A CHLORINE BALANCE FOR THE NETHERLANDS

PART II: SUBSTANCE DOCUMENTS FINAL REPORT

TNO-report
STB/95/040-II-e

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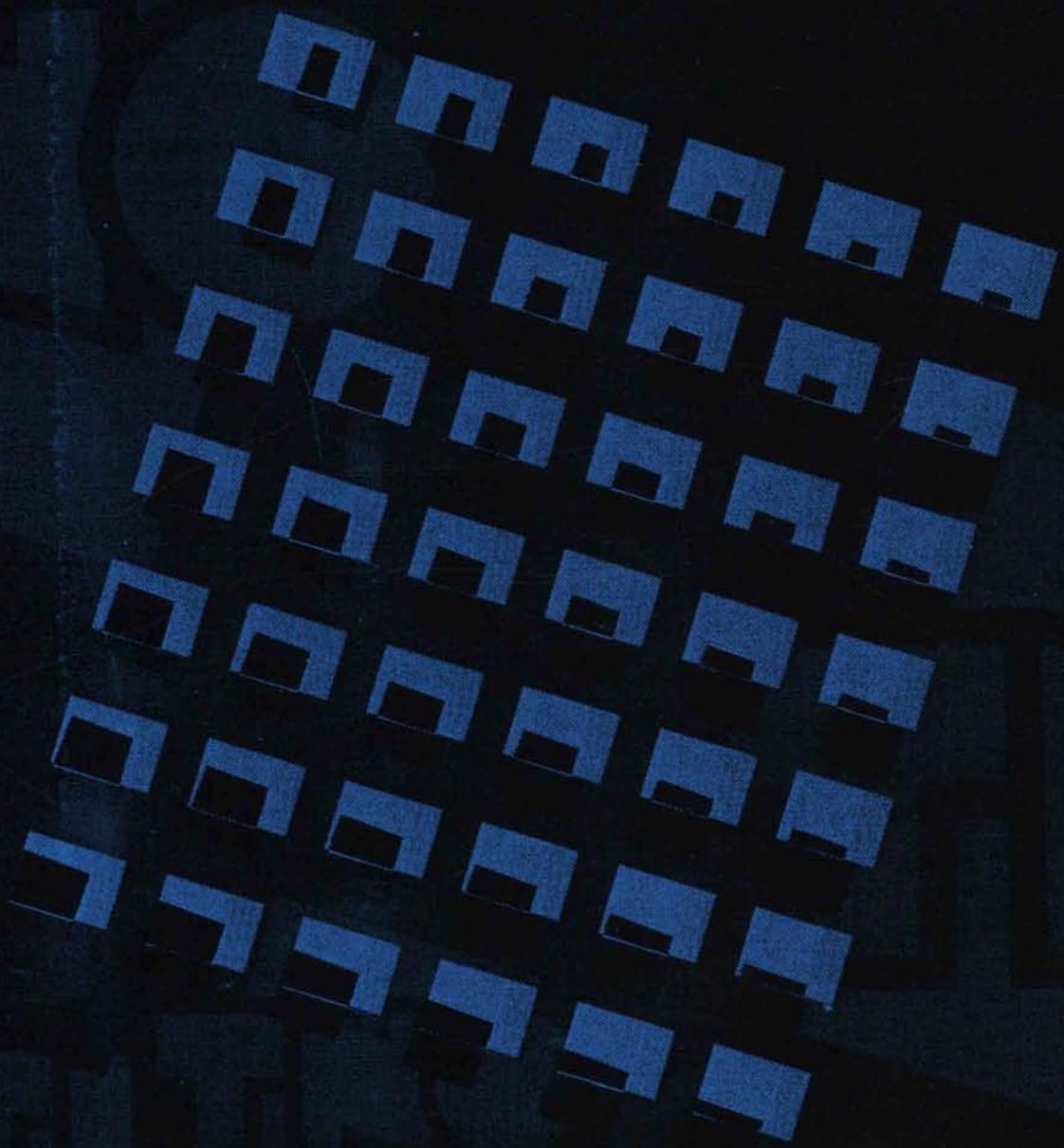
Part II: Substance documents

Final report



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Part II: Substance documents

Final report

Commissioned by the Ministries of Housing, Spatial Planning and the Environment (VROM), Economic Affairs and Transport, Public Works and Water Management

Apeldoorn/Leiden, 16 November 1995

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The Standard Conditions for Research Instructions given to TNO, as filed at the Registry of the District Court and the Chamber of Commerce in The Hague shall apply to all instructions given to TNO.

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PART II:

SUBSTANCE DOCUMENTS

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November 1995

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STRUCTURE AND COMPOSITION OF SUBSTANCE DOCUMENTS

1 INTRODUCTION

For the purposes of this study the chlorine chain was divided into 46 segments. Each segment describes a part of the processes or consumption applications in the Netherlands' chlorine chain. Before presenting the 46 substance documents, this section describes the structure of the documents and the procedure for collecting information.

Each segment generally consists of four subsections:

1. Introduction
2. Processes
3. Substance flows
4. Comments and points for discussion.

The introduction discusses the position of the chlorine application in the chlorine chain and where appropriate, explains the major companies and processes. Sub-section 2 describes the process. Sub-section 3 explains the substance flows and emissions. Other relevant issues are discussed in a concluding sub-section.

All consumption applications by chlorine compound are generally described in a single document. In these documents sub-sections 2 and 3 are combined in a subsection 'processes and substance flows', which describes the processes and emissions by consumption application.

The method of collecting information for each sub-section is described briefly below.

2 PROCESSES

The sub-section Processes describes the process in which the chorine or chlorinated compound is used. The purpose of the descriptions is to explain the description of the substance flows and there is no pretence that they are complete. The description is compiled from various sources. In many cases, the results of the Collaborative Project for the Description of Industrial Processes in the Netherlands (SPIN) were used. SPIN was carried out by RIVM in cooperation with the Ministry of Housing, Spatial Planning and the Environment (VROM) and the Institute for Inland Water Management and Wastewater Treatment (RIZA) with

the aim of describing the most relevant processes for environmental policy. Many processes involving chlorine have been or will be described in the context of SPIN.

Another important source of information is the companies which were approached in the course of the project. In some cases, process descriptions provided for licensing purposes or environmental impact assessment (EIA) procedures could be used for the purposes of this project.

If descriptions are not based on these sources, the RIVM/TNO study into halogenated hydrocarbons, the German Handbook of Chlorine Chemistry or general literature on chemical technology were used [ECOTEC 1991, Bremmer 1988].

3 SUBSTANCE FLOWS AND EMISSIONS IN 1990

3.1 Production processes

In production processes in which chlorine or chlorinated products are converted into other compounds, TNO requested relevant companies to prepare a macro chlorine balance for the process. Such a balance gives an insight into the main flows of chlorine: the use of chlorine or chlorine compounds and the quantity of chlorine that flows out in the form of product, is released into water as chloride or is produced as a by-product in the form of HCl. Import and export figures from the CBS and EUROSTAT were then used to estimate the domestic market for the compound produced [CBS 1991]. Production figures provided by companies were compared with the consumption figures in adjoining links in the chain. Production figures from the individual emission record [ER-I] provided an extra means of comparison. For reasons of confidentiality the figures in the report are sometimes aggregated.

Emissions to water and air (except releases of chloride) are not usually included in such a balance as they often account for less than one percent of the volume of chlorine. Most companies further found it too difficult, too time-consuming or undesirable to produce an extensive list of emissions. Emission figures were therefore taken from the individual emission record (ER-I) and the RIZA's emission registration system (WIER) [ER-I 1994, RIZA 1994b]. If emissions to water for the same substance were measured in both the ER-I and WIER, preference was given to the figure in WIER. WIER bases itself on the emission measurements taken in connection with emission licences. These figures are regarded as the more reliable by those concerned in both ER-I and WIER. In some

cases the emission figures are supplemented with data from a SPIN document. In appropriate cases this is noted in the text.

The emission picture is not complete. Neither ER-I nor WIER pretends to describe all (potential) emissions of chlorine-containing compounds. ER-I focuses on the major known emissions. WIER concentrates on monitoring 11 priority organic chlorine compounds drawn up in the framework of the North Sea Action Programme/Rhine Action Programme (RAP/NAP). For the purposes of this project it was impossible to conclusively demonstrate whether there were unintentional by-products apart from registered emissions. Attention was given to the occurrence of other emissions only in so far there was easily accessible literature concerning them. Dioxins and polychlorinated biphenyls (PCBs) in particular could be covered [Bremmer 1994, Raad 1993].

In principle, emission data at process level from the ER-I and WIER are confidential. They are therefore not stated in this report or are given in aggregated form.

3.2 Consumption applications

There are too many companies involved in the area of consumption applications to approach them individually. This would have been altogether too difficult for consumer applications. To make estimates for consumption applications we therefore used earlier studies, figures from industry, SPIN documents, the Collective Emissions Record (ER-C), previous surveys conducted by third parties or other monitoring activities. For many consumption applications, emissions factors to water, air and waste can be found in studies conducted in the framework of ER and SPIN. The volume disposed of with waste and the leakage into water and air can be estimated on the basis of estimated consumption. The volume discharged with waste was compared as far as possible with figures from the notification records of hazardous substances of the National Notification Centre for Waste Substances (LMA) [LMA 1994, Stap 1994a, v.d. Steen 1991, EUROSTAT 1991, Tukker 1993a, Verhage 1991].

In some cases it was impossible to allocate, for instance, the last 10% of a substance to a specific consumption application. In such cases the leaks were estimated on the basis of the average emission factors for the other sectors.

4 SUBSTANCE FLOWS AND EMISSIONS UNDER ENVISAGED POLICY

For the segments which contribute most to the scores in 1990, we investigated the influence of envisaged policy on the pattern of emissions.

Only 'hard' measures established as of the reference date of 1 January 1995 were included. 'Hard' measures were regarded as being target reductions which could be enforced by or by virtue of regulation or to which both the government and the relevant target groups had formally committed themselves. These were:

- requirements with respect to emission reductions in a reference year in the future imposed when a licence was issued;
- agreements in existing Integrated Environmental Targets (IMTs) and covenants, unless discussions with the target group had raised questions about the technical feasibility of certain objectives;
- reduction targets in Dutch or supranational regulations.

In some cases (e.g. the Dry cleaners Environmental Management Decree) no reduction objectives (prescribed targets) are prescribed but rather steps to be taken to counter emissions. In such cases the likely reduction in emissions is estimated on the basis of available background literature.

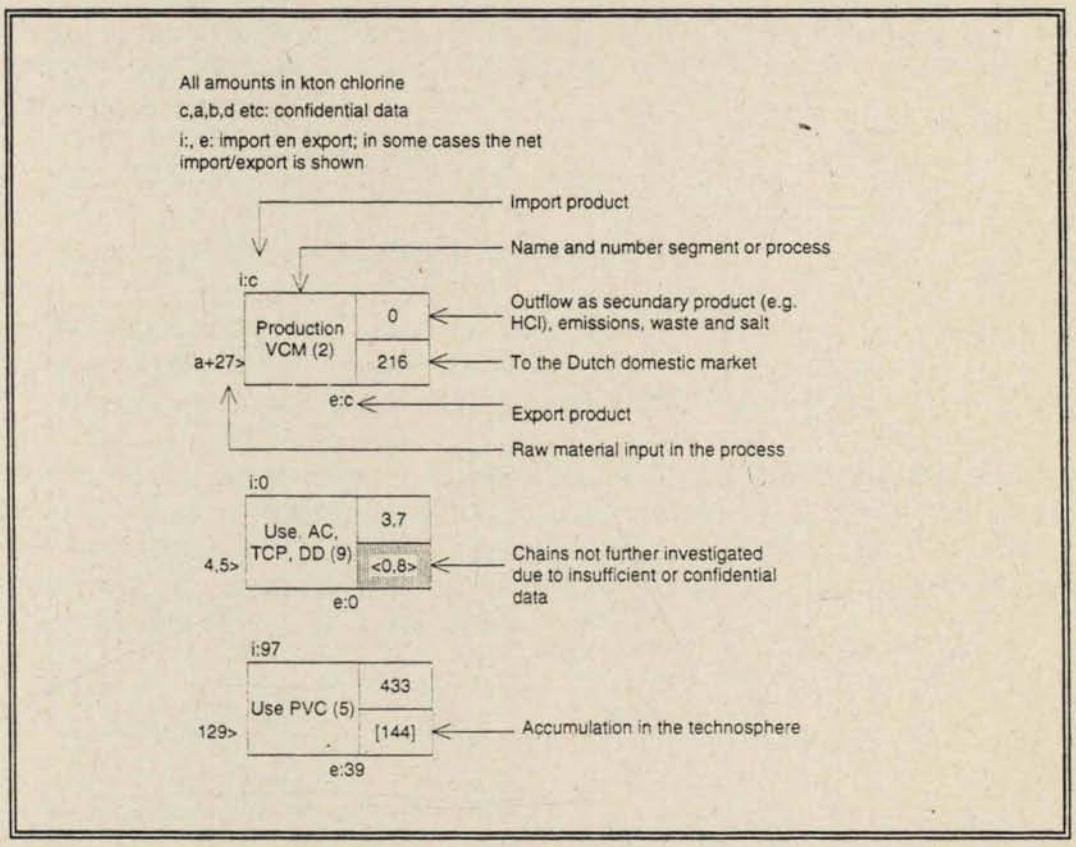
Targets and objectives which are still under discussion (for example, the proposal to ban dichloromethane (DCM) in paint remover) do *not* count. The same applies for 'soft' projections with respect to lower output arising from proposed technical measures by companies, the implementation of which is not 100% certain, etc. Wherever 'hard' information about emission reductions was lacking, the emission figures for 1990 from phase 1 are maintained. No account has been taken of changes in emissions as a result of economic growth or other autonomous developments within the target group. To sum up, in effect the emission figures in 1990 are revised for the cases referred to in sub-section 2.2 to the situation after implementation of the envisaged policy from 1 January 1995.

5 REMARKS AND POINTS FOR DISCUSSION

The sub-section on comments and points for discussion deals with uncertainties in the figures. It also indicates whether the situation described has changed or will change dramatically as a result of government policy that has been implemented, measures expected to be taken by the company or other reasons.

Each segment closes with a detailed substance flow diagram. The legend to this diagram is given below.

Legend for substance flow diagrams (quantities in kt chlorine, excluding internal recycling, 1990)



SEGMENT 1: PRODUCTION OF CHLORINE

1 INTRODUCTION

Five companies produce chlorine in the Netherlands. These are Akzo Nobel (at 3 plants), General Electric Plastics and Solvay. Chlorine and sodium hydroxide and hydrogen are produced by means of electrolysis of kitchen salt. The following reaction takes places:

$$2\ NaCl + 2\ H_2O \longrightarrow 2\ NaOH + H_2 + Cl_2$$

There are three methods of electrolysis:

- mercury electrolysis (Solvay and Akzo Nobel Hengelo);
- diaphragm process (Akzo Nobel Delfzijl);
- membrane process (Akzo Nobel Rotterdam and General Electric).

The difference between these processes lies in the separation of the anode and cathode liquid. In mercury electrolysis this separation occurs with the aid of mercury. In the other methods the electrodes are separated by means of a diaphragm and a membrane. The following sub-section describes the three processes in a little more detail [SPIN, 1993c].

2 PROCESSES

2.1 Mercury electrolysis

In the mercury cell electrolysis process there are two cells. A concentrated NaCl solution flows through the primary cell. The mercury cathode flows along the bottom of this cell. During the electrolysis process the NaCl decomposes, chlorine is produced on the anode and sodium on the cathode. The chlorine is removed and purified. Sodium an amalgam with mercury on the surface of the mercury electrode (Na(Hg)x).

The amalgam flows from the bottom of the cell to the decomposition cell where it decomposes according to the reaction:

$$2\ Na(Hg)x + 2\ H_2O \longrightarrow 2\ NaOH + 2\ H_2 + x\ Hg$$

This produces very pure caustic soda. The mercury is fed back into the electrolysis cell.

The products (caustic soda, chlorine and hydrogen) are purified in a number of steps. Chlorine is cooled, dried with sulphuric acid and liquified. Filtration is used to remove the mercury from the caustic soda. Hydrogen gas is cooled and if necessary compressed. Partly as a result of stringent EU legislation the emissions of mercury during this process have been sharply reduced.

2.2 Diaphragm process

In the diaphragm process the electrolytes are separated by an asbestos diaphragm. The diaphragm separates the chlorine from the caustic soda and hydrogen gas produced during the electrolysis of brine. The cathode process results in a solution of caustic soda in brine, from which soda can be prepared. If necessary, the salt can be (partially) crystallised through the evaporation of the water; however, this leaves caustic soda contaminated with salt behind. The evaporation does not take place in the Netherlands.

2.3 Membrane process

The membrane technology is the latest development in the production of chlorine alkali. The structure of the process is similar to the diaphragm process, with the difference that the barrier between the electrodes is formed by an ion-exchanging membrane. This membrane conducts electric current through the transport of sodium ions. However, OH ions also diffuse through the membrane. These ions are undesirable, and are neutralised by adding hydrochloric acid. The separation with the aid of membranes means that the strength of the caustic soda formed cannot be affected during its formation. The strength of the caustic soda is around 20% by weight and will therefore have to be reduced by evaporation. After evaporation deferrization takes place by mean of filtration over graphite. The chlorine gas formed is cooled, dried with sulphuric acid and compressed. The hydrogen gas is washed to remove the caustic soda, and then again dried, cooled and compressed. The advantages of this process are:

- the process uses less energy than the other two processes;
- the caustic soda is very pure (compared with the diaphragm process);
- substances like asbestos and mercury are not used.

The disadvantages are the substantial investment costs involved and the degree to which the necessary purity can be achieved.

3 SUBSTANCE FLOWS AND EMISSIONS IN 1990

3.1 Production and import/export

Two chlorine producers have supplied figures on the quantities of chlorine they produce. For this study, Akzo Nobel provided a figure for the total quantity of chlorine *sold* as reported in the EUROCHLOR survey for 1990[1]. The amount sold includes the quantity of chlorine imported by Akzo Nobel, which is practically the same as the CBS figure for chlorine imports. Production by Akzo Nobel is calculated from the previously mentioned sales figures minus the CBS figures for chlorine imports to the Netherlands.

These figures show that in 1990 the Netherlands produced 550,600 tonnes of chlorine, around 90,000 tonnes less than previous estimates based on the existing production capacity [SPIN 1993c; Berends 1990]. The figures given here by producers are in fact within a few percent of the figures recorded in the ER-I and are within 56,000 tonnes of the figure for chlorine production in the Netherlands reported by EUROCHLOR [ER-I 1994, EC/BSM/TAUW 1992]. We therefore do not expect there are any major errors in the numbers given here.

On the basis of the ratio between production figures in ER-I for the various Akzo Nobel plants, we estimated the quantity of chlorine which is produced by type of process. Together with the figures given by GEP and Solvay, the following global distribution of Dutch chlorine production by type of process emerges:

-	mercury electrolysis	182,000 tonnes
-	diaphragm process	89,000 tonnes
-	membrane process	279,600 tonnes
	Total	550,600 tonnes

According to the CBS, exports totalled 92,500 tonnes [CBS 1991]. Solvay reported exports of 94,000 tonnes. Neither GEP nor Akzo Nobel exported chlorine in 1990.

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[1] EUROCHLOR is the trade association for European chlorine producers. A number of small inaccuracies in the figures given to EUROCHLOR were corrected in consultation with Akzo Nobel.

It is assumed that Solvay's export figures are the more accurate and Solvay's figure is therefore adopted throughout. Imports amounted to around 29,400 tonnes [CBS, 1991]. With production of 550,600 tonnes, it follows that Dutch consumption was 486,000 tonnes of chlorine.

Table 1.1 shows the sales of chlorine to the other segments based on the statements of the market parties that use chlorine. For reasons of confidentiality, the figures have been aggregated or are not given. Under No. 13 the table includes a quantity of chlorine which is used in the pesticides and specialty division of Shell Nederland Chemie. These production units were closed down in 1992/1993 and are therefore not further discussed in this study. See further the description in the other segments.

3.2 Emissions

Emissions to air occur through the expulsion of air containing chlorine gas. These gases are washed with caustic soda so that hypochlorite is produced from chlorine. Some producers purify chlorine by absorption/distillation, using tetra as absorption agent. This causes emissions of tetra. In 1990 cooling was still done cooling plants which contained CFCs: this is the reason for the CFC emissions from chlorine production recorded in ER-I. Such emissions are not included here but in the segments describing the consumption of tetra and CFCs.

Emissions to air have been taken from ER-I; emissions to water from WIER [ER-I, 1994, RIZA 1994a]. In so far as ER-I covers more substances than WIER, emission figures were supplemented with those from the ER-I.

Table 1.1: Sale of 486,000 tonnes chlorine in 1990 (in tonnes)

Segment no.	Process	Quantity	Segment no.	Process	Quantity
2	EDC/VCM	149,200	18	Production HCFC-22	p.m.
8	AC/ECH/Epoxy	131,000	19	Production te-flon	p.m.
11	Polycarbonate(incl. MDI)	62,527	21	Production CFC 113/114 (incl 18 and 19)	7,473
12	MDI (aggregated with 11)	p.m.	40	Hypochlorite	14,165
13	TDC/aramide	16,000[1]	42	Titanium dioxide	2,000[2]
14	Monochloro-acetic acid (incl. MCPA/MCPP)	32,140	43	Inorganic chlorine compounds	18,608
15	MCPA/MCPP (aggregated with 14)	p.m.		Stock- and rounding off differences	2,100 [3]
17	Production DCM, chloroform, tetra, PER	49,625			

1 Aggregated with quantity of chlorine used in the hex- and specialty division of Shell (since closed down)

2 Estimate by TNO

3 E.g. Solvay reported increased stocks. This discrepancy is regarded as a normal inaccuracy and otherwise disregarded.

More than one process is carried out at the plants of Akzo Nobel (Delfzijl, Hengelo and Rotterdam) and Solvay. Emissions to air are recorded by process in the ER-I. Emissions to water from all processes, however, occur at one location via a single treatment plant. Emissions to water are somewhat arbitrarily allocated to individual processes as follows:

- According to ER-I, dichloromethane (DCM) is used as a solvent by Solvay in another process. It is assumed that this process accounts for the EOCl emission in WIER.
- Akzo Nobel Delfzijl had only very minor emissions of EOCl in 1989 and 1991. In 1990 releases of chloroform and DCM [Wunderink 1993] were unusually high following a calamity and these can be allocated to the halogenated hydrocarbons (HHC) factory. ER-I allocated a limited emission 'HHC, unknown' to chlorine production. On the basis of this figure, 50 kg of the EOCl emission from WIER is allocated to the chlorine production.
- For Akzo Nobel Hengelo emissions of monochloroacetic acid (MCA) and other hydrocarbons are allocated to MCA production.
- For Akzo Nobel Rotterdam the emissions of individual substances are allocated on the basis of causality to the EDC and pesticide production. The EOCl is allocated entirely to EDC (see segment 2).

Table 1.2 gives a list of emissions which can be allocated to the production of chlorine, aggregated over the five companies. For reasons of confidentiality no emissions from individual companies and processes are listed. The table shows that the losses of chlorine are minimal compared with the continued use. However, there are losses due to the disposal of NaCl (salt) with the caustic soda from the diaphragm process, for example. In fact, this is a throughflow of NaCl which is not converted into chlorine during the electrolysis process. It is irrelevant for the purposes of this study which is after all concerned with the Netherlands chlorine balance and not the salt balance. For simplicity's sake, therefore, the net input of NaCl has been retained and equated with the production of chlorine. Figure 1.1 shows the complete substance flow.

Table 1.2 Chlorine-containing emissions to water and air during the production of chlorine in 1990 (kg chlorine; in brackets: kg of substance)

Compound	Air	Water
Chlorine	15.100	p.m.
HCl	542 (588)	
EOCl		50
Total chlorine: 15.692	15.642	50

4 EMISSIONS AFTER ENVISAGED POLICY

The measures to reduce emissions established as of 1 January 1995 are discussed below. The emissions remaining after implementation of this policy have been estimated on the basis of the emission situation in 1990. No account has been taken of changes in emissions as a result of economic growth or other autonomous developments in the target group.

The emissions occurring during the production of chlorine listed in the table below do not appear in the Integrated Environmental Targets (IMT) for the chemical industry, but one underlying Corporate Environmental Plan (BMP) contains an emission scenario for these substances. The emissions in the scenario after implementation of the envisaged policy have been calculated on the basis of the objectives for the year 2000 in the BMP. Measures to reduce emissions which were implemented between 1990 and 1995 have also been taken into account.

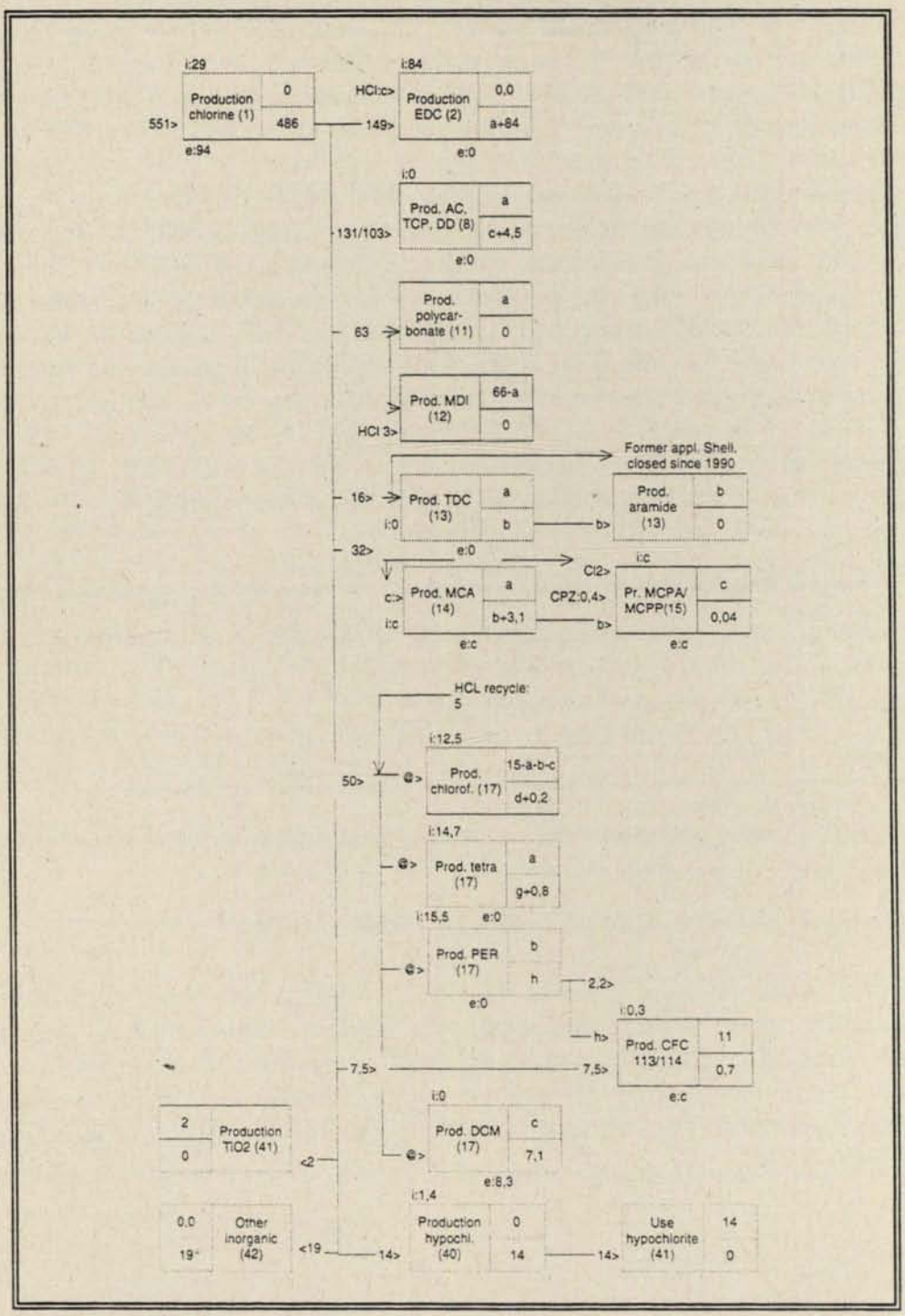
Table 1.3 *Emissions containing chlorine to water and air during production of chlorine after implementation of envisaged policy (kg chlorine; in brackets: kg of substance)*

Compound	Air	Water
Chlorine	7.723	p.m.
HCl	542 (588)	
EOCl		50
Total chlorine: 8.315	8.265	50

5 REMARKS AND POINTS FOR DISCUSSION

Waste water generally contains salt, active chlorine and caustic soda. Bromide, naturally present in brine, is quantitatively converted into bromide by the existing Cl_2, some of which can be converted into bromates (BrO_3). The combination of Cl_2 and Br_2 in the presence of a carbon source can also lead to the formation of trihalomethanes. The degree to which this process occurs is still being studied [SPIN 1993c].

Figure 1.1: Substance flows during production and consumption of chlorine (in kt chlorine, 1990)



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SEGMENT 2: PRODUCTION OF EDC AND VCM

1 INTRODUCTION

ROVIN is the sole producer of dichloroethane (EDC) and vinylchloride monomer (VCM) in the Netherlands. ROVIN is a joint venture of Shell and Akzo Nobel. Production is located at Akzo Nobel's plant in Botlek. The production of EDC and VCM are closely interrelated and have therefore been dealt with in the same substance document. VCM is principally used by ROVIN itself in the production of PVC. The other Dutch manufacturer of PVC, the Limburgse Vinyl Maatschappij (LVM) in Geleen, does not produce VCM but imports it from Belgium (see segment 3: PVC production).

