

**THE LIFE-CYCLE OF CHLORINE:  
PART I AND II**

by

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# THE LIFE-CYCLE OF CHLORINE: PART I<sup>1</sup>

## Abstract

Chlorine is an important industrial chemical. Not only is it a component of many important products, it is also needed for many chemical manufacturing processes, even where it does not appear in the final product. But many chlorine chemicals, especially organo-chlorines, are toxic, carcinogenic, teratogenic or otherwise disturbing (or potentially disturbing) to the environment. For this reason, some environmentalists — notably Greenpeace — have seriously proposed and lobbied for a ban, not just on some products, but on all uses of elemental chlorine itself. The chemical industry is taking this threat seriously, and mounting a vigorous defense. But the debate so far is not illuminating the issues effectively, because both sides are selectively using questionable and unverifiable data.

The fact that there are scientific uncertainties is not really the problem. The problem is that data in the public domain and accessible to environmentalists and even regulatory authorities is of very poor quality. Thanks to industry secrecy, much crucial information is unavailable and much of what is available is wrong. The purpose of this paper, and the two that follow, is to elucidate the information requirements for an adequate life-cycle analysis of chlorine and its uses. The present paper deals with electrolytic chlorine production and the chlorine-mercury connection. The next paper deals with conversion processes and losses and further chemical industry uses of chlorine. The third and final paper deals with end uses of chlorine and their environmental consequences.

## Part I. Background

Chlorine is a chemically active element that is invariably combined with other elements, usually sodium or calcium, but occasionally potassium and magnesium. Its major compound in the environment is sodium chloride (NaCl) or ordinary table 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 rare in the earth's crust. Its role in biochemistry is equally limited. While salt is a necessary component of every diet, and chloride ions constantly circulate through the bloodstream, and through every cell, its biological role is limited. It 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.

There are several hundred organo-chlorine molecules of natural origin, mostly produced in minute quantities by marine organisms. The most important of these is chloromethane, which seems to be produced at the rate of about 4 million t/y [SRC 1989]. However, organo-chlorines are not found in the tissues of vertebrates or any terrestrial animals [Neidleman & Geigert 1986; Vallentyne 1989]. Hence terrestrial animals do not metabolize them or detoxify them efficiently, due to lack of evolutionary "experience".

Also, a number of organo-chlorines are biologically active in the sense that they are capable of interfering with certain normal biochemical functions. 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 (starting with DDT) and herbicides (such as 2-4 D) during the 1950s and 1960s. In other cases, the toxic or carcinogenic effects turned up be accident, as in the case of the widely used solvent 1-1-1-trichloroethane (a potent neurotoxic), 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 antigens). All that can be said at present, with some confidence, is that the biological activity of organo-chlorine molecules is related to their physical structures (i.e. shapes). This follows 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. For instance, only one of the isomers of benzene hexachloride (BHC) is biologically active; the rest are essentially inert. (The active isomer, in purified form, is the insecticide lindane). Similarly, only one of the numerous congeners of TCDD ("dioxin") is known to be biologically active, namely the 2,3,7,8 TCDD.

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 food chain. This is why eagles, ospreys, falcons and game fish were the main victims of 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 PCBs.

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 chemical reactions involving chlorine, from pulp bleaching to incineration (and accidental fires) that cause the greatest public concern — justified or not. The chlorinated dioxins (TCDDs) and dibenzo-furans (TCDFs) are among the candidate villains. Apart from its biological activity, chlorine has been implicated in the destruction of stratospheric ozone. The details of the chemical mechanism involved need not detain us here. It is only of interest that chlorine is only transported into the stratosphere in the first place by virtue of the great stability (i.e. persistence) of chlorofluorocarbons (CFCs) in the presence of atmospheric oxygen and OH<sup>-</sup> radicals. Whereas most organic chemicals are rapidly oxidized, this is not true of the CFCs. These are compounds used widely as refrigerants, foam blowing agents and solvents (and formerly as aerosol propellants) precisely because of this stability.

There are environmental/health arguments against the use of chlorine for bleaching paper pulp, and against the dissipative use of chlorinated pesticides, chloro-carbon solvents and chloro-fluorocarbons. Because of these problems the industrial use of chlorine itself is being challenged, especially by the environmental organization Greenpeace [Thornton 1991, 1993]. The chlorine industry, feeling threatened, is mounting an active defense [Amato 1993]. It is indisputable that alternatives can be found to most of the well-known major uses of chlorine. But there are at least 15,000 chlorinated compounds in commerce, some of which might be very hard to replace. It is by no means clear how costly the substitutes would be and whether the costs would be justified by the presumed benefits.

A total ban on chlorine use would certainly be disruptive in the short term and probably

excessively costly in relation to the benefits achieved [MIT 1993]. For example, in western Europe chlorine is used for treatment of 98% of the drinking water, and is used in the manufacturing process for 96% of crop protection chemicals, 85% of health care products and 55% of all chemical products [Eurochlor 1995]. While some of these claims are disputable in detail, it would be advisable to undertake a much more complete and sophisticated life-cycle analysis of the chlorine industry than anything yet attempted along these lines.

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 chemical 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 PVCs). The extent of the data gaps and difficulties is clearly indicated in the following. 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. Without such data the requisite analysis cannot be carried out and intelligent public policy cannot be made.

## **Production and consumption of chlorine**

Chlorine and caustic soda (sodium hydroxide) are usually co-products of the electrolysis of sodium chloride, mainly in the form of brine made by solution mining of underground salt (halite) deposits.<sup>2</sup> World production and consumption of chlorine in 1991 was 35.701 MMT, of which the U.S. accounted for 29% and western Europe 25% [Tecnon 1993]. A detailed breakdown of capacity, production and demand by region is given in *Table I*. Although the table does not show it, both production and consumption have peaked and begun to decline in Europe and North America. However demand is rapidly growing in other parts of the world, especially Latin America and Asia.

Given the focus of this paper on life cycle analysis, some comments on the data in the table are appropriate. It will be noted that the only officially published government data that is international in scope is the UN *Industrial Statistics*. This source is also by far the least reliable, since it is assembled by UN-crats from data provided by national statistical offices of member countries which the UN statisticians are not permitted (for political reasons) to challenge. It is well-known among practitioners that most centrally planned countries submitted figures from 5-year plans, rather than actual data. Many other countries simply did not bother to provide data. Because of political sensitivities, some egregious errors were—and still are—promulgated without comment. In particular, the UN reported no chlorine production for a number of producing countries, including Argentina, Australia, China and Taiwan. For a number of other countries the most recent data was from earlier years, although the UN statisticians did extrapolate regional totals. On the other hand, the UN reported production in the former USSR, attributed entirely to the Ukraine, ranging from 26,697 kMT

in 1982 to 20,298 kMT in 1990 (the last year reported). These absurd figures were duly added to the other regional totals, leading to equally absurd global totals to which the Ukraine contributed over half in some years!

Fortunately, data on production capacity is also available from different sources (the industry magazine *Informations Chimie*, published in Paris), which confirm that the actual production capacity of the former USSR is only about 3000 kMT. Moreover, the UN itself independently publishes data on the output of caustic soda (NaOH), which is a co-product of chlorine. 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.<sup>3</sup> While 1991 data are not available, UN reports caustic soda production in the former USSR for 1990 as 2974 kMT (of which only 443 kMT was from the Ukraine). This would correspond to chlorine output of 2660 kMT, approximately. The latter is consistent both with capacity estimates and with demand estimates reported by MIT [MIT 1993]. In other cases where chlorine production data was unavailable or questionable, I used caustic soda production data to estimate it. In one case (Australia), lacking other information, I assumed near-capacity production (300 kMT). The resulting world total of 36,109 kMT for 1991 is very close to the survey-based estimate (35,701 kMT) by Tecnon Ltd, a major industry consulting group [Tecnon 1993]. This remarkable coincidence tends to confirm the value of consistently using materials balance methodology for verification of questionable data points.

## Production processes for chlorine

Primary chlorine is almost entirely (94% in Europe) produced by electrolysis of sodium chloride salt (brine), with sodium hydroxide (caustic soda) as a co-product. Minor amounts are produced from potassium salts and in the production of sodium or potassium metal. There are three important variants of the basic electrolytic process, viz. the mercury cell, the diaphragm cell and the membrane cell. The three types of cell are summarized in terms of inputs and outputs in *Table II*. In the decades since World War II, perhaps the largest consumptive use of mercury has been in the manufacture of chlorine and sodium hydroxide by electrolysis. This technology was commercialized as early as 1894, with Hamilton Castner's "rocking cell", which was the dominant electrolytic method in the first quarter of this century. Most new chlor-alkali plants constructed in the 1920s, 1930s and 1940s utilized diaphragm cells, rather than mercury cells.

The economics of the mercury cell changed dramatically with the advent of the DeNora cell, developed in Italy and licensed by Monsanto shortly after World War II. Olin Mathieson Chemical Company also developed a new mercury cell design. Chlorine production since the 1940s has risen enormously, spurred by burgeoning demand for chlorinated pesticides (like DDT, aldrin, dieldrin, endrin and chlordane), herbicides (like 2-4-D and its relatives), and plastics, notably PVC. Roughly half of the new capacity added in the U.S. in the 1950s and 1960s utilized mercury cells (see *Figure 1*) .

By 1970 there were 25 mercury cell chlor-alkali plants in the U.S., producing 2.5 million tons (2.2 MMT) of chlorine per annum, or about 28% of U.S. production [USEPA 1971]. Production of chlorine in the U.S. rose very rapidly from 1946 through 1970 or so. Since the

early 1970s has remained fairly constant, although the use of the mercury cell has declined slowly, to about 17% in 1991. In fact, whereas U.S. production is dominated by the diaphragm cell, European production was, and still is, primarily via the mercury cell (63.1% of 1988 European capacity). Of the remainder, 28% of European capacity is based on the diaphragm cell and 5.3% of European capacity uses the newer membrane cell.

The mercury cell was, for many years, a significant source of environmental pollution, since some mercury is lost in the process. Inorganic mercury can be metabolized to highly toxic methyl-mercury ( $\text{CH}_3$ )<sub>2</sub>Hg by anaerobic bacteria and this substance is bio-accumulated in the marine food chain. It can reach dangerous concentrations in the tissues of fish or fish-eating sea-birds.<sup>4</sup> The biological mercury cycle is summarized in *Figure 2*.

Because of the Minimata experience, the mercury cell was phased out altogether in Japan and to some extent in the U.S., since the early 1970s. In 1970 there were 25 mercury cell plants in the U.S. The number had dropped to 19 in 1989. Historical data on chlorine production by cell type in the U.S. is shown in *Figure 1*. Data on U.S. use of mercury for this process is shown in *Table III*, taken from publications of the U.S. Bureau of Mines. The chlor-alkali industry was the largest domestic user of mercury in the years 1989-90, despite the fact that only 17% of U.S. production used the mercury cell. An obvious implication is that mercury consumption by the European chlor-alkali industry must be considerably higher than U.S. consumption. Unfortunately, consumption data is not available for Europe or any other country.

At first glance, it would appear that mercury consumption for chlorine production should be equal to mercury emissions to the environment. However, it is not so simple. Before the hazardous nature of mercury emissions was fully recognized, actual emissions from the mercury cell averaged 300 mg/kg of product, or 3 kg/tonne. In response to tighter regulation and better housekeeping, the emissions rate had declined to 150 mg/kg, or 1.5 kg/tonne by 1971 [ibid]. A 1974 EPA publication uses the same figure [Martin 1974]. This figure was adopted by the World Health Organization (WHO) for its 1982 guidelines for rapid assessment of sources of air, water and land pollution [WHO 1982].<sup>5</sup>

As a cross check, one can compare these rates with reported mercury consumption. In the pre-regulation days of 1970, the loss rate for mercury cells was acknowledged to be 300 mg/kg. Given a production level of 2.2 MMT via the mercury cell, this loss rate would have required a mercury replacement of 660 metric tons. Actual reported mercury consumption by the chlor-alkali industry in that year was slightly less, viz. 517 metric tons [USBM 1975], which implies a loss rate of 235 mg/kg. It is not unreasonable to assume that the level of 150 mg/kg taken from the 1974 EPA document (and assumed by the WHO) was realistic. The consumption and emissions figures for 1970 and 1974 are therefore roughly consistent with each other.

The German data (such as it is) tell a similar story. In 1973 the German chlor-alkali industry consumed 128 metric tons of mercury. There was a gradual but sporadic decline through 1985, when consumption was 41.8 tonnes [Rauhut 1988]. This reflects a reasonable, but not spectacular, improvement in the "housekeeping" of the industry with respect to mercury. Where did it go? In that year, Rauhut suggests that 1 tonne of mercury was lost to water, 4 tonnes to air and 40 tonnes to "Deponie", which translates as land deposition [ibid]. The minor difference between losses and consumption reflects stock changes.

According to the industry, however, mercury emissions have continued to decline. One European author associated with the industry claims an emissions level of 2.47 mg/kg by

1988, as shown in *Table IV*. [Manzone 1993]. Other estimates of current mercury emissions in chlorine manufacturing range from 0.47 mg/kg to 3 mg/kg (*Table V*). I have serious reservations about these claims, however, for reasons discussed below.

Consider the largest (most conservative) of the emission rate estimates for 1988 or later in *Table V*, viz. 3 mg/kg, which happens to come from the Stanford Research Institute's Chemical Economics Handbook [SRI 1989]. U.S. chlorine production in 1988 was 10.2 MMT, of which about 20% or 2 MMT, was apparently produced by mercury cells. If mercury losses had been only 3 mg/kg then makeup requirements for mercury would have been a mere 6 metric tons. But, according to the U.S. Bureau of Mines, mercury consumed in chlor-alkali production in 1988 was 445 metric tons. Simple arithmetic shows that the actual use of mercury for chlor-alkali production in that year was nearly 75 times SRI's "theoretical" loss rate.

