorine use. All of this has combined to create an apparent potential shortage of caustic soda. Prices in the spot market reflect such expectations.

In response to the Greenpeace attack, the chemical industry — through the Chlorine Institute — has rallied strongly in defense of chlorine as an indispensable component of modern technological society. The truth is that some uses are surely not indispensable. Indeed, several have been banned outright for a number of years. The chances of a total ban still seem remote, at this point. Restrictions on certain uses of chlorine (e.g. solvents and PVC packaging) would seem to make more sense. But such things are not always decided rationally, and there is always the possibility of further scientific discoveries implicating chlorine.<sup>9</sup> It would therefore be advisable for government and academia to begin consideration, in cold blood, of the possible implications of such a ban.

To permit such a study, however, the chemical industry will have to cooperate by making available much more data than it has traditionally been willing to release to the public. The industry consistently refuses to publish production, consumption, trade and stockpile data even for extremely toxic compounds that have long been banned (such as DDT and PVC's). The argument that such information must remain proprietary for "competitive reasons" rings

hollow. The more likely explanation is that the industry prefers to keep the numbers hidden for fear of embarrassment. It seems very unlikely that the public will be persuaded to support the industry position on the basis of technical and economic arguments that depend entirely on "proprietary" data that cannot be released for scrutiny. In the present circumstances, Greenpeace may be able to make a persuasive case that the industry must have something nasty to hide. The only way for industry to take and hold the "moral high ground" is to release the data.

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## Endnotes(9)

1. We wish to acknowledge the valuable assistance of Donald Rogich, Director, Office of Mineral Commodities and, especially, Dennis Kostick, commodity specialist for salt, Bureau of Mines, U.S. Department of the Interior, Washington D.C.
2. One source calculates that annual volcanic emissions amount to approximately 11 million metric tons of HCl.

3. However, the presence of organo-chlorine molecules in the environment may have been overlooked. "According to Dr. Gordon Gribble of Dartmouth, there are nearly 2000 different organo-chlorides and organo-halogen chemicals that naturally occur in our biosphere, 700 of which were discovered in the last 10 years. For example, about 100 different halogen compounds are in one species of edible Hawaiian seaweed. One species of Florida Gulf acorn worm produces 20 different organo-halogen compounds....He states that biomass generates about 5 million tons of natural methyl chloride annually...." [Kostick 1994 p]
4. In this connection, chlorine from industrial activities is not necessarily the only source, As mentioned in a previous footnote, as much as 11 million metric tons of HCl is liberated annually by vulcanism. While HCl is normally washed out of the troposphere by rain, volcanic eruptions can (and do) sometimes pierce the troposphere and inject quantities of material into the stratosphere where it has the potential of interacting with ozone. This problem is most acute in the polar regions, where the stratosphere is closer to the earth's surface than in the tropics.
5. In the early 1990's several Wyoming producers of sodium carbonate (from evaporite Trona deposits) began producing sodium hydroxide by reacting sodium carbonate with lime, with by-product calcium carbonate (that is recycled to lime by calcination). This continued until the market for electrolytic caustic soda returned to balance [Kostick 1994 p]
6. The surprisingly large production of inorganic chlorine chemicals in Japan may be partly attributable to large-scale production of sodium chlorate.
7. There may be some hazard associated with plasticizers and other additives, including cadmium.
8. The most important PVC plasticizers are Di (2-ethyl hexyl) phthalate (DEHP) and t-dioctyl phthalate (DOP). Production of DEHP in Germany in 1986 was 360 KMT, with net exports of 150 KMT. Production of DOP in 1986 was 234 KMT, with net exports of 141 KMT. Both domestic production and exports were used primarily in PVC [Balzer & Rauhut 1987]
9. In this connection, recent epidemiological evidence of a decline in male fertility, among both human and non-human species, has convinced some scientists that the likely culprit is not one chemical but a whole class of "estrogen-like" chemicals including poly-aromatic hydrocarbons (PAH's) and especially their chlorinated derivatives. The latter — of which DDT and PCB's are examples — seem to cause problems primarily by virtue of being very stable and nearly immune to attack by micro-organisms. As a consequence of both properties they tend to bio-accumulate in the fatty tissues of higher animals where they can interfere with normal hormonal functions, including reproductive functions.