2 PROCESSES

The vinylchloride monomer (VCM) is produced from ethene, chlorine and oxygen according to the following overall reaction:

(1) $2\ CH_2 = CH_2 + Cl_2 + ½\ O_2 \longrightarrow 2\ CH_2 = CHCl + H_2O$

There are a number of distinct steps in this process, which are illustrated in figure 2.1. The intermediate product dichloroethane (EDC) plays a central role in this process. EDC is prepared by direct chlorination or oxychlorination:

- in direct chlorination, ethylene and chlorine are used:

  (2) $CH_2 = CH + Cl_2 \longrightarrow CH_2Cl\text{-}CH_2Cl$

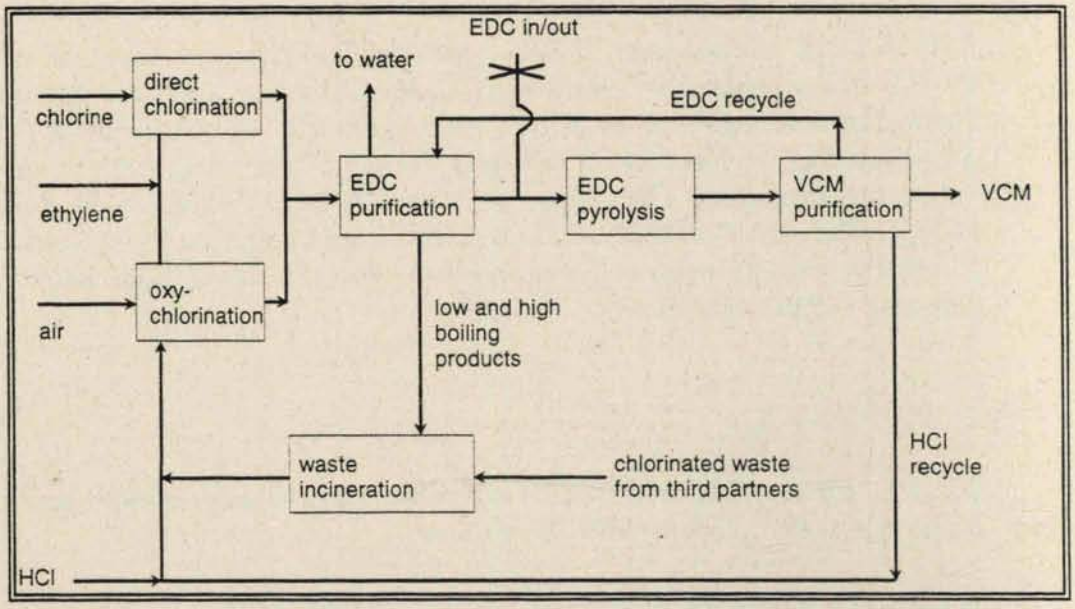
  EDC acts as a solvent. The two gaseous reactants are added to the solution in almost equal measures at around 50°C. The reaction heat is used to evaporate the EDC that is produced. Iron chloride is used as a catalyst.

- in oxychlorination, ethylene, hydrogen chloride and oxygen are used.

  (3) $CH_2 = CH_2 + 2\ HCl + ½\ O_2 \longrightarrow CH_2Cl\text{-}CH_2Cl + H_2O$

  This reaction occurs at 220-240°C and under increased pressure (4 bar). Iron chloride is used as a catalyst.

Figure 2.1: Diagrammatic representation of the production of VCM



The EDC that is produced is cooled and then washed with water and caustic soda to remove HCl, Cl_2 and contaminants that are soluble in water. Water is removed from the EDC by distillation. Once removed, the water is cleaned using a stripper and a biological treatment with activated carbon.

In the above reactions, chloroethane, trichloromethane, tetrachloromethane, 1,1,2-trichloroethane and tetrachloroethane are produced as by-products, as well as traces of chlorinated aromates. The EDC is cleaned of these contaminants by distillation. The by-products together account for less than 2.5% (ECETOC 1991). The by-products, together with highly chlorinated waste from third parties, are treated in an incinerator for liquid and gaseous waste, during which HCl is recovered and then used again in the oxychlorination.

After being treated, the EDC is converted into VCM by pyrolysis at around 500°C and 10 bar.

(4) $CH_2Cl\text{-}CH_2Cl \dashrightarrow CH_2 = CHCl + HCl$

This produces various chlorinated and non-chlorinated by-products. These, together with non-reacted EDC, are returned to the process. The HCl that is released is used in the oxychlorination. During the process solid waste is released in the form

of carbon from process filters, calcium chloride from the drying of process flows and sewage sludge. This waste is incinerated as chemical waste at AVR-Chemie (editor's note: AVR-Chemie is the most important Dutch hazardous waste management company).

3 SUBSTANCE FLOWS AND EMISSIONS

3.1 Substance flows

ROVIN provided an aggregated balance for the flows in figure 2.1. This shows the inflow of chlorine, EDC (excluding internal recycling) and HCl (excluding internal recycling but including the HCl recovered from waste from third parties) and the outflow of EDC and VCM. According to ROVIN, there are no emissions of chloride (salt) into water of any significance for the balance.

There is a discrepancy of around 10% between the figures for VCM production supplied by ROVIN and those in the ER-I and the report 'PVC and Chain Management' [Caesar 1992]. The latter source refers to an annual production of 430,000 tons of VCM.

The Limburgse Vinyl Maatschappij (LVM) imports (and is the sole Dutch company to do so) a substantial quantity of VCM. This figure is not reported by the CBS but was supplied to TNO/CML by LVM. The CBS does report exports of VCM (214,000 tons in 1990). This figure is lower than ROVIN's figure for the volume exported. The export figure given in the report 'PVC and Chain Management' falls between the figures given by ROVIN and by the CBS. The discrepancies can be reasonably explained by changes in stocks, the delay between the time a contract is concluded with a foreign country and when the shipment actually occurs, differences in the definition of import/export or transhipment, etc.

For the purposes of this study, we have adopted the figures provided by ROVIN. The principal reason for doing so is that the figures supplied by ROVIN and LVM produce a figure for domestic PVC consumption which accords reasonably closely with the report 'PVC and Chain Management' [Caesar 1992]. The alternative would be to adopt lower VCM production, lower exports of VCM and higher domestic PVC production on the basis of production figures from the ER and export figures from the CBS. The emission data in the ER and WIER, and consequently the results of the emission assessment, are the same in both variants. For the purpose of prioritising leaks, which is the principal objective of this study, it therefore makes no difference which option is taken.

In 1990, ROVIN's consumption of chlorine for VCM amounted to 149,200 tons. The HCl used by ROVIN and acquired externally came from other chlorine processes. This recycling has taken place since the 1970s. No figures are given for the use of HCl or production of VCM for reasons of confidentiality. The same applies for VCM imports by the LVM. Table 2.1 shows the overall consumption of VCM in the Netherlands.

The HCl used by ROVIN includes 6,500 tons derived from the conversion of 10,000 tonnes of waste from third parties. We were unable to ascertain the precise source of this waste. Some of it comes from Shell and some from abroad [LMA 1994, Stap 1994]. Segment 7 shows that in 1993 Shell supplied a quantity of trichloropropane which contained 2,600 tons of chlorine. For simplicity's sake, TNO and CML have adopted the same volume for 1990; it was assumed that the remainder of the waste was imported.

The imports of EDC amounted to 112,000 tonnes, according to the CBS [CBS 1991]. According to Eurostat, however, *exports* of EDC to the Netherlands from EU countries alone totalled 130,000 tonnes [EUROSTAT 1991]. This figure possibly includes transhipments. The volume of EDC used at ROVIN exceeded the sales of EDC; net imports of EDC (calculated as chlorine) for use in VCM production in 1990 were 26,830 tons. Table 2.1 presents a summary of EDC consumption on the basis of segments 2, 5 and 6. Although consumption is slightly higher than the CBS figure for imports, the difference falls within a reasonable margin of error. It is assumed that 116,800 tons of EDC was imported. Figure 2.2 shows the substance flows in the production of EDC and VCM.

Table 2.1 *Substance flows for EDC and VCM in 1990 in tonnes of chlorine (between brackets: in tonnes of product)*

Substance	Production	Import/export	Consumption	Application
EDC	-	83,740(116,800)	83,740 (116,800)	26,830 VCM 56,600 Amines 310 Other
VCM	*	*	216,000 (380,000)	213,000 PVC 3,000 Copolymers

* Confidential

3.2 *Emissions*

Figures for emissions have been taken from ER-I and WIER. We have corrected them for a value for diffuse emission of VCM which later proved incorrect (see also sub-section 4). The emissions to air from the ER processes 'production of VCM' and incineration of waste substances, including the generation of processing steam, are allocated entirely to VCM production. The emissions to water in the ER and WIER have been aggregated and have to be allocated to the processes taking place at Akzo Nobel Rotterdam (production of chlorine, VCM and pesticides). Emissions of EDC and EOCl have been allocated entirely to VCM production. Although EOCl may also be produced during production of pesticides, the use of chlorine in this process is negligible compared with VCM production. There are small emissions of chlorobenzenes, which are allocated to the pesticide production on the basis of information from Berbee [1987].

According to Evers [1989] and Greenpeace [undated], dioxins may be produced during the production of EDC. According to RIZA, around 1 g TEQ of dioxins was released into water in 1985 [Wunderink 1993]. This quantity has since been sharply reduced by the commissioning of a treatment plant [Wunderink 1993]. The annual emission of dioxins to water at an EDC/VCM plant in Norway is around 0.1 g TEQ [SFT 1993]. Sources of emissions of dioxins to air were the subject of an extensive national study and measurement programme [Bremmer 1994]. The report confirmed Akzo Nobel's statement that emissions of dioxins as a result of the incineration of chemical waste at Akzo Nobel amounted to 0.09 g TEQ TCDD a year [Akzo Nobel 1994; Bremmer 1994]. According to Bremmer's study, process emissions of dioxins from the chemical industry are minor compared with those from their vapour treatment plants and incinerators. It is therefore assumed that the incinerator is the major source of dioxins during EDC production.

LCA databases consulted generally give less detailed emission figures than those we acquired and used as described above. In one case an emission of $6.58 * 10^{-11}$ grams of chlorobenzenes per kg of PVC produced was reported during the production of EDC/VCM/PVC, which would represent an emission of around 25 grams of chlorobenzenes for the Netherlands. This quantity does not contribute significantly to the scores on the themes, so that the accuracy of this figure was not investigated further. The figure was not used in the calculations.

4 EMISSIONS UNDER ENVISAGED POLICY

The measures to reduce emissions established as of 1 January 1995 are discussed below. The emissions remaining after implementation of this policy have been

estimated on the basis of the emission situation in 1990. No account has been taken of changes in emissions as a result of economic growth or other autonomous developments in the target group.

Chlorine and HCl are not mentioned in the IMT. An emission scenario for these substances is given in the underlying corporate environmental plan (BMP). Since 1990 the company producing them has implemented a number of measures which have reduced the emissions. We have based the calculation of the emissions for the situation after implementation of the envisaged policy on:

- the objectives for the year 2000 in the BMP;
- information provided by the company concerned about the measures already taken for substances which are not included in the BMP.

An important measure already taken is the flaring out and incineration of the emissions from the tank storage of 1,2-dichloroethane. Another reason why the emission figures under envisaged policy are a bit lower than the figure for 1990 in the ER-I is an error in the reporting of emissions for the ER in 1990. In the calculation of the diffuse emission of vinyl chloride in 1990 some emissions were counted twice because the results of a screening measurement were added to the diffuse emissions calculated with the EPA method.

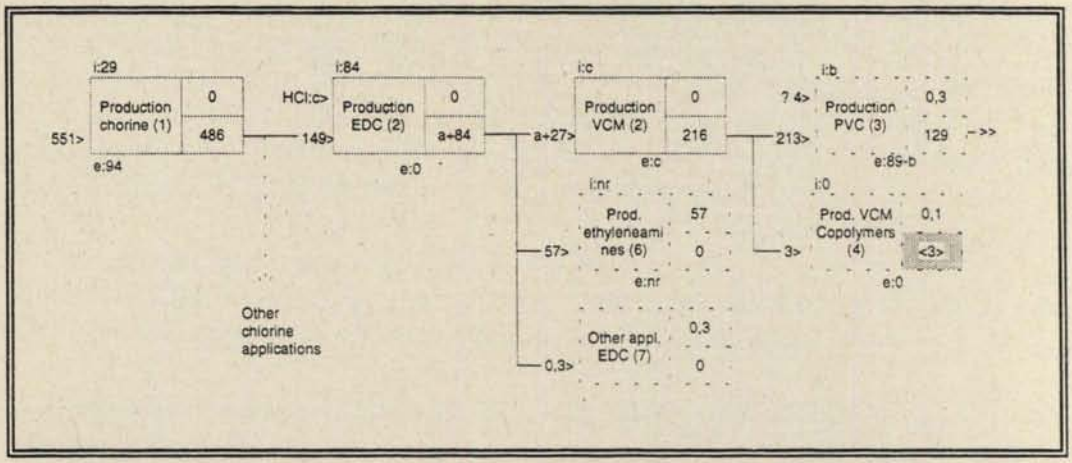
The ER-I also includes an emission of chlorohydrocarbons (CHCs) which is not further specified. This is not mentioned in the BMP. Given the nature of the measures for the other substances (such as the flaring out and incineration of respiratory losses and waste gases) it can in fact be assumed that emission reductions comparable to those for the substances referred to in the BMP will be achieved. The approach to the reduction in emissions of CHCs is therefore to adopt the general reduction percentage included in the IMT for volatile organic substances (VOS) under the theme of acidification.

5 COMMENTS AND POINTS OF DISCUSSION

The incinerator at Akzo Nobel also incinerates waste from third parties. The allocation of emissions from the incinerator to the VCM production is therefore somewhat arbitrary.

Emission figures at the process level from ER-I and WIER can not be published without the consent of the company concerned. Since in this case the process takes place at only one company in the Netherlands, it is impossible to disguise the figures by aggregating them. The company concerned declined a request by TNO/CML to publish the emission figures adopted for 1990 and the future situation in this report.

Figure 2.2: Substance flows in production of EDC and VCM (in kt chlorine, 1990)



SEGMENT 3: PRODUCTION OF PVC

1 INTRODUCTION

Two companies in the Netherlands produce polyvinylchloride (PVC) from vinyl chloride monomer (VCM). These are the Limburgse Vinyl Maatschappij (LVM) and ROVIN, a joint venture of Shell and Akzo Nobel. LVM is a subsidiary of the Belgian concern Tessenderloo Chemie. Its plant is located in the DSM factory in Geleen. The ROVIN plant is in the grounds of Shell-Pernis.

2 PROCESSES

ROVIN produces its VCM at Akzo Botlek and transports it to the production site by pipeline. LVM receives VCM, also by pipeline, from its parent company in Belgium.

The VCM is fed to a reactor in doses, together with a suspension stabiliser, a pH buffer, an anti-foam agent and an initiator (organic peroxides). VCM reacts to PVC as follows:

(1) n $CH_2 = CHCl \longrightarrow CH_2 - CHCl - CH_2 - ChCl -$

When a conversion rate of 80 to 90% is reached, the polymerization is stopped with the aid of an inhibitor. After recovery of unconverted VCM, the suspension is filtered and temporarily stored. Residues of VCM are then stripped with open steam and transported to a gasometer. In fact, all water flows with a VCM content are treated in this way before being pumped to a water treatment plant. According to statements by the companies, after stripping the water is "VCM-free". In view of the high vapour pressure of VCM (3.4 bar at 20°C) this seems likely. There will probably be some emissions to water of the auxiliary substances (organic peroxides, interfacial active substances, inhibitor, methanol, pH buffers and anti-foam agent) [SPIN 1993e].

The VCM-free suspension is processed into dry PVC powder by centrifugation and drying. The air used for this is released into the atmosphere via a bag filter. VCM is recovered from various gas flows containing VCM using a condenser. PVC is produced in batches. Before the reactor is refilled it is first rinsed with water to remove residues of PVC.

During production, PVC is released as waste as a result of the filtering of the "lumps" formed in the suspension. These lumps are disposed of at an incineration plant for chemical waste. The cleaning of the reactors also produces PVC waste: a certain amount of PVC clings to the walls despite the fact that they have a coating to prevent this.

3 SUBSTANCE FLOWS AND EMISSIONS IN 1990

According to ROVIN and LVM, 213,000 tons of VCM (calculated as chlorine) was used for the production of PVC in 1990. Scarcely any chlorine is lost during the production of PVC except through minor (in relation to the output) process emissions and waste flows. Table 3.1 shows the production and import/export of PVC based on figures from ROVIN, LVM and CBS [1991]. The discrepancy accords reasonably with the domestic market volume according to Caesar [1992]. There is a discrepancy of around 2% which can be explained by inaccuracies and uncertainties in the various figures (see, inter alia, the discussion on the volume of VCM production in Segment 2, sub-section 3). An additional factor is that in converting quantities of PVC into quantities of chlorine, those supplying the figures appear to have rounded off the conversion factors in different ways. In the overall balance of the Netherlands' chlorine chain, the discrepancy of 4,359 tons is treated as imports.

Table 3.1 Substance flows for PVC in 1990 (in tons of chlorine; between brackets: tons of PVC)

Compound	Production [Akzo 1994, LVM 1994]	Net exports [CBS 1991]	Inaccuracies	Domestic consumption [Caesar 1992]
PVC	213,000 (369,500)	88,700 (154,000)	4,359 (7,500)	128,571 (223,000)

The major emissions to air are of VCM and PVC powder. There are further small emissions of methanol, secondary butyl alcohol and freon. Most of the emissions come from numerous small sources, such as leakages through seals and during maintenance work. The major points for emissions of PVC powder are the outlets of the washing towers. Emissions of PVC powder also occur during the ventilation of bunkers [SPIN 1993d].

For LVM, the VCM emissions to air are taken from ER-I. ROVIN renovated its plant in mid-1992 which led to a considerable improvement in the situation with regard to emissions compared with 1990. At ROVIN's request, the post-1992 emission figures for VCM have been adopted [see e.g. Caesar 1992, SPIN 1993e]. Emissions of PVC powder, external disposal of PVC coagulate for incineration and landfill with sewage sludge have been calculated from figures provided by the companies concerned and/or the literature [SPIN 1993e]. Although there are generally no figures for 1990, it has been assumed that those for 1990 will not differ significantly. Emissions to water appear to be zero on the basis of the description in SPIN. Table 3.2 lists the emissions. Figures have not been broken down by individual company for reasons of confidentiality. Figure 3.1 presents a substance flow diagram for the production of PVC.

Table 3.2 Emissions containing chlorine into water, air and waste during production of PVC in 1990 (in tonnes of chlorine; in brackets: tonnes of substance)

Compound	Air	Water	Waste
VCM	55.3 (90)	-	-
PVC powder	80 (140)	-	-
PVC coagulate	-	-	43 (76)
PVC in sewage sludge	-	-	114 (200)
Total: 292.3	135.3	0	157

4 EMISSIONS UNDER ENVISAGED POLICY

The measures to reduce emissions established as of 1 January 1995 are discussed below. On the basis of the emission situation in 1990, the emissions remaining after implementation of this policy have been estimated. No account has been taken of changes in emissions as a result of economic growth or other autonomous developments in the target group.

Of the emissions occurring during the production of PVC mentioned in the table below, reduction targets for vinyl chloride are included in the Integrated Environmental Target (IMT). The calculation of the emissions for the situation

after implementation of the envisaged policy are based on the objectives for the year 2000 in the BMPs. PVC powder is not mentioned in the IMT or the BMPs. The emissions for these are all assumptions. Table 3.3 shows the future emission situation based on these assumptions.

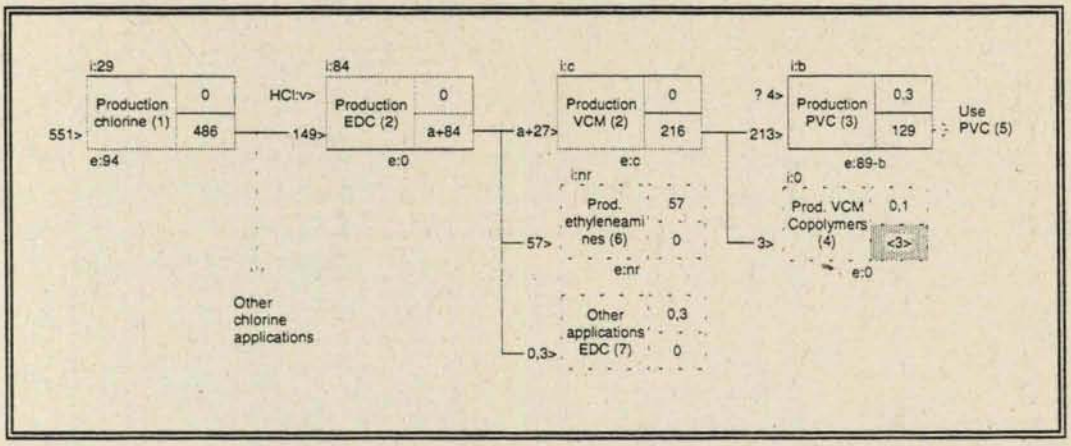
Table 3.3: Chlorine-containing emissions to water and air during the production of PVC after envisaged policy (tonnes chlorine; in brackets: tonnes of substance)

Compound	Air	Water
VCM	39 (69)	-
PVC powder	80 (140)	-
Total chlorine:	119	0

5 COMMENTS AND POINTS FOR DISCUSSION

The production of PVC receives little attention in most of the literature on organic by-products containing chlorine [Greenpeace, Bremmer 1994]. A more recent study by Greenpeace does not exclude the possibility that PVC could be contaminated with dioxins. Greenpeace refers to a concentration of 0.86 to 8.69 ppt TEQ in PVC suspension, based on a study by the Swedish Environmental Protection Agency [Greenpeace 1994]. We found no further reference to this in any of the literature.

Figure 3.1: Substance flows in production of PVC (in kt chlorine, 1990)



SEGMENT 4: PRODUCTION OF PVC COPOLYMERS

1 INTRODUCTION

Two companies, BASF Nederland and VINAMUL in Geleen produce copolymers of vinylchloride monomer (VCM). The following sub-section discusses the steps in the process in more detail. The description is primarily based on the SPIN document on BASF [SPIN 1993a].

2 PROCESSES

PVC latex is produced by means of polymerization by doses. The following raw materials are used:

- VCM;
- acrylates;
- emulsifiers;
- initiator;
- water.

The overall reaction formula is as follows:

VCM + acrylic esters -----▸ PVC / acrylic polymer (dispersion)

The monomers are mixed in a mixing tank. The polymerization is then initiated. After reaching a conversion rate of around 98% the product is stripped with steam. The water containing VCM is cleaned in a vacuum with the aid of steam stripping. The water is then taken to the chemical-physical treatment plant. The water and the vapour from the vacuum system are taken to a VCM recovery unit. The VCM is almost entirely absorbed by means of active carbon.

3 SUBSTANCE FLOWS AND EMISSIONS IN 1990

During the production of PVC copolymers, all chlorine is in principle incorporated in the product. Losses only occur due to misbatches, etc. A total of 5,500 tonnes of VCM is used. This corresponds with around 3,000 tonnes of chlorine. On the basis of data from both companies, the percentage of waste in the worst-case scenario is 3% (90 tonnes of chlorine). According to figures from one of the

companies the waste is entirely composed of material from depolymerized material which can be disposed of as industrial waste [Tel. inf. 1994].

Given the very small quantity of chlorine compared with other chlorine-containing polymers, the product was not followed any further. Imports and exports of PVC copolymers are disregarded. The destination of the 2,910 tonnes of chlorine in the product is classified as 'unknown' in the overall analysis in Part 1.

The ER-I only lists one company, for which a VCM emission to air is recorded. This is small compared with that recorded for the production of EDC/VCM and PVC. For reasons of confidentiality this figure is not published here. There is no record for either company in WIER for releases of chlorinated compounds to water.

Figure 4.1 gives the substance flow diagram.

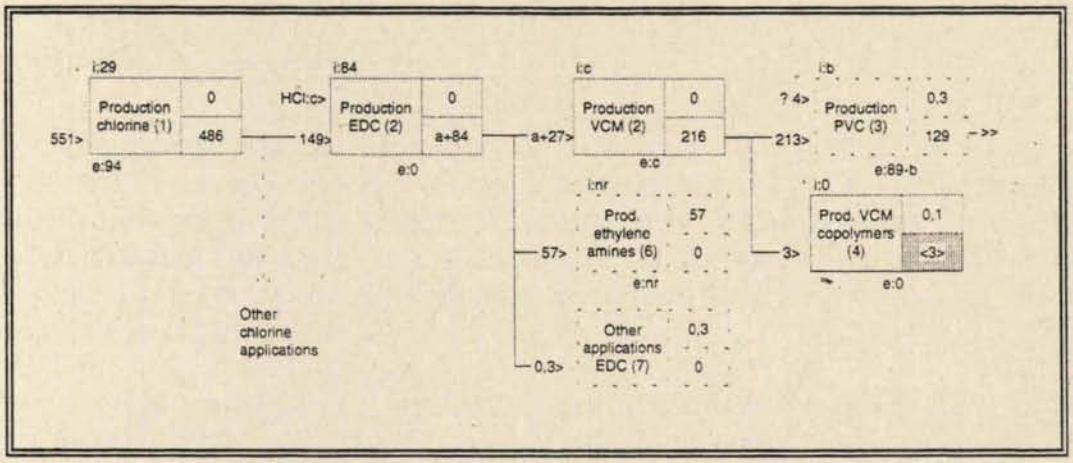
4 EMISSIONS UNDER ENVISAGED POLICY

The emissions from the process in this segment make no real contribution to the score on environmental themes for the situation in 1990. For simplicity's sake, the emission figures for 1990 have also been used in the assessment of the situation arising after implementation of the policy established as of 1 January 1995.

5 REMARKS AND POINTS FOR DISCUSSION

Neither company is regarded as a priority company for the purposes of the RAP/NAP [Wunderink 1993]. During a national measurement programme carried out by RIZA in 1992 a small quantity of AOX was measured in the effluent at one company. The quantity of EOCl was below the detection limit. The other company was not covered.

Figure 4.1: Substance flows in production of PVC copolymers (in kt chlorine, 1990)



SEGMENT 5: CONSUMPTION APPLICATIONS OF CHLORINATED POLYMERS

1 INTRODUCTION

This segment covers the application of polymers containing chlorine, which are generally used in long-life products. In terms of a substance flow analysis, this means that the output is added to an existing stock in the economy. Each year a certain quantity of the material is discarded from the stock as it reaches the waste stage. As far as long-life applications are concerned, however, these quantities bear no relation to the output.

In terms of volume, PVC is by far the most important chlorinated polymer. Other polymers containing chlorine, such as PVC copolymers and neoprene, are disregarded for the purposes of further discussion. The following sub-section discusses the areas of application of PVC. The waste flows are discussed in sub-section 3.

2 APPLICATIONS OF PVC

2.1 Description

Pure PVC is a hard, brittle material which degrades at around 100°C and is sensitive to deterioration under the influence of light and air. Pure PVC is therefore supplemented with additives, which improve PVC's properties and allow it to be processed. With the right choice of additive, it is possible to tailor the material to various applications. There are many types of additive. Examples include plasticizers (especially phthalic acid esters), pigments (titanium white, lead chromates, cadmium pigments), heat and light stabilizers (usually organic substances based on lead, tin, zinc, barium, potassium and cadmium), lubricants (wax, fatty alcohols, fatty acid esters), fillers (chalk, china clay, talcum, magnesium oxide), flame retardants (antimony trioxide, aluminium hydroxide, magnesium oxide, chloroparaffins), impact modifiers and fibres used as reinforcing materials. In terms of weight, the plasticizers are the most important additives. The plasticizer content of PVC normally accounts for between 20 and 40% of the weight of PVC, although there are soft PVC formulas which consist for more than 60% of plasticizers.

The range of applications of PVC and its various formulas is wide and varied. In Western Europe in 1992 around 18% of PVC was used in packaging, 55% in the building trade and 27% in other applications.

A distinction is usually made between short-life and long-life applications and between hard PVC and soft PVC (with a high percentage of plasticizer). In Western Europe, 13% of the total volume of PVC has a useful life of less than 2 years and 25% lasts between 2 and 15 years. The remaining 62% of PVC articles have a useful life of longer than 15 years.

PVC is used in, among others, the car industry, the health care sector and the sport and recreation sector. Long-life applications of PVC are generally found in the building trade (cable insulation, pipes, gutters and window frames).

2.2 Substance flows

In 1990, 223,000 tonnes of PVC powder was processed in the Netherlands. Including 72,000 tons of additives, the total volume was 295,000 tons of PVC. Table 5.1 gives a breakdown of the use of PVC among the various applications, as well as the import/export balance. Figures from Caesar [1992] have been converted into volumes of PVC and chlorine. A distinction has been made between long-life applications (which fall under the total PVC stock in the economy) and short-life applications, especially packaging. According to Caesar [1992], the current stock of PVC in the economy exceeds one million tons.

There are no figures available on imports and exports of PVC in goods other than those specifically mentioned in the table. In sub-section 4, these are derived indirectly from the production figures, estimates on accumulation and the known quantity of waste, and are estimated at 96,700 tons.

Emissions containing chlorine from a number of the processors of PVC included in the ER are nil, as is more or less to be expected with this inert polymer. Here it has been assumed that processing of PVC causes no significant (chlorine-containing) emissions. Any emissions caused by the use of solvents and adhesives are dealt with in the segments describing the consumption applications of halogenated hydrocarbons (segments 22 - 36).