A far lower (i.e. more optimistic) emissions rate, 0.47 mg/kg, has been recommended for use in life cycle analyses by a Swiss government publication [Habersatter & Widmer 1991]. If this emissions rate were assumed to be applicable in the U.S. (where environmental controls in this area are more rigorous than in Europe) the makeup requirements for mercury in 1988 would have been slightly less than 1 metric ton. What happened to the other 444 tons that were consumed? The emissions rates claimed in *Table V* are clearly not consistent with reported mercury consumption for 1988 and later years.

To dig deeper, one can compare mercury consumption by the U.S. chlor-alkali industry, as reported by the U.S. Bureau of Mines, with mercury emissions reported by the same industry to the Environmental Protection Industry (the so-called Toxic Release Inventory, or TRI). The comparison is shown in *Table VI*. Evidently, most of the mercury consumed by the chlor-alkali industry has somehow disappeared from these statistics. A detailed breakout of reported *total* mercury releases and transfers for 1992, obtained from the published TRI book, is reproduced in *Table VII* (converted from pounds to metric tons). It does not help much. It merely confirms, again, that most of the mercury consumed in 1992 in the U.S. (621 metric tons) is unaccounted for in the TRI statistics.

What happens to the missing mercury? Probably most of it is accumulated in semi-solid or solidified sludges from process water treatment. The latter may be stored on site, buried on site or shipped to a landfill. According to the TRI data base for 1992, "transfers to off-site treatment and/or disposal" outweighed "emissions to air and water" by a factor of 12. Nevertheless, these two routes accounted for only 108 metric tons in 1992 *from all industrial consumers*, not just the chlor-alkali producers.

The mystery was only partly resolved when EPA tightened its controls in 1991 and explicitly banned the disposal of mercury-containing sludges from waste-water treatments at chlor-alkali facilities. In the same year, EPA expanded its reporting requirements for TRI to include a section on "source reduction and recycling". For 1991 the industry reported 350 metric tons of mercury recovered on site, and for 1992 about 320 metric tons.<sup>6</sup> The recovered mercury had been accumulating in wastewater sludges, previously unreported.

The statistical discrepancies are still unresolved. If large amounts of mercury were being recovered on-site, then consumption of new mercury would fall. The TRI statistics do not reveal a consistent pattern of recovery. Nearly 3/4 of this reported recovery in 1991 occurred at a single site: Occidental Chemical Corp's, plant in Muscle Shoals, Ala. Virtually all of the remainder came from just 3 other sites. The majority of plants did not report either recycling or off-site treatment. In fact, many did not report at all.

It must be concluded that, either the chlor-alkali producers do not know what is happening to the mercury they use, that they have been deliberately under-reporting emissions, or that the mercury is still accumulating in wastewater sludge ponds. Both of the first two possibilities must be taken seriously, but the most likely is the third. If the latter is the case (it seems probable) then the stored mercury gradually "leaks" into water or volatilizes into air, over a period of years. In short, the unreported mercury is still effectively being emitted to air and/or water.

The diaphragm cell is also known to be a source of pollution, namely of 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 were some operational problems in early installations, has been little growth in demand in Europe and America since the early 1970s and because existing facilities are fully depreciated but still functional. New facilities in Asia and Latin America tend to be based on "tried and true" western technologies, rather than newer and riskier ones.

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## Endnotes

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. There are several other minor routes to chlorine, mainly electrolysis of HCl and MgCl. In Europe, these routes altogether accounted for only 3.4% of 1988 chlorine capacity.
3. Admittedly, 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. However this would not change the chlorine/caustic ratio very much.
4. This happened in the 1950s in Minimata bay in Japan, due to the discharge of some mercury (a spent catalyst) into the bay by a chemical plant. A number of people — mostly fisher-folk — became seriously ill and some were disabled. Mercury poisoning is now known as "Minimata disease".
5. The 1982 WHO publication is still the basis of UN environmental planning guidelines, worldwide.
6. I am grateful to Stephen Jasinski, the mercury specialist at USBM, for calling my attention to the statistical change that occurred in 1991 [Jasinski 1994].

**Table I: Chlorine & caustic soda (kMT)**

Chemical Region	Chlor-alkali capacity 1991 InfoCh. <sup>a</sup>	Chlorine		Caustic soda production 1991 UN <sup>b</sup>
		production 1991 UN <sup>b</sup>	demand 1990 MIT	
<b>World (reported)</b>	<b>43 811</b>	<b>35 701<sup>c</sup></b>	<b>37 433</b>	<b>36 090</b>
<b>(summed)</b>		<b>35 487</b>		<b>38 064</b>
W. Europe	11 257	8 978	9 760	9 060 <sup>b</sup>
Germany	4 674	3 684	3 739	4 130 <sup>b</sup>
E. Europe	2 117	1 550	1 460	1 735
C.I.S.	3 000	2 660 <sup>b</sup>	2 697	2 974
N. America	15 180	12 410 <sup>b</sup>	12 551	13 204 <sup>b</sup>
U.S.	13 179	10 361 <sup>d</sup>	11 009	11 023
S. America	1 625	1 308 <sup>b</sup>	1 500	1 466
Brazil	1 070	1 034 <sup>est</sup>	980	1 147
Africa	538	71.3	346	80
S. Africa	232	—	225	—
Middle East	730	(e)	750	(e)
Asia	9 035	8 210 <sup>b</sup>	8 214	9 209
Japan	3 136	3 370 <sup>b</sup>	3 550	3 788
China	3 365	3 160 <sup>b</sup>	2 930	3 541
Oceania	319	300 <sup>est</sup>	155	336 <sup>b</sup>

- a. Capacities as reported in Info Chimie Sept. 1989, including capacity additions under construction at that time and presumably operational by 1991.
- b. UN statistics are very incomplete; e.g. no production figures for Argentina, China, the Mid-East or Oceania; Japanese production as liquid chlorine only. chlorine production for C.I.S. as 20,298 kMT (1990, Ukraine), which is clearly erroneous (see capacity data). To fill in gaps in UN chlorine production data, we have used caustic soda data as a surrogate, assuming 1.12 tonnes of caustic soda per tonne of chlorine. Where the UN has both chlorine & caustic soda data and they are inconsistent, we have taken the larger (chlorine equivalent) as being more likely to be correct.
- c. World total from Tecnon Ltd., an industry consulting group.
- d. Source for US data is USBM Minerals Yearbook, 1991, page 1301.
- e. Included in Asia.

**Table II: Processes for the production of chlorine**

<b>A. CHLORINE: BY ELECTROLYSIS OF NA CL IN DIAPHRAGM CELLS</b>				
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>B. CHLORINE: BY ELECTROLYSIS OF NA CL IN MEMBRANE CELLS</b>				
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	
<b>C. CHLORINE: BY ELECTROLYSIS OF NA CL IN MERCURY CELLS</b>				
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 III: Mercury consumption in chlorine production**

Year	Hg used for Cl 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 1992]

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]

**Table IV: Mercury emissions in chlorine production (g/MT)**

<i>Effluent</i>	<i>1972</i>	<i>1975</i>	<i>1980</i>	<i>1984</i>	<i>1988</i>
Waste water	28	9	1	0.2	0.06
Waste air	15	13	6	2.2	2.0
Via main products (Cl <sub>2</sub> -H <sub>2</sub> -NaOH)	24	8	1	0.5	0.4
<b>Total</b>	<b>64</b>	<b>30</b>	<b>8</b>	<b>2.9</b>	<b>2.46</b>

Source: [Manzone 1993]

**Table V: Various estimates of mercury emissions per ton of chlorine**

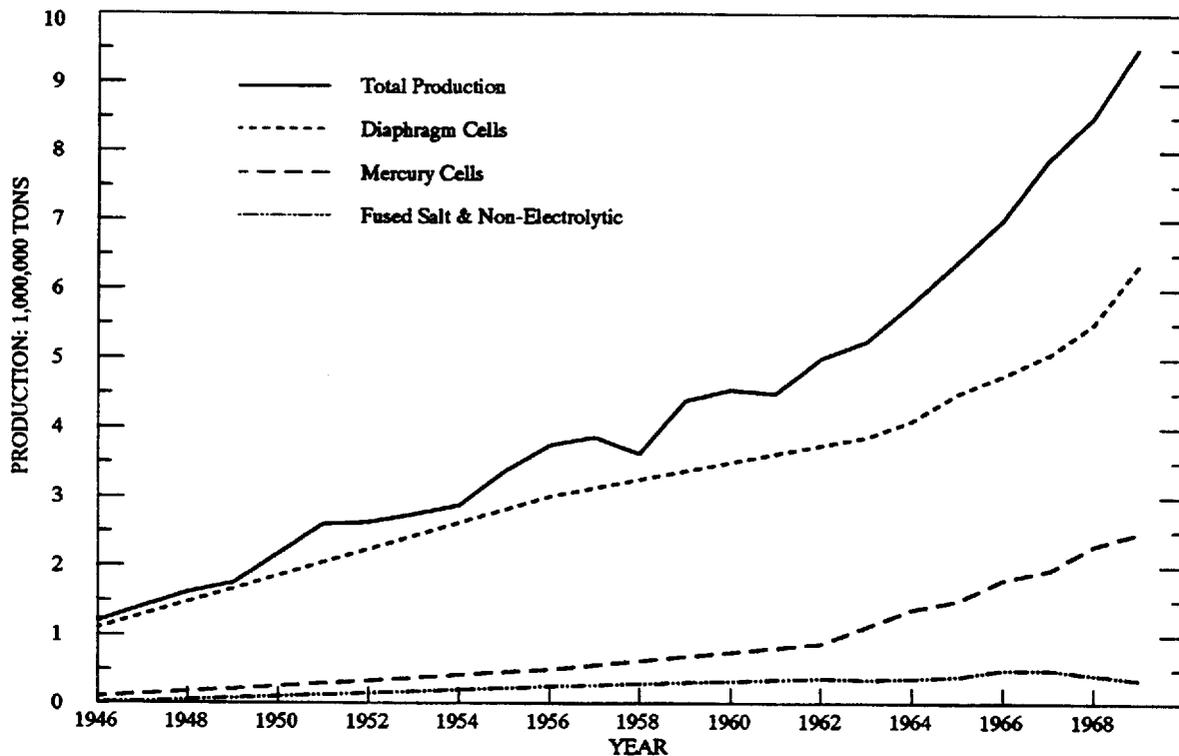
<i>Loss rate (mg/kg)</i>	<i>Source</i>
150	WHO 1982, based on Martin 1974
3	SRI 1989
2.47	Manzone 1993
0.6	Tellus 1992, based on USEPA 1982
0.47	Habersatter & Widmer 1991

**Table VI: Where has the mercury gone?**

<i>Mercury in SIC 2812 (Chlorine Production) USA metric tons</i>					
<i>Year</i>	<i>USBM Minerals Yearbooks Consumption</i>	<i>USEPA TRI Data Base as reported by</i>			
		<i>EPA Office of Pollution Prevention &amp; Toxics Releases</i>	<i>U.S. Bureau of Mines</i>		
			<i>Releases</i>	<i>Transfers</i>	<i>Total</i>
1987	311	23.7			
1988	445	15.7			
1989	381	10.7	11.3	52.9	64.2
1990	247	11.0	11.0	58.5	69.5
1991	184	7.9	8.5	56.0	64.5
1992	209	6.3	4.5	8.7	13.2

**Table VII: Transfers of TRI metals and metal compounds, metric tons, 1992**

Chemical	Transfers to recycling	Transfers to energy recovery	Transfers to treatment	Transfers to POTW's	Transfers to disposal	Other off-site transfers	Total transfers
Mercury & its compounds	23.3	0	33.6	.001	74.8	.001	134.0



Total only for 1947-1955 and 1957-1961

(Specific cell types interpolated)

Figure 1. Chlorine production in the U.S. by cell type Source: [USEPA 1971]

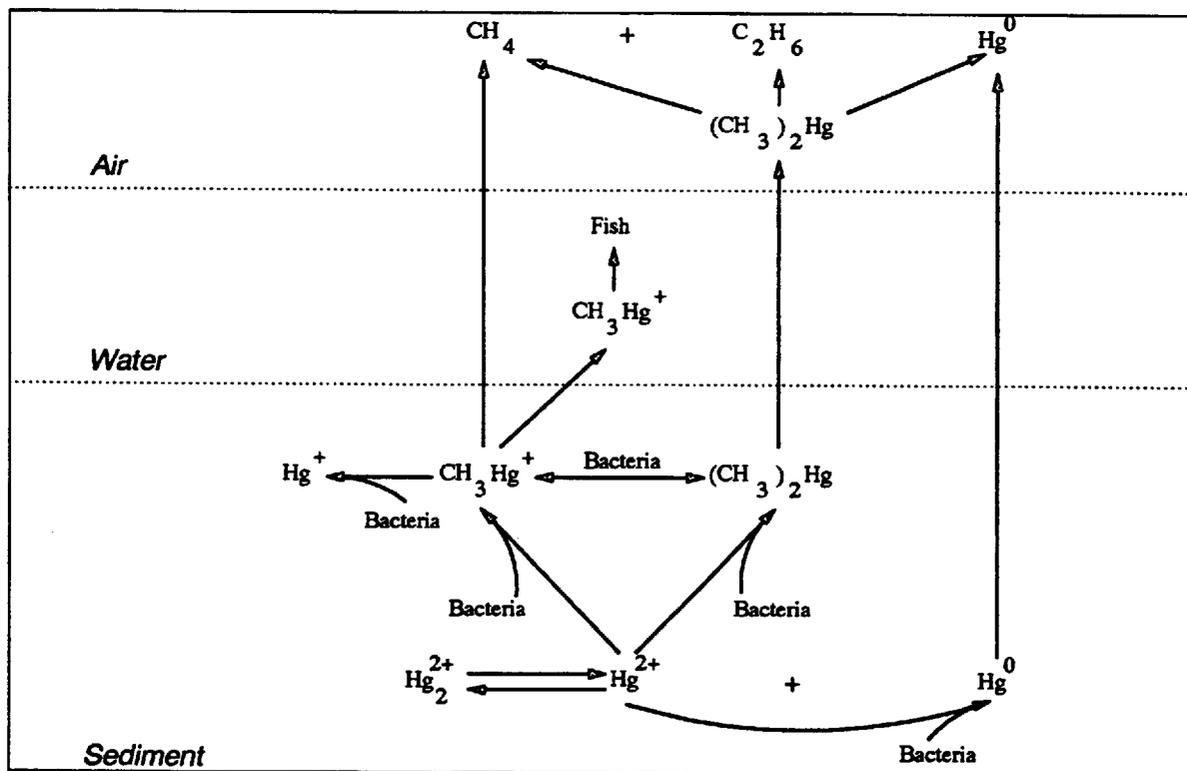


Figure 2. Biological cycle for mercury Source: [Wood 1974]

# **THE LIFE-CYCLE OF CHLORINE: PART II<sup>1</sup>**

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## **ABSTRACT**

In this paper we describe the chlorine chemical industry in Europe and its major conversion processes and emissions. Five major process chains, beginning with methane, ethane, ethylene, propylene and benzene are analyzed in detail, along with four important "stand-alone" processes. A self-consistent "version" of the industry is constructed for 1992, based on data from a variety of different sources. Mass balance conditions are satisfied. Emissions, by type, are calculated. It is of interest to note that of 8566 kMT of chlorine produced in Europe during 1992, we have specifically accounted for 7378 kMT. Of this subtotal, 1859 kMT was used to manufacture inorganic chemicals and 5519 kMT was used to manufacture organic chemicals, for a subtotal of 7378 kMT. Within this subtotal, 5 major process chains and 4 important "stand-alone" processes accounted for 6767 kMT of chlorine. A total of 4575 kMT (Cl) was embodied in products and 2192 kMT (Cl) was emitted to the environment in chlorinated waste products arising from this subset of chains and processes. The breakdown was as follows: 107 kMT (Cl) was embodied in identified organic compounds, 847 kMT (Cl) was in the form of sodium chloride, 299 kMT (Cl) was embodied in other identified inorganic compounds and 938 kMT (Cl) was embodied in unidentified wastes. The largest single source of chlorinated waste products was the propylene chlorination chain, which generated 974 kMT (Cl) of wastes, mostly unidentified, but probably mainly as NaCl. A further 147 kMT was embodied in "light and heavy ends" that were probably recycled or pyrolyzed for recovery of hydrochloric acid.

# 1. Introduction

For any produced chemical (indeed, any material) material, there are two possible fates. The chemical may "converted" i.e. transformed chemically to make something else. Or the chemical may be used as it is. Again, there are two possibilities. The chemical may be consumed in a production process (without being converted) or it may be used by a "final" consumer. If it is either converted into another product, or consumed in the process (e.g. as a solvent, a lubricant or a catalyst) it is called an *intermediate good*. If, on the other hand, it is used by a consumer it is called a *final good*.

Those products that are not transformed further must ultimately become wastes, either sooner or later. Some products, such as solvents and pesticides are dissipated immediately after use. On the other hand others, like PVC used for cable insulation, pipe, flooring or window frames, may have an effective lifetime of several decades.

However, it is analytically convenient to distinguish between losses and wastes that occur in the manufacturing process, *vis à vis* losses that occur in subsequent consumptive use. The former are discussed in the present paper (Part II). The latter are discussed in a later paper (Part III of the series).

Major uses of chlorine in the U.S. are summarized for 1992 in the pie chart *Figure 1* [Thornton 1993]. A more detailed breakdown is available for the World, and for Europe, for the years 1989-1992 as shown in *Table I* and *Table II* [Tecnon 1993]. Our own revised estimate for Europe is also presented in pie-chart form (*Figure 2*). As noted below, our results are based largely on Tecnon data, but with two revisions resulting from consistency requirements.

A few major regional differences in use patterns are worthy of comment. (See *Table III* [USBuMines 1994]). According to this source, 25% of Japanese chlorine consumption is apparently used for inorganic chemicals, as compared to only 8-10 % for Europe, the U.S. and the rest of the world. This is somewhat mysterious. Another difference is that pulp and paper bleaching accounted for only 1% of European chlorine consumption — in elemental form — in 1994 (5.8% in 1987) vs 9% in the U.S. (14% in 1989) and 5% in Japan.<sup>2</sup> On the other hand, water treatment accounted for 4% of chlorine use in Europe (where ozone also has a significant market), 5% in the U.S. and Japan, but 11% in the rest of the world.

Of the final products that embody chlorine, in Europe, just over 60% (in terms of chlorine content) consists of the plastic PVC [ibid]. The remainder consists of solvents (18%), other organics (15%) and inorganics, such as bleaches (6%) [ibid]. Expressed in terms of primary chlorine inputs, PVC accounts for  $0.60 * 0.515 = 0.31$  (31%) of western European elemental chlorine production. VCM and PVC production by region are given in *Table III*. For instance, U.S. production in 1991 was 4157 kMT, while western European production was 5006 MMT; the world total was 16,087 kMT in that year (the last for which we have global data). The chlorine content of PVC is 56.7%, so this product apparently accounted for  $2360/10,361 = 22.5\%$  of gross U.S. chlorine output,  $2840/8978 = 31.6\%$  of gross west European chlorine output and  $9130/35,700 = 25.6\%$  of gross global chlorine output.

Of the apparent HCl supply in Europe (about 5566 kMT for 1992), over 80% was used as a process reactant — mostly in the EDC/VCM chain — 14% was used for pH adjustment and neutralization, and the rest for miscellaneous purposes (including sale outside the industry). Uses of HCl in Europe in 1989 are shown in a pie chart *Figure 3* [ECOPLAN undated]. We analyze the year 1992 in greater detail below.

## 2. Data sources and data problems

It is important to note, here, that while government sources do provide gross production and consumption figures for major chemicals, including chlorine and hydrochloric acid, detailed data on chlorine *uses* are not routinely available from any U.S. or European government agency. They are only available from private sources, either the industry itself (e.g. [Euro Chlor 1995]) or market consulting firms that do surveys from time to time. Data on wastes and losses are collected, in principle, by the U.S. Environmental Protection Agency and its counterparts in Europe and Japan. As a practical matter, there is only one source of such data, namely the chemical industry itself. Considering that the industry is almost pathologically secretive, even about production and consumption statistics, it should not be surprising that emissions data effectively do not exist, at least in the public domain.

The major purpose of this paper is to construct a plausible emissions profile for the industry by indirect means. In fact, this exercise requires chemical process data, most of which are also obscure or unpublished. Process schematics and "recipes" are normally available only from chemical engineering textbooks, patents or private consultants. Fortunately chemical processes can also be simulated via chemical process design software (e.g. Aspen Plus®) that is commercially available. The results presented hereafter were obtained by systematically scanning the published literature for process information, which was subsequently subjected to a detailed element-by-element "balancing" process using a methodology that has been described more fully in previous papers [Ayres 1995; Wolfgang & Ayres 1995]).

There are two fundamental problems with the private unpublished market data. In the first place, survey methodologies are not adequately described or tested. For instance, it is unclear whether the numbers in published pie charts and tables refer to inputs to a "process chain", or to chlorine embodied in outputs.

To understand the importance of the ambiguity, we consider the implications of two alternative interpretations. Let Case A refer to the possibility that Tecnon's chlorine numbers can be interpreted as the chlorine *inputs* to the respective process chains. Let Case B refer to the other possibility, namely that the numbers refer to the chlorine embodied in either the *final* product of the chain (where the latter actually contains chlorine) or the chlorine consumed in the production process for that final product, where the final product does not actually contain chlorine. There are two feasible consistency tests, viz. total chlorine production and by-product hydrochloric acid production. In both cases we can compare implied totals for case A and case B with actual (i.e. published) totals for the reference year, 1992.

Details of the calculations are given in the Appendix, but the "bottom line" (*Table IV*) is that both consistency tests seem to rule out case B. In case A, the major processes and process chains (discussed in detail later) account for 7378 kMT of chlorine for Europe in 1992, compared with Tecnon's basic estimate of 7546 kMT for this subgroup out of an apparent total production level of 8760 kMT. The difference between our calculations and Tecnon's estimate is tolerable (about 2.2%). But case B implies that the same subgroup of chains and processes would require 9511 kMT of chlorine, about 26% too much (and more than 100% of the total amount of chlorine produced).

The second consistency test (by-product hydrochloric acid) is slightly less straightforward. As in the first case, the difference between the two cases is non-trivial, as shown in *Table V*. Comparing the two cases, it can be seen that the total HCl output implied by Case B is again considerably larger than the total implied by Case A. We do not have 1992 data on HCl production and consumption in Europe. However a recent survey covering 76% of the

European chlorine industry (61 locations) found secondary production of HCl for 1991 amounting to 4113 kMT, chlorine content [ECOTEC 1995]. If the ECOTEC survey results can be extrapolated, it would appear that the 1992 total for Europe would have been about 5566 kMT (total) or about 5400 kMT chlorine content. The survey also found that 96.5% of the total European HCl supply originated from by-products, while the other 3.5% was recovered from pyrolysis of chlorinated hydrocarbon wastes (CHCs). Sources of HCl according to this survey were the EDC/VCM chain (59.4%), the phosgene chain (11.3%), the chloromethane chain (5%) and other chains (20.4%).<sup>3</sup>

Our own calculations, based on the 1992 Tecnon production data mentioned above, plus process data from other sources, accounted for 4164 kMT of HCl in case A and 5294 kMT in case B. (See *Table V*). Here, our case B estimates for the subgroup of processes and chains coincide fairly closely to the extrapolation of *total* production of HCl extrapolated from ECOTEC (although there are significant differences for particular chains). Only 272 kMT of HCl is left unaccounted for in case B. This is certainly too little, since some of the omitted chains are significant. For instance, we know that chloroprene polymerization yields hydrochloric acid, probably about 80 kMT in 1992. Similarly, about 290 kMT of HCl was a by-product of fluorocarbon production in 1989 (not included in our analysis), and the corresponding figure for 1992 was probably not less than 200 kMT.<sup>4</sup>

By contrast, in case A the missing processes and chains would still have to account for 1400 kMT (or about 25%) of the total apparent (i.e. extrapolated) output of HCl. This is possible albeit somewhat implausible. Nevertheless, it appears that case A is the only consistent possibility, and we use it hereafter, with certain exceptions. We suspect that total by-product HCl production in 1992 was actually somewhat less than the extrapolated quantity 5566 kMT. The discrepancy arises from the unavoidable "big company" bias of ECOTEC's survey. (In short, we suspect that the unsurveyed sites on average are smaller, less integrated, and generate more waste and less by-product HCl per unit of chlorine consumed, than the surveyed sites).

A second difficulty is that the Tecnon data for Europe (interpreted as inputs — case A) differs significantly from data published by European chlorine industry association Euro Chlor [Euro Chlor 1995] and the European Chlorinated Solvents Association [ECSA 1993]. We have used the ECSA data as our primary source for the four major tonnage solvents (below). However, the process information available to us (which may be obsolete) suggests that the Tecnon data may involve some double counting. In particular, we have assumed that methyl chloride, attributed by Tecnon to the methane chlorination chain, is actually produced from methanol and recycled HCl. Second, we have assumed that carbon tetrachloride is produced mainly as a by-product of ethylene chlorination. The net effect of these assumptions is to reduce the overall chlorine requirements for the methane chlorination chain, and to shift some chlorine away from the chloromethane chain and into the chloroethylene chain. Whether or not our assumptions are correct, they would seem to be internally consistent and efficient i.e. a "possible universe".

To illustrate other discrepancies, for 1992 Tecnon reported chlorine production of 8760 kMT (*Table IV*) whereas Euro Chlor reported 8610 kMT [Euro Chlor 1995]. Tecnon reported that 358 kMT of chlorine was used for water treatment in Europe; Euro Chlor reported only 251 kMT for this purpose [ibid]. In the case of the four major solvents [methylene (di)chloride, trichloroethylene, perchloroethylene, 1,1,1 trichloroethane (methyl chloroform)] Tecnon reported total consumption of 433 kMT, while Euro Chlor reported 405 kMT [ibid]. In the case of chlorinated polymers (including PVC, PVDC and chlorinated polyethylene PE), Tecnon reports 3197 kMT for vinyl chloride monomer (VCM), the precursor of both PVC and PVDC, plus 10 kMT chlorinated polyethylene (PE); for this category Euro Chlor reports 3716

kMT, presumably including some other polymers [ibid]. Obviously the discrepancy regarding chlorinated polymers is much too large to explain so easily. Nevertheless, for reasons noted above, we use Tecnon data except where otherwise specified.

### 3. Mass balances for chlorine chemicals in Europe, 1992

Many, if not most, uses of chlorine and its products are intermediate. That is, chlorine and its organic compounds are mostly transformed into other products. The intermediate uses and conversion processes are discussed in this section. There are significant losses of chlorine and its products during the various conversion processes. We have constructed detailed balances of chlorine inputs and outputs for five major chains and several stand-alone processes, discussed below. Most of the "lost" chlorine is actually converted to hydrochloric acid (HCl), which can be recycled within the industry quite easily. A very high percentage of HCl is produced as a by-product.

The internal production and consumption of HCl in the chemical industry 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.

Ethylene dichloride (EDC) is the most important chlorinated intermediate in tonnage terms, if we disregard hydrochloric acid. However, according to *Table III* almost all EDC (95.9% in Europe, 1992) is consumed in the production of vinyl chloride monomer (VCM). VCM, in turn, is polymerized to make the durable plastic PVC. PVC accounts for nearly 31% of European elemental chlorine output. The biggest single use of chlorine is in the manufacture of vinyl chloride, the monomer for the plastic polyvinyl chloride or PVC (30.7% in Europe, 24% in the U.S.).

Other intermediate organic chemical categories were as follows (*Table II*): chlorinated methyl ( $C_1$ ) compounds accounted for 10.5%; chlorinated ethane and ethyl ( $C_2$ ) compounds other than vinyl chloride (12.1%); chlorinated  $C_3$  compounds (epichlorohydrin and propylene oxide by the chlorohydrin route), 13.2%; phosgene derivatives (5.5%); other higher order chloro-carbons (2.1%). Inorganic chemicals accounted for 8.4%, with hydrochloric acid (2.8%) and sodium hypochlorite (2.5%) the major items.