Table 5.1: *PVC substance flows in 1990 in tonnes of chlorine (between brackets: in tonnes of PVC, excluding additives).*

Area of application	Production	Net exports	Domestic consumption		
			Long-life	Short-life	
				excl. additives	incl. additives
Hard PVC					
Building applications and pipes	63,997 (111,000)[1]	1,730 (3,000)	62,267 (108,000)		
Packaging	28,251 (49,000)[2]	20,102 (34,866)		8,149 (14,134)	(15,000)
Soft PVC					
Cables, floor coverings, other[4]	34,593 (60,000)[3]	16,853 (29,230)	15,375 (26,668)	2,365 (4,102)	(8,000)
Production waste	1,730 (3,000)			1,730 (3,000)	(3,000)
Total	128,571 (223,000)	38,685 (67,096)	77,636 (134,668)	12,244 (21,236)	(26,000)

1. This figure includes the addition of 12,000 tons of additives
2. This figure includes the addition of 3,000 tons of additives
3. This figure includes the addition of 57,000 tons of additives.
4. Packaging and waste are classified as short-life. The volume of short-life was adjusted to correspond with the quantity of short-life PVC waste (see Table 5.2) by supplementing from the category "Cables, etc". The volume of additives per type of short-life use is estimated pro rata to the total quantity of additives per area of application.

3 WASTE FLOWS

The ultimate purpose of the PVC varies. Only short-life applications (especially packaging) return in the form of waste within a period of 1 to 2 years. Other applications are added to the volume of PVC in circulation in society. At the end of the life of the long-life applications, the PVC is disposed of as waste. The volume of waste does not, however, bear any relation to the output or imports/exports.

In waste policy, waste substances are generally classified according to the source. The categories described below are those of relevance for PVC. All quantities stated in this sub-section relate to the volume of PVC in waste, in other words *including* additives.

Household waste
Household waste (HW) is the normal "waste in sacks" from households. It contains PVC in the form of packaging and other, more long-life applications. Separated collection and recycling of plastics did not yet exist and has been ignored. According to Caesar [1990], in 1988 the volume of PVC in HW totalled 31,000 tonnes, of which 13,000 tonnes was packaging waste (short-life) and 18,000 tonnes was long-life PVC. This figure has been maintained for 1990. Nagelhout [1992] stated that in 1990 37% of the plastic waste in HW was incinerated and 63% was landfilled. It has been assumed that these proportions also applied for PVC.

Bulk household waste
Bulk household waste (BHW) consists to a large extent of discarded durable goods. These may contain PVC. It has been assumed that only long-life applications are involved. According to Caesar [1990], the volume of BHW in 1988 amounted to 6,000 tonnes; for the sake of simplicity this figure has also been adopted for 1990. Of the plastic waste in bulk household waste in 1990, 63% was landfilled and 37% was incinerated. There was no recycling [Nagelhout 1992].

Office, shop and service waste
This waste flow originates from offices, shops and services (OSS). A large share of the waste consists of packaging, paper and putrescible waste. It contains PVC in the form of packaging and other, more long-life, applications. In 1988 the total volume was 13,000 tonnes [Caesar 1990]. In 1990 the ratio of incineration to landfill was 24:76 [Nagelhout 1992]. Recycling of PVC has been ignored. The ratio of short-life (packaging) to other waste has been estimated on the basis of the volume of plastic packaging in OSS according to Joosten [1989] and the quantity of plastic waste according to Van Duin [1991]. It has been assumed that this ratio also applies for the PVC share.

Industrial container waste
This waste flow originates from industry and involved a total of 12,000 tonnes in 1988 [Caesar 1990]. This figure has also been taken for 1990. The waste concerned is production waste during the processing of PVC and other, usually long-life, products. For simplicity's sake, only the 3,000 tonnes of production waste referred to in sub-section 2 as short-life waste has been included. In 1990 7.5% of industrial waste was incinerated and 92.5% was landfilled [Nagelhout 1992]. It has been assumed that these proportions also apply for PVC. It has also been assumed that recycling of PVC in 1990 can be ignored.

Car wrecks

Car wrecks were almost entirely shredded in 1990. After separating the ferrous and non-ferrous materials, the remaining waste, including the PVC it contained, was landfilled. Shredder waste was not yet incinerated in 1990 [Nagelhout 1992]. According to Caesar [1990], car wrecks contained around 8,000 tonnes of PVC in 1988. This figure has also been maintained for 1990.

Building and demolition waste

Building and demolition waste (BDW) generally contains long-life PVC. BDW was partly dumped and partly separated, after which the brick-like share was recycled. The remainder was usually landfilled [AOO 1992]. It has been assumed here that the volume of PVC in BDW amounts to 16,000 tonnes [Caesar 1990], consists entirely of long-life materials and that all of it is landfilled.

In this way, we estimate that in 1988 (the most recent figures!) there was a total of 86,000 tonnes of PVC waste. It has been assumed that the same volume can be adopted for 1990. Table 5.2 presents a breakdown by type of waste flow. The figures include additives. According to Nagelhout [1989], PVC in waste (including additives) has a chlorine content of 50%. It follows from this that 43,000 tonnes of chlorine in the form of PVC reaches the waste stage; according to Table 5.2, 34,100 tonnes of this is landfilled and 8,900 tonnes is incinerated. There was a limited amount of external recycling in 1990 (one thousand tonnes). This is further ignored.

Table 5.2 Source of PVC in waste in 1988 (in tons of PVC, including additives). Source: [Caesar 1990][1]

Type of waste	Volume			Landfilled	Incinerated
	Short-life	Long-life	Total		
Household waste	13,000	18,000	31,000	19,500	11,500
Bulk household waste		6,000	6,000	3,700	2,200
OSS waste	10,000	3,000	13,000	10,000	3,100
Industrial waste	3,000	9,000	12,000	11,100	900
Building and demolition waste		16,000	16,000	16,000	
Car wrecks		8,000	8,000	8,000	
Total	26,000	60,000	86,000	68,300	17,700
Total chlorine	12,244[2]	30,756[4]	43,000[3]	34,100[3]	8,900[3]

1. It is assumed that figures for 1990 are comparable.
2. See volume of chlorine in Table 5.1 under 'short-life, excl. additives'
3. According to the Memorandum on plastic waste [Nagelhout 1989], around 50% of PVC, including plasticisers and additives, consists of chlorine.
4. Calculated from total minus short-life.

4 COMPARISON OF PRODUCTION, ACCUMULATION AND WASTE FLOW

In theory, the volume of short-life PVC in the waste stage should be equal to the short-life PVC applications. Comparison of Tables 5.1 and 5.2 shows that these quantities can be made to correspond without having to make forced assumptions.

According to Table 5.2, around 30,756 tonnes of chlorine are released as waste from long-life applications. Building and piping are important long-life applications. From Table 5.1 it can be seen that these account for 108,000 tonnes of PVC, to which around 12,000 tonnes of additives are added. The volume of chlorine equivalent is 62,267 tonnes, which represents a chlorine content of around 52%. Table 5.2 shows that some 16,000 tonnes of PVC is released as building and demolition waste. If it is assumed that the chlorine content of this waste is also 52%, we arrive at a figure of around 8,300 tonnes of chlorine. To summarise, for the building industry this signifies an inflow of 62,267 tonnes, an outflow of around 8,300 tonnes and therefore an accumulation of approximately 54,000 tonnes of chlorine in PVC. This represents an accumulation of 90% of the inflow, which

corresponds with the generally accepted estimates of the use of PVC in building and piping [Bhairo 1994] and also seems reasonable, for instance, on the basis of the useful life of products (see sub-section 2).

With a total of 30,756 tonnes of chlorine in PVC waste and 8,300 tonnes of chlorine in PVC in building and demolition waste, around 22,400 tonnes of chlorine comes from waste from other long-life PVC applications. Table 5.1 shows, however, that the *inflow* is only 15,375 tonnes, which is unusual since it is generally accepted that PVC in fact *accumulates*. Estimates have been made at the European level of the net accumulation rate for various long-life PVC applications (e.g. agriculture, motor industry and other applications). The weighted average is around 80% [Bhairo 1994]. With this percentage, an outflow of 22,500 tonnes to waste is only explicable with an inflow of 112,000 tonnes and an accumulation of 89,600 tonnes. With a net domestic inflow of 15,375 tonnes, there must therefore be diffuse imports in products of around 96,700 tonnes of PVC expressed as chlorine.

This figure is naturally only a rough estimate. It can, however, be explained on the basis of reasonable assumptions and is defensible. Since the figure has no influence whatever on emissions from the chlorine chain, and therefore on ultimate priority setting, we have chosen not to devote too much effort to providing a more solid foundation for the diffuse imports of PVC.

Overall, this estimate leads to an accumulation of around 143,600 tonnes of PVC: 54,000 tonnes in building and piping and 89,600 tonnes in other applications.

5 EMISSIONS UNDER ENVISAGED POLICY

The emissions from the processes in this segment only contribute to the score on landfill for the situation in 1990. In consultation with the steering committee it was decided not to present a survey of the policy measures with respect to this segment. For simplicity's sake, the emission figures for 1990 have also been used for the assessment of the situation arising after implementation of the policy established as of 1 January 1995.

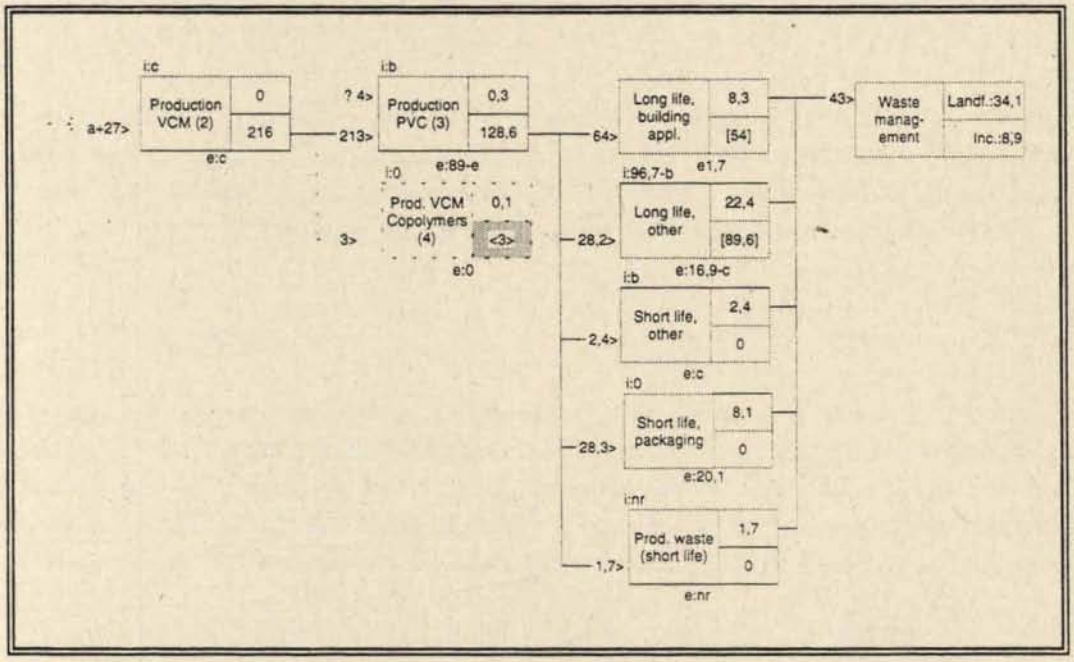
In practice this means that four developments, which have mutually contradictory effects on the volume of landfill, are ignored. These are:

- the market for short-life applications, such as packaging, is declining. This effect leads to a lower supply of PVC in the waste phase;
- the PVC market as a whole has grown slowly since 1993, probably mainly in long-life applications [Tukker 1995]. In the long term this could lead to a greater supply of PVC in the waste phase;
- there is a growing volume of accumulated PVC in society. At a certain point in time this will be released as waste which will lead to a greater supply of PVC in the waste phase;
- the government has reached agreement with various sectors of industry for the recycling of PVC. This concerns mainly long-life applications, such as window frames and tubes. This will lead to a decline in the supply of PVC which has to be processed as final waste.

6 COMMENTS AND POINTS FOR DISCUSSION

The volume of recycled PVC waste was still very small in 1990. The recycling of PVC is steadily increasing. Significant steps have been taken to encourage recycling, especially of PVC products and applications used in the building industry. The target is to recycle 100% of these products. Recycled PVC is generally used again in building materials, such as wall elements.

Figure 5.1: Substance flows in applications of PVC (in kt chlorine, 1990)



SEGMENT 6: PRODUCTION OF ETHYLENEAMINES

1 INTRODUCTION

Ethyleneamines are produced at DOW Benelux in Terneuzen and Delamine in the Akzo Nobel plant in Delfzijl. Delamine is a joint venture of Akzo Nobel and Tosoh. The following sub-section describes the stages in the production process. The description is based on the SPIN document for this process [SPIN 1993b].

2 PROCESSES

Ethyleneamines are produced at DOW Benelux in Terneuzen and at Delamine in Delfzijl by the ethylenedichloride process. This involves ethylenedichloride (EDC) reacting at 140°C and 140 bar with an overmeasure of ammonia (NH_3). The by-product vinylchloride produced during the process is incinerated. The reaction produces a mix of aminohydrochloride salts. Some of the possible reactions are:

$$\underset{\text{EDC}}{CH_2Cl\text{-}CH_2Cl} + 2\ NH_3 \longrightarrow Cl^-.H_3N^+\text{-}CH_2\text{-}CH_2\text{-}^+NH_3.^-Cl + 2\ NaOH \longrightarrow$$

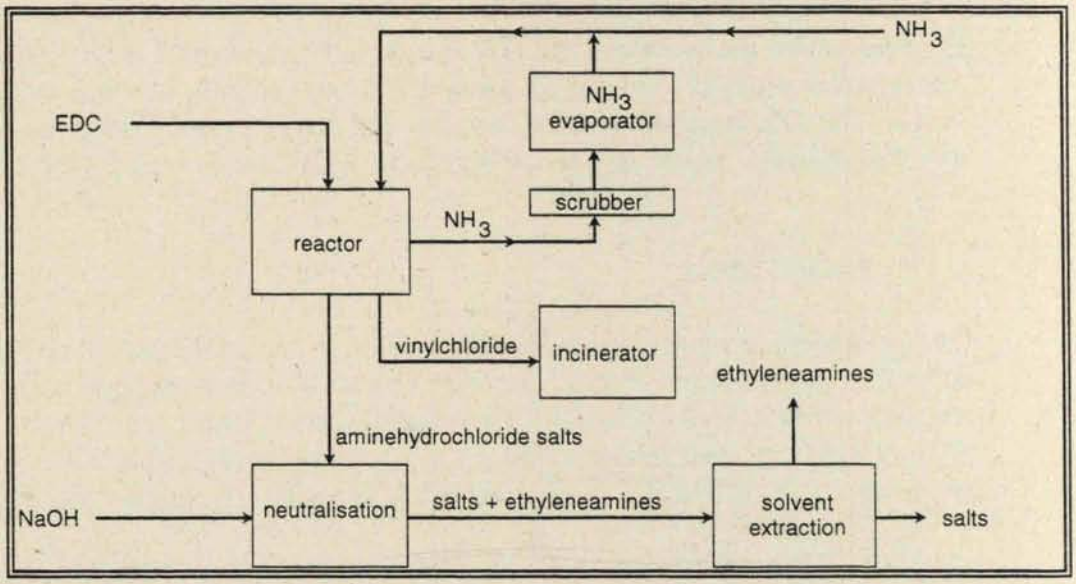
$$\underset{\text{Ethylenediamine}}{H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2}. + 2\ NaCl + 2\ H_2O$$

These salts are neutralised with caustic soda, creating free ethyleneamines and inorganic salts (primarily NaCl). After the amines of the organic salts have been separated with the aid of solvent extraction, the various fractions of ethyleneamines are separated and purified by means of distillation.

The proportions of the reaction products can be varied by using the NH_3 overmeasure and reactor dimensions. Reaction products might be: ethylenediamine (EDA), piperazine (PIP) diethylenetriamine (DETA), aminoethylpiperazine (AEP), triethylenetetramine (TETA), tetraethylenepentamine (TEPA) and other polyamines.

A diagram of the process in given in Figure 6.1.

Figure 6.1 Diagram of the production of ethyleneamines



3 SUBSTANCE FLOWS AND EMISSIONS IN 1990

According to figures from Delamine and DOW Benelux 56,608 tonnes of EDC (expressed as chlorine) were used in the production of ethyleneamine in 1990. About 56,600 tonnes were released as Cl. The losses in the form of emissions to water and air constituted a negligible quantity in the balance.

Delamine is not covered by the ER in view of its lack of priority and weight. DOW Benelux is included. The ER figures correspond closely with those given by DOW Benelux. The DOW Benelux has sharply reduced EDC emissions since 1990 with the introduction of floating roofs on storage tanks.

The emissions to water from both DOW Benelux and Delamine are included in WIER. In both cases, the record involves total emissions from all processes taking place at the factories in Terneuzen and Delfzijl respectively.

Besides ethyleneamines, in 1990 DOW Benelux also produced vinylidenechloride (VDCM). The emissions to water included in WIER for trichloroethene,

tetrachloroethene, trichloroethane, tetra and chloroform are allocated to production of VDCM. According to the SPIN document and ER-I figures for emissions to air these substances are in fact released during the production of VDCM.

According to figures from DOW Benelux EOCl is released during VDCM production, the eythleneamine production and other processes in the approximate ratios of 40:30:30. The quantity of EOCl reported in WIER is allocated to the various processes in these proportions. Besides ethylenamine, chlorine and chlorinated solvents are also produced at the plant in Delfzijl. The emissions to water in 1990 were largely the result of a calamity which can be allocated to the production of halogenated hydrocarbons. For pragmatic reasons, all the EOCl emissions at Akzo Nobel have been allocated to the production of halogenated hydrocarbons.

Table 6.1 gives of list of emission figures. Because they cannot be disguised through aggregation, emissions to air are not included in the table.

Table 6.1 Chlorine-containing emissions to water and air during production of ethyleneamines in 1990 (kg of chlorine)

Compound	Air	Water
Chlorine	*	-
HCl	*	-
VCM	*	-
EDC	*	-
EOCl	-	348
Total chlorine	p.m.	348

4 EMISSIONS UNDER ENVISAGED POLICY

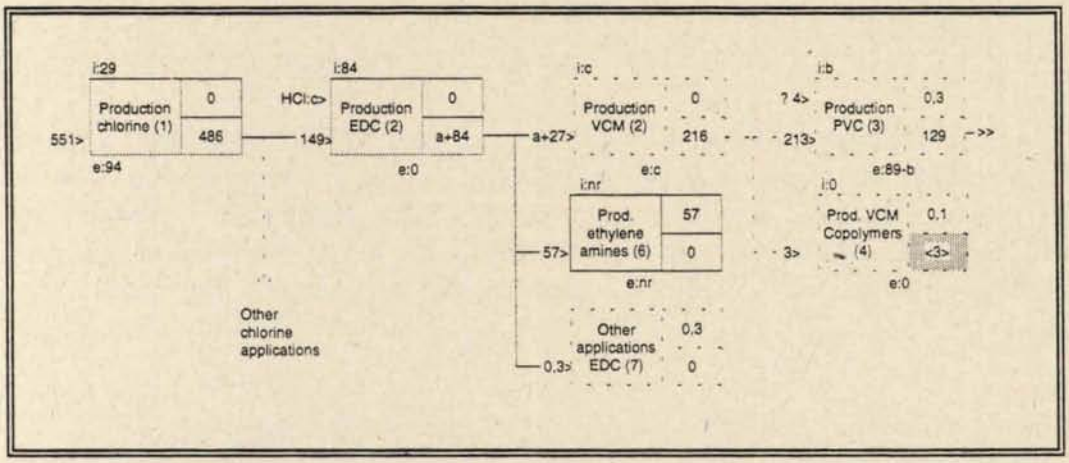
The emissions from the process in this segment make no essential contribution to the score on environmental themes for the situation in 1990. For simplicity's sake, the emission figures for 1990 have also been used in the analysis of the situation arising after implementation of the policy established as of 1 January 1995.

5 COMMENTS AND POINTS FOR DISCUSSION

Akzo Nobel Delfzijl (where Delamine is established) and DOW Benelux were included in the AOX/EOX measurement programme carried out by RIZA in mid-1992. At Akzo Nobel the quantity of EOX and AOX was similar to the quantity of chlorine which was released to water in the form of known individual compounds. At DOW Benelux the quantity of EOX and AOX was a factor of 5 to 8 higher [RIZA 1994a and b]. The reasons for this could be measurement errors, (e.g. inorganic) chlorine which was incorrectly identified with EOX/AOX or emissions of organic chlorine compounds which could not be individually measured.

Emission figures at process level from ER-I and WIER can not be published without the consent of the relevant company. In this case emission figures could not be disguised by aggregation. The companies concerned declined a request from TNO/CML to publish the emission figures adopted for 1990 and the future situation in this report.

Figure 6.2: Substance flows in production of ethyleneamines (in kt chlorine, 1990)



SEGMENT 7: OTHER CONSUMPTION APPLICATIONS OF EDC

1 INTRODUCTION

Small quantities of 1,2 EDC are used for purposes other than the production of VCM or ethyleneamine. It is used by one company as a solvent; the pharmaceutical industry uses EDC for, among other things, the production of phenylglycylchloride, and a third firm uses it to produce flavourings. These applications are discussed in this substance document. EDC is also used as scavengers in leaded petrol.

2 PROCESSES AND SUBSTANCE FLOWS IN 1990

Solvent
1,2 EDC is used as a solvent by a chemical company. According to the company's own statement, practically all EDC leaves the company as waste. The emission to air is limited, according to ER-I. According to WIER, the company releases a few kilos of EOCl, possibly originating from other processes [ER-I 1994, RIZA 1994a]. The company was covered by the AOX/EOX measurement programme conducted by RIZA in mid-1992. A very high annual freight of AOX was measured [RIZA 1994b].

Pharmaceuticals
EDC is used as a solvent in the pharmaceutical industry. Most is used in the production of phenylglycylchloride (FGZ). A tetra/EDC mix is used in the production of this compound. There is an emission to air of around 180 tonnes [ER-I 1990, SPIN 1992b]. A further 2 tonnes is disposed of as waste with the solvent layer from a phase separator. It is recycled as far as possible by distillation. EDC and tetra are probably also disposed of in the distillation residue. The quantity is not reported in the SPIN document or by the National Notification Centre for chemical waste. They are otherwise disregarded here [SPIN 1992a, LMA 1994]. According to the SPIN document on the pharmaceutical industry a number of other smaller emissions to air occur in other processes. The total emission to air is 198 tonnes according to the SPIN document on phenylglycylchloride and the pharmaceutical industry. Emission to water is 0.55 tonnes [SPIN 1992a and 1992b].

Production of flavourings
The ER-I reports an emission of 88 tonnes to air at a producer of fragrances and flavourings. There are no figures for the quantity of waste and the total consumption. They have been estimated by TNO and they are presented in Table 7.1.

Use as scavenger in leaded petrol
EDC is used as a scavenger in leaded petrol. According to Bremmer [1994] the chlorine concentration in leaded petrol is around 50 mg/litre, which amounts to 90 tonnes of chlorine at an annual consumption of 1.8 billion litres of petrol, mainly due to the use of EDC. These scavengers are not produced in the Netherlands but are imported. The chlorine is chiefly emitted as HCl. There are also emissions of dioxins [Marklund 1990]. Bremmer [1994] estimates the emissions in the Netherlands at 7 g TEQ TCDD. Raad [1993] concludes for the time being that in the absence of positive indications there are no emissions of PCBs from traffic.

Table 7.1 Use of 1,2 EDC as solvent in 1990 in tonnes of chlorine (in brackets: in tonnes of substance)

Target group	Consumption	Air	Water	Waste
Chemical industry	14 (19)[1]	0.029 (0.041)		14 (19)
Pharmaceutical industry	144 (201)[2]	142 (198)	0.39 (0.55)	1.4 (2)
Fragrances and flavourings industry	64 (90)[3]	63 (88)		1.4 (2)
Traffic/scavenger	90 (133)	[4]		
Total:	312 (443)	205 (276)	0,39 (0,55)	16,8 (23)

1) Company's statement. Emission to air according to ER-I.
2) Total emissions in SPIN document on the pharmaceutical industry and phenylglycylchloride.
3) Emission to air according to ER-I. TNO estimate of waste based on pharmaceutical industry.
4) Emission of 90 tonnes of chlorine as HCl, 7 g. TEQ TCDD.

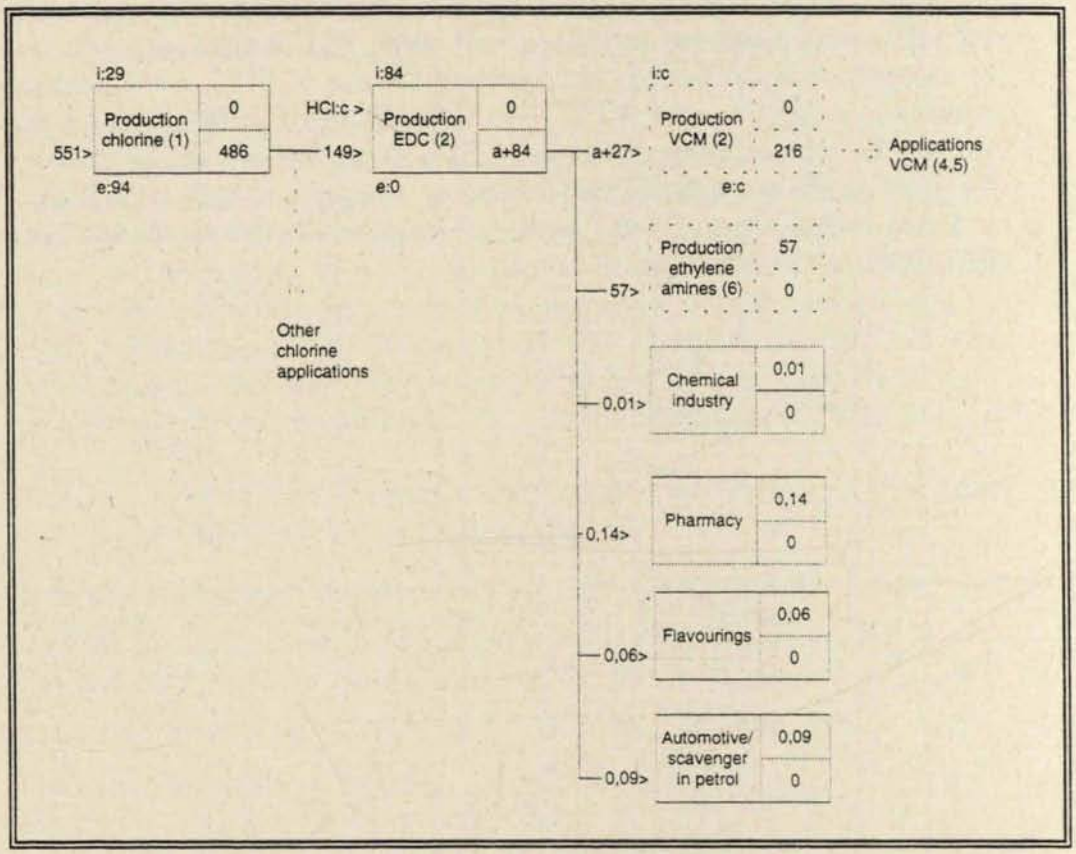
3 EMISSIONS UNDER ENVISAGED POLICY

The emissions from the process in this segment make no essential contribution to the score on environmental themes for the situation in 1990. For simplicity's sake, the emission figures for 1990 have also been used in the analysis of the situation arising after implementation of the policy established as of 1 January 1995.

4 COMMENTS AND POINTS FOR DISCUSSION

Apart from VCM production, tank storage and production of ethyleneamines, the ER-I does not include any processes from which EDC is emitted. Previous studies of halogenated hydrocarbons only refer to the use of EDC in the production of scavengers in leaded petrol [ECTOTEC 1991, Bremmer 1988]. We were informed verbally by the compilers of ER-I and EDC producers that this process is not in fact used in the Netherlands. Scavengers are mainly imported from England and added to leaded petrol. On this basis, it is assumed that there are no other major EDC users in the Netherlands.

Figure 7.1: Substance flows in other applications of EDC (in kt chlorine, 1990)



SEGMENT 8 PRODUCTION OF ALLYLCHLORIDE, EPICHLOROHYDRINE AND EPOXY

1 INTRODUCTION

Epichlorohydrine (ECH, 1-Chlorine-2,3-Epoxypropane) is the most important raw material for the production of epoxy resin. In the Netherlands ECH is produced for this purpose by Shell Nederland Chemie (SNC). Until recently, ECH was also used as a raw material for glycerine in the Netherlands. This application was phased out at the end of the 1980s [SPIN 1993e]. ECH is produced from chlorine and propene. An intermediate product is allylchloride (AC, 1-chlorine-2-propene); by-products are trichloropropane (TCP), dichloropropane and dichloropropene (DD-mix).

The production of AC, ECH and epoxy resin are dealt with in the same document. They are all produced at the same locations and SNC only provided aggregated figures for these processes. AC, ECH, TCP and DD are also used externally. According to SNC, figures for **1990** are difficult to find. For this segment, therefore, **1993** has been taken as the reference year.