Unfortunately the rest of the intermediate product breakdown shown in *Tables I, II* and *Figures 1 & 2* is almost meaningless to anyone except an industrial chemist, and its implications are anything but clear. The sorts of questions one would like to answer include: how much chlorine is contained in "final" products that are sold to other sectors and not transformed further? (The plastic PVC is an obvious example, but there are many others). What is the ultimate fate of that embodied chlorine? How much chlorine is lost to the environment in conversion processed within the chemical industry? Again, in what forms? These questions are at the heart of a life cycle analysis of chlorine. As noted above, only process losses are considered in this paper. The fate of final products is considered in the third and last paper.

The situation is complicated by the fact that a chlorine atom may be recycled within the chemical industry several times before being embodied in a final product or discarded in a

waste. Chlorine is recycled in several ways, although by far the most important is as hydrochloric acid (HCl), which is used in enormous quantities, most of which is a by-product of some other production process. In fact, chlorinated intermediates are utilized in the production of a number of final products that contain no chlorine, i.e. all the chlorine is discarded along the way (mostly as HCl). Examples include polyurethanes, polycarbonates, epoxies, propylene oxide, fluorocarbons, titanium dioxide and ultrapure (electronic grade) silicon. Some of these are discussed later.

Apart from recycling via hydrochloric acid, there are several other less important possibilities. In the first place, some secondary chlorine (about 3.4% in Europe) is produced from by-product HCl by electrolysis (the Kel-chlor process). In addition, salt itself is recycled to a small extent, mainly where it is a major waste product (as in polycarbonate production). A small amount of EDC is recycled from VCM production. Finally, some over-chlorinated products are recycled by hydrogenation or pyrolysis, again yielding HCl/Cl<sub>2</sub> which is recycled.

The most important single chain is the one that begins with chlorination of ethylene and ends with PVC and some by-products. However the analysis is again complicated by the fact that there are several other by-products of the chain, including vinylidene chloride (VDC), 1,1,1 trichloroethane, trichloroethylene, perchloroethylene and carbon tetrachloride. The last four products are also made by other processes (e.g. ethane chlorination). Also, we know that vinyl chloride monomer (VCM) is not made exclusively from EDC (in Europe some is made by direct chlorination of acetylene).

We had no direct information on the mix of processes that was used, but we do know a few other useful facts. As mentioned above, there are two major processes involved in the production of EDC, namely direct chlorination of ethylene and oxychlorination of ethylene using hydrochloric acid. The main process for making vinyl chloride monomer (VCM) in turn is pyrolysis of EDC, which produces hydrochloric acid as a by-product. We know that these three processes are normally carried out jointly, in the same facility, so that the HCl produced from the EDC pyrolysis process is then utilized next door in the oxychlorination process to make EDC. There is no *net* output of HCl from these combined processes beyond the plant boundary itself. This enables us to allocate the EDC output among the two principal production processes: about 53.7% of the virgin EDC is made by direct chlorination of ethylene, the remainder being from the oxychlorination process. Carbon tetrachloride is recovered as a by-product of the direct chlorination process. The carbon-tetrachloride, in turn, is the primary feedstock for production of chloro-fluorocarbons (CFCs).

As noted, 96% of the EDC is converted to vinyl chloride monomer, VCM. The remainder of the EDC — about 4% — is divided between the monomer vinylidene chloride (from which several products, including "saran" are made) and the two solvents, trichloroethylene and perchloroethylene. Similarly, we know that another solvent, 1,1,1 trichloroethane, is manufactured partly from VCM itself. (It can also be made from vinylidene chloride, but we have ignored that route, since it involves an extra step).

All three of these solvents can also be made by direct chlorination of ethane. Again, we have no direct information on the allocation of chloroethane solvent output among alternative processes. However, we do know the total European production of the three above-mentioned solvents for 1992, shown in *Table VI* [ECSA 1993], and of course their chlorine content is easily calculated: viz. 80.95%, 85.51% and 79.73% respectively. We also know the amount of chlorine allocated to these three chemicals according to the Tecnon survey (*Table II*). Subtracting the latter from the totals reported by ECSA left significant differences in all cases. We interpreted these differences to be the chlorine content of the by-product contributions from EDC and VCM. These amounted to 72 kMT for trichloroethylene, 120 kMT for perchloroethylene and 128 kMT for 1,1,1 trichloroethane, respectively.

We had no direct data on the production of vinylidene chloride (VDC). However, to estimate it we subtracted the imputed uses of EDC for trichloroethylene and perchloroethylene production (72 kMT and 120 kMT chlorine content, respectively) which left 152 kMT of EDC (109 kMT chlorine content) to be accounted for. From a description of the VDC process, [SRI 1989] we were able to calculate that 188 kMT of molecular chlorine was also used, and that total output of VDC must have been 187 kMT (137 kMT chlorine content). By-product hydrochloric acid output must have been 82 kMT (79 kMT chlorine).

We also had no data on acetylene consumption for VCM production. To balance the entire system we made the arbitrary assumption that VCM via the acetylene hydrochlorination route, together with VCM polymerization, consumed exactly 82 kMT of HCl (the amount available from vinylidene chloride production). This implies about 73 kMT net HCl input to acetylene chlorination, which would require an acetylene input of 58 kMT. This last calculation is probably not correct, but it is internally consistent and plausible.

Combining all of the inputs and outputs, then, using process yield data for EDC and VCM production from various published and unpublished sources, we arrived at *Figure 4* and the following summary:

#### Extended EDC-VCM-PVC Chains (*Figure 4*)

- Direct chlorine inputs to the extended EDC chains: 3562 kMT
- Chlorine in recycled EDC: 227 kMT
- Chlorine in HCl produced (and entirely consumed) in the chain: 2795 kMT
- Chlorine embodied in VCM: 2752 kMT (of which 45 kMT to 1,1,1 trichloroethane)
- Chlorine embodied in PVC: 2680 kMT
- Chlorine embodied in vinylidene chloride, VDC: 137 kMT
- Chlorine embodied in per- and tri-chloroethylenes: 120 kMT and 72 kMT
- Chloride embodied in carbon tetrachloride: 162 kMT
- Chlorine embodied in 1,1,1 trichloroethane from this chain: 128 kMT
- Chlorine in HCH "heavy ends & "light ends": 92 kMT
- Chlorine in wastes: 171 kMT (of which 124 kMT was inorganic)

Taking into account by-products, this chain accounted 40.7% of the chlorine consumed in western Europe in 1992.

Analysis of the other chains followed a similar methodology. We omit the details. The next largest final output of chlorine products from the chemical industry in Europe in 1992 was chlorinated solvents, as shown in *Table VI* [ECSA 1993]. Total output of these four for 1992 amounted to only 768 kMT, of which only about 80% — or 608 kMT — was chlorine. (Production and sales of solvents are declining steadily). Apart from by-products of ethylene chlorination, solvents are produced by chlorination of methane or ethane.

The chloroethane series, including chloroacetic acid, is displayed graphically in *Figure 5*. In this case, we calculate chlorine consumption of 311 kMT (3.5%). A composite diagram of the chloromethane series is shown as *Figure 6*. It consumed 339 kMT (3.9%) of chlorine in Europe in 1992, according to our calculations (based on Tecnon, case A). Together, these two chains consumed 650 kMT of chlorine in 1992. However, the two chains do not correspond exactly to solvents output. On the one hand, some solvents are produced as by-products of the chlorination of ethylene (chain). On the other hand some other chemicals, including chloroform and chloroacetic acid are also derived from these two chains. The summary results are as follows:

### Extended Chloroethane Chains (*Figure 5*)

- Chlorine consumed in the chloroethane chain: 311 kMT
- Chlorine in HCl produced by the chains: 151 kMT
- Chlorine embodied in 1,1,1 trichloroethane: 30 kMT
- Chlorine embodied in trichloroethylene: 29 kMT
- Chlorine embodied in perchloroethylene: 61 kMT
- Chlorine embodied in chloroacetic acid: 11 kMT
- Chlorine in HCl and other Cl wastes: 21 kMT

### Chloromethane Chains (*Figure 6*)

- Chlorine consumed in the chloromethane chain: 339 kMT
- Chlorine in HCl consumed in the chain: 173 kMT
- Chlorine in HCl produced by the chain: 90 kMT
- Chlorine embodied in methyl chloride (from methanol): 156 kMT
- Chlorine embodied in methylene chloride from the chain: 141 kMT
- Chlorine embodied in chloroform from the chain: 59 kMT
- Chlorine embodied in carbon tetrachloride from the chain: 46 kMT
- Chlorine embodied in light and heavy ends: 14 kMT
- Inorganic chlorine wastes (NaCl): 4 kMT

The gross output of HCl from the chloromethane and chloroethane chains together was  $90 + 151 = 241$  kMT (Cl). As a percentage of the total by-product HCl, this is 4.5%. Added to the 2797 kMT already accounted for by the EDC-VCM-PVC chain (52%), we have accounted for 3038 kMT (Cl content), or 56.5% of the reported total, without including the CHC recovery.

An important inorganic product that contains chlorine is "hypochlorite" (95% sodium, 5% calcium) an important category of industrial and household bleaches. Input chlorine was 246 kMT, of which 117 kMT was embodied in hypochlorites. Outputs included 115 kMT in the form of HCl (Cl), 1 kMT "pure" salt and 13 kMT in the form of other wastes.

As was noted previously, there are a number of important instances of the use of chlorine (and HCl) as an intermediate in the production of chemicals that do not themselves contain chlorine. For such products, it necessarily follows that *all* chlorine ends up in by-products such as HCl that are used in other processes or in wastes. Examples are as follows:

*Polyurethanes* are polymers of either *toluene diisocyanate* (TDI), or *methylene diphenyl diisocyanate* (MDI). These monomers are made by reacting a feedstock (e.g. toluene diamine) with a chlorine-containing intermediate (*phosgene*,  $\text{CCl}_2\text{O}$ ), yielding HCl as a by-product. (In this case the HCl is recycled to hydrogen and chlorine by electrolysis.)

*Polycarbonates* are co-polymers of *phosgene* with *bisphenol A* with HCl as a by-product. The phosgene chain is shown schematically, along with the *chlorobenzene* process in *Figure 7*. The phosgene chain alone accounted for 755 kMT or 8.6% of European chlorine consumed in 1992 according to our calculations, based on Tecnon data, case A. *Chlorobenzenes* consumed an additional 93 kMT. These were mostly used to manufacture pesticides and herbicides.

### Extended Phosgene/Chlorobenzene Chains (*Figure 7*)

- Chlorine consumed in the phosgene/chlorobenzene chain: 848 kMT
- Chlorine in HCl produced by the chains: 671 kMT
- Chlorine embodied in phosgene: 747 kMT (0 kMT leaves chain)
- Chlorine embodied in monochlorobenzene: 31 kMT
- Chlorine embodied in dichlorobenzene: 12 kMT (4 kMT leaves chain)
- Chlorine in Cl wastes: 142 kMT

*Propylene oxide (epoxipropane)*, is an important intermediate feedstock for several products. It is made by two processes. The older "chlorohydrin" process proceeds via *dichloropropene* (DCP). In the dominant version, HCl is a by-product of the second stage, but it is neutralized with calcium hydroxide, producing  $\text{CaCl}_2$  as a waste. In one case (Dow) the propylene oxide facility is co-located with a salt electrolysis facility. Instead of producing NaOH commercially by dehydration of the cell liquor, it is used to neutralize the HCl from the chlorohydrin process, regenerating NaCl brine that is fed back into the electrolysis. The newer peroxidation 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 of this process, whence the Oxirane process only accounts for about 4% of worldwide capacity as of 1989-90 [Fonds Chem. 1992].

*Epoxies* are co-polymers of *bisphenol A* with *epichlorohydrin*. The latter is derived from *allyl chloride*, from direct chlorination of propylene. Not only does the production process for *epichlorohydrin* itself generate large quantities of HCl, so does the final polymerization process [Fonds Chem 1992]. A schematic diagram of the propylene chlorination chain is shown in *Figure 8*. The propylene chlorination chain taken as a whole (see also above) accounted for 1108 kMT of chlorine, or 12.7% of European chlorine consumed in 1992, based on Tecnon data (case A). The allyl chloride sub-chain accounted for 153 kMT of chlorine or about 1.7% of 1992 European chlorine consumption.

### Extended Propylene Chlorination Chains (*Figure 8*)

- Chlorine consumed in the propylene chlorination chain: 1108 kMT
- Chlorine in HCl produced by the chains: 72 kMT
- Chlorine in HCl consumed in the chain: 22 kMT
- Chlorine embodied in allyl chloride: 54 kMT (5 kMT leaves chain)
- Chlorine embodied in epichlorohydrin: 41 kMT (0 kMT leaves chain)
- Chlorine embodied in "ends": 6 kMT
- Chlorine in Cl wastes: 974 kMT

*Butyl rubber* is another case. It is *polychloroprene*, a polymer of *chloroprene*, which is a chlorinated product of butadiene, a  $\text{C}_4$  hydrocarbon. Inputs to the chlorination process were 82 kMT; of which 37 kMT was embodied in chloroprene and the remainder is apparently waste. No chlorine is contained in the polymer itself. The polymerization process therefore generates additional chlorine, probably in the form

of HCl.

*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 direct chlorination to titanium tetrachloride ( $\text{TiCl}_4$ ) as an intermediate step. The chloride is then "burned" at high temperatures (above  $1000^\circ\text{C}$ ), or reacted with high temperature steam, to produce the oxide. In the case of direct oxidation, most of the chlorine is recycled internally. In the case of reaction with steam, hydrochloric acid is generated. In this case HCl is apparently not recycled, but is neutralized by an alkali; the waste product is either sodium chloride (salt) or magnesium chloride [Fonds Chem 1992]. The waste stream also includes small amounts of ferric chloride (from iron impurities in the ore). This process consumed 104 kMT of chlorine in 1992 or about 1.2% of elemental chlorine in Europe.

*Fluorocarbons (FCs, HFCs)* are made by direct fluorination of chlorocarbons or CHCs, mainly carbon tetrachloride, releasing chlorine or HCl [Fonds Chem 1992]. Production is included under "solvents", although the main source is probably by-product  $\text{CCl}_4$  from EDC production.

*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 hydrochloric acid (HCl) for recycling [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].

*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 other silicon chemicals. However the final fate of the chlorine is unclear. We have described this complex system is described in more detail in another publication [Ayres *et al*, 1995, Chapter 10].

Summarizing, it is interesting to present the various chains in an integrated form. This is done in *Figure 9*.

## 4. LOSSES OF CHLORINE DURING PRODUCTION

Regarding HCl production as a recycling loop, it follows that chlorine inputs to the chemical industry taken generally may be divided into primary inputs (i.e. "virgin" chlorine

from NaCl) and secondary inputs, consisting of secondary chlorine and HCl. Based on the ECOTEC numbers, the former accounts for 64% and the latter for 36% of the total chlorine input [ECOTEC, *ibid*]. Looking at the composite outputs of the chemical industry, again 36% of the chlorine content is recycled, 41% is embodied in primary products and 23% is lost.

According to ECOTEC, most of the chlorine losses within the industry occurs as sodium chloride [*ibid*]. This results from neutralization reactions between hydrochloric acid HCl and caustic soda, NaOH. Certainly, most of the NaOH consumed in the chemical industry ends up reacting with and neutralizing one of the strong acids, either HCl or H<sub>2</sub>SO<sub>4</sub>.<sup>5</sup> Of total NaOH production, 29% in Europe and 36% in America is used within the chemical industry, mostly for this purpose [USBuMines, 1994]. Actually, there is reason to believe that large quantities of calcium chloride, CaCl<sub>2</sub> are also generated, resulting from the use of lime (CaO) as a neutralizing agent.

It should be pointed out, however, that 8% of the chlorine output consists of chlorine embodied in chemical intermediates, other than HCl, that are also used inside the chemical industry. From a flow perspective, therefore, it can be concluded that only  $(41-8)/64 = 51.5\%$  of the primary chlorine produced is ultimately embodied in "final" products sold to other industries or to final consumers, while the rest (48.5%) is consumed within the industry and ultimately lost to waste streams within the industry.

Assuming these percentages hold at the global level, it would follow that if global output of chlorine is 36 MMT, then about 4.5 MMT is embodied in intermediates, 18.5% is embodied in final products and 17.5 MMT is finally carried off in process wastes from within the chemical industry. While most of the latter may consist of aqueous solutions of sodium or calcium chloride, which are comparatively harmless to the environment (depending on location and quantity, of course), there remains a significant quantity of chlorinated hydrocarbon (CHC) wastes. In the most advanced countries, the latter are recovered and pyrolyzed to recover HCl and chlorine (as noted above). For instance, according to the ECOTEC survey, representing 76% of the industry, 136 kMT of HCl was recovered by pyrolysis of CHC's in Europe in 1992. This amounts to roughly 4% of the HCl consumed but only 1.4% of the chlorine flux in the sector.

Our own calculations, based on Tecnon data from *Table II* offer a far more detailed picture, albeit only for a subset of the chemical industry. For our subset of 5 chains and 3 stand-alone processes, chlorine inputs were 6600 kMT, and chlorine embodied in "useful" outputs, excluding HCl (most of which is recycled within the industry) was 4109. See *Tables IV & V (Case A)*. However, not all of these outputs are final products. For instance, some CHC's are converted into CFCs; others are converted into non-chlorinated products, such as butyl rubber, silicones, and so on. For the subset we have analyzed, identifiable wastes amount to 2192 kMT, as shown in *Tables VII & VIII*. The breakdown was as follows: 107 kMT (Cl) was embodied in identified organic compounds, 847 kMT (Cl) was in the form of sodium chloride, 299 kMT (Cl) was embodied in other identified inorganic compounds and 938 kMT (Cl) was embodied in unidentified wastes. The largest single source of chlorinated waste products was the propylene chlorination chain, which generated 974 kMT (Cl) of wastes, mostly unidentified, but probably mainly as NaCl. A further 147 kMT was embodied in "light and heavy ends" that were probably recycled or pyrolyzed for recovery of hydrochloric acid.

The composition of the CHC wastes cannot be characterized precisely in molecular terms by our imperfect mass-balance methodology. Of particular concern are emissions of EDC and VCM, both of which are produced in extremely large quantities *en route* to PVC. Both of these chemicals are highly toxic, while VCM is both toxic and also carcinogenic.<sup>6</sup> The dangers have been recognized for some time, and strict standards have been enforced, in

Europe and America, both on worker safety and on the allowable content of unpolymerized VCM in PVC products. However, according to our calculations, in *Table VIII*, about 28 kMT of EDC was lost or unaccounted for in production wastes (pre-treatment) in Europe in 1992, or about 0.5% of total production. Similarly, our calculations suggest that roughly 1% of input VCM is not converted to PVC; of this 0.75% of the produced VCM, or 35 kMT is probably lost in process wastes (although some of this may be incorporated in the PVC itself). Clearly, emissions controls at the plant level can — and presumably does — reduce these losses.

There are other scattered data that offer some confirming clues. We have no specific information on EDC emissions, unfortunately. As regards VCM, 330 tonnes was released to the environment in Germany during 1989 [Claus *et al* 1990]. This would be around 0.03% of German production. One plant in Sweden emitted 140 tonnes of VCM in 1991 according to its own environmental report [Norsk Hydro 1992], while another in the U.K. emitted 1700 tonnes of VCM in 1991 [ICI 1992]. This is probably not less than 0.5% of production. For Europe as a whole (where standards are less tight than in Germany) it is plausible that VCM emissions still amount to 0.2-0.3% of production.

As regards other wastes, the foregoing analysis represents a likely upper limit to useful products and, hence, a lower limit to CHC production and waste generation. Chlorine not embodied in products and not converted to HCl, of course, ends up as inorganic chlorides (NaCl, CaCl<sub>2</sub>) or as unrecovered CHCs. One can estimate the NaCl wastes directly in the case of processes using NaOH (for instance, the epichlorohydrin chain). In the case of propylene chlorination and some inorganic products, we do not have enough information to characterize the wastes more precisely. This would be a useful object of future research.

## ENDNOTES

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. However, sodium chlorate (NaClO<sub>3</sub>) — which yields chlorine dioxide on site — is also produced and used in significant quantities for pulp bleaching. This chemical is *not* produced from chlorine, however. It is made by electrolysis of salt. Sodium hypochlorite (NaClO) is another widely used bleach, though we are not aware of any use in pulp bleaching.
3. In this case the EcoTec survey is contradicted by another industry consultant, ECOPLAN. According to ECOPLAN (1989), about 200 kMT of HCl was produced by direct reaction of chlorine with hydrogen and another 270 kMT was produced by the old process of reacting sulfuric acid with salt. Together, these two processes accounted for 7.8% of apparent 1989 production in Europe.
4. This data also comes from SRI (1989). Fluorocarbons are produced from various chlorocarbons (notably carbon tetrachloride and 1,1,1 trichloroethane) by reaction with hydrofluoric acid (HF), yielding HCl as a by-product.
5. The latter reaction yields sodium sulfate, which is a product that has a significant market in the paper industry. However it has no importance for this analysis, except insofar as it accounts for part of the NaOH that is produced initially as a by-product of chlorine production.
6. At least 157 deaths had been attributed to VCM poisoning in Germany, up to 1990, and at least 140 additional deaths were anticipated before 2020 [Kollmann *et al* 1990].

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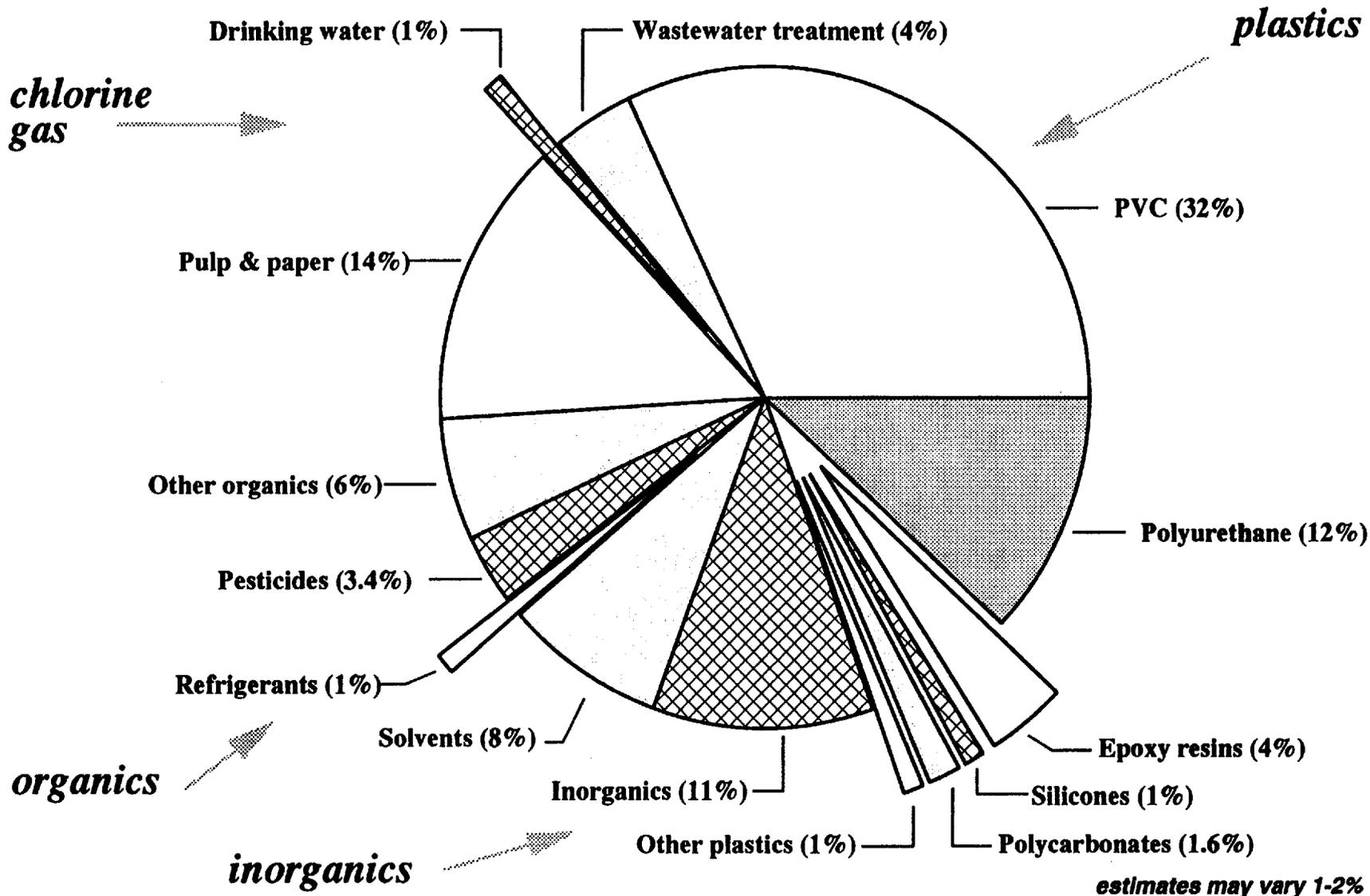


Figure 1: U.S. chlorine end uses, 1992  
 Source: [Thornton 1993]

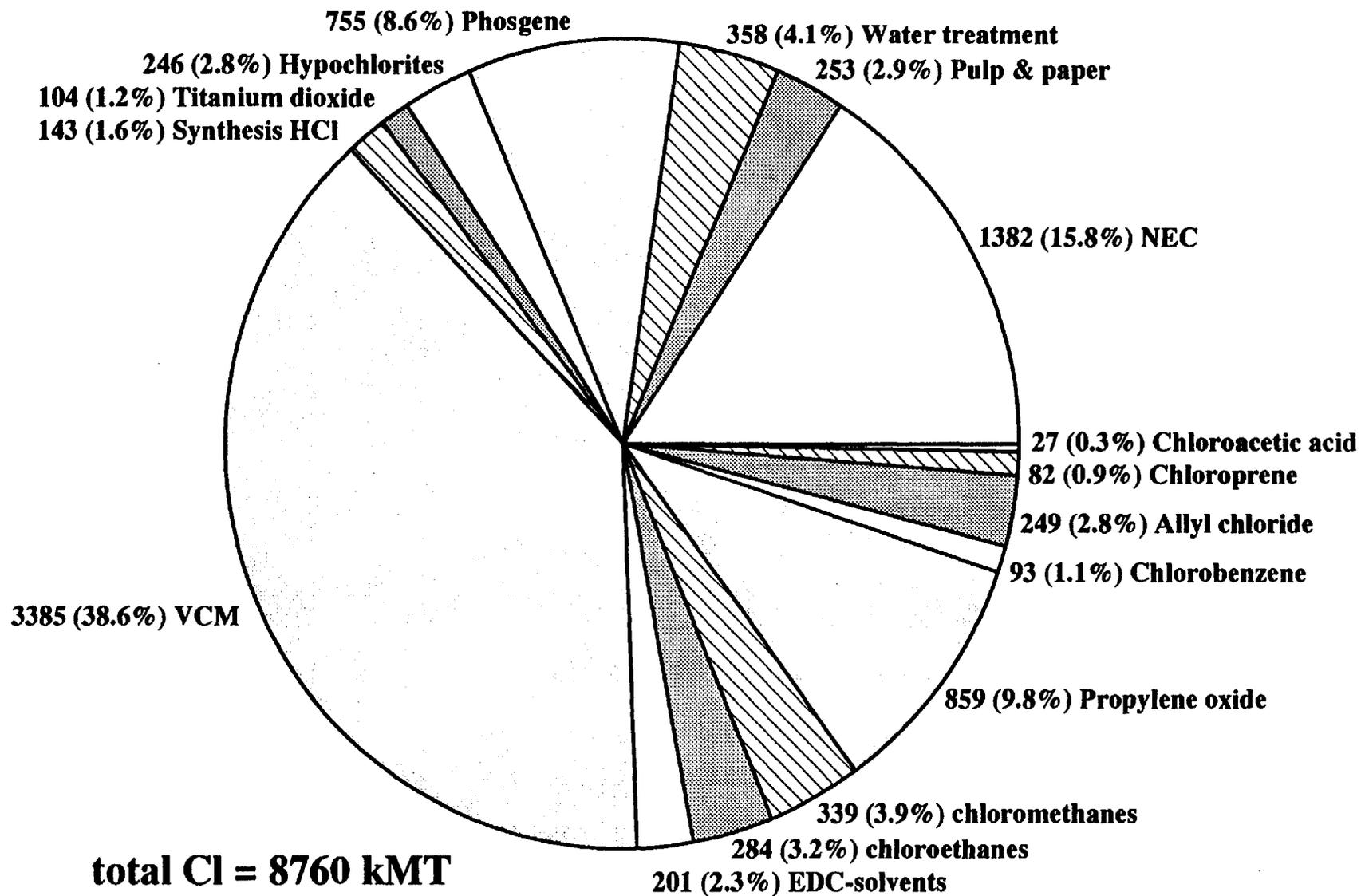


Figure 2: Western European chlorine end-use, 1992 (kMT Cl-content)