2 PROCESSES

2.1 Production of AC and ECH

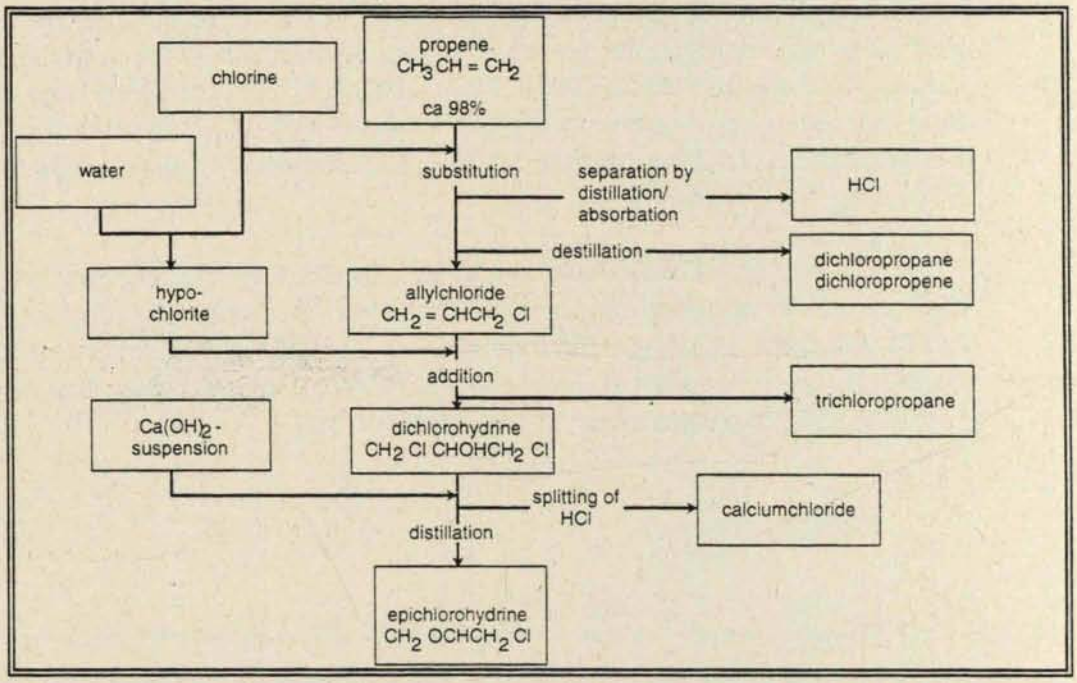
Epichlorohydrine (ECH) is prepared via the intermediate products allylchloride (AC) and dichloroydrine (DCH) from the raw material propene and chlorine. Figure 8.1 presents a diagram illustrating the process [Bremmer 1988].

Raw AC is produced from the raw materials propene and chlorine. The production units consist of two parallel reactor trains, one of which is always in operation while the other is cleaned. Waste water flows are given an initial treatment and then taken to the biological treatment plant (CWZ).

During the reaction the by-products hydrochloric acid (HCl) and a blend of 1,3-dichloropropene and 1,2-dichloropropane (DD-mix) are produced. After separating a propene/hydrochloric acid fraction in a prefractionator, AC is distilled to remove DD, among other things. The "light end" (LE) fractions are burned in two incinerators, during which hydrochloric acid is recovered.

Crude dichlorohydrine is then prepared from purified AC and hypochlorite, which is produced from chlorine and water. 1,2,3-trichloropropane is formed as a by-product of this.

Figure 8.1 Diagram of production of AC, ECH, DD and TCP [Bremmer 1988]

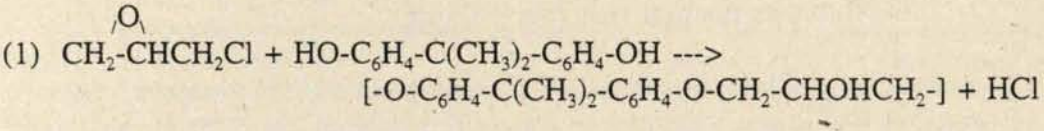


ECH is formed by allowing the raw DCH to react with lime milk ($Ca(OH)_2$). This produces $CaCl_2$, which is released to water. The crude ECH, which is contaminated with DCH and TCP, is stripped from the water with steam and then purified by distillation. DCH and TCP are produced during this process as bottom drainage. DCH is then recirculated internally.

The by-products of AC and ECH production, DD and TCP, are purified with the aid of a film-evaporator. The 'heavy ends' (HE) of this purification are burned in the previously mentioned incinerator. Both the dirty water flows from the occasional cleaning of the crude allylchloride units and the water from the ECH strippers are taken after pre-treatment to the waste water treatment installation. The water is then successively cooled, neutralised with hydrochloric acid so that fixed substances such as $Ca(OH_2)$ and $CaCO_3$ dissolve, and finally decomposed in a stripper of CO_2 [SPIN 1993d].

2.2 *Internal use of ECH and DD*

ECH is used internally to produce epoxy resins. Epoxy resin is generally prepared by a reaction of ECH with bisphenol A under the influence of caustic soda and with the separation of NaCl (salt) according to:



(1) $CH_2\text{-}CHCH_2Cl + HO\text{-}C_6H_4\text{-}C(CH_3)_2\text{-}C_6H_4\text{-}OH \rightarrow [\text{-}O\text{-}C_6H_4\text{-}C(CH_3)_2\text{-}C_6H_4\text{-}O\text{-}CH_2\text{-}CHOHCH_2\text{-}] + HCl$

DD is purified in a film evaporator and distilled. During this purification waste is produced consisting mainly of chlorinated hydrocarbons. This waste is incinerated. Dichloropropane is produced during treatment, which is sold externally.

3 SUBSTANCE FLOWS AND EMISSIONS 1993/1990

3.1 Production

Because of an upgrading of the factory it was felt to be pointless to draw up a balance for 1990. Furthermore, according to Shell the relevant figures can not be found. *Given this situation, we chose 1993 as the reference year for the production of AC, ECH and related products such as DD and TCP. The external uses of the products (segments 10, 11 and 12) have also been described for 1993.*

For the purpose of this study flows which are internally circulated, such as HCl, DCH and other chlorine-containing by-products, are not significant. The same applies for the various 'light ends' and 'heavy ends' (waste flows) which are burned in the company's own incinerators. Shell has therefore prepared an aggregated substance balance for 1993 for the production of AC, ECH and epoxy resins.

For 1990, the incoming chlorine stream was 131,000 tonnes. In 1993 this was 102,700 tonnes [Shell, 1994]. For commercial reasons, the outward flow of TCP, ECH, DD and AC were only provided to TNO/CML in aggregated form. The balance provided by Shell was closed, at 400 tonnes of chlorine. Bremmer [1988] gives key figures for the quantities of by-products, including HCl, which are released during the production of ECH. On the basis of quantities of HCl released reported by Shell and with the aid of the key figures, an estimate of the production of each substance was prepared. These were, expressed in quantities of chlorine:

- 22,000 tonnes HCl sold externally (Shell figure)
- 7,100 tons ECH sold externally
- 800 tonnes AC sold externally
- 2,600 tonnes TCP sold externally
- 10,500 tonnes ECH for production of epoxy resins
- 5,800 tonnes DD mix incinerated or processed internally
- 2,500 tonnes internal HCl (Shell figure)

According to Shell, in the AC/ECH production 51,000 tonnes of chlorine in the form of $CaCl_2$ are released into water. The internal use of ECH, HCl and DD led to releases to water of 17,700 kt Cl (salt). A further 1,100 tonnes of product, calculated as product, are sold externally. This is probably dichloropropene. In net terms, the use of 102,700 tonnes of chlorine in the ECH plant thus gives us:

- 22,000 tonnes of HCl sold externally;
- 7,100 tonnes of ECH sold externally
- 800 tonnes AC sold externally
- 2,600 tonnes of TCP sold externally
- 1,100 tonnes of dichloropropene sold externally
- 51,000 tonnes $CaCl_2$ to water
- 17,700 tonnes Cl to water.

The difference in the balance of 400 tonnes is treated as a normal discrepancy. According to Shell, these estimates are accurate enough for the purpose of this study.

3.2 Import, export and domestic consumption

Imports of AC are not recorded separately by the CBS. AC falls under the category 'Other saturated chlorinated acyclical hydrocarbons'. In 1990 these imports were practically entirely accounted for by 1,1,2-chloroethane, a raw material for VDCM production (see segment 28). The exports in this category were less than 1,000 tonnes in 1990 [CBS 1991]. The production of dichloropropene by Shell is almost equal to the figure for consumption in agriculture [NEFYTO 1993]. Imports and exports of dichloropropene, AC and TCP are therefore assumed to be zero. CBS does not give export figures for ECH. According to the European counterpart of the CBS, EUROSTAT, other EU countries reported imports of 16,000 tonnes from the Netherlands in 1990 [EUROSTAT 1991]. For 1993, including exports to non-EU countries, exports of 18,000 tonnes are assumed. The import and export of AC, DD, TCP and ECH is

shown in Table 8.1. Figure 8.2 illustrates the overall substance flow of AC, ECH and other products.

Table 8.1: Substance flows of DD, AC, TCP and ECH in 1993 in tonnes of chlorine (between brackets: tonnes of product)

Substance name	Production	Import[1]	Export	Consumption
AC	800	-	-	800
TCP	2,600	-	-	2,600
DD	1,100 (1,700)	-	-	1,100 (1,700)
ECH[2]	7,100 (18,500)	2,000 (6,800)	6,900 (18,000)	2,800 (7.300)

[1] Import in 1993 according to CBS [1994a]

[2] Excluding internal use by Shell

3.3 Emissions

Emissions have been taken from the ER-I and WIER. They are figures for 1990, because figures for 1993 are not yet entered in ER-I and WIER. Since the process emissions have no effect on the balance, they are of no further significance.

All releases to air from SNC reported in ER-I, except those releases which are clearly derived from the ER-I processes 'production of VCM' 'production of cyclical hydrocarbons' and 'production of pesticides' are allocated to the production of AC/ECH and epoxy resin. The production of VCM is described separately in segment 4. The production of cyclical hydrocarbons (hexachlorocyclopentadiene) and pesticides has since stopped. Emissions related to it are therefore excluded from this study. Furthermore, emissions from cooling plants (CFCs) and solvents during other processes (e.g. production of polypropylene) are covered in the segments describing the applications of CFCs and solvents. All chlorine-containing emissions from Shell's incinerators are attributed to the ECH process. Because waste from the pesticide section is also incinerated in this oven, this means the emissions are overestimated. According to Shell's figures, dioxin emissions of 1 gram TEQ/year to air occur. This figure accords with data from the national dioxin programme [Bremmer 1994]. This dioxin emission will be reduced to 0.02 g TEQ/year after 1996 [Shell 1994].

A complicating factor for emissions to water is that releases take place via a central water treatment plant owned jointly by SNR (Shell Nederland Refinery) and SNC. The emission of chlorine-containing compounds are in fact almost entirely attributable to the ECH plant and to the pesticides division [Berbee 1987, Canton 1979]. Emissions of chlorobenzenes are allocated, on the basis of (likely) causality, to the pesticides division. Since this production has been stopped they are otherwise ignored. The other emissions to water included in the ER can be allocated on the basis of causality to the production of AC/ECH etc. (see also Berbee [1987] and Canton [1979]. According to Shell's figures, there was a dioxin release of 0.3 g 2,3,7,8-TCDD-equivalent [Shell 1994]. In 1985 this was estimated by RIZA at 1 g [RIZA 19894]. The release of EOCl amounted to 20 tonnes in 1990. This has been reduced to a little more than 10 tonnes/year [Wunderink 1993].

4 EMISSIONS UNDER ENVISAGED POLICY

The measures to reduce emissions established as of 1 January 1995 are discussed below. On the basis of the emission situation in 1990, the emissions remaining after implementation of this policy have been estimated. No account has been taken of changes in emissions as a result of economic growth or other autonomous developments in the target group.

Of the emissions that occur during the production of allylchloride, epichlorohydrine and epoxies, target reductions for emissions have only been included in the integrated environmental target (IMT) for dichloroethane.

An emission scenario has been prepared for a number of other substances in the underlying Corporate Environmental Plan (BMP). Furthermore, since 1990 a number of measures have been taken in the production company which have reduced emissions. The calculation of the emissions for the situation after implementation of the envisaged policy is based on the objectives for the year 2000 in the BMP. During this study it appeared that the BMP of the company concerned took no account of a relevant measure already taken. Shell has executed a so-called "dirty air" project aimed at reducing diffuse emissions of allylchloride and epichlorohydrine, among others. There are no hard figures for the reductions achieved. For the sake of caution, therefore, only the reductions included in the BMP are incorporated for the situation in the year 2000 and no account has been taken of the potential effects of the 'dirty air' project.

The ER-I also records an emission of chlorohydrocarbons (CHCs) which was not further specified. This is not mentioned in the BMP. Given the nature of the

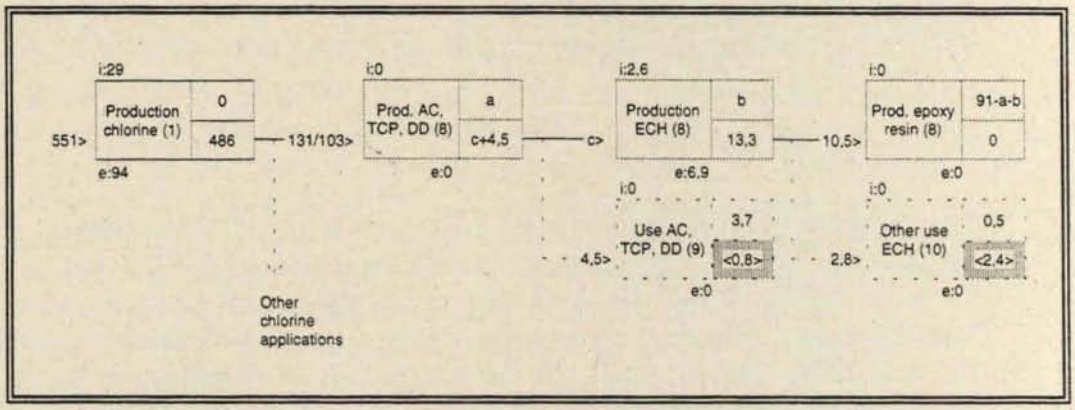
measures for the other substances (such as the encapsulation and incineration of losses of breath and waste gases) it can in fact be assumed that emissions will be reduced in line with the substances that are referred to in the BMP. The approach taken to the reduction of emissions of CHCs is therefore to adopt the general reduction percentage included in the IMT for VOS under the theme acidification.

5 COMMENTS

The company was included in the AOX/EOX measurement programme carried out by RIZA in mid-1992. The quantity of chlorine measured as EOX and AOX is in the same order of magnitude as the quantity of chlorine released into water in the form of known individual compounds. These are mainly hexachloropropylethers [Canton 1979, Berbee 1987]. In the absence of a classification factor, these emissions are not otherwise included in the assessment. The EOCl emissions to water are the subject of discussions between Shell and RIZA.

Emission figures at the process level from ER-I and WIER can not be published without the consent of the company concerned. Since in this case the process takes place at only one company in the Netherlands, it is impossible to disguise the figures by aggregation. The company concerned declined a request by TNO/CML to publish the emission figures adopted for 1990 and the future situation in this report.

Figure 8.2: Substance flows in production of AC, ECH and epoxy resin (in kt chlorine, 1993)



SEGMENT 9: APPLICATIONS OF DICHLOROPROPENE, TCP AND AC

1 INTRODUCTION

Dichloropropene, tricholoropropane (TCP) and allylchloride (AC) are used in various processes. This substance document discusses them. As with the production of ECH the reference year is **1993**.

2 PROCESSES AND SUBSTANCE FLOWS IN 1990

Allylchloride
Allylchloride is used mainly for the production of ECH. Other possible applications are in the production of pesticides and pharmaceuticals. According to Bremmer [1988], they are probably not used in these sectors in the Netherlands. Another possible application is the production of allylalcohol. A telephone survey for this study failed to discover any Dutch users of AC. Shell informed us verbally that some of the AC is exported to Belgium [Shell 1994]. No quantities were mentioned. TNO and CML have designated the destination of the entire volume of 800 tonnes of AC (expressed in chlorine) as 'unknown'.

Trichloropropane
TCP is a compound with little commercial value. According to figures from Shell, TCP is sometimes exported as a raw material for the production of pesticides. It is usually incinerated as chemical waste.

In the period 1990-1992, according to the National Notification Centre for Waste Substances a sizeable amount of liquid halogenated waste was deposited by Shell, largely with Akzo Nobel [LMA 1994, Stap 1994]. According to Akzo Nobel it processed around 10,000 tonnes of waste for third parties in 1990, corresponding to around 6,500 tonnes of chlorine. For simplicity's sake, it is assumed here that all TCP from Shell was incinerated at Akzo Nobel (2,600 tonnes of chlorine in 1993). It is further assumed that the volume in 1990 did not differ from 1993. Emissions during this incineration have already been covered in segment 2.

Dicholoropropene
In the past a mix of dichloropropane and cis/trans dicholoropropene was used as a soil decontaminant in agriculture. In the mid-1980s this involved 5,000 to 6,000 tonnes of DD mix per year [ER-C 1994, Bremmer 1988]. Since the beginning of the 1990s only dichloropropene may still be used. Segment 8 assumes the use of 1,700 tonnes of dichloropropene in agriculture (corresponding to 1,100 tonnes of

chlorine). This figure accords reasonably with the consumption of soil decontaminants for 1992 given by NEFYTO [NEFYTO 1993]. In the context of the legislation on pesticides, the entire quantity represents a permitted leak into the environment. This is discussed further in segment 37 (pesticides application).

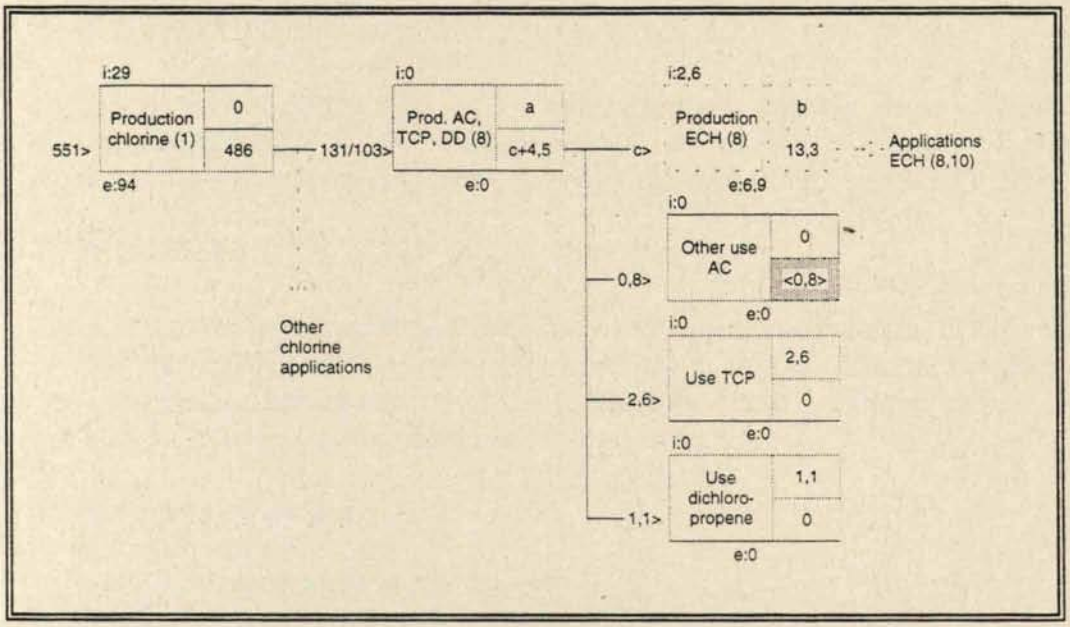
3 EMISSIONS UNDER ENVISAGED POLICY

The emissions from the processes in this segment do not contribute to the score on the environmental themes for the situation in 1990. The use of dichloropropene will be dealt with in segment 38: Pesticides, and no emissions are included for the other substances for 1990. For simplicity's sake, these figures for 1990 are also adopted for the analysis of the situation arising after implementation of the envisaged policy as of 1 January 1995.

4 COMMENTS AND POINTS FOR DISCUSSION

None.

Figure 9.1: Substance flows in applications of AC, TCP and dichloropropene (in kt chlorine, 1993)



SEGMENT 10: OTHER PRODUCTION WITH ECH

1 INTRODUCTION

The production of epoxy resin is the most important application of epichlorohydrine (ECH). ECH is also used as a raw material for a number of other processes. This substance document discusses the other applications of ECH.

2 PROCESSES

According to the information document on halogenated hydrocarbons, ECH is also used for the production of glycerine [Verhage 1991]. This application was phased out in the Netherlands at the end of the 1980s [SPIN 1993e]. For the purposes of this study a number of other applications were traced:

- production of (co)polymer;
- production of flocculant;
- production of other ECH derivatives.

Production of copolymer
According to the manufacturer's figures, all chlorine remains in the product during the production of the copolymer. Because the quantity of chlorine in copolymers is small compared with bulk polymers like PVC, this product was not followed any further.

Production of flocculant
During the production of flocculant chlorine is converted into chloride, which is released to water when the flocculant is used.

Production of other ECH derivatives
Other ECH derivatives are produced by Chemische Fabriek Zaltbommel and by Servo Delden. In the production of derivatives chlorine remains bound in organic form. In one case, dichloropropanol is formed as a by-product which is used as a solvent in the pharmaceutical sector. The ECH derivatives are mainly used for modifying starch and cellulose. These modified compounds are used mainly in the paper industry. In this process, the manufacturer states that in one of the ECH derivatives, the organically bound chlorine is converted into chloride and is released as salt into water. For the other derivatives it is unclear whether, and if so how, the chlorine reacts.

3 SUBSTANCE FLOW AND EMISSIONS IN 1990

Around 4,500 tonnes of ECH were used in total in these processes (1,717 tonnes of chlorine). Assuming a domestic market of 7,300 tonnes of ECH (2,800 tonnes chlorine; see substance document 8) this means that the destination of around 2,800 tonnes ECH is not known (1,083 tonnes chlorine).

The ECH used is converted into (expressed in chlorine):

- 168 tonnes polymer;
- 108 tonnes dichloropropanol;
- 453 tonnes chloride (flocculant and some ECH derivatives);
- 988 tonnes chlorine in ECH derivatives.

The destination of the polymer and the 988 tonnes of chlorine in ECH derivatives has been classified as 'unknown'. The fate of the dichoropropanol used in pharmaceuticals is also not known.

The four companies which use ECH are included in the ER-I, from which emissions have been taken. Several processes were recorded at one company. Releases of ECH and a release of a chlorooctane to water are allocated to the process in which ECH is used. The release of the latter substance can not be explained by the other processes. An EOCl emission of a number of kilos included in WIER is allocated by this company to another process. Neither company reported the existence of significant quantities of chlorine-containing waste. Table 10.1 gives an aggregated list of the emissions from the ER-I. For reasons of confidentiality no emissions are listed for individual companies.

Table 10.1: Chlorine-containing emissions to water and air in other ECH applications in 1990 (kg chlorine; in brackets: kg substance)

Compound	Air	Water
ECH	325 (855)	
Chlorooctane		239 (999)
Total chlorine: 564	325	239

4 EMISSIONS UNDER ENVISAGED POLICY

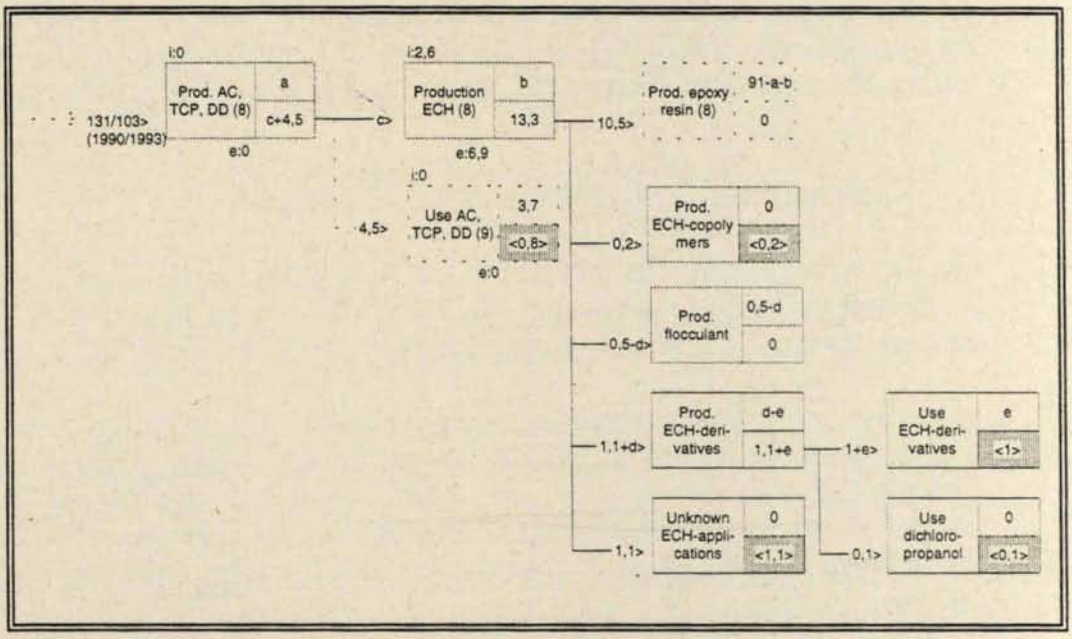
The emissions from the process in this segment make no essential contribution to the score on environmental themes for the situation in 1990. For simplicity's sake, the emission figures for 1990 have also been used in the analysis of the situation arising after implementation of the policy established as of 1 January 1995.

5 COMMENTS AND POINTS FOR DISCUSSION

One of the companies was included in the AOX/EOX measurement programme conducted by RIZA in mid-1993. A very high annual freight of AOX was measured, while EOX emissions were below the detection limit [RIZA 1994b].

Measurements by RIZA record increased EOCl and AOX emissions in the paper industry. These emissions are partially caused by contaminants in paper pulp, for example due to imports of paper pulp which is bleached with chlorine. German research shows however that the application of cellulose improvers based on ECH are the major source of AOX forms in the paper industry [Mobius 1990a and 1990b].

Figure 10.1: Substance flows in other applications of ECH (in kt chlorine, 1993)



SEGMENT 11: PRODUCTION OF POLYCARBONATE

1 INTRODUCTION

General Electric Plastics B.V. in Bergen op Zoom is the only producer of polycarbonate in the Netherlands. The polycarbonate is produced from phosgene and bisphenol-acetone sold under the brand name LEXAN in the form of granules or plates. The major customer is the car industry which manufactures a number of parts, such as bumpers and dashboards, from the granules. Other market sectors are packaging, building and construction, household appliances, computers and communication systems, electrical and electronic equipment, material conveyance, medical appliances, aircraft and furniture.

2 PROCESSES

GEP produces chlorine by electrolysis from salt in situ (see segment 1). Through a reaction with steam in a reformer, carbon monoxide is produced from natural gas. Carbon monoxide and chlorine react to phosgene according to:

(1) $CO + Cl_2$ ----------> $COCl_2$

The installation for both the chlorine and the phosgene process are in a separate, completely gas-tight and slightly under-pressured plant [SPIN 1993]. Polycarbonate is produced from bisphenol-acetone (BPA) and phosgene in a solution of dichloromethane (DCM):

(2) $Cl\text{-}CO\text{-}Cl + HO\text{-}C_6H_4\text{-}C(CH_3)_2\text{-}C_6H_4\text{-}OH \xrightarrow{25^oC}$
$[\text{-}O\text{-}C_6H_4\text{-}C(CH_3)_2\text{-}C_6H_4\text{-}O\text{-}CO\text{-}]_{80 \text{ tot } 100} + 2HCl$

After being washed and centrifuged the polycarbonate is precipitated and post-dried to polycarbonate powder. This powder forms the basic raw material for the production of LEXAN. During the precipitation drying the last residues of solvent are removed from the product using steam. Vapours with DCM from the solvent recovery installation are purified in two washers, and then the washing water is fed again into the steam stripper in the recovery installation.

The raw waste water of the polycarbonate production contains residues of solvent, salt and some other elements. The solvent is concentrated via an integrated system within the process of washing and steam stripping. It is then reused in the process.

After this treatment, the waste water is conducted over carbon beds and then released.

The polycarbonate powder is extruded in strands, while additives are blended in, which are processed by means of mincing machines to LEXAN granules or modifications thereof. Additives can consist of pigments, fillers, stabilisers, and possibly other polymers.

3 SUBSTANCE FLOWS AND EMISSIONS IN 1990

For reasons of confidentiality, the chlorine balance for the production process of polycarbonate is aggregated with the balance for the production of MDI (see segment 12). Table 11.1 presents the aggregated chlorine balance, for which Figure 11.1 presents the substance flow diagram. The chlorine used in the production of polycarbonate is converted into chloride (kitchen salt) and released into the Western Schelde. Imports or exports of phosgene, the raw material containing chlorine used in the production, play no role.

The ER-I only records the emission of salt and solvents such as DCM. Emissions of such solvents are not covered here but in the segment describing the applications of DCM and other halogenated hydrocarbons. The company is not a priority company in the context of the Rhine and North Sea Action Programme (RAP/-NAP) and is not covered by WIER. The company is included in the AOX/EOX measurement programme conducted by RIZA in mid-1992. The quantity of EOX was below the detection limit. The AOX freight is a factor of 2 to 3 higher than the quantity of chlorine related to the DCM emission recorded in ER-I [RIZA 1994b, ER-I 1994].

Table 11.1 Aggregated chlorine balance for the production of polycarbonate and MDI in 1990 (tonnes of chlorine)

Compound		Amount of ingoing chlorine	Amount of outgoing chlorine
In:	chlorine (Cl_2)	62,527	
	HCl	3,267	
Out:	HCl (by-product)		30,642
	chloride (Cl^-; to water)		35,152
Total		65,794	65,794

Emission figures at the process level from ER-I and WIER can not be published without the consent of the company concerned. Since in this case the process takes place at only one company in the Netherlands, it is impossible to disguise the figures by aggregation and the emission figures for the process are therefore not published here.