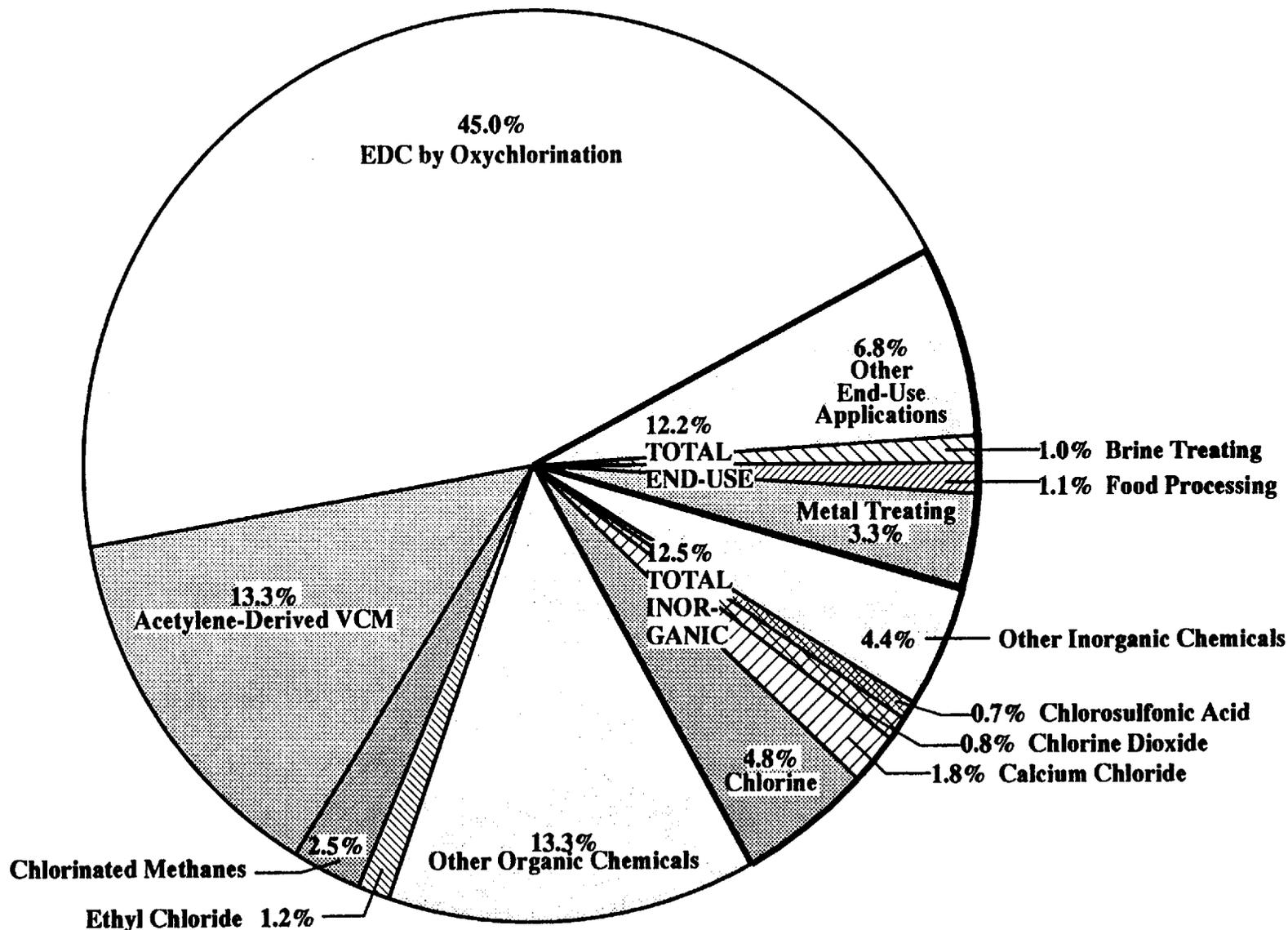
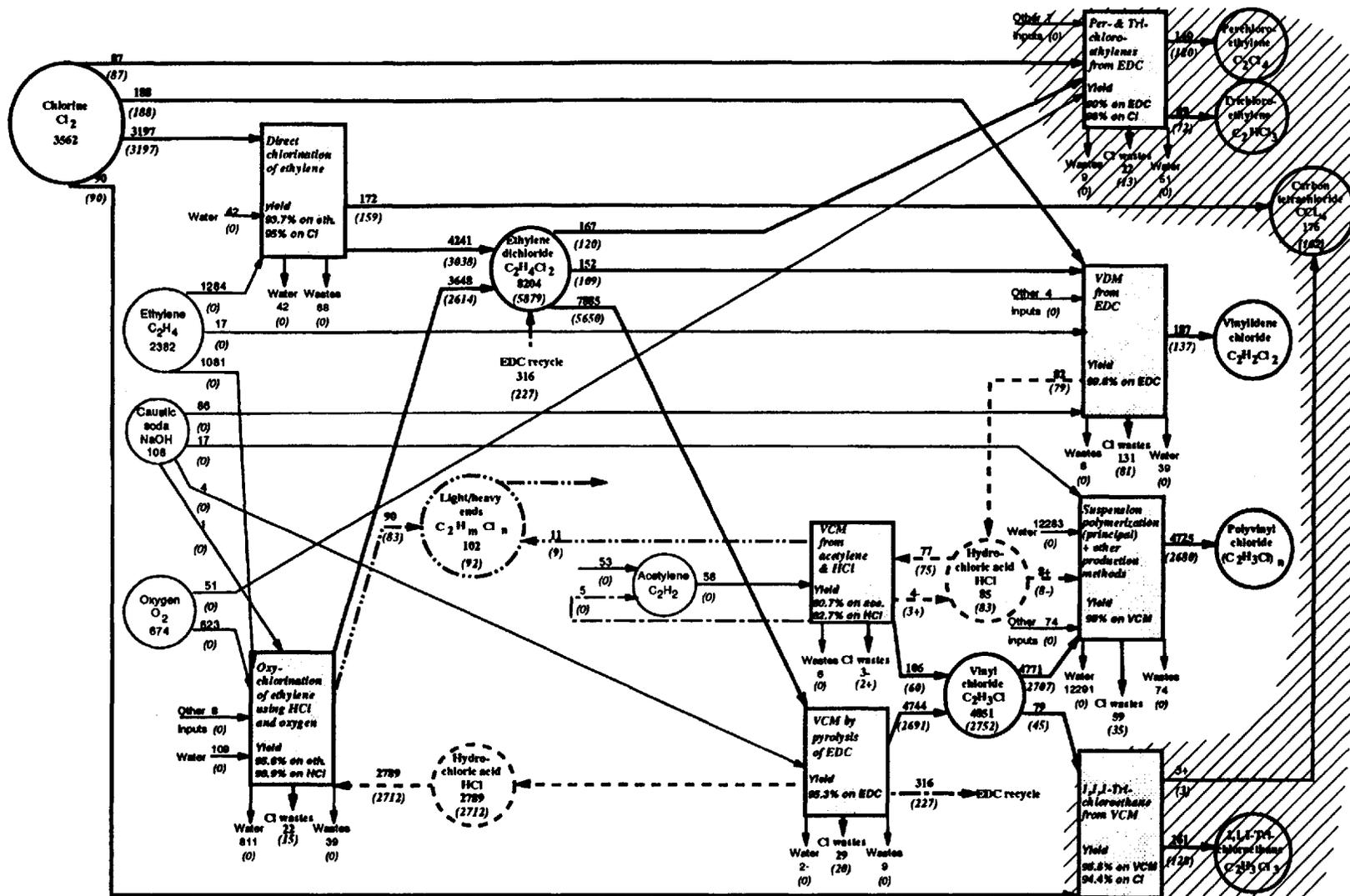
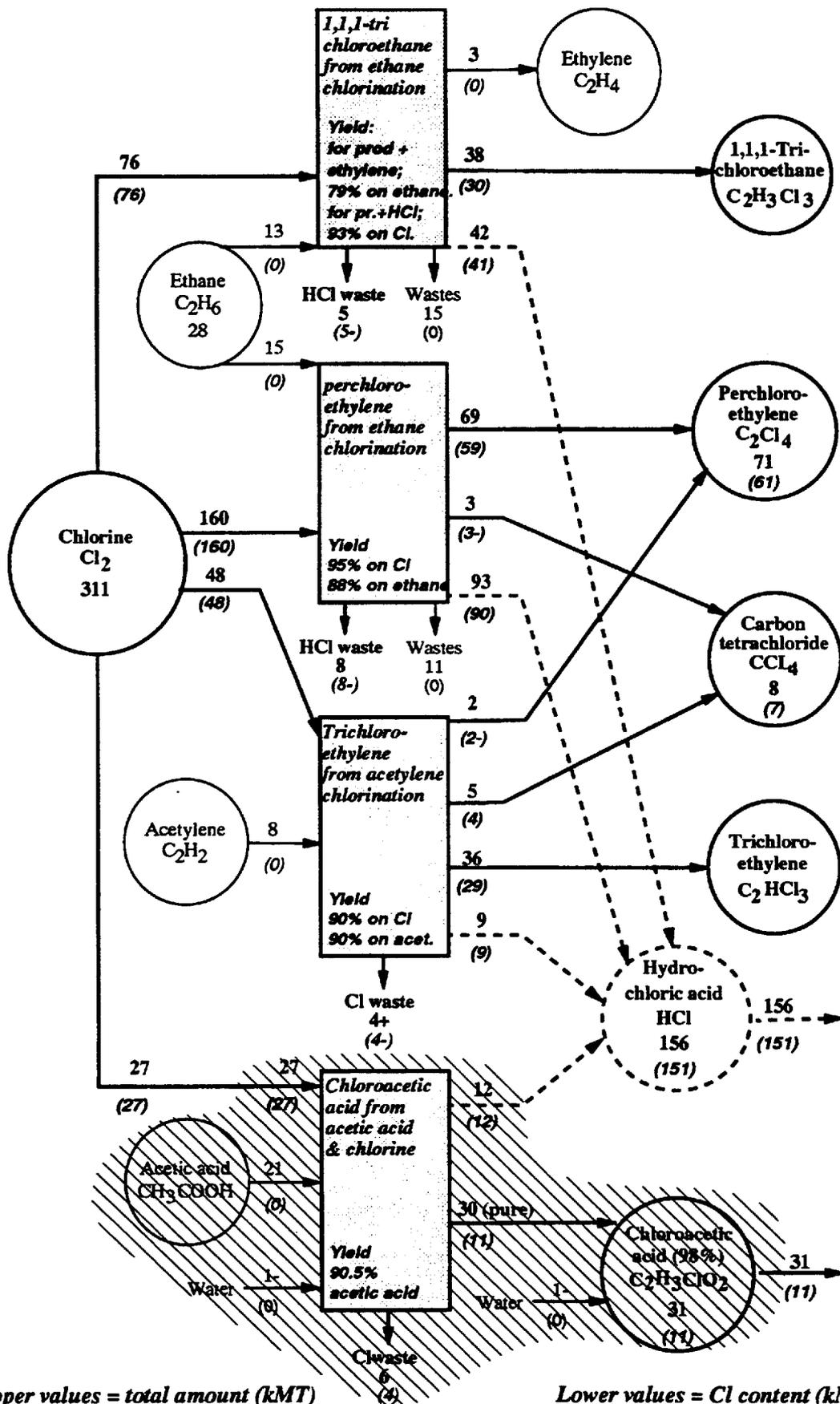


Figure 3: Western European consumption of hydrochloric acid by end-use, 1989  
 Data Source: ECOPLAN



Upper values = total amount (kMT)  
 Lower values (in parentheses) = Cl content (kMT)

Figure 4: VCM & EDC process-product flows; Western Europe, 1992



Upper values = total amount (kMT)

Lower values = Cl content (kMT)

Figure 5: Chloroethane (including chloroacetic acid) process-product flows, Western Europe 1992

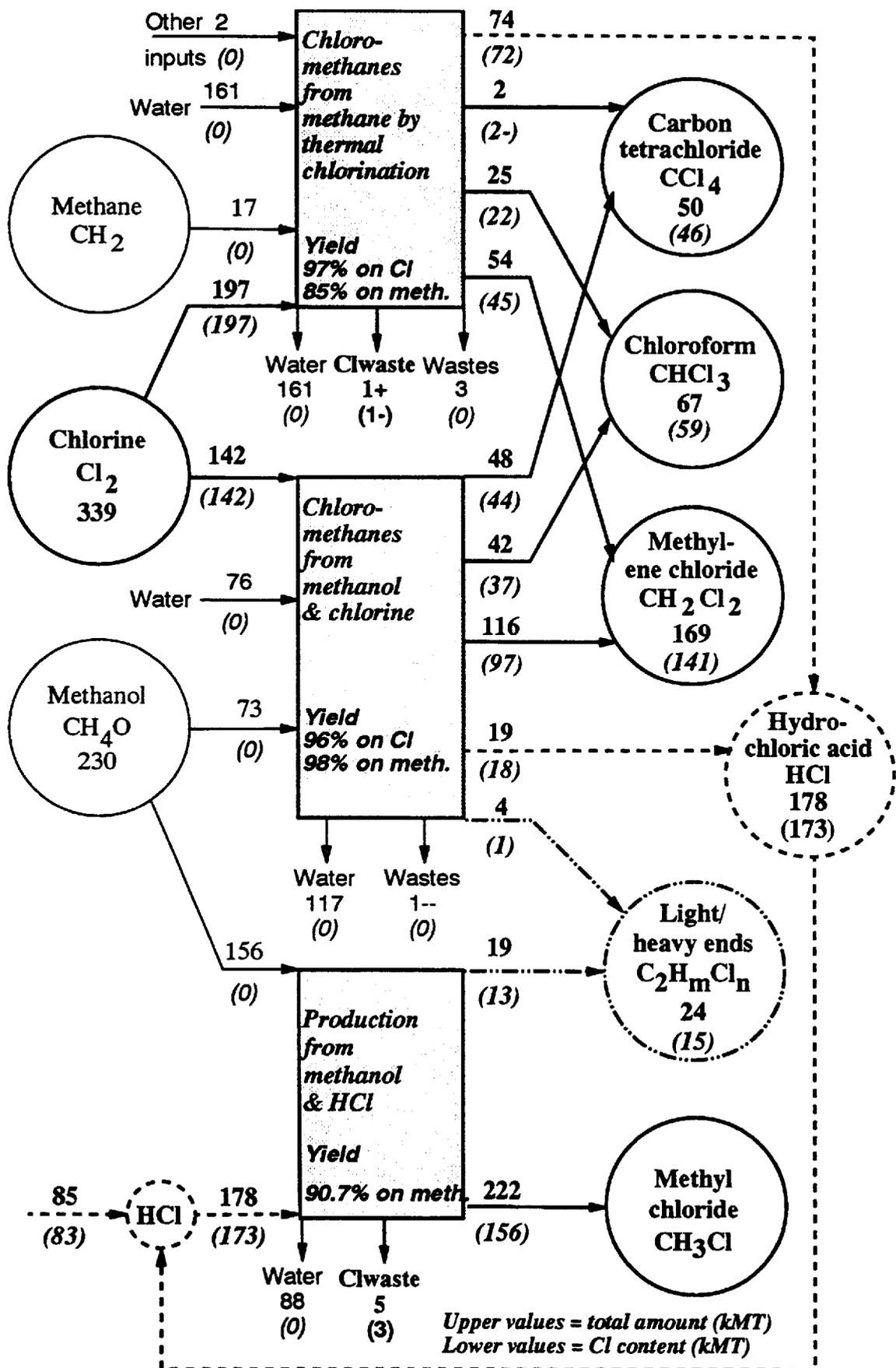


Figure 6: Chloromethane process-product flows, Western Europe 1992

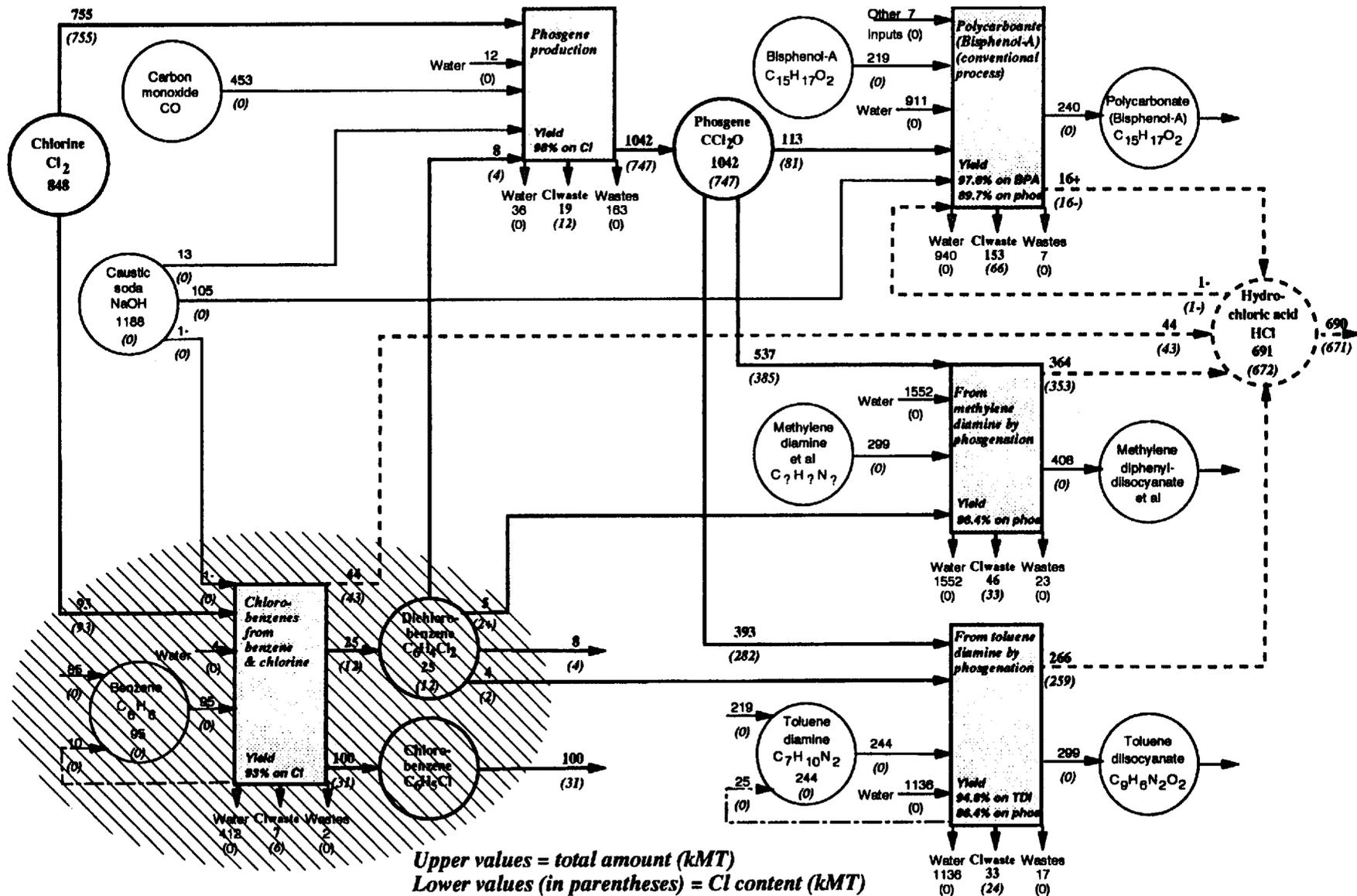


Figure 7: Chlorobenzene & phosgene process-product flows, Western Europe, 1992

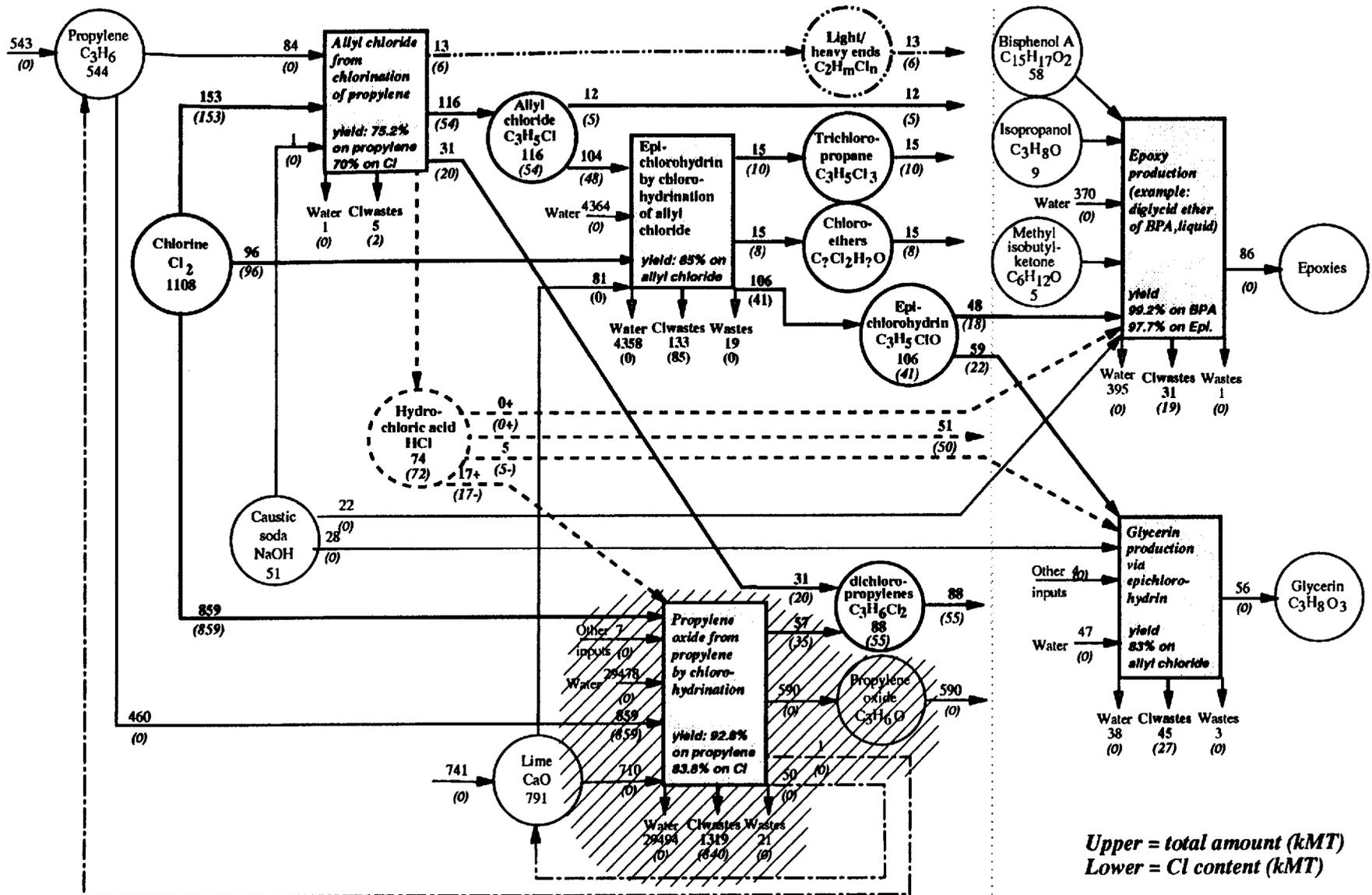


Figure 8: Allyl chloride & propylene oxide process-product flows, Western Europe 1992

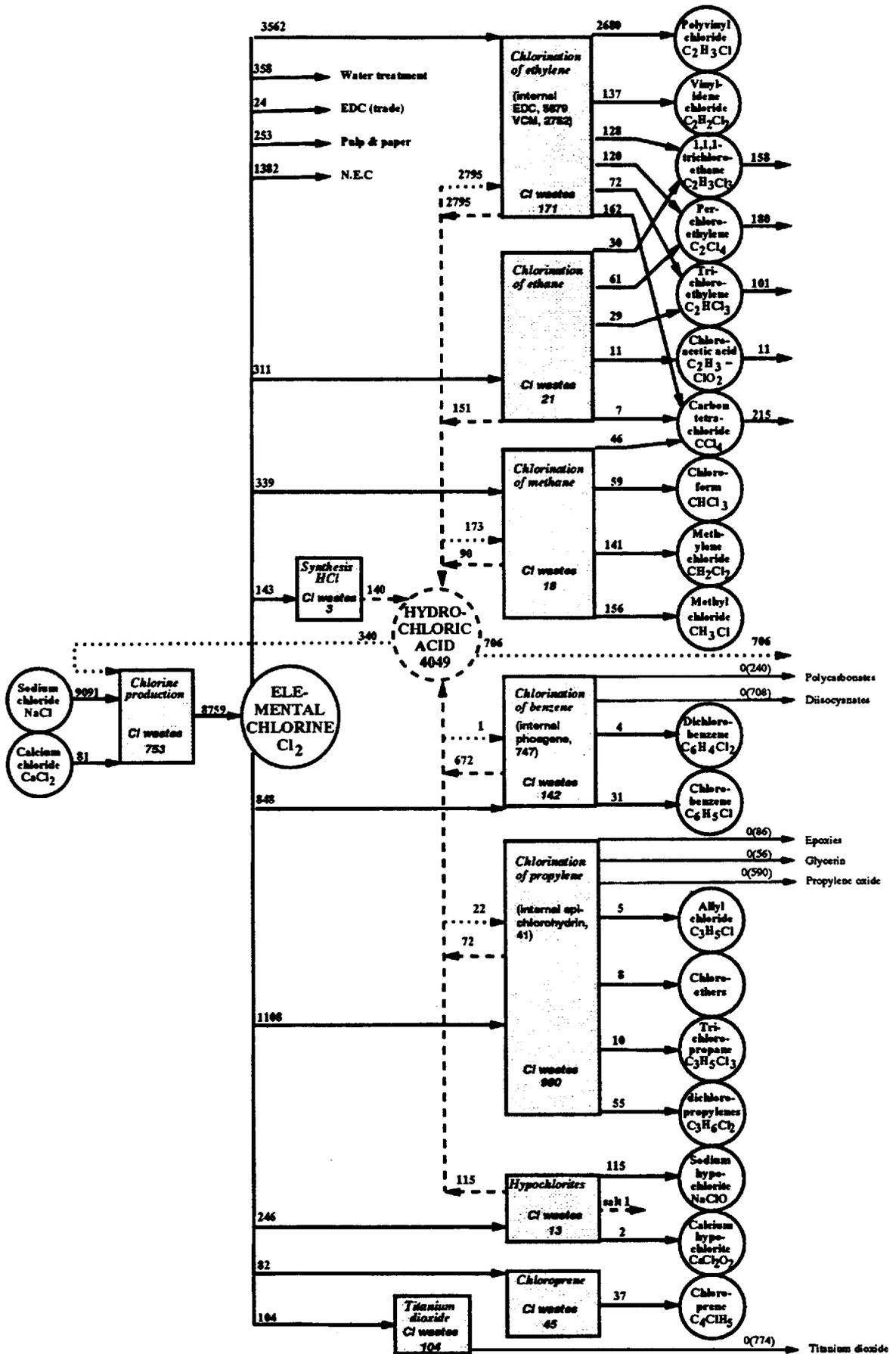


Figure 9: Chlorine process-product flows, Western Europe 1992 (kMT Cl-content)