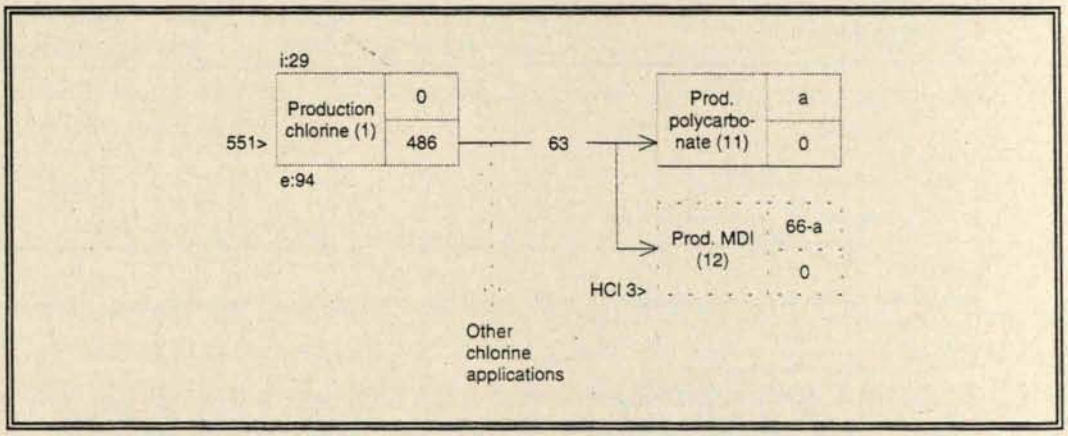
4 EMISSIONS AFTER ENVISAGED POLICY

The emissions from the process in this segment make no essential contribution to the score on environmental themes for the situation in 1990. For simplicity's sake, the emission figures for 1990 have also been used in the analysis of the situation arising after implementation of the policy established as of 1 January 1995.

5 COMMENTS AND POINTS FOR DISCUSSION

In 1988 a major programme started to reduce emissions of solvents to air (toluene and dichloromethane) by 75% compared with levels in 1988. This involves measures such as optimising processes, waste gas treatment, recovery, etc. A lot has also been done to reduce the diffuse emission of dichloromethane by using better gaskets on flanges and pumps, reducing the number of flanges and the total replacement of equipment. The reduction objective has been achieved. The Chemiewinkel of the University of Groningen has studied whether there are alternative solvents to DCM. It appears not, or the solvents concerned introduce risks such as the risk of fire and ecotoxic properties (dioxane, cyclohexanone) [Ree 1990].

Figure 11.1: Substance flows in production of polycarbonate (in kt chlorine, 1990)



SEGMENT 12: PRODUCTION OF MDI

1 INTRODUCTION

ICI in Botlek uses chlorine as a raw material for the production of MDI (ethylene-diphenyldiisocyanate). MDI is a raw material for PUR foams. The following subsection describes the stages in the process [ECTOTEC 1991, ICI 1994].

2 PROCESSES

Chlorine is acquired from Akzo Nobel by pipeline (see substance document on chlorine). The chlorine is converted with carbon monoxide transported by pipeline into phosgene as follows:

(1) $CO + Cl_2 \xrightarrow{\text{C. 80oC}} COCl_2$

Diaminodiphenylmethane (DADPM) is prepared in situ. This involves the use of hydrochloric acid (HCl). MDI is prepared from DADPM and phosgene according to the following reaction:

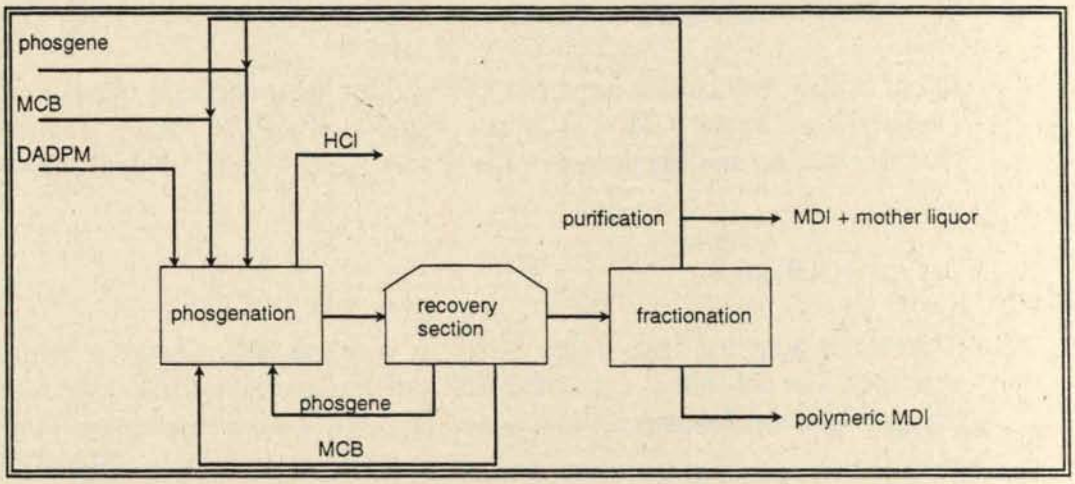
(2) $NH_2\text{-}C_6H_4\text{-}CH_2\text{-}C_6H_4\text{-}NH_2 + 2\ COCl_2 \xrightarrow{\text{50-100oC}} OCN\text{-}C_6H_4\text{-}CH_2\text{-}C_6H_4\text{-}NCO + 4\ HCl$

The reaction to isocyanate takes place in the solvent monochlorobenzene (MCB). The reaction blend goes to the processing section where the phosgene and MCB are removed under a higher temperature and lower pressure.

The product is then fractionated under low pressure. The bottom product has a relatively high content of polyfunctional isocyanate groups. It is stored in bulk as 'polymeric MDI', The 4-4' MDI ('pure' MDI) and the mother liquor, a mix of 4-4' and 2-4' MDI is produced from the top product. The MDI, mother liquor and polymeric MDI are stored in bulk for internal processing or transport to customers.

Phosgene, MCB and/or HCl are separated from various residue flows. Phosgene and MCB are returned to the process. HCl is sold externally.

Figure 12.1: Diagram of production of MDI



The waste gases from the preparation of the phosgene and MDI are neutralised in a caustic soda scrubber or hydrolysed, during which sodium chloride, carbonate and sometimes hypochlorite are formed. This is taken to the water purification plant (WPP) with other waste water after the MCB is removed in a steam stripper. Waste flows containing MCB are processed externally. Figure 12.1 illustrates the process.

3 SUBSTANCE FLOWS AND EMISSIONS IN 1990

For reasons of confidentiality the chlorine balance for the production process of MDI is aggregated with the balance for the production of polycarbonate (see segment 11). Table 12.1 presents the aggregated chlorine balance. Figure 12.2 shows the substance flow chart. The chlorine consumed and the HCl used are converted during the production of MDI into chloride (salt) which is released into the Nieuwe Waterweg, and HCl which is sold externally.

Table 12.1 Aggregated chlorine balance for the production of polycarbonate and MDI in 1990 (in tonnes of chlorine)

Compound		Amount of ingoing chlorine	Amount of outgoing chlorine
In:	chlorine (Cl_2)	62.527	
	HCl	3.267	
Out:	HCl (by-product)		30.642
	chloride (Cl^- ; to water)		35.152
Total		65.794	65.794

The ER-I reports no emissions to air and water (other than salt) [ER-I 1994]. The company is not a priority company in the context of RIZA's Rhine and North Sea Action Programme (RAP/NAP) and is not registered in WIER [Bakker 1992, RIZA 1994a]. Emission figures at the process level from ER-I and WIER can not be published without the consent of the company concerned. Since in this case the process takes place at only one company in the Netherlands, it is impossible to disguise the figures by aggregating them.

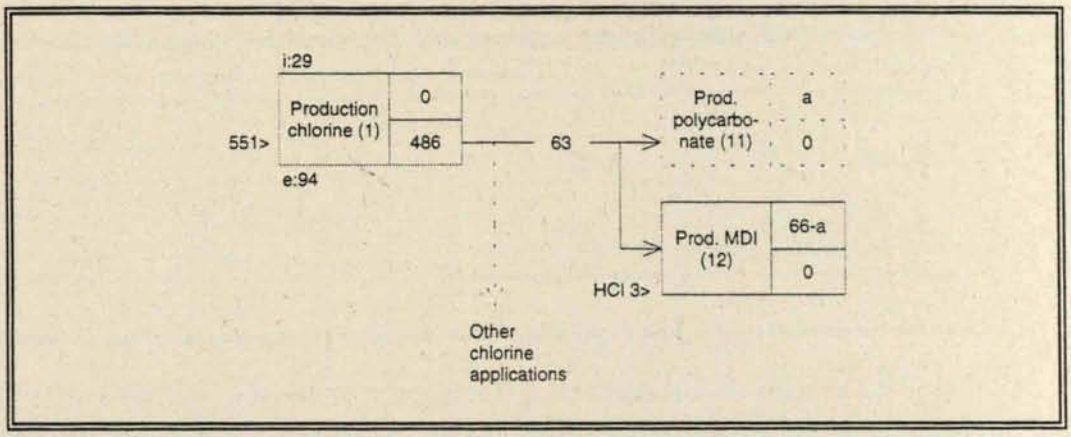
4 EMISSIONS UNDER ENVISAGED POLICY

The emissions from the process in this segment make no essential contribution to the score on environmental themes for the situation in 1990. For simplicity's sake, the emission figures for 1990 have also been used in the analysis of the situation arising after implementation of the policy established as of 1 January 1995.

5 COMMENTS AND POINTS FOR DISCUSSION

According to Slooff [1991], there are emissions of MCB to water. These are not allocated to the MDI production but to segment 36: Application of aromatic chlorine compounds. The company was included in the AOX/EOX measurement programme conducted by RIZA in mid-1992. The quantity of EOX was a number of times greater, and the quantity of AOX more than ten times greater than the quantity of chlorine which according to Slooff [1991] was released in the form of MCB [RIZA 1994b]. This could indicate the release of organic halogenated compounds that have not yet been registered.

Figure 12.2: Substance flows in production of MDI (in kt chlorine, 1990)



SEGMENT 13: PRODUCTION OF TDC AND ARAMIDES

1 INTRODUCTION

The Aramidemaatschappij V.O.F. (now: Aramide Products) in Delfzijl produces terphtaloyldichloride (TDC) from P-Xylene and chlorine. This is a raw material for aramide. The next sub-section describes the process in more detail. The process description is based on [Assies 1991] and material from the TNO Plastics and Rubber Institute (KRI) [Preston 1985, Volbracht 1976 and 1989]. Akzo Nobel (90%) and the N.O.M. are shareholders in the company, which is established in the Akzo Nobel grounds in Delfzijl. It is included separately in the ER and WIER, however.

2 PROCESSES

2.1 Production of TDC

TDC is produced via the following reactions:

$$\underset{\text{p-xylene}}{H_3C\text{-}C_6H_4\text{-}CH_3} + 6\ Cl_2 \xrightarrow{UV} \underset{\text{HCPX}}{Cl_3C\text{-}C_6H_4\text{-}CCl_3} + 6\ HCl \quad (1)$$

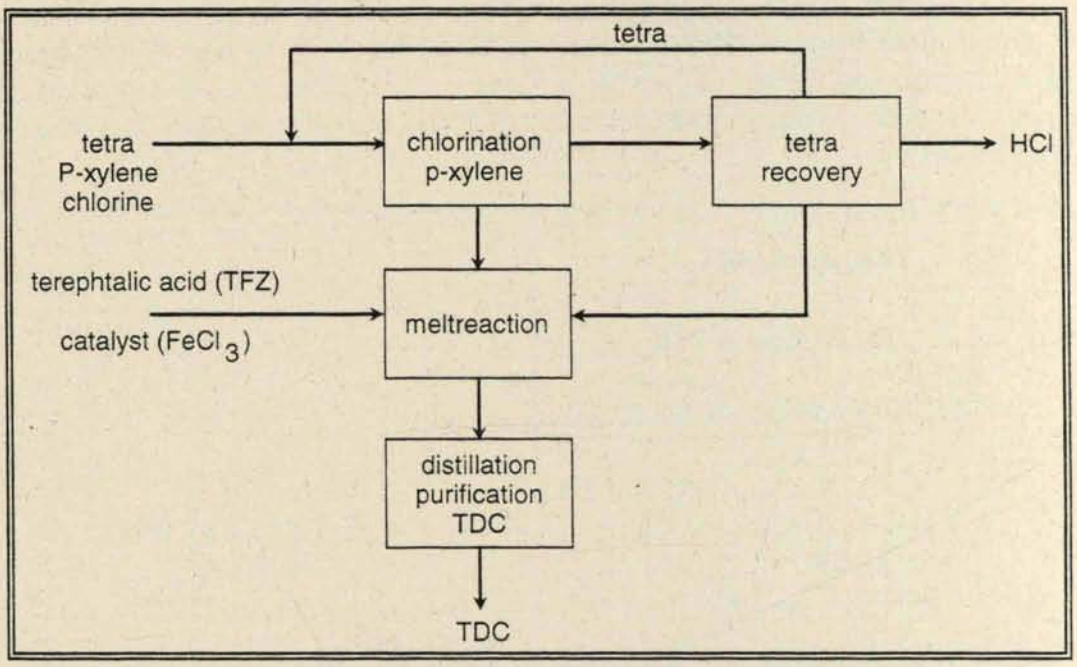
$$\underset{\text{HCPX}}{Cl_3C\text{-}C_6H_4\text{-}CCl_3} + \underset{\text{TFZ}}{HOOC\text{-}C_6H_4\text{-}COOH} \xrightarrow{FeCl_3} 2\ \underset{\text{TDC}}{ClOC\text{-}C_6H_4\text{-}COCl} + 2HCl \quad (2)$$

P-xylene is chlorinated in batches to hexachlorine-P-xylene (HCPX). To prevent side-reactions and rust forming, the process is conducted in an inert tetra atmosphere. The reaction is catalysed by UV light. Waste flows containing tetra are neutralised with NaOH and separated and then the tetra layer is distilled. The tetra vapour is cleaned in a caustic soda scrubber and fed back into the process.

After the chlorination, terephtalic acid (TFZ) is added to HCPX in a batch reactor (reaction 2). The waste gas from this reaction contains N_2, HCl TDC, HCPX and TPA. This mixture goes to the HCl processing system. Raw TDC is conducted to an evaporator and then to a rectification column. The vapour is condensed and this produces quality TDC. Like off-spec batches, in 1990 the bottom product was processed elsewhere as chemical waste (including at Akzo Nobel in Botlek with

recovery of HCl). These flows are now incinerated in Akzo Nobel's incinerators. Figure 13.1 illustrates the preparation of TDC.

Figure 13.1 Diagram of TDC production



2.2 *Production of aramide*

Poly p-phenylene terephthaloyl amide (PPTA) is the raw materials for super-strength fibres, such as Twaron (Akzo Nobel) and Kevlar (DuPont). These fibres will be referred to as aramide fibres for short. Aramide is synthesised from equimolar quantities of p-phenylenediamine (PDD) and terephthalic acid dichloride (TDC) in an N-methylpyrolidon (NMP)/calcium chloride mixture.

The process is performed in batches. The individual steps are illustrated in figure 13.2.

In the first step, liquid or finely ground TDC is mixed with a solution of PPD in NMP/$CaCl_2$. Because the reaction is strongly exothermal, the reaction mix is cooled. Together with the other components of the reaction medium, the aramide formed creates a highly viscous jelly-like mass, from which the polymer, after intensive mixing with water, is settled, filtered off, washed and dried. The filtrate is neutralised with calcium hydroxide during which the HCl bound to NMP is converted into water and $CaCl_2$. Regeneration occurs partly by liquid-liquid extraction with dichloromethane (DCM) and otherwise by evaporation. The top product consists of water, $CaCl_2$ and traces of NMP and DCM, which is further processed. Some of the $CaCl_2$ is fed back into the process. The remainder is released to water. The intermediate product NMP is also fed back into the process. The bottom product consists of DCM, NMP and water. This is distilled in a separate column.

The aramide resin is spun into fibres elsewhere. Since the aramide is chlorine-free, this product is not followed any further.

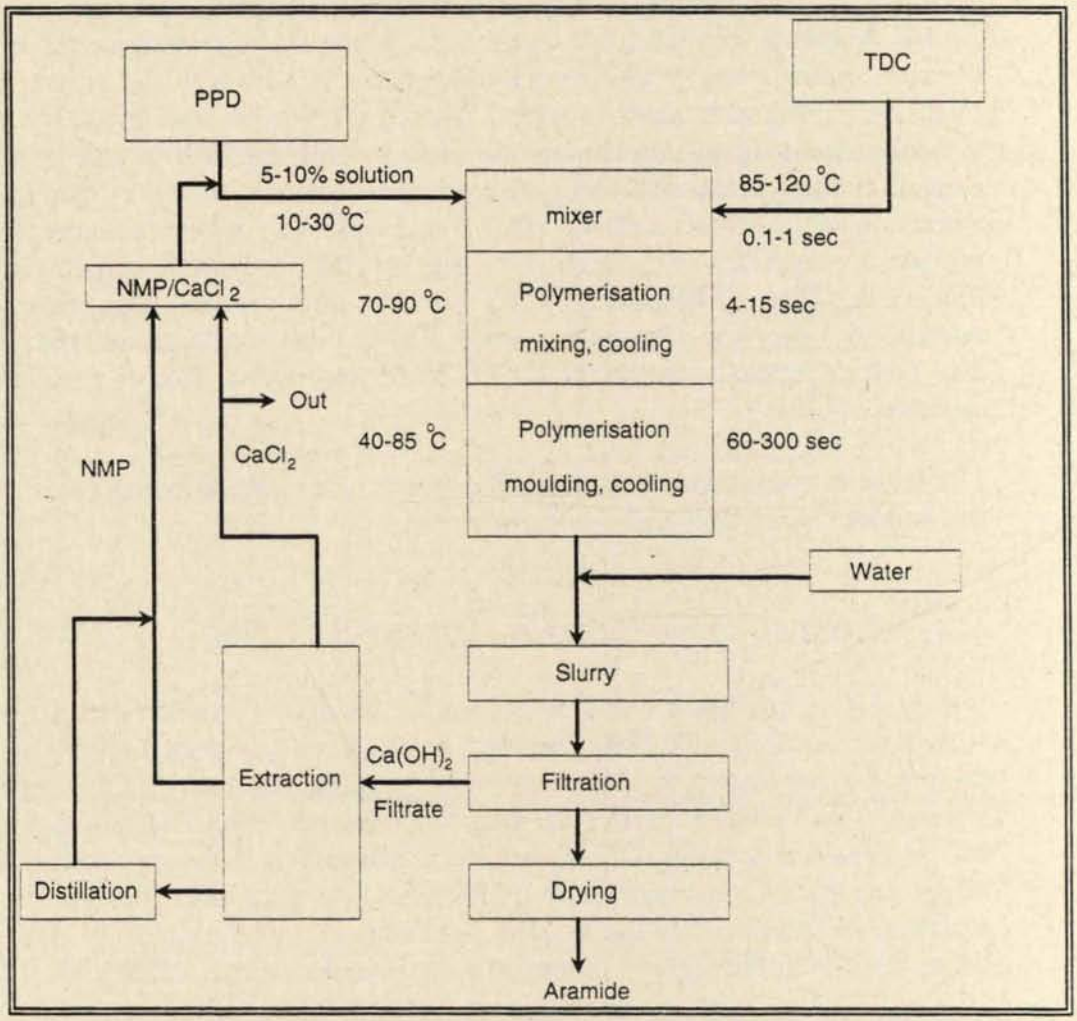
3 SUBSTANCE FLOWS AND EMISSIONS IN 1990

V.O.F. Arami supplied a chlorine balance for the above processes for 1993. The chlorine consumption for 1990 is known; on this basis a balance for 1990 has been estimated. The figures for 1993 are based on processing of TDC waste in the company's own incinerator. In 1990 the waste released during TDC production was still processed externally. This difference is discounted in the calculation below. Moreover, thanks to recycling the HCPX yield has since been increased to 99% compared with 1990. The use of DMC and tetra as solvent is not included here, but is dealt with for all applications in substance documents 25 and 30.

For reasons of confidentiality no figures are given here for chlorine consumption or emissions. There are no import and export figures for the intermediate product TDC, but they are being considered for the future. All TDC is processed into aramide. The chlorine consumed in this segment is released as follows:

- 3,843 tonnes as chloride (NaCl into water or HCl for use elsewhere);
- the remainder as halogen-containing waste (for external incineration).

Figure 13.2 Diagram of aramide production



The quantities of waste reported by Arami are of the same order of magnitude as the figures in the notification records for chemical waste [LMA 1994].

The company was not registered in the ER in 1990 [ER-I 1994]. This means the company was not one of the 350 leading Dutch companies in terms of impact based on measured emissions and is not regarded as a priority company by the licensing authorities for any other reason. Emissions to water are recorded in WIER and included in this study [RIZA 1994a].

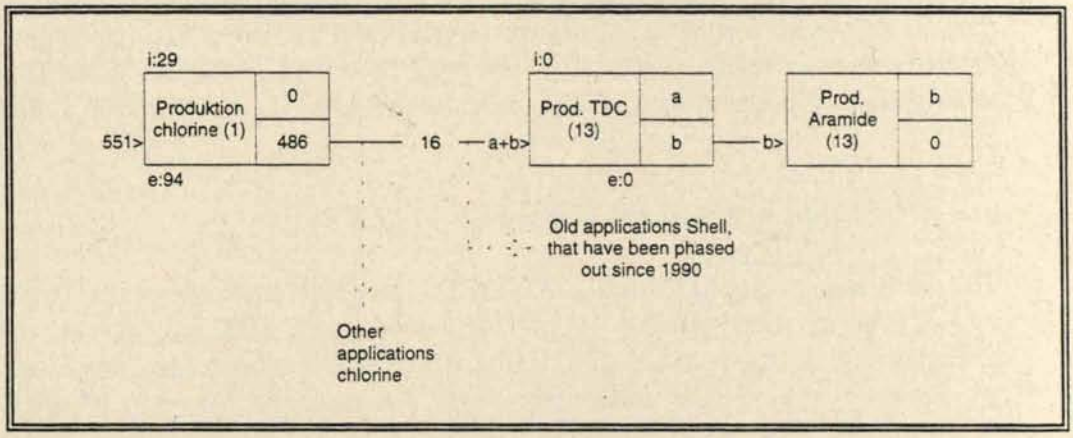
4 EMISSIONS UNDER ENVISAGED POLICY

The emissions from the process in this segment make no essential contribution to the score on environmental themes for the situation in 1990. For simplicity's sake, the emission figures for 1990 have also been used in the analysis of the situation arising after implementation of the policy established as of 1 January 1995.

5 COMMENTS AND POINTS FOR DISCUSSION

The company was included in the AOX/EOX measurement programme conducted by RIZA in mid-1992 [RIZA 1994b]. The quantity of EOX is of the same order of magnitude as the quantity of chlorine which is released in the form of already known emissions of individual substances. The measured quantity of AOX is a factor of 3 to 4 higher.

Figure 13.3: Substance flows in production of TDC and aramide (in kt chlorine, 1990)



SEGMENT 14: PRODUCTION OF MONOCHLOROACETIC ACID

1 INTRODUCTION

Akzo Nobel-Hengelo produced monochloroacetic acid from chlorine and hydrochloric acid. The following sub-section describes the steps in the process.

2 PROCESSES

Monochloroacetic acid is produced by the chlorination of acetic acid:

$$(1)\quad CH_3COOH + Cl_2 \xrightarrow[\text{catalyst}]{85\ ^\circ C} ClCH_2COOH + HCl$$

The reaction temperature is around 85°C. Catalysts are used, on the one hand to convert the acetic acid as completely as possible, and on the other to limit as far as possible the formation of dichloroacetic acid. HCl is released during the reaction. The HCl is processed and sold externally. MCA is separated from the reaction mix. Dichloroacetic acid which is formed is converted into MCA by reduction with hydrogen. The pure end product is acquired by distillation and is an odourless, white substance.

3 SUBSTANCE FLOWS AND EMISSIONS IN 1900

Akzo Nobel provided a chlorine balance for the process for 1993. The chlorine consumption in 1990 is known: on the basis of this a balance has been estimated for 1990. For reasons of confidentiality, the use of chlorine in the production of MCA is aggregated with the use in the production of the pesticides MCPA and MCPP (segment 15).

According to Akzo Nobel, 32,140 tonnes of chlorine were used for MCPA, MCPP and MCA. The outflow for these two aggregated processes is shown in Table 14.1. Neither the National Notification Centre for Waste Substances nor the producer reports deposits of significant quantities of waste from this process [LMA 1994].

Table 14.1: Substance flows in MCA, MCPA and MCPP production in 1990 (in tonnes chlorine)

	Input into process	Product	Chloride
HCl			14.242
Chlorine	32,140		
Chloropropionic acid	370		
MCPA, MCPP and MCA		14,536 [1]	
Chloride			3,732 (water)
Total	32,510 =	14,536 +	17,974

[1] Domestic consumption MCPA 44 tonnes [ER-C 1994]. Less use of MCA for the production of MCPA and MCPP.

The CBS reports a significant export surplus for MCA [CBS 1991]. The reported production of MCA corresponds closely to the export surplus and the domestic consumption of MCA for the production of pesticides and starch/cellulose derivatives. Table 14.2 shows the consumption per application.

Table 14.2 Substance flows for MCA in 1990 (in tonnes of chlorine)

	Production of MCA	Net export	Dutch consumption
Segment 15	a	b	-
Segment 15			3.039
Segment 16			c
Discrepancies and inaccuracies			101
Total	a -	b =	3.140 + c

a,b and c: confidential

Emission figures are derived from the ER-I [ER-I 1994]. There is more than one process at the plant in Hengelo (including production of chlorine and hypochlorite). This segment only covers the emissions during the production processes 'production of MCA (sodium chloride)' and 'production of hydrochloric acid'.

The ER-I records only an emission to water via the central water treatment for all processes together. The emission to water of MCA is allocated to the production of MCA. The emission to water of chlorine is allocated to the chlorine production. The ER-I also records an emission of EOCl but it is unclear which process this should be allocated to and is otherwise not considered.

The company is not registered in WIER or regarded as a priority source of emissions to water under the Rhine and North Sea Action Programme (RAP/NAP). RIZA did not include the company in the AOX/EOX measurement programme it conducted in mid-1992.

4 EMISSIONS UNDER ENVISAGED POLICY

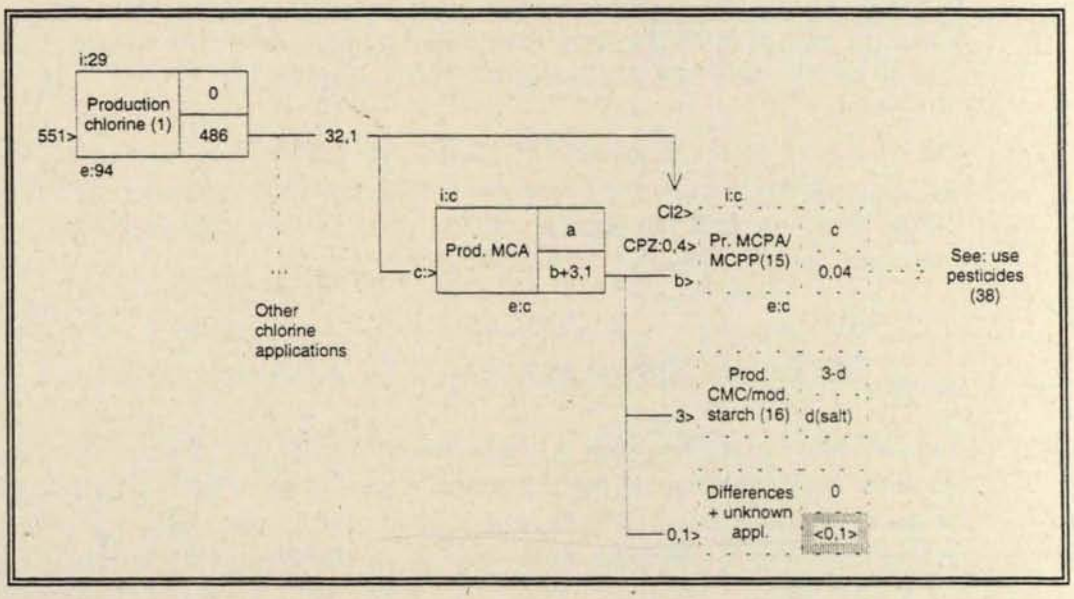
The emissions from the process in this segment make no essential contribution to the score on environmental themes for the situation in 1990. For simplicity's sake, the emission figures for 1990 have also been used in the analysis of the situation arising after implementation of the policy established as of 1 January 1995.

5 COMMENTS AND POINTS FOR DISCUSSION

It is assumed that all MCA is exported as acid and not as sodium chloride. If there is a sizeable export of the heavier sodium chloride, domestic consumption is larger than indicated here. According to the producer of MCA, segments 17 and 18 in fact cover all the major Dutch consumers. It is therefore unlikely that exports of MCA are much lower than has been assumed above.

Emission figures at process level from ER-I and WIER can not be published without the consent of the relevant company. In this case emission figures could not be disguised by aggregation. The companies concerned declined a request from TNO/CML to publish the emission figures adopted for 1990 and the future situation in this report.

Figure 14.1: Substance flows in production of MCA (in kt chlorine, 1990)



SEGMENT 15 PRODUCTION OF MCPA AND MCPP

1 INTRODUCTION

Akzo Nobel Rotterdam is one of three Dutch producers of pesticides. MCPA and MCPP are produced from MCA, chloropropionic acid, chlorine and some non-chlorine-containing raw materials.

2 PROCESSES

MCPA, 4-chlorine-2-methyl-phenoxyhydrochloric acid is produced by means of a reaction of monochlorohydrochloric acid (MCA) with 2-methyl-4-chorophenol:

(1) $ClCH_2COOH + Cl\text{-}C_6H_4\text{-}OHCH_3 \text{ ----> } CLCH_3\text{-}C_6H_4\text{-}OCH_2COOH + HCl$

MCPP, 4-chlorine-2-methyl-phenoxypropionic acid is produced by a reaction of chloropropionic acid with 2-methyl--chlorophenol:

(2) $ClCH_2CH_2COOH + Cl\text{-}C_6H_4\text{-}OHCH_3 \text{ ----> } CLCH_3\text{-}C_6H_4\text{-}OCH_2CH_2COOH + HCl$

MCA is acquired from elsewhere (especially the plant in Hengelo);chloropropionic acid is imported. Various chlorocresoles, which act as intermediate products, are produced in situ and involve the use of chlorine. A small portion of the substances reach the effluent. During the production processes of MCPA and MCPP (hydrogen) chloride is released. This is released with the effluent after extensive treatment via the central water treatment plant.

3 SUBSTANCE FLOWS AND EMISSIONS IN 1990

Akzo Nobel provided a chlorine balance for the process for 1993. The chlorine consumption in 1990 is known; on the basis of this a balance for 1990 has been estimated. For reasons of confidentiality, the use of chlorine in the production of MCPA and MCPP has been aggregated with the use in the production of MCA (segment 14).

Table 15.1 Substance flows in MCPA and MCPP production in 1990, in tonnes chlorine

	Input in process	Product	Chloride
HCl			14,242
Chlorine	32,140		
Chloropropionic acid	370		
MCPA, MCPP and MCA		14,536 [1]	
Chloride			3,732 (water)
Total	32,510 =	14,536 +	17,974

[1] Domestic consumption MCPA 44 tonnes [ER-C 1994]. Less use of MCA for production of MCPA and MCPP.

Figures from Akzo Nobel show that 32,140 tonnes of chlorine were used in the production of MCPA, MCPP and MCA. The outflow for these two aggregated processes is shown in Table 15.1. Chloropropionic acid is imported. Almost the entire output of MCPA and MCPP is exported. The ER-C adopts an annual consumption of 44 tonnes of active substance MCPA/MCPP in the Netherlands (expressed as chlorine) [ER-C 1994].

The emission figures are taken from the ER-I and WIER. The emissions to air from the ER processes 'production of pesticides' are allocated entirely to the processes discussed here. Neither the National Notification Centre for Waste Substances nor the producer reports deposits of significant quantities of waste from this process [LMA 1994]. Process waste is possibly incinerated in the company's own incinerator. Because this incinerator generally burns waste from the production of EDC/VCM the emissions are allocated to this process.

The emissions to water in the ER-I and WIER are the total figures for all the processes that take place at Akzo Nobel Rotterdam (production of chlorine, VCM and pesticides). Emissions of EDC and EOCl are allocated entirely to the VCM production. Although EOCl is possibly produced during the production of pesticides the use of chlorine is negligible compared with VCM production. There is a small emission of chlorobenzenes. On the basis of information from Berbee [1987] this is allocated to the pesticide production. According to Wunderink [1993] around 1 g TEQ of dioxins were released to water in 1985, probably

entirely from the EDC/VCM production. This quantity has since been sharply reduced with the commissioning of the treatment plant.

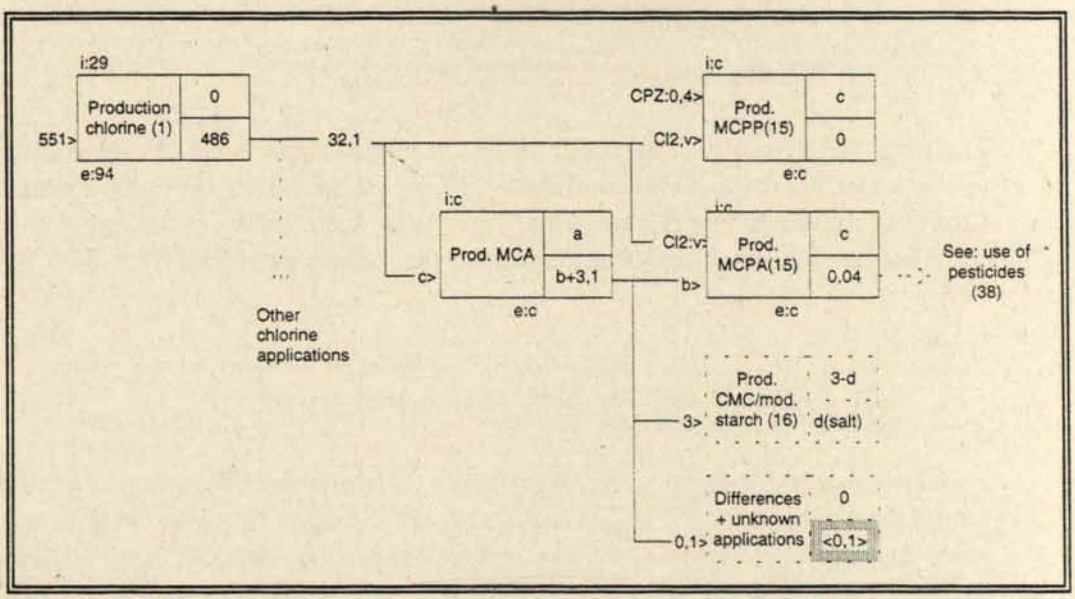
4 EMISSIONS UNDER ENVISAGED POLICY

The emissions from the processes in this segment make no essential contribution to the score on environmental themes for the situation in 1990. For simplicity's sake, the emission figures for 1990 have also been used in the analysis of the situation arising after implementation of the policy established as of 1 January 1995.

5 COMMENTS AND POINTS FOR DISCUSSION

Emission figures at the process level from ER-I and WIER can not be published without the consent of the company concerned. Since in this case the process takes place at only one company in the Netherlands, it is impossible to disguise the figures by aggregation. The company concerned declined a request by TNO/CML to publish the emission figures adopted for 1990 and the future situation in this report.

Figure 15.1: Substance flows in production of MCPA and MCP(in kt chlorine, 1990)



SEGMENT 16: PRODUCTION OF CARBOXYMETHYLCELLULOSE AND MODIFIED STARCHES

1 INTRODUCTION

Carboxymethylcellulose (CMC) is produced in the Netherlands by Akzo Nobel (in Arnhem) and Metsa Serla (Nijmegen). CMC is prepared from monochloroacetic acid (MCA) and cellulose. Modified starch is prepared in a similar fashion by a number of other companies in the Netherlands (including Avebe in Drenthe/Groningen and Zetemeelfabriek de Bijenkorf in Koog aan de Zaan).

This sub-section describes the steps in the process in more detail [SPIN 1994a].

2 PROCESSES

2.1 CMC Production

The production of CMC can be divided into the pre-treatment of the cellulose, the preparation of CMC, the de-alcoholisation of CMC to technical CMC, the preparation of pure CMC and the finishing.

Cellulose is ground to the required size of particle. The ground cellulose is put into a reactor. The cellulose is alkalised to sodium cellulose with the aid of caustic soda. After this reaction, monochloroacetic acid (MCA) dissolved in ethanol is added to the reactor. When the temperature is increased the following reaction occurs:

(1) $NaOH + ClCH_2COOH \longrightarrow ClCH_2COONa + water$;

(2) natroncellulose + $ClCH_2COONa \longrightarrow$ Na-CMC + keukenzout.

The most important by-products formed are sodium glycolates and kitchen salt. In the case of technical CMC all reaction products are dried and used as such. In the production of pure CMC the by-products are washed out with an ethanol-water mixture. After the ethanol is recovered the product is dried. During the purification the by-products such as kitchen salt are disposed of in the effluent. Around half of all CMC output is purified and so half of the chlorine used via MCA is released via the effluent as chloride.

2.2 *Production of carboxylised starch*

To produce carboxylised starch, starch is treated with sodium hydroxide. During the alkalisation, the precise ratios of starch, sodium hydroxide and water must be maintained. In the process, so-called alkali starch is produced, which is later filtered off to react in a reactor with the sodium chloride of monochloroacetic acid (sodium MCA, $ClH_2CCOONa$). The reaction products are sodium chloride, sodium glycolates and carboxylised starch. The physical details are determined by the degree of polymerisation, substitution and uniformity of the polymer chains.

The following reactions occur:

(3) $NaOH + ClCH_2COOH \dashrightarrow ClCH_2COONa$ + water;

(4) starch + $ClCH_2COONa \dashrightarrow$ carboxylised starch + kitchen salt.

3 SUBSTANCE FLOWS AND EMISSIONS IN 1990

The precise consumption of MCA was provided by three companies (calculated as chlorine, MCA or sodium MCA). If necessary, these have been converted to a volume of chlorine. One company, with a relatively small total consumption, only gave a total for the use of chlorinated compounds. It is assumed that 50% of this was MCA. According to MCA producer Akzo Nobel there are no major consumers in the Netherlands besides the companies identified.

Table 16.1 shows the use of MCA in various processes. For reasons of confidentiality, figures for the use of MCA in the production of CMC and modified starch are aggregated. All chlorine from MCA is converted into chloride and either incorporated in the product or released to water.

Neither the companies themselves nor the National Notification Centre for Waste Substances report deposits of chemical waste with a chlorine content from these processes [LMA 1994]. ER-I and WIER report no releases to water from the companies concerned other than chloride.

Table 16.1 Substance flows in production of CMC and modified starch in 1990 (in tonnes of chlorine)

Process	Use of MCA	Discharge Cl^- to water or absorbtion as Cl^- in product
CMC	*	*
Modified starch	*	*
Total	3,039	3,039

* Confidential

4 EMISSIONS UNDER ENVISAGED POLICY

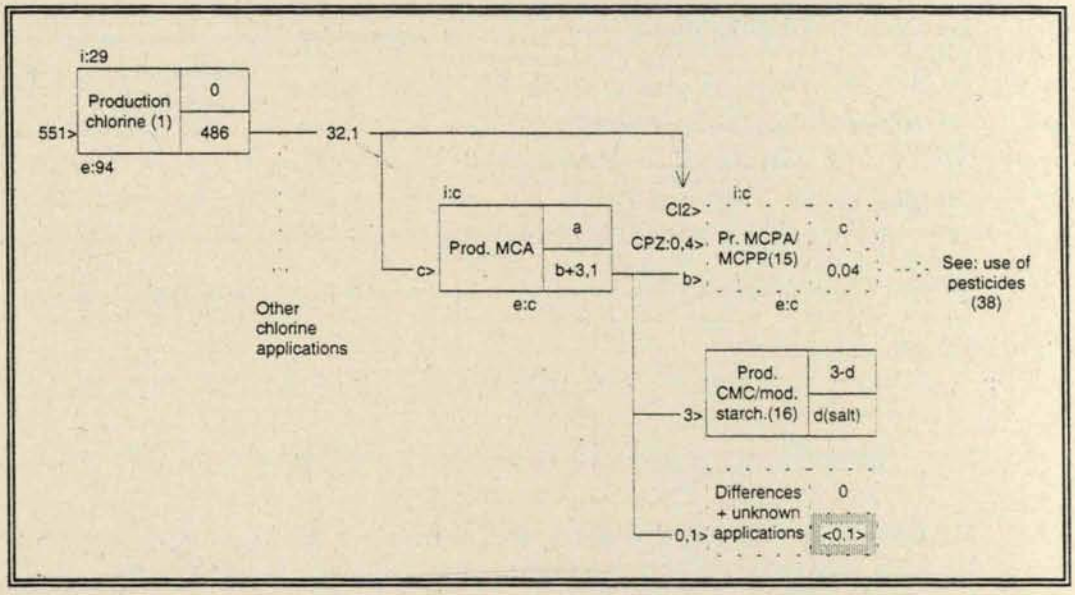
The emissions from the process in this segment make no essential contribution to the score on environmental themes for the situation in 1990. For simplicity's sake, the emission figures for 1990 have also been used in the analysis of the situation arising after implementation of the policy established as of 1 January 1995.

5 COMMENTS AND POINTS FOR DISCUSSION

According to SPIN [1994a], the waste water from the CMC production may be contaminated with sodium glycolate, sodium acetate, alcohol, acetic acid, monochloroacetic acid, kitchen salt and product residues.

At one starch processing company RIZA measured an emission of EOCl to water during a national measurement programme. The same company, however, used large quantities of hypochlorite. This appears a more likely source for the formation of EOCl than the relatively limited amount of MCA used. At a producer of CMC, AOX was measured in the effluent during the programme. The concentration of EOX was below the detection limit [RIZA 1994b]. The two other companies were not included. The companies concerned are not among the priority companies or the major sources of releases of chlorinated compounds under the Rhine and North Sea Action Programme [Wunderink 1993].

Figure 16.1: Substance flows in production of CMC and modified starch (in kt chlorine, 1990)



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SEGMENT 17: PRODUCTION OF CHLORINATED SOLVENTS

1 INTRODUCTION

Akzo Nobel is the only Dutch producer of chlorinated solvents (halogenated hydrocarbons - HHCs). Chloroform and tetra are produced in Delfzijl via the intermediate product methylchloride dichloromethane (DCM). Until mid-1990 tetrachloroethene (PER) was also produced in a combined PER/tet(ra) process. The plant has since been closed. The following sub-section describes the steps in the process in greater detail [SPIN 1994b, Bremmer 1988]. Besides the primary production, a very small amount of chlorinated solvents are produced in the Netherlands through distillation of waste. Sub-section 2.2 discusses this recycling.

2 PROCESSES

2.1 Production of Primary HHCs

Figure 17.1 illustrates the production of chlorinated hydrocarbons.

Methanols and a return flow of hydrochloric acid (HCl) react to methyl chloride and water. The gaseous reaction mix is cooled so that most of the water condenses. Some of the surplus chlorinated hydrogen dissolves in this water so that a thinned hydrochloric acid solution is produced. This is stripped of methanol, and processed to 30% hydrochloric acid. The methylchloride gas is dried with concentrated sulphuric acid and used entirely in the methylene-chloroform factory.

In this factory, the methyl chloride reacts with chlorine to DCM and chloroform. The by-products tetra and HCl are produced. By using an overmeasure of methylchloride all chlorine is removed in the reaction. The reaction mixture is separated by condensation into a liquid and a gas phase. The gas phase consists mainly of HCl and methyl chloride and is largely fed back into the methyl chloride production.

The liquid phase is separated by means of distillation into DCM, chloroform and tetra. Methyl chloride and HCl released at this time are fed back into the process.

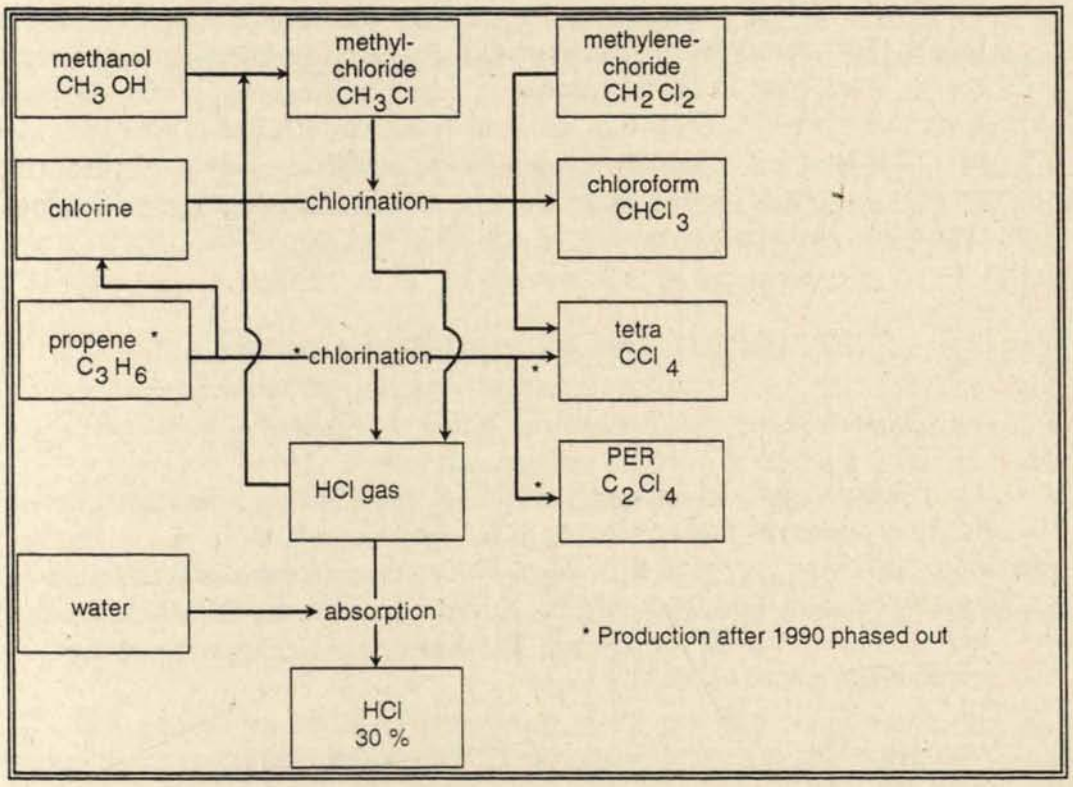
Until 1990 propene was chlorinated to tetra and PER with gaseous chlorine in the PER/tetra plant. This produced HCl which was separated and processed to 30% hydrochloric acid.

Methylene chloride, chloroform, tetra and (until 1990) PER are then mixed with 10% caustic soda to neutralise residues of chlorine and HCl. As a last step, the damp, purified chlorohydrocarbons are dried.

Since mid-1990 Akzo Nobel has been using an incinerator to process waste gas flow containing chlorohydrocarbons. These are waste gases from storage tanks and the methylene chloride/chloroform factory. The waste gases from the incinerator are conveyed to an absorber where hydrochloric acid is produced, which is either processed and sold or neutralised and released. After absorption, the waste gases are fed through an alkali scrubber and then released into the outside air. The waste flow created here, chlorine bleaching soda, is processed in the electrolysis factory.

The process effluent (caustic soda discharge, and washing water from scrubbers) released from the chlorohydrocarbon production plant undergoes a physical/chemical treatment. Discontinuous flows are drainage and cleaning water and acid and caustic soda streams. Caustic soda is added to the process effluent to neutralise acid, whereupon sedimentation takes place. At this point the chlorohydrocarbons are largely separated. The effluent is then added to a solvent separator. The chlorinated hydrocarbons released during the sedimentation and in the solvent separator are processed and then recycled in the company. After the solvent separator the effluent is treated in a steam stripper at which point the stripped chlorohydrocarbons are fed back into the process.

Figure 17.1 Diagram of the production of halogenated hydrocarbons



2.2 *Recycling and distillation of HHCs*

Many companies that use HHCs regenerate them after internal use by means of distillation. An example is the use of DCM as a solvent in the pharmaceutical industry. The recycling is around 6 to 7 times the quantity purchased annually [VNCI/McKinsey 1991]. Internal recycling is ignored for the purposes of this substance flow analysis because the recycling is linked to the relevant application.

External recycling takes place if the waste containing HHCs is distilled externally. When the original supplier gets the distilled material back this is known as 'distillation for pay'. The distiller can also sell the regenerated solvent directly on the market. In that case the regeneration falls under the waste substances legislation and the quantities processed must be reported to the National

Notification Centre for Waste Substances (LMA)[2]. Information in the LMA shows that around 1,000 tonnes of waste containing HHCs is distilled annually [Stap 1994]. The 'distillation for pay' circuit has a similar volume [Tukker 1993a]. The waste consists for 30% of HHCs [Verhage 1991]. Assuming a yield of 80% from distillation, this represents around 500 tonnes of recycled HHCs. Almost half of this is PER from PER sludge from dry cleaners [Stap 1994]. The remainder is mainly from waste from the mechanical and electrical engineering industry. The most important solvent in this sector in 1990 was 1,1,1-tri. DCM was used to a limited extent, and chloroform and tetra not at all (see segment 21-36). External recycling of DCM, chloroform and tetra is therefore negligible compared with production at Akzo Nobel.

3 SUBSTANCE FLOWS AND EMISSIONS IN 1990

3.1 Estimated production at Akzo Nobel

Akzo Nobel supplied a chlorine balance for 1993. Because the PER/tet plant is no longer in operation, this only refers to the production of DCM and chloroform, and the by-products tetra and HCl. Akzo Nobel can not provide production or sales figures for 1990. For 1990 only the chlorine input in the DCM/Chloroform plant and the PER/Tet plant are known. These were 47,101 tonnes and 2,602 tonnes respectively, a total of 49,703 tonnes.

Akzo Nobel has estimated figures for 1990 from the 1993 balance and the chlorine input for 1990. Because of the closure of the PER/Tet plant, the production of each substance in 1990 can not be automatically estimated from the production ratios in 1993. By combining production figures from the ER, consumption figures which are regarded as reliable, figures for imports/exports from CBS and the chlorine input in 1990, we have estimated the production for 1990 as closely a possible. This was done as follows:

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[2] With the entry into force of the Waste Substances chapter of the Environmental Management Act on 1 January 1994, it is also compulsory to notify and be licensed for 'service distillation'. Note for the translated text: 'destillation for pay' was a system in Dutch hazardous waste management, where an owner of a spent solvent could ask a waste management company to distill the solvent for him. Since the ownership of the solvent was not transferred, there formally was no waste handed over to an other party - which ment under the old Hazardous Waste Management law that no permit was necessary.

1. The PER/Tet plant supplied around 700 tonnes of chlorine-containing solid waste which was disposed of in salt mines in 1990 [LMA 1994]. It is assumed that this corresponds with 237 tonnes of chlorine.

2. 2,602 tonnes of chlorine was used in this factory. Less 237 tonnes in waste, this leaves 2,365 tonnes. This is assumed to be entirely converted to PER and tetra.

3. Akzo Nobel has estimated the production of chloroform/dichloromethane on the basis of production figures for 1990 and the chlorine input for 1990. It is assumed that the figure for DCM derived in this way is correct. TNO has estimated the quantity of the by-product HCl in the same way.

4. The Netherlands' consumption of tetra is known. TNO has received figures on the use of tetra for the production of CFC-11 and CFC-12. The other consumption (as solvent) is monitored under the CFC action programme [CFC Commission 1994]. The production for 1990 was derived from the total consumption and the import surplus according to CBS [1991].

5. The remaining chlorine is converted into PER or chloroform. The ratio of PER and chloroform has been chosen in such a way that the production corresponds to the consumption in segments 21-36.

The total production of DCM, chloroform, tetra and PER calculated in this way comes to over 45,000 tonnes of product. According to the ER, the output of the chloroform/DCM plant and the PER/tetra plant amounts to over 44,000 tonnes of product. The estimate leads to a domestic supply which corresponds with the consumption.

Table 17.1 shows the chlorine balance for the production of HHCs. The table also shows the domestic supply, taking into account 200 tonnes of PER from the recycling circuit and the net imports according to the CBS [1991]. Table 16.2 shows the consumption of HHCs in the production of (H)CFCs and other applications based on segments 21-36. For reasons of confidentiality, figures for the application in the (H)CFC production and therefore also the figure for the output of DCM, chloroform and tetra have been aggregated.

Table 17.1 Chlorine balance in HHC production and import/export of chlorinated solvents in 1990 (tonnes of chlorine)

Substance name	Production	Production by means of distillation	Net import [CBS 1991]	Consumption
DCM	15,400	p.m.	- 8,300	7,100
Chloroform		-	12,470	
Tetra	Σ: 24,566	-	14,700	Σ: 67,436
PER		200	15,500	
HCl	9,500 [1]			
Waste	237			
Total	49,703			

[1] Net HCl production. Methylchloride, the basic raw material for DCM, chloroform and tetra, is prepared entirely by use of HCl. We can conclude from this that 5,286 tonnes of chlorine are recycled internally as HCl.

Table 17.2 Domestic applications of HHCs in 1990 (expressed in tonnes chlorine; in brackets: tonnes of product)

Substance	Total	Raw material CFC's	Other
DCM	7,100	-	7,100 (8,500)
Chloroform			203 (210)
Tetra	Σ: 67,436	Σ: 64,273	716 (777)
PER			2,244 (2,600)

3.2 Emissions

Emissions to air occur mainly during maintenance at the chlorohydrocarbons plant. The incinerator is also taken out of commission at that time so that air containing HHCs originating from storage, loading and a number of atmospheric process tanks is released without treatment. These periodic emissions encompass around 90% of the total emissions to air of HHCs from Akzo Nobel Delfzijl. Effluent is

released after physical-chemical treatment. It contains (small quantities of) methyl chloride, DCM, chloroform and tetra. There is also an (untreated) emission of methanol and methyl chloride via a methanol stripper.

Akzo Nobel in Delfzijl has a large number of production processes. The ER-I lists emissions by process. Emissions to water, however, take place via a single treatment plant. The figures from the ER-I and WIER are somewhat arbitrarily allocated as follows [ER-I 1994, RIZA 1994a]:

- ER-I allocates a limited emission "Hydrocarbons, chlorinated, not specified" to the production of chlorine. On the basis of this figure, 50 g of the EOCl emission in WIER is attributed to chlorine production.
- all other emissions to water can be allocated to the production of HHCs on the basis of causality.

4 EMISSIONS UNDER ENVISAGED POLICY

The measures to reduce emissions established as of 1 January 1995 are discussed below. On the basis of the emission situation in 1990, the emissions remaining after implementation of this policy have been estimated. No account has been taken of changes in emissions as a result of economic growth or other autonomous developments in the target group.

Of the emissions that occur during the production of chlorinated solvents the Integrated Environmental Target (IMT) sets out targets for reducing emissions of tetrachloromethane, chloroform, dichloromethane, PER, hexachlorobenzene and hexachlorobutadiene. The last two are the result of an historic emission (soil remediation) and are therefore not included further in this study.

The calculation of the emission in the situation after implementation of the envisaged policy is based on the BMP tables. Account has also been taken of the measures already implemented to reduce emissions as reported by the company. These measures relate to substances not listed in the BMP.

5 COMMENTS AND POINTS FOR DISCUSSION

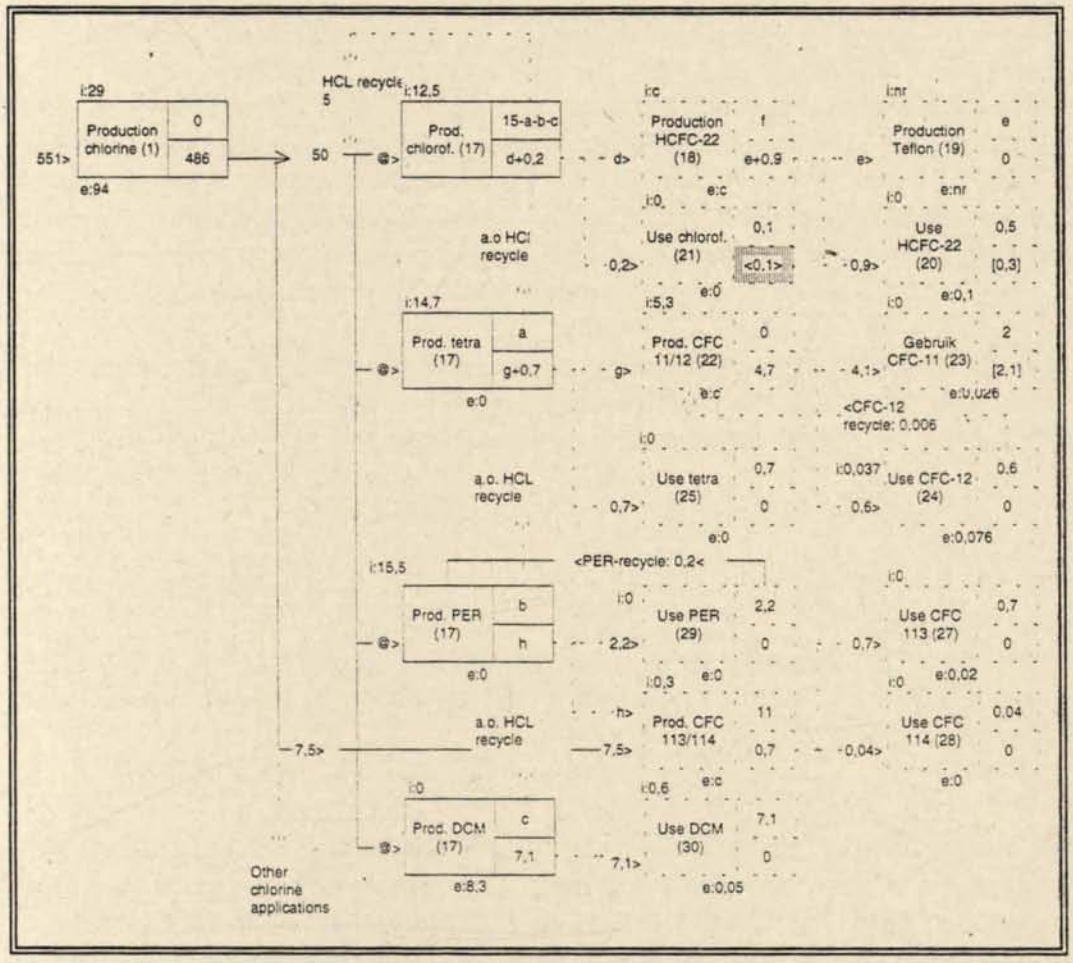
The emissions to water of DCM, chloroform and EOCl in 1990 were higher than in 1989 and 1991 because of a calamity. The difference compared with 1992 is smaller. The emission figures adopted here possibly reflect an incidentally unfavourable situation.

The quantity of EOX to water is in the same order of magnitude as the quantity of chlorine which is released in the form of previously known emissions of individual substances [RIZA 1994b, ER-I 1994].

Hexachlorinated compounds were released in the past. With the closure of the PER/Tet plant they are no longer released. Because the soil in the Akzo Nobel grounds is still polluted with these compounds they are still released through springs. Because this is an historical emission it has not been included in the study. Through specific treatment of this effluent the releases have in fact been reduced to practically zero.

Emission figures at the process level from ER-I and WIER can not be published without the consent of the company concerned. Since in this case the process takes place at only one company in the Netherlands, it is impossible to disguise the figures by aggregation. The company concerned declined a request by TNO/CML to publish the emission figures adopted for 1990 and the future situation in this report.