**Table I: World chlorine use data (kMT)**

	<b>1988</b>	<b>1990</b>	<b>1991</b>	<b>1992</b>
Capacity to produce chlorine	41361	43405	43336	43160
Production	36756	36853	35701	35550
Total consumption	36756	36843	35682	35566
Total inorganic	13825	13423	13063	12580
Pulp & paper	4546	3889	3571	3362
Water treatment	1963	1955	1961	1976
Phosgene	1685	1860	1865	1928
Hypochlorite	934	933	913	913
Other inorganic	4697	4786	4753	4401
Titanium dioxide	522	583	607	632
Bromine	228	230	232	233
Synthesis HCl	283	445	508	468
N. E. C. (inorganic)	3664	3528	3406	3068
Total organic	22931	23420	22619	22986
VCM	10428	11474	11406	12278
EDC (solvents)	746	642	624	602
Chloroethanes	1523	1380	1180	1000
111 Trichloroethane	478	545	481	427
Trichloroethylene	368	276	251	208
Perchloroethylene	677	559	448	365
Chloromethanes	2470	2132	2000	1732
Methyl chloride	451	537	536	479
Methylene chloride	498	468	395	304
Chloroform	535	502	481	484
Carbon tetrachloride	986	625	588	465
Propylene oxide	2265	2334	2490	2594
Chlorobenzene+phenol	814	827	766	803
Chlorobenzene	800	813	752	789
Chlorinated phenol	14	14	14	14
Other organic	4685	4644	4211	3976
Chlorinated polyethylene	20	30	34	38
Allyl chloride	608	651	670	690
Chloroprene	273	258	226	217
Chloroacetic acid	69	71	69	70
Agrochemicals	384	284	282	282
Seasonings/MSG	63	62	59	59
Dyes & intermediates	248	253	255	257
N. E. C. (organic)	3020	3035	2616	2363
EDC (trade)	4	-4	-47	14

*Data Source: TECNON*

**Table II: Western Europe - chlorine use data (kMT)**

	1988	1990	1991	1992
Capacity to produce chlorine	11900	11613	11488	11267
Production	10440	9773	9224	8759
Total consumption	10437	9759	9235	8760
Total inorganic	3226	3076	2974	2545
Pulp & paper	649	492	338	253
Water treatment	368	359	359	358
Phosgene	669	742	725	755
Hypochlorite	259	256	256	246
Other inorganic	1281	1227	1296	933
Titanium dioxide	80	99	104	104
Bromine	25	25	25	25
Synthesis HCl	58	102	121	143
N.E.C. (inorganic)	1118	1001	1046	661
Total organic	7211	6683	6261	6215
VCM	3303	3239	3032	3197
EDC (solvents)	390	330	314	294
Chloroethanes	532	410	362	281
111 Trichloroethane	87	88	86	76
Trichloroethylene	171	93	83	48
Perchloroethylene	274	229	193	157
Chloromethanes	1032	834	776	677
Methyl chloride	191	191	184	173
Methylene chloride	230	210	164	152
Chloroform	178	158	147	137
Carbon tetrachloride	433	275	281	215
Propylene oxide	813	884	917	859
Chlorobenzene+phenol	143	137	108	105
Chlorobenzene	131	125	96	93
Chlorinated phenol	12	12	12	12
Other organic	882	839	786	778
Chlorinated polyethylene	3	7	9	10
Allyl chloride	143	149	151	153
Chloroprene	93	100	89	82
Chloroacetic acid	25	26	26	27
Agrochemicals	12	13	13	13
Seasonings/MSG	0	0	0	0
Dyes & intermediates	11	12	12	12
N.E.C. (organic)	595	532	486	481
EDC (trade)	116	10	-34	24
Inventory change	-2	0	12	-1
Net Trade	5	14	-3	0
Chlorine exports	361	381	362	291
Chlorine imports	356	367	365	291

*Data Source: TECNON*

**Table III: World demand for chlorine by end-use, 1994**

<i>Use Category</i>	<i>Europe</i>	<i>US</i>	<i>Japan</i>	<i>Rest of World</i>
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%

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

**Table IV: Chlorine consumption, Western Europe 1992, kMT(Cl<sub>2</sub>)**

	<i>TECNON</i>	<i>Case A</i>	<i>Case B</i>
<b>Total consumption</b>	<b>8760</b>	<b>8760</b>	<b>8760</b>
Consumption N.E.C.	1214	1382	-751 !
Consumption accounted for	7546	7378	9511
<i>Total inorganic</i>	<i>2545</i>		
Inorganic N.E.C.	686		
Inorganic accounted for	1859	1859	2140
Pulp & paper	253	253	253
Water treatment	358	358	358
Phosgene	755	755	763
Hypochlorite	246	246	516
Titanium dioxide	104	104	104
Synthesis HCl	143	143	146
<i>Total organic</i>	<i>6215</i>		
Organic N.E.C.	528		
Organic accounted for	5687	5519	7371
VCM	3197	3385	4032
EDC (solvents)	294	177	88
EDC (trade)	24	24	24
Chloroethanes	281	284	690
Chloromethanes	677	339	460
Propylene oxide	859	859	842
Chlorobenzene	93	93	275
Allyl chloride	153	249	712
Chloroprene	82	82	183
Chloroacetic acid	27	27	64

**Table V: HCl flows within the chlorine industry: Western Europe 1992**

	<i>Ecotec</i>			<i>Case A</i>		<i>Case B</i>	
	<i>kMT-Cl</i> (76%)	<i>kMT</i> <i>HCl</i>	%	<i>kMT</i> <i>HCl</i>	%	<i>kMT</i> <i>HCl</i>	%
<b>VCM(PVC)</b>							
HCl produced	2441	3303	59.3%	2888	69.4%	3353	63.3%
HCl consumed	2672	3606	64.8%	2880	83.7%	3343	85.0%
<b>EDC (Solvents)</b>							
HCl consumed		10	0.2%	8	0.2%	9	0.2%
<b>Chloroethanes</b>							
HCl produced				144	3.5%	364	6.9%
Chloroacetic acid							
HCl produced				12	0.3%	28	0.5%
<b>Chloromethanes</b>							
HCl produced	232	314	5.6%	93	2.2%	157	3.0%
HCl consumed	122	165	3.0%	178	5.2%	197	5.0%
<b>Phosgene</b>							
HCl produced	465	629	11.3%	647	15.5%	654	12.3%
HCl consumed				1	0.0%	1	0.0%
<b>Chlorobenzenes</b>							
HCl produced				44	1.1%	131	2.5%
<b>Allyl chloride (Epichlorohydrin)</b>							
HCl produced				74	1.8%	211	4.0%
<b>Propylene Oxide</b>							
HCl consumed				23	0.7%	32	0.8%
<b>Hypochlorites</b>							
HCl produced				119	2.8%	249	4.7%
<b>Other process chains</b>							
HCl produced	839	1135	20.4%				
HCl consumed	340	460	8.3%				
<b>Direct HCl production</b>							
HCl produced				144	3.5%	147	2.8%
<b>Chlorine production from salt</b>							
HCl consumed	186	252	4.5%	349	10.2%	349	8.9%
<b>Other industry uses</b>							
HCl produced	136	184	3.3%				
HCl consumed	575	778	14.0%				
<b>TOTAL in this table<sup>a</sup></b>							
HCl produced	4113	5566	100.0%	4164	100.0%	5294	100.0%
HCl consumed	3995	5231	100.0%	3439	100.0%	3932	100.0%

a. Differences between consumption and production arise from sources and uses external to the set of processes and chains explicitly considered.

**Table VI: 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

Data Source: ECSA

**Table VII: Wastes and potential wastes from analyzed processes by process chain kMT of chlorine content, Western Europe 1992**

	<i>Total</i>	<i>Ethylene</i>	<i>Ethane</i>	<i>Methane</i>	<i>Benzene</i>	<i>Propylene</i>	<i>4 single</i>
		<i>EDC,</i>	<i>chloro-</i>	<i>chloro-</i>	<i>chloro-</i>	<i>allyl</i>	<i>hypochlorite,</i>
		<i>PVC</i>	<i>ethanes,</i>	<i>methanes</i>	<i>benzenes,</i>	<i>chloride,</i>	<i>chloroprene,</i>
			<i>chloroacetic</i>		<i>phosgene</i>	<i>propylene</i>	<i>TiO<sub>2</sub>,</i>
			<i>acid</i>			<i>oxide</i>	<i>chlorine</i>
<b>CHLORINATED</b>	<i>kMT-Cl</i>	<i>kMT-Cl</i>	<i>kMT-Cl</i>	<i>kMT-Cl</i>	<i>kMT-Cl</i>	<i>kMT-Cl</i>	<i>kMT-Cl</i>
CHCs	52	47	1.6	3.4			
other chlorinated organic	55		2.2		53		
Sodium chloride	847	96		0.7		46	705
Hydrochloric acid	22		17.5		4		
other chlorinated inorganic	277	28				85	164
Unidentified chlorinated	938				84	843	11
<i>Total chlorinated waste</i>	<i>2192</i>	<i>171</i>	<i>21.2</i>	<i>4.2</i>	<i>142</i>	<i>974</i>	<i>880</i>
<i>Ends</i>	<i>147</i>	<i>92</i>		<i>14.5</i>		<i>6</i>	<i>34</i>
<b>Chlorinated waste including ends</b>	<b>2339</b>	<b>264</b>	<b>21.2</b>	<b>18.6</b>	<b>142</b>	<b>979</b>	<b>915</b>
<b>NON-CHLORINATED</b>	<i>kMT</i>	<i>kMT</i>	<i>kMT</i>	<i>kMT</i>	<i>kMT</i>	<i>kMT</i>	<i>kMT</i>
(CH) <sub>n</sub> hydrocarbons	35	20	3.0		2.4		9.3
C <sub>n</sub> H <sub>m</sub> hydrocarbons	214	186		2.7	25		
other identified	894	13	0.4	0.2	176	0.6	704
other unidentified	93				6.9	42	44
<b>Total non-chlorinated waste</b>	<b>1235</b>	<b>219</b>	<b>3.4</b>	<b>2.9</b>	<b>211</b>	<b>43</b>	<b>757</b>
<b>Water out: waste and/or dilution</b>	<b>74147</b>	<b>13241</b>	<b>0</b>	<b>367</b>	<b>3668</b>	<b>34286</b>	<b>22585</b>

**Table VIII: Wastes and potential wastes from analyzed processes by chemical Western Europe 1992**

	<i>kMT</i>	<i>kMT-Cl</i>
1,1,1,2-Tetrachloroethane	0.10	0.08
1,1,1-Trichloroethane	11	9
1,1-Dichloroethylene	0.04	0.03
1,2-Dichloroethylene	0.17	0.13
Carbon tetrachloride	91	84
Methyl chloride	21	14
unidentified=C <sub>n</sub> Cl <sub>j</sub> H <sub>m</sub>	90	40
<b>TOTAL ENDS</b>	<b>212</b>	<b>147</b>
1,1,1,2-Tetrachloroethane	0.02	0.02
1,1,1-Trichloroethane	2.7	2.1
1,1,2-Trichloroethane	5.0	4.0
1,1-Dichloroethylene	0.01	0.01
1,2-Dichloroethylene	0.04	0.03
Carbon tetrachloride	2.2	2.0
Ethylene dichloride	28	20
Methyl chloride	4.8	3.4
Perchloroethylene	0.56	0.48
Vinyl chloride	35	20
Chloroacetic acid	0.56	0.21
Dichloroacetic Acid	3.6	2.0
Phosgene	74	53
Sodium chloride	1396	847
Hydrochloric acid	22	22
Ammonium chloride	44	29
Calcium chloride	259	165
Cuprous chloride	0.02	0.01
Mercuric chloride	0.11	0.03
Titanium tetrachloride	110	82
unidentified-Cl <sub>j</sub> + X	1518	938
<b>TOTAL CL WASTE</b>	<b>3508</b>	<b>2192</b>
Propylene oxide process	1319	840
Titanium dioxide process	146	104
Chlorine production process	1178	718
<b>CL WASTE FROM CL PRODUCTS</b>	<b>865</b>	<b>529</b>
Ammonium nitrate	14	
Calcium hydroxide	0.8	
Carbon, activated	0.21	
carbon dioxide	863	
caustic soda	11	
Di-n-propylamine	3.8	
Sodium carbonate	0.82	
Sulfuric acid	0.53	
(CH) <sub>n</sub> hydrocarbons	35	
C <sub>n</sub> H <sub>m</sub> hydrocarbons	214	
unidentified	93	
<b>TOTAL OTHER WASTE</b>	<b>1235</b>	
<b>TOTAL WASTE ACCOUNTED FOR</b>	<b>4743</b>	<b>2192</b>
<b>TOTAL ENDS</b>	<b>212</b>	<b>147</b>
<b>WASTE=ENDS + WASTE ACCOUNTED</b>	<b>4955</b>	<b>2339</b>
<b>FROM CL PRODUCTS</b>	<b>865</b>	<b>529</b>
<b>FROM CL<sub>2</sub> PRODUCTION</b>	<b>1178</b>	<b>718</b>
<b>FROM NON-CL PRODUCTS</b>	<b>2912</b>	<b>1091</b>
<b>TOTAL WATER (WASTE + DILUTION)</b>	<b>74147</b>	