Figure 17.2: Substance flows in production of chloromethanes/PER and their consumption applications (in kt chlorine, 1990)



SEGMENT 18: PRODUCTION OF HCFC-22

1 INTRODUCTION

DuPont de Nemours in Dordrecht is a producer of HCFC-22 (difluorochloromethane). This substance is included as a transition substance in the Protocol of Montreal and is treated separately in the HCFC-halon prohibition. HCFC-22 is used partly in refrigeration and partly as a raw material for the manufacture of the monomers tetrafluoroethene (TFE) and hexafluoropropene (HFP), which are raw materials for the production of fluorinated polymers like teflon.

The following sub-section describes the steps in the process in more detail. The process description is based on the earlier RIVM/TNO study, the draft SPIN document on Du Pont and the Handbuch Chlorchemie [Bremmer 1988, SPIN 1994c, ECOTEC 1991].

2 PROCESSES

HCFC-22 is produced from chloroform and hydrogen fluoride (HF). Antimonypentachloride is used as a catalyst. The reaction is:

(1) $CHCl_3 + 2\ HF \longrightarrow CHF_2Cl + 2\ HCl$

The reaction mixture is conducted to an HCl column where the hydrochloric acid gas is separated and processed in the cooler absorbers with water to a commercially acceptable 30% HCl solution. The bottom product in the HCl column is purged of HF in the water scrubber. From this, 15% HF solution is produced for sale.

The remaining acid and traces of Cl_2 are neutralised with an alkaline buffer solution and disposed of via the process sewage pipe. HCFC-22 is dried and purified in a distillation column and then stored in tanks. Dissolved HCFC-22 in the watery flows (alkaline solution and 15% HF) is recovered. Waste acid (HCl), which is released via a separate acid outlet pipe, together with other alkaline waste flows are purged of residues of fluorohydrocarbons and halogenated compounds by means of strippers. Active carbon filters ensure that the halogenated components are recorded. All watery flows from the HCFC-22 plant are released directly and contain no substances which can be decomposed in a biological treatment installation.

3 SUBSTANCE FLOWS AND EMISSIONS IN 1990

The input and output of chlorine compounds in the process are confidential. They concern the consumption of chloroform and chlorine and the production of HCFC-22, HCl and releases of chloride. The figures acquired by TNO and CML are therefore not published here. For the same reasons, the CBS does not publish figures for the exports of HCFCs or net import figures. Some of the HCFCs are sold for the consumption application market, and some are used internally in the production of teflon. Table 18.1 shows the use in consumption applications for 1990 on the basis of the CFC action programme [CFC Commission 1994].

Table 18.1 Production, import and export of chlorinated solvents in 1990 (tonnes chlorine; in brackets: tonnes of substance)

Substance name	Production	Net import	Consumption
HCFC-22 (consumption applications)	*	*	896 (2,120)
HCFC-22 (teflon production)	*	*	*

* Confidential

The emissions occurring during the production process consists of emissions of chloride as salt to the surface water, releases of HCl in the surface water and chloroform emissions to water. The emissions to air consist of volatile organic substances (VOS), including HFC-23, HCFC-23, HCFC-21 and chloroform.

The ER-I only records emission figures for a combined process 'emission of freons', where the emissions related to the production of CFC-113 and CFC-114 are also included. Emissions of C_2-compounds are allocated to the CFC-113/114 production because this involves production of C_2 compounds. Emissions of C_1 compounds are allocated to the production of HCFC-22. The ER-I also reports emissions of DCM and CFCs in other processes (such as cooling). Such emissions are not included here but in the segments describing the consumption applications of DCM and CFCs.

Emissions to water are taken from WIER, supplemented with an item for 'CFCS not further known' from the ER-I. They are total figures for all processes at Du Pont. They must be allocated to the production of CFC-113/114, HCFC-22 and teflon. In the absence of anything better they are allocated to the three processes in the ratio 40:50:10 on the basis of global chlorine input.

4 EMISSIONS UNDER ENVISAGED POLICY

Du Pont has drawn up a Corporate Environmental Plan (BMP). This describes emission objectives for the production of HCFC-22 in the year 2000. When this report was being compiled the BMP had not yet been approved and was not public. The objectives will probably not change however [FO-Industrie, 1995]. The calculation for the situation after implementation of the envisaged policy is therefore based on the figures from the draft BMP that were available in May 1995. These emission figures can not be published for the moment for reasons of confidentiality.

The substance groups in the BMP are less detailed than the emission figures for 1990 from the ER and WIER. Discrepancies and problems of allocation were dealt with as follows:

- the BMP gives an overall objective for emissions of HCFCs to air, without a breakdown by individual substance. The same applies for the emissions of CFCs. We assumed that the total emission budget for HCFCs or CFCs can be allocated to individual HCFCs or CFCs in accordance with the actual ratio of emissions in 1990;
- the BMP gives a combined total for the quantity of emissions of EOCl to water from the production of HCFCs and Teflon[3]. A ratio of 40:10 for emissions of EOCl from HCFC and Teflon production was adopted in sub-section 3. This ratio is also maintained for the year 2000;
- the BMP gives no specific reduction target for chloroform to water. This emission was included in WIER for 1990. The same applies for an emission to water of FCHCs - not further known in the ER. It is assumed that the chloroform and FCHC emissions will be reduced by the same percentage between 1990 and 2000 as the EOCl emissions.

5 COMMENTS AND POINTS FOR DISCUSSION

The quantity of chlorine measured as EOCl was more than 10 times higher in 1990 than the quantity of chlorine which was released in the form of known individual compounds. This discrepancy can probably be explained by the item 'CFCs - not further known' in the ER-I.

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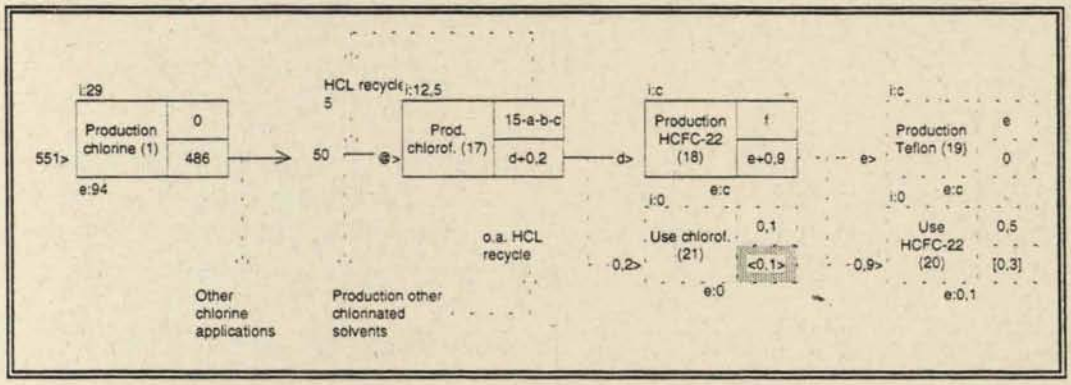
[3] EOCl emissions from the CFC-113/114 plant are no longer relevant since it closed in 1994.

Emission figures at the process level from ER-I and WIER can not be published without the consent of the company concerned. Since in this case the process takes place at only one company in the Netherlands, it is impossible to disguise the figures by aggregation. The company concerned declined a request by TNO/CML to publish the emission figures adopted for 1990 and the future situation in this report.

Figure 18.1: Substance flows in production of HCFC-22 (in kt chlorine, 1990)



SEGMENT 19: PRODUCTION OF TEFLON

1 INTRODUCTION

Teflon is produced in the Netherlands by DuPont de Nemours. Teflon (PTFE, polyfluoroethene) is produced from tetrafluoroethene (TFE) in a watery environment. HCFC-22 is the raw material for TFE. Copolymers of PTFE are formed from TFE and HFP (hexafluoropropene).

The following sub-section describes the steps in the process in more detail.

2 PROCESSES

First, the processes which take place in the TFE-HFP monomers plant will be described. The process relating to the teflon production will then be discussed. Figure 19.1 illustrates the entire process in diagrammatic form.

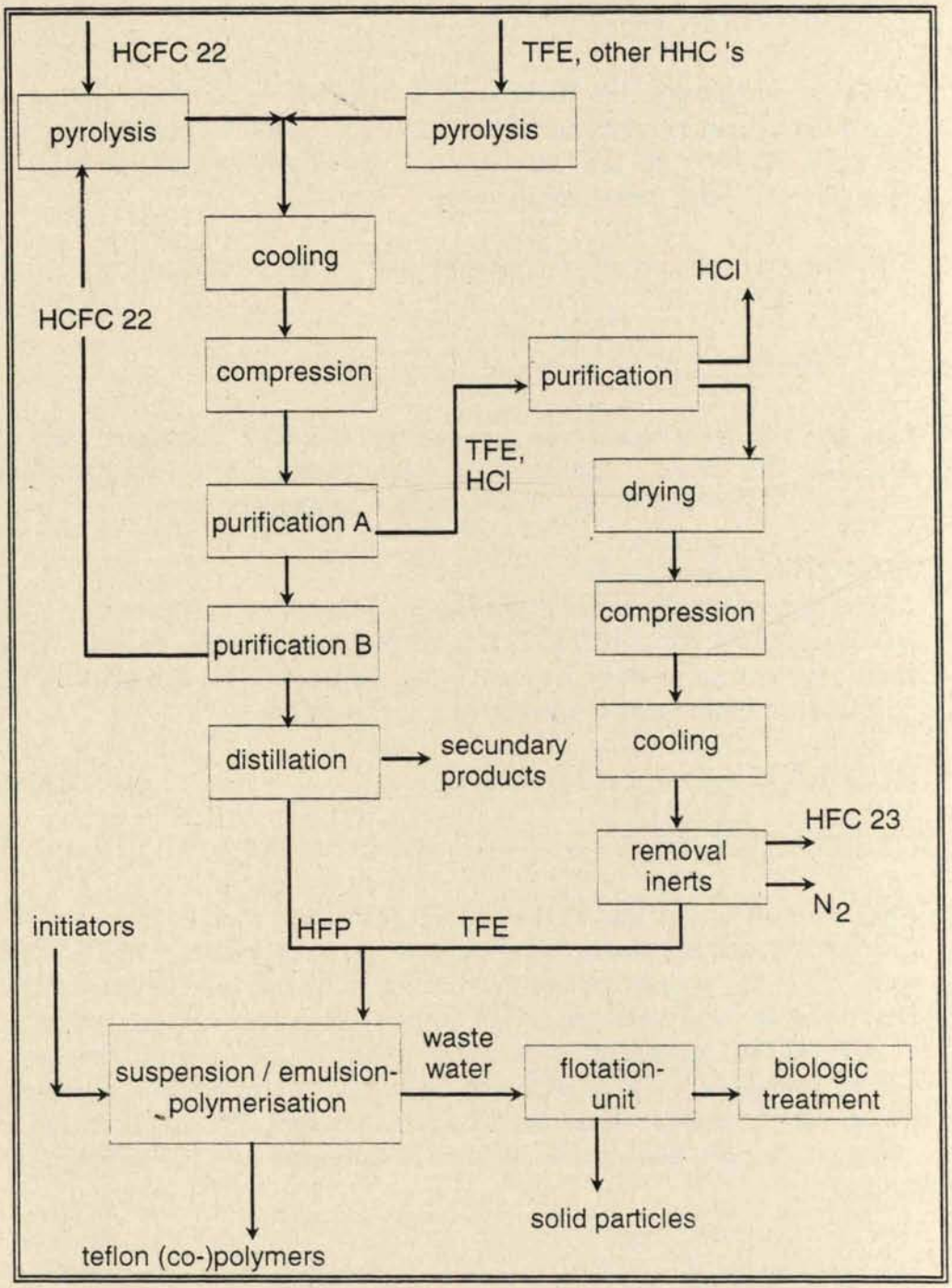
TFE/HFP Monomers plant
TFE is prepared by pyrolysis of HCFC-22, followed by purification in which the quantity of unconverted HCFC-22 is again fed into the pyrolysis ovens in purified form. HFP is then prepared by means of pyrolysis of TFE and other HFCs. The comparative reactions of this process are given below:

(1) $2\ CHF_2Cl \longrightarrow F_2C{=}CF_2 + 2\ HCl$ (production TFE)

(2) $CHF_2Cl + F_2C{=}CF_2 \longrightarrow CF_2{=}CF{-}CF_3 + HCl$ (production HFP)

After the synthesis ovens, TFE and HFP are largely purified in a joint process. Cooling and compression is followed by the first separation of TFE as azeotrope with HCl in the primary column (A). This product can be safely stored in tanks. Depending on the demand for TFE in the polymer factories and for the preparation of HFP, HCl is then removed with water (5% HCl is now released, but from 1995 will be sold as 30%), after which traces of HCl are removed in a caustic soda washer (discontinuous release via the process sewage). This is followed by drying of the gas, compression, cooling and removal of inerts (HFC 23 and N_2) in the gas stripper.

Figure 19.1 *Diagram of teflon production and the production of copolymers of teflon*



The bottom product of the primary column (A) is purged in a column of unconverted HCFC-22 and contains HFP, high boiling and very high boiling substances. Pure HFP is separated from the many by-products via four different distillation columns. The high boiling substances are partly re-cracked to HFP, among other things, whereupon the remainder is released into the atmosphere at a height of 65 metres via a central chimney after detoxification of the toxic PerFluorIsoButene (PFIB). The very high boiling substances are also (separately) detoxified and incinerated externally. HFP is stored in a storage tank.

TEFLON production
Teflon and its copolymers are formed from TFE, and in the second case also from HFP in a watery environment. Teflon is formed according to the following reaction:

(3) $n\ F_2C{=}CF_2 \longrightarrow -CF_2-CF_2-CF_2-CF_2-$

Because of the danger of explosion (TFE is extremely reactive) and the fairly high polymerisation temperature, teflon production occurs in a watery environment at temperatures of 20-100°C and pressures of 0.2 to 1.5 mPa, with even lower pressures often sought for safety reasons. Persulphates, manganese acid, redox systems or perfluorated organic peroxides can be used as initiators. The polymerisation process in a watery environment can be either an emulsion polymerisation or a suspension polymerisation process. The effluent contains dispersal agents and coagulants. To remove solid particles the flows are treated via a flotation unit before going to the biological treatment installation.

3 SUBSTANCE FLOWS AND EMISSIONS IN 1990

The quantity of HCFC-22 used in the production of teflon (co)polymers is confidential. Figures acquired by TNO and CML are therefore not being published. The chlorine from HCFC-22 was almost entirely converted into chloride (salt) which was released. A further 4 tonnes of waste and 121 tonnes of other emissions (expressed in tonnes of chlorine) were produced.

The major emissions to air in the production of monomers are volatile organic substances (VOS) including (C)FHCS. These are registered in ER-I as a separate process, so that there are no problems with allocation. Emissions to water have been taken from WIER supplemented with the item 'CFCs - not further known' from the ER-I. These are total figures for all processes at DuPont. They must be allocated to the production of CFC-113/114, HCFC-22 and teflon. In the absence

of anything better, they have been allocated to the three processes in the ratio 40:50:10 on the basis of the global chlorine input.

4 EMISSIONS UNDER ENVISAGED POLICY

Measures are already being taken to reduce emissions. Measures in the production process for HCFC-22 are described in segment 19.

DuPont has drawn up a Corporate Environmental Plan (BMP), which includes emission objectives for the production of teflon monomer and teflon in the year 2000. At the time this report was compiled, the BMP had not yet been approved and published. The objectives are not expected to change [FO-Industrie, 1995]. In the calculations for the situation after implementation of the envisaged policy, therefore, the figures available in May 1995 from the draft BMP have been used. These emission figures can not be published at the moment for reasons of confidentiality.

The substance groups in the BMP are less detailed than the emission figures for 1990 from the ER and WIER. Discrepancies and problems of allocation were dealt with as follows:

- the BMP gives an overall objective for emissions of fluorochlorohydrocarbons (FCHCs) to air from the teflon monomer plant without any breakdown for each individual substance. We have assumed that the total emission budget for FCHCs can be allocated to individual FCHCs in accordance with the actual ratio of emissions in 1990;
- the BMP gives a combined total for the quantity of emissions of EOCl to water from the production of HCFCs and Teflon[4]. In sub-section 3 a ratio of 40:10 was adopted for emissions of EOCl from HCFC and Teflon production. This ratio has also been retained for the year 2000;
- the BMP gives no specific target for reduction of emissions of FCHCs- not further known to water. This emission was recorded in the ER for 1990. It is assumed that the chloroform and FCHC emission will be reduced by the same percentage as the EOCl emission between 1990 and 2000.
- in 1990 the ER recorded an emission of PER from teflon production. The BMP gives no specific objective for emission of PER in teflon production, but gives one for DuPont as a whole. For simplicity's sake, the total emission of PER in the year 2000 is allocated entirely to teflon production;

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[4] EOCl emissions by the CFC-113/114 plant are no longer relevant since it was closed in 1994.

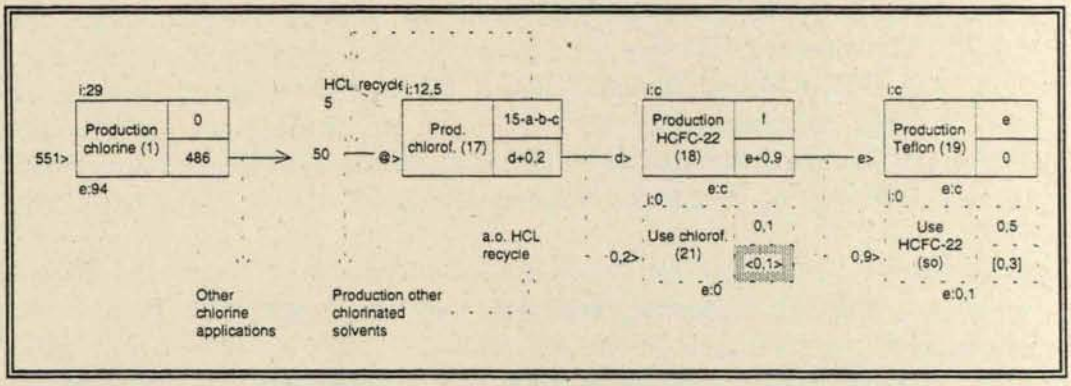
- for the year 2000, the BMP refers to a new emission of a FCHC to air compared with the BMP reference years of 1985 and 1992. This was also not included in the ER in 1990. This is added as an extra emission for the year 2000;
- an emission of another CFC from the teflon production which was important in 1992 will be reduced to zero in the year 2000 according to the BMP. All CFCs still emitted in 2000 according to the BMP are already allocated to HCFCs (segment 18). It is therefore assumed that the emission in the ER for 1990 will no longer occur in the year 2000.

5 COMMENTS AND POINTS FOR DISCUSSION

The quantity of chlorine measured as EOCl in 1990 was over 10 times higher than the quantity of chlorine which was released in the form of known individual compounds. This discrepancy can probably be explained by the item 'CFCs - not further known' in the ER-I.

Emission figures at the process level from ER-I and WIER can not be published without the consent of the company concerned. Since in this case the process takes place at only one company in the Netherlands, it is impossible to disguise the figures by aggregation. The company concerned declined a request by TNO/CML to publish the emission figures adopted for 1990 and the future situation in this report.

Figure 19.2: Substance flows in production of teflon (in kt chlorine, 1990)



SEGMENT 20 CONSUMPTION APPLICATIONS OF HCFC-22

1 INTRODUCTION

HCFC-22 is used as an industrial cooling agent and as an aerosol. HCFC-22 is used as a substitute for CFC-11 and CFC-12 because it has far less effect in depletion of the ozone layer and the substitution can be made without major technical modifications.

2 PROCESSES AND SUBSTANCE FLOWS

In 1990 an estimated total of 2,120 tonnes of HCFC-22 was consumed [CFC Commission 1994]. According to estimates by KPMG [1994], around 60% of the consumption was as a cooling agent and 40% in aerosol products (1,270 and 850 tonnes respectively). The various applications are described below. Table 20.1 presents a summary of consumption and emissions.

Cooling agent for industrial purposes
The cooling agent HCFC-22 is used as a substitute for so-called hard CFCs in industrial refrigerators. The volume used in 1990 was 1,270 tonnes. Besides supplementary losses through leaks, the market is also growing (new building and conversions). A rating for the emission to air, disposal with waste and growth of the market can be derived from the VNCI-McKinsey study in 1991. On this basis, the growth in the market is fixed at 656 tonnes. Of the remainder, 96.5% is emitted to air and 3.5% disposed of as waste [VNCI/McKinsey 1991].

Aerosol
In 1990 an estimated 850 tonnes of HCFC-22 was used as aerosol/propellant for foams. According to estimates by KPMG [1994] around 65% of this was used for PUR aerosols and 35% in other aerosol products. As a result of an export surplus the consumption of aerosols in the Netherlands is only 66% of the production [Tukker 1993b]. It is assumed that this also applies for the aerosols dealt with here. It is assumed that the entire volume is emitted to air.

Table 20.1: Use of HCFC-22 in 1990 (tonnes of chlorine; in brackets: tonnes of substance)

Target group	Consumption	Imp./exp.	Accumulation[1]	Air	Water	Waste
Industrial cooling	521 (1270)		269 (656)	243 (593)		9 (21)
PUR-aerosol	226 (550)	- 77 (-187)		149 (363)		
Other aerosols	123 (300)	- 42 (-102)		81 (198)		
Total:	869 (2120)	- 119 (-289)	269 (656)	473 (1154)		9 (21)

1) In 1990 there was a growth market of 656 tonnes in the cooling target group. This amount accumulated in society.

3 EMISSIONS UNDER ENVISAGED POLICY

On 16 March 1993 the "Provisions for the leak-proofing of cooling plants Regulation" was published in the Government Gazette. The purpose of the regulation was to prevent emissions of cooling agents. To this end, further provisions were drawn up with respect to the leak-proofing of cooling plants (with a capacity greater than 500 Watt).

In December 1994 the European Commission adopted a new integrated regulation concerning substances that deplete the ozone layer (PbEG 3093/94 of 15 December 1994). This also covered HCFCs, for which the European Union included provisions for the reduction which went further than the reductions agreed in the Protocol of Montreal. The regulation is based on a phased reduction in the use of HCFCs from the level in the reference year of 1989. The regulation states that from 1 January 2015 no chlorofluorohydrocarbons may be marketed or used by a company itself.

Six months after the regulation entered into force the use of HCFCs was banned, with the exception of applications as a cooling agent, solvent, propellant for the manufacture of insulating hard foam and integrated foam for safety purposes, in laboratories and as a carrying gas for decontaminants in closed systems.

From 1-1-1996 HCFCs may no longer be used as cooling agent in open systems with direct evaporation, or household refrigerators and freezers, or in climate

control equipment in cars and vehicles for public transport by road produced after this date. Applications as a solvent in open systems and aerosols are also prohibited.

From 1-1-1998 HCFCs may no longer be used in equipment produced after 31-12-1987 for applications as carrying gas for decontaminants in closed systems and as climate control instruments in vehicles for public transport by rail.

From 1-1-2000 there is a ban on the application of HCFCs as a cooling agent in cooling refrigeration plants or equipment with an axle capacity of 150 kW or more produced after this date.

The regulation contains measures which will only be implemented in the medium term. It is however established policy which is no longer open to discussion. We therefore chose to regard the situation after implementation of this policy as the future situation and did not opt for a point in time when HCFCs are still used. Ultimately, there will be zero emissions for all applications after implementation of the policy established as of 1 January 1995. Table 20.2 shows this.

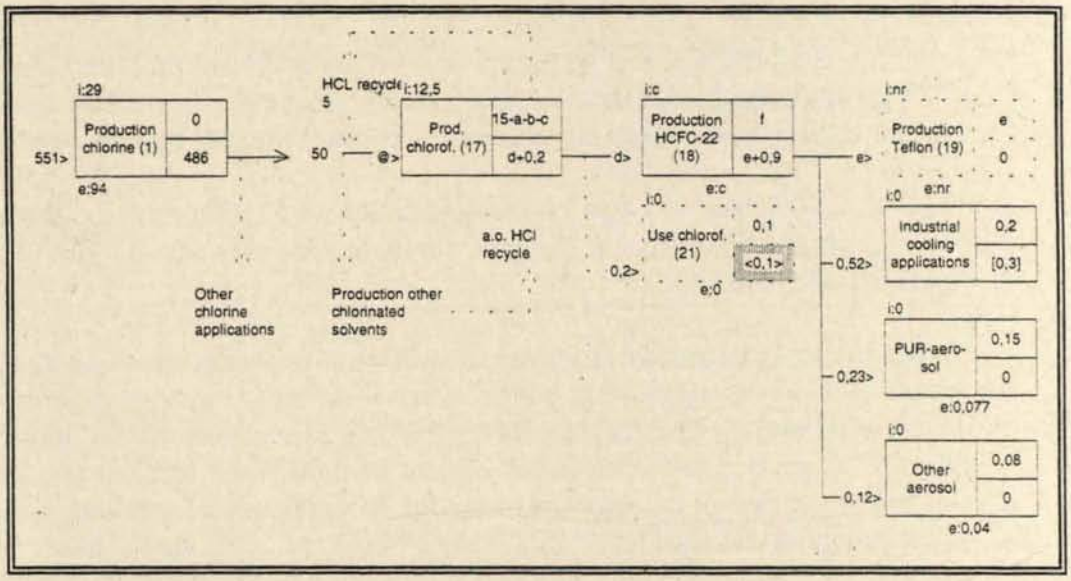
Table 20.2 Emissions of HCFC-22 under envisaged policy (tonnes chlorine; in brackets: tonnes of substance)

Target group	Consumption (tonnes)	Imp./exp. (tonnes)	Stock formation (tonnes)	Air (tonnes)	Water (tonnes)	Waste (tonnes)
Diverse	p.m.	p.m.	p.m.	0	0	0
Total:	p.m.	p.m.	p.m.	0	0	0

4 COMMENTS AND POINTS FOR DISCUSSION

None.

Figure 20.1: Substance flows in consumption applications of HCFC-22 (in kt chlorine, 1990)



SEGMENT 21: CONSUMPTION APPLICATIONS OF CHLOROFORM

1 INTRODUCTION

Chloroform is mainly used for the production of HCFC-22 (see segment 18). The use of chloroform in consumption applications has declined sharply since the mid-1980s. Bremmer [1988] mentions its use in the pharmaceutical industry as an important application, while a recent study of the effluent problems in the pharmaceutical industry by the CUWVO regards the use of chloroform as negligible [CUWVO 1993].

2 PROCESSES, SUBSTANCE FLOWS AND EMISSIONS IN 1990

According to segment 17, the use of chloroform in consumption applications amounts to around 229 tonnes per year. This sub-section discusses the known consumption figures in the target groups:

- the pharmaceutical industry;
- yarns and fibres industry.

Pharmaceutical industry
In the pharmaceutical industry the consumption of chloroform is minimal. The ER-I records an emission from the industry of around 1 tonne [ER-I 1994, Berdowski 1993]. Emission to water is disregarded on the basis of the CUWVO report [1993]. Figures for the disposal as water are not known and are disregarded.

Yarns and fibres industry
According to figures from the Emission Reduction in the Chemical Industry Project (PERC) 115 tonnes of chloroform were emitted to air and 0.2 tonnes to water in 1985 [Comprimo 1991; VROM/Comprimo 1992]. These emissions have also been taken for 1990.

Other
Based on a consumption of 210 tonnes in 1990, there remains a volume of 94 tonnes for the item 'Applications not known'. In the absence of data or indications no estimate has been made of emissions to water, air and waste.

Table 21.1 presents a summary of these figures.

Table 21.1: Use of chloroform in 1990 (tonnes of chlorine; in brackets: tonnes of substance)

Target group	Consumption (tonnes)	Imp./exp. (tonnes)	Air (tonnes)	Water (tonnes)	Waste (tonnes)
Pharmaceutical industry	0.9 (1)		0.9 (1)		
Yarns/fibres industry	102 (115)		102 (115)	0.18 (0.2)	
Unknown	100 (113)				
Total:	203 (229)		103 (116)	0.18 (0.2)	

3 EMISSIONS UNDER ENVISAGED POLICY

The measures adopted for each target group as of 1 January 1995 to reduce emissions are discussed below. On the basis of the emission situation in 1990, an estimate has been made of the emissions that will remain after implementation of this policy. No account has been taken of changes in emissions as a result of economic growth or other autonomous developments within the target group.

Pharmaceutical industry
EU Directive 94/60/EC contains a ban on the use of chloroform in concentrations of 0.1% or more in mass in substances and preparations intended for sale to the general public. A number of exceptions are made for certain medicines and cosmetic products.

In 1990 the pharmaceutical industry emitted 1 tonne of chloroform to air. The companies in the pharmaceutical sector have signed the 'Memorandum of Understanding for the implementation of an environmental policy in the chemical industry'. These companies are therefore bound by the expected emission reduction on the basis of the draft BMPs. At the time this report was compiled these BMPs had not all been approved. The objectives are not expected to be changed however. The emissions to air are to be reduced by 90% [FO-Industrie 1995]. The future emission of chloroform by the pharmaceutical industry will then be 0.1 tonne.

Yarns and fibres industry
The yarns and fibres industry emitted 115 tonnes of chloroform to air and 0.2 tonnes to water in 1990. The companies in the sector have also signed the 'Memorandum of Understanding for the implementation of environmental policy in the chemical industry'. These companies are therefore also bound by the target

emission reductions based on the BMPs. For emissions to air this is expected to be 90% and for emissions to water 80% [FO-Industrie 1995]. This means that the future emission of chloroform by the yarns and fibres industry in 2000 will be 11.5 tonnes to air and 0.04 tonnes to water.

Other/unknown
There was a consumption of 94 tonnes of chlorine in 1990 for unknown applications. In the absence of data or indications no estimate has been made of emissions to air, water and waste. Nor has any estimate been made for the situation after implementation of established policy.

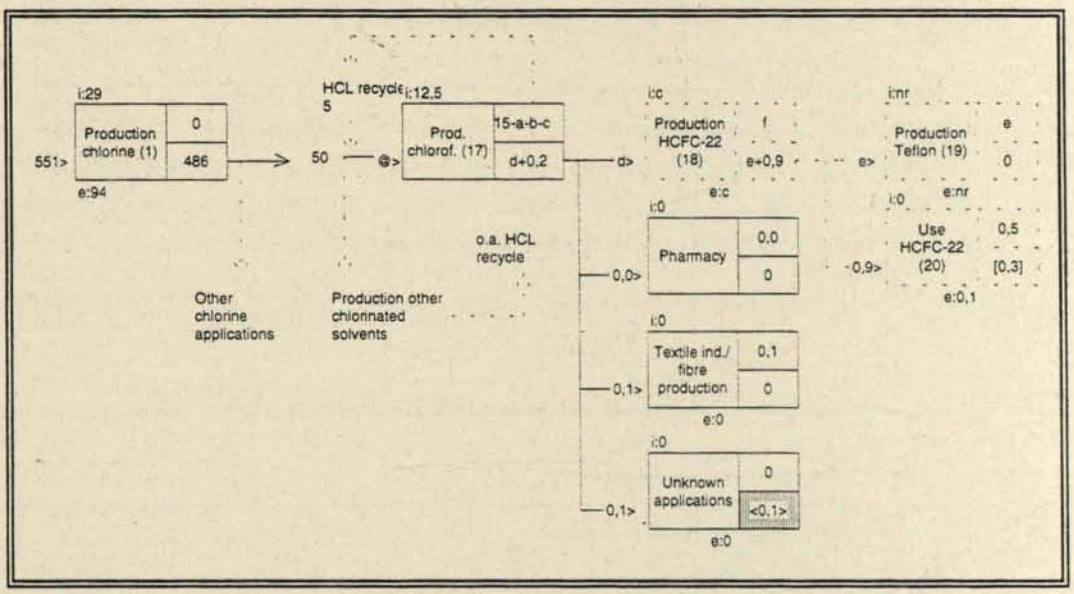
Table 21.2: Emissions of chloroform under envisaged policy (tonnes chlorine; in brackets: tonnes substance)

Target group	Consumption (tonnes)	Imp./exp. (tonnes)	Air (tonnes)	Water (tonnes)	Waste (tonnes)
Pharmaceutical industry	p.m.	p.m.	0.09 (0.1)		
Yarns and fibres industry	p.m.	p.m.	10.2 (11.5)	0.04 (0.04)	
Other / unknown	p.m.	p.m.			
Total:	p.m.	p.m.	10.29 (11,6)	0.04 (0.04)	

4 COMMENTS AND POINTS FOR DISCUSSION

According to a study by RIZA there is a diffuse emission of chloroform to water via households. Measurements taken during the period 1984 to 1987 showed releases of 2.3 tonnes of household effluent into the sewage system [Teurlinckx 1991]. This figure must be interpreted cautiously. The emission figures have possibly been overtaken because immediately after the period in which the measurements were taken the quantity of chloroform in consumption applications is likely to have declined sharply. The formation of trihalomethanes during the use of hypochlorite could also have contributed to the chloroform burden [ODWM 1989, FIFE 1993]. Without new measurements and further study it is impossible to assess the size and sources of emissions of chloroform to water from households.

Figure 21.1: Substance flows in consumption applications of chloroform (in kt chlorine, 1990)



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SEGMENT 22: PRODUCTION OF CFC-11 and CFC-12

1 INTRODUCTION

Allied Signal in Weert (formerly an Akzo subsidiary) produces CFC-11 (trichlorofluoromethane) and CFC-12 (dichlorofluroromethane). The use of these substances has been halted by virtue of the Protocol of Montreal and its implementation in the EU as of 1 January 1995, with a number of exceptions. Allied Signal will continue to produce these CFCs for those applications.

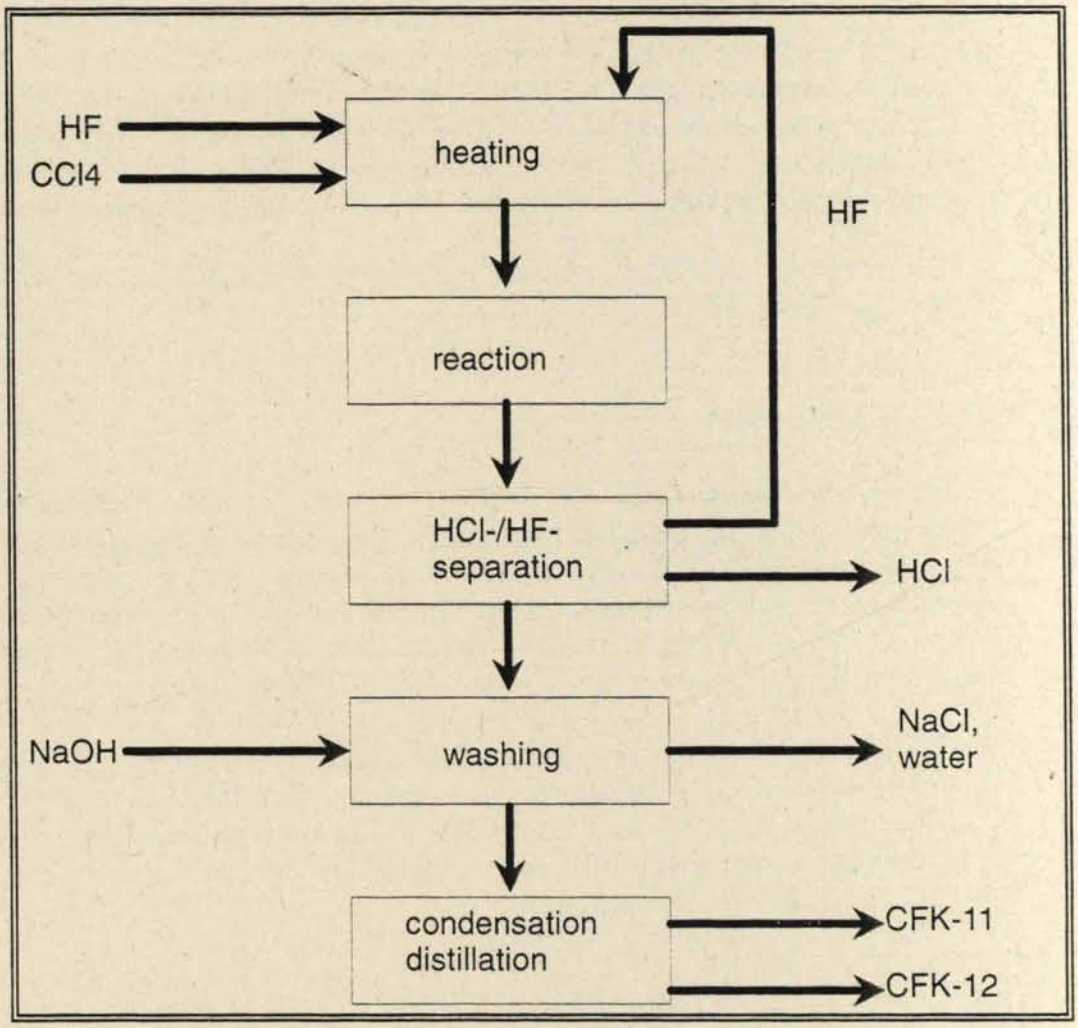
The following sub-section describes the steps in the process in more detail [Bremmer 1988, ECOTEC 1991].

2 PROCESSES

The raw material for CFC-11 and CFC-12 is tetra. Almost all the tetra produced and imported to the Netherlands is used in the process. By substituting chlorine with fluoride, both CFCs are produced from tetra. Gaseous HF and tetra are put into a rotating oven. Reaction takes place at around 150°C with the aid of a catalyst. Process conditions such as temperature, pressure and the proportions of the raw materials in the mix determine which CFCs are produced.

After the reaction the gaseous products are separated from the by-product, hydrochloric acid, and washed with caustic soda. The different CFCs are separated by distillation. HF is returned to the process. The manufacturing process for CFC-11 and CFC-12 is shown in the diagram below. A very small quantity of CFC-13 is also produced as a by-product.

Figure 22.1: Diagram of production of CFC-11 and CFC-12 [ECTOTEC 1991]



3 SUBSTANCE FLOWS AND EMISSIONS IN 1990

In 1990, 7,720 tonnes of HCl (expressed as chlorine) were produced in the production of CFC-11 and CFC-12. The volume of tetra used and the quantity of CFC-11 and CFC-12 produced are confidential.

A number of tonnes of CFC-13 are released as a by-product. This quantity is disregarded here.

Table 22.1 shows the imports for 1990 according to the CBS. The monitoring programme of the CFC action programme provides an insight into the consumption in 1990 [CFC Commission 1994]. The CBS does not produce figures for exports of CFCs because there is only one producer [CBS 1991]. Figure 22.2 gives a summary of these figures.

Table 22.1: Production, import and export of CFC-11 and CFC-12 in 1990 in tonnes chlorine (in brackets: tonnes of product)

Substance name	Production	Import [CBS 1991]	Export	Consumption [CFC Commission 1994]
CFC-11	*	4,475 (5,779)	*	4117 (5,317)
CFC-12	*	812 (1,385)	*	612 (1,043)

* Confidential

The ER-I indicates that emissions to air are the most significant [ER-I 1994]. These are emissions of CFC-11, CFC-12, CFC-13 and tetra. Emissions to water are taken from WIER and if necessary supplemented on the basis of ER-I [RIZA 1994a].

Emission figures at the process level from ER-I and WIER can not be published without the consent of the company concerned. Since in this case the process takes place at only one company in the Netherlands, it is impossible to disguise the figures by aggregation. The company concerned declined a request by TNO/CML to publish the emission figures adopted for 1990 and the future situation in this report.

3 EMISSIONS UNDER ENVISAGED POLICY

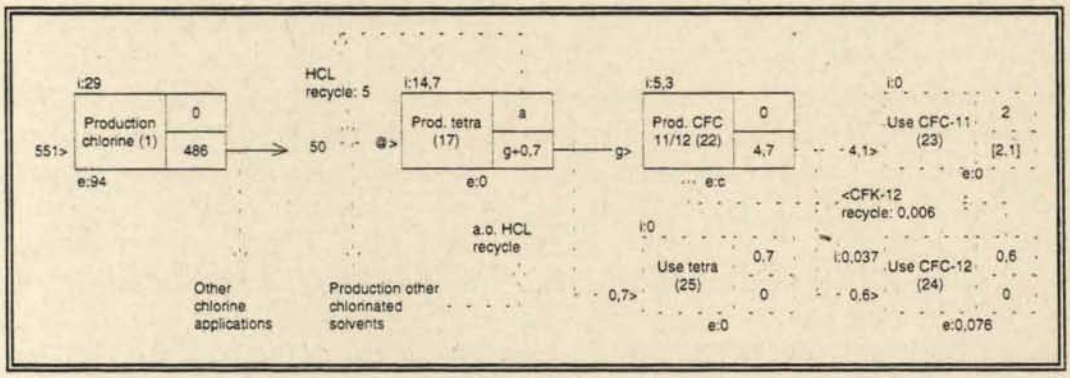
The Protocol of Montreal prohibits the use and production of new CFCs and tetra from 1 January 1996. The EU has prepared a regulation which gave effect to this ban from 1 January 1995 (EU Regulation 3093/94). The substance may now only be used for a small number of essential applications. Allied Signal still produces for these applications. These exceptions will become more limited over time.

For the time being, no date has been given for when Allied Signal will stop producing CFCs. Although the level of production is falling there will be no major changes in the emissions to air compared with 1990. The installation of an MPPE unit on 1/7/1995 will reduce emission to water by 90%. For the situation after implementation of the envisaged policy from 1 January 1995, emissions to air will be assumed to be the same as in 1990 and emissions to water will be based on a reduction of 90% compared with 1990 [Allied Signal 1995].

4 COMMENTS AND POINTS FOR DISCUSSION

From the figures in ER-I and WIER in 1990 the quantity of chlorine measured as EOCl was around 10 times greater than the quantity of chlorine which was released into water in the form of previously known individual compounds [RIZA 1994a, ER-I 1994]. This discrepancy can probably be explained by the item, "CFCs - not further known" in the ER-I. The company was included in the AOX/EOX measurement programme conducted by RIZA in mid-1992. The quantity of EOX was a factor of 4 lower than in 1990 [RIZA 1994b].

Figure 22.2: Substance flows in production of CFC-11 and 12 (in kt chlorine, 1990)



SEGMENT 23: CONSUMPTION APPLICATIONS OF CFC-11

1 INTRODUCTION

CFC-11 has several different uses, the most important being its use as a propellant for various synthetic foams. Relatively small amounts of CFC-11 are used in dry cleaning, aerosols, cooling agents and diverse other products.

2 PROCESSES, SUBSTANCE FLOWS AND EMISSIONS IN 1990

According to the CFC Commission's annual report [1994] a total of 5,317 tonnes of CFC-11 were used in 1990. Details of the use, accumulation, import and export of products containing CFC-11 and emissions classified by application are given below. Table 23.1 gives an outline summary.

Dry Cleaning
The use of CFC-11 in chemical laundries and industrial textile cleaners amounted to an estimated 14 tonnes in 1990 [CFC Commission 1994]. This total is made up of waste and emissions to air or water in the same proportions as adopted for CFC-113 in the report 'Cleaning and degreasing with HHC's in small firms' [van der Most 1993]. An estimated 11 tonnes of CFC-11 are emitted to air and 0.2 tonnes to water. Approximately 2.8 tonnes is disposed of as waste.

Aerosols
According to the CFC action programme a total of 479 tonnes of CFC-11 and CFC-12 were used in the production of aerosols in 1990. KMPG states that CFC-11 accounted for about 20% (96 tonnes) of this amount. Due to an export surplus the use of spray cans in the Netherlands is only 66% of the production [Tukker 1993b]. Therefore only 63 tonnes of CFC-11 in all are used in aerosol products in the Netherlands.

Synthetic foams
The total use of CFC-11, -12, -113 and -114 in production of synthetic foams came to 5,353 tonnes in 1990 [CFC Commission 1994]. Of this total, 44 tonnes were CFC-114 and 115 tonnes CFC-12. The CFC Commission gives a breakdown by application for 861 of the 983 tonnes CFC-113 used in 1991. It is assumed that the remaining 13% was used in foam. On the basis of the 1,197 tonnes of CFC used in 1990 this amounts to 157 tonnes. This indicates that 4,937 tonnes of CFC-11 remains in foam (see the relevant segments). The SPIN document 'Production of synthetic foam' lists the use of CFC-11 in various kinds of PUR and XPS foam

in addition to the occurring emissions. The propellant in soft PUR and XPS diffuses so quickly that the emission can be considered equal to the use. In PUR and other PUR-types CFC-11 is mainly absorbed by the foam and diffuses over a period of decades. The accumulation in the economy and the emissions released directly to the air during production were taken from the SPIN document [SPIN 1993d]. This leaves an outstanding item of 140 tonnes of CFC-11 for other foams, whereby it is assumed that the propellant was all emitted to air. There is no difference between the import and export of hard PUR-foam materials which means that no corrections are needed on account of possible stock formation [CBS 1991].

Emissions from the amount of synthetic foam accumulated in society
As indicated above, a significant share of CFC-11 is absorbed in hard PUR foams and diffuses slowly into the environment. Assuming a similar production rate per capita as in the United States, about 34,000 tonnes of CFC-11 has been taken as the figure for Dutch production of hard PUR foam since 1960 [EPA 1998]. In the 1990 annual report of the CFC action programme, the Dutch stock of CFCs in insulating foam was estimated at 50,000 tonnes [CFC Commission 1991]. Some of this stock will by now have been emitted to the air either through diffusion or damage depending on the application. The EPA estimates this amount to be 50% [EPA 1988]. This would lead to a remaining amount of between 17,000 and 25,000 tonnes CFC-11 in hard PUR. Based on a remaining lifespan of 45 years, an average of 360 to 530 tonnes will be emitted each year. We have adopted an annual volume of 445 tonnes. Specialised processing centres did not start recovering CFC-11 from PUR foam until 1992.

Cooling
A total of 737 tonnes of CFCs were used in cooling plants in 1990, according to the CFC action programme. Subtracting the consumption of CFC-12 and CFC-115 leaves a figure of 143 tonnes of CFC-11 used as a cooling agent. It is further assumed that about 50% involves replacement of an amount lost through leakage and 50% expansion of the cooling market.

Other uses
An entry of 127 tonnes remains for 'other applications'. In view of the proportions in the other groups it is assumed that this remaining entry is emitted entirely to the air.

Table 23.1: Application of CFC-11 in 1990 (tonnes chlorine; in brackets: tonnes substance)

Target group	Consumption (tonnes)	Imp./exp. (tonnes)	Stock formation (tonnes)	Air (tonnes)	Water (tonnes)	Waste (tonnes)
Dry cleaning	11 (14)			9 (11)	0.15 (0.2)	2.2 (2.8)
Aerosols	74 (96)	-26 (-33)		49 (63)		
PUR-soft	466 (602)			466 (602)		
PUR-hard	2245 (2900)	zero	2133 (2755)	112 (145)		
PUR-other	310 (400)	zero	288 (372)	22 (28)		
XPS-foam	693 (895)			693 (895)		
Other foams	108 (140)			108 (140)		
Hist. foam emissions		zero	-345 (-445)	345 (445)		
Cooling	111 (143)			111 (143)		
Other	98 (127)			98 (127)		
Total:	4117 (5317)	-26 (-33)	2076 (2682)	2012 (2599)	0.15 (0.2)	2.2 (2.8)

3 EMISSIONS UNDER ENVISAGED POLICY

A number of measures limiting the use of CFC's have already been implemented in the period 1990-1995. With effect from 1 January 1993 a ban was imposed on the production and marketing of insulating plates or panels containing CFCs (polyurethane and polystyrene). This was extended to cover other insulating materials containing CFCs on 11 July 1993. Furthermore, since 1 January 1992 the use of sprayed insulating material which contains CFCs is not permitted for floor or cavity wall insulation. A 'spray can covenant agreement' between VROM and Dutch Aerosol Union (NAV) dating from 5 January 1988 stipulated a reduction in the use of CFCs. With the exception of technical and medical sprays, which were not covered by the agreement, the CFC use in consumer aerosols ended in 1991.

The Montreal Protocol forbids the use of new CFCs and tetra from 1 January 1996. The EU drew up a regulation to enforce this with effect from 1 January

1995 (EC Regulation 3093/94). CFC-11 should therefore also be phased out in the Netherlands from this date.

The substance is only permitted for a limited number of essential uses. These exceptions will be gradually restricted. Recycled CFCs and tetra may still be used after 1 January 1995. In effect, it is accepted that the volume of CFCs present in the Netherlands on 1 January 1996 will be used up. In 1990 the CFC Commission estimated the existing store of CFCs in closed applications (particularly cooling systems) at about 5,000 tonnes [CFC Commission, 1990]. Given the sharp decline in use over the period 1990-1994, we estimate the amount since 1 January 1995 to be significantly smaller, and negligible in comparison with the 17,000 to 25,000 tonnes still stored in foam.

Recycling of CFCs from foam is still only carried out on a small scale. Only some foam from refrigerators is processed; this is however a very limited amount. There is therefore no policy to tackle the historical emissions from foam.

In conclusion, the emission from all uses which remains after implementation of the envisaged policy from January 1 1995 is fixed at zero. The historical emissions from foam are an exception. Without a supplementary policy these will continue for decades and are therefore seen as a *future* emission. Table 23.2 gives the future emission scenario.

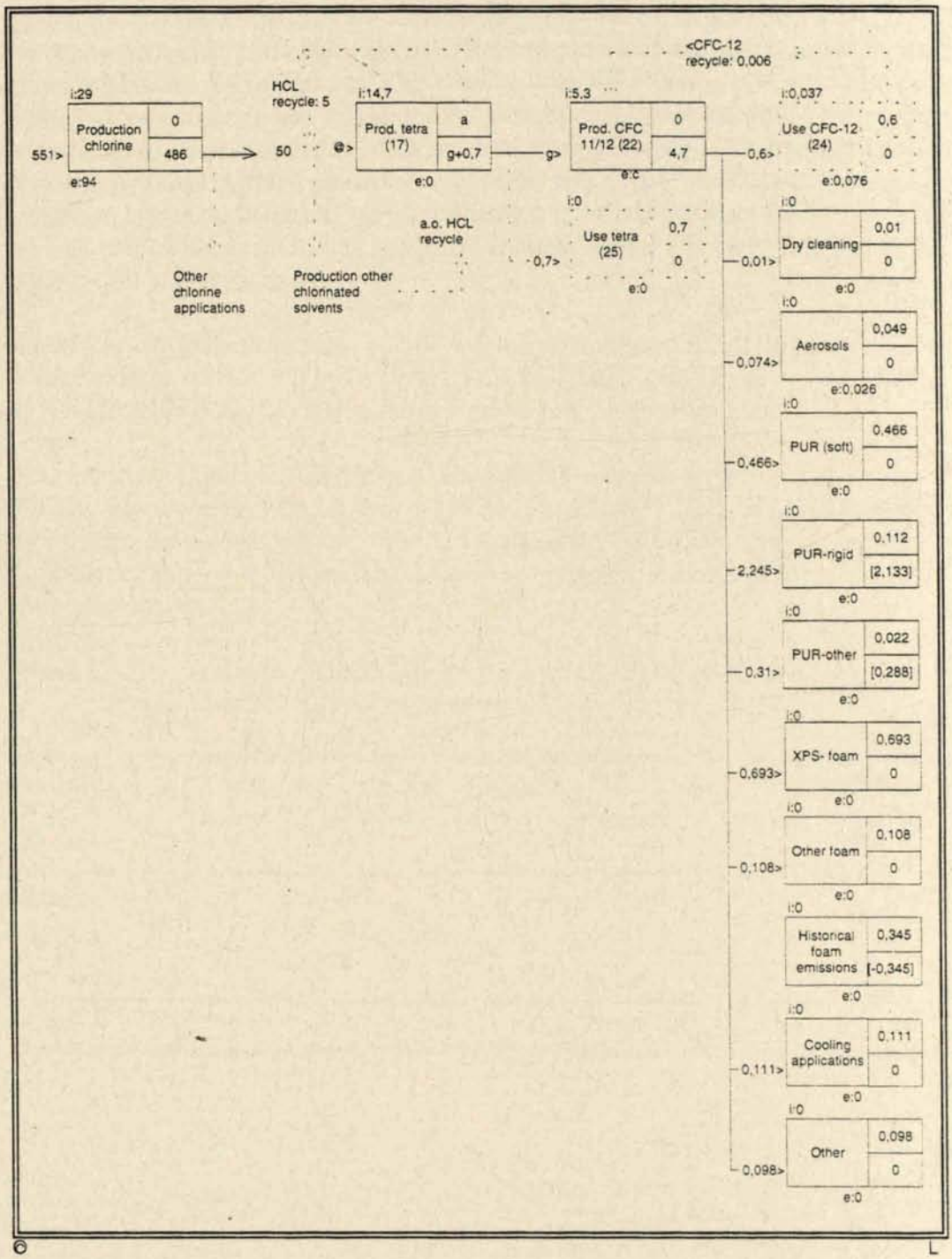
Table 23.2: Emissions of CFC-11 under envisaged policy (tonnes chlorine; in brackets: tonnes substance)

Target group	Consumption (tonnes)	Imp./exp. (tonnes)	Stock formation (tonnes)	Air (tonnes)	Water (tonnes)	Waste (tonnes)
Other				0	0	0
Hist. foam emissions		zero	-345 (-445)	345 (445)		
Total:				345 (445)	0	0

4 COMMENTS AND POINTS FOR DISCUSSION

It is interesting that in 1990 more than half of the CFC-11 is not emitted but accumulates in society in the form of PUR foam. This effect is not usually included in accounts of the total Dutch emissions of substances which deplete the ozone layer. In the Ministry of VROM's annual Environmental Programmes and the study 'Environmental performance indicators' the emissions of CFC-11 are equated with the usage reported by the CFC Commission, which represents an overestimate of 40% [VROM 1993e, Adriaanse 1993]. However, unless measures are taken to process foam containing CFC, an annual emission of a few hundred tonnes of CFC-11 will continue.

Figure 23.1: Substance flows in consumption applications of CFC-11 (in kt chlorine, 1990)



SEGMENT 24: CONSUMPTION APPLICATIONS OF CFC-12

1 INTRODUCTION

CFC-12 has the following uses:
- cooling agent for domestic requirements;
- cooling agent for industrial requirements;
- sterilisation gas;
- aerosol;
- propellant for foams.

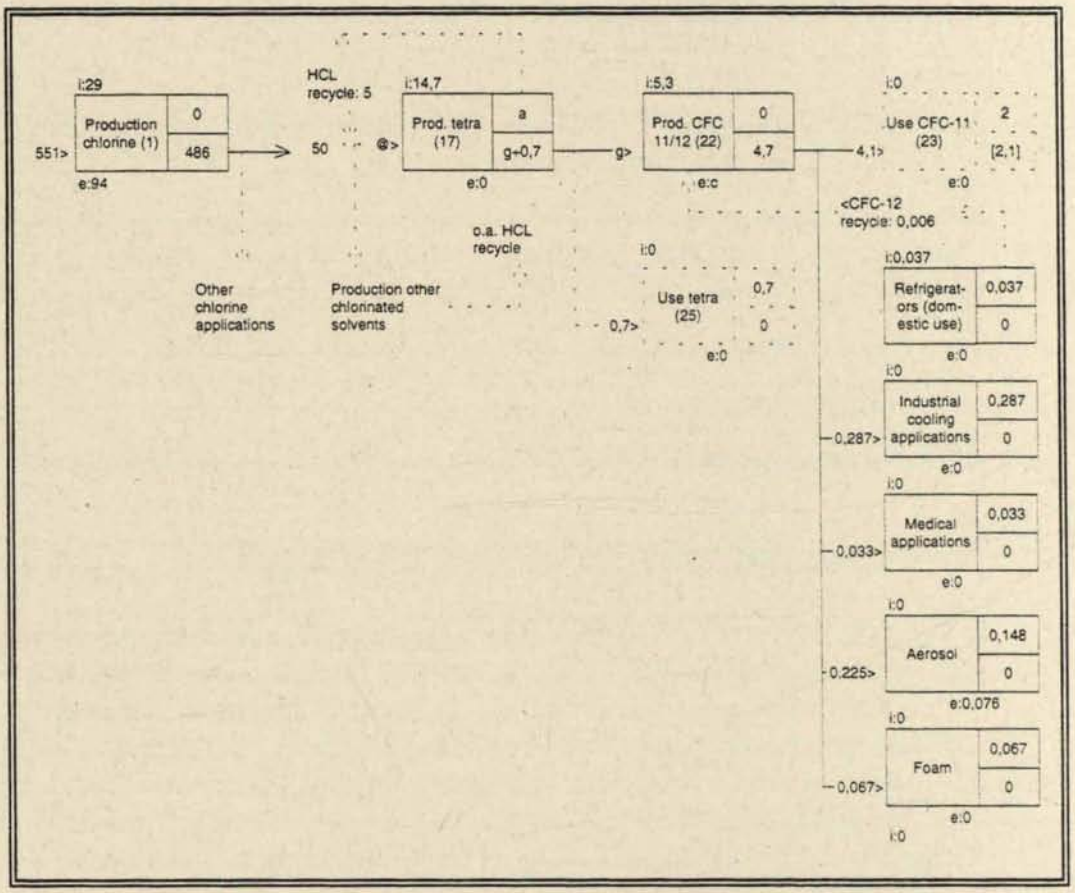
2 PROCESSES, SUBSTANCE FLOWS AND EMISSIONS IN 1990

Total consumption of CFC-12 came to about 1,043 tonnes in 1990 [CFC Commission 1994]. Details of the amounts and emissions per application are given below. Table 24.1 gives a summary of quantities, imports and exports in products as well as emissions to air and water and waste.

Household equipment
The market for domestic refrigerators is a replacement market. More than 500,000 refrigerators are discarded and replaced annually. No cooling elements are made in the Netherlands. They are imported (along with the CFCs). Each contains about 120 grams CFC-12. We have assumed imports of 62.9 tonnes CFC-12 [v.d. Velde 1993]. According to v.d. Velde about 10.5 tonnes of CFC-12 is recovered from discarded refrigerators. We have taken this figure also for 1990. The number accords reasonably with the estimate that CFCs were tapped from more than 160,000 refrigerators in 1990, whereby about 60 grams is extracted from each refrigerator. TNO regards the difference between the amount imported (and subsequently 'discarded') and the quantity of CFCs drawn off as an emission to air. This possibly leads to an overestimate of the emissions in the Netherlands as a large number of discarded refrigerators may be sold second-hand outside the country. This seems an acceptable simplification as CFCs contribute to a global environmental problem and only a small amount is involved.

Industrial cooling machines
According to the annual reports of the CFC action programme, an estimated 489 tonnes of CFC-12 were used for (industrial) cooling in 1990 (excluding on-site regeneration by installers). It can be assumed that the amount used in industrial cooling is equal to the replacement of losses through leakage. For this reason we conclude that 100% is emitted to the air.

Figure 24.1: Substance flows in consumption applications of CFC-12 (in kt chlorine, 1990)



1 INTRODUCTION

Almost all of the carbon tetrachloride (tetra) produced and imported in the Netherlands is used to make CFC-11 and CFC-12 (see segment 20). A small portion is used elsewhere, mainly as a solvent in the pharmaceutical sector. We will discuss these applications in this segment.

2 PROCESSES, SUBSTANCE FLOWS AND EMISSIONS IN 1990

According to the CFC Commission [1994], 777 tonnes of tetra were used in consumption applications in 1990. This amount excludes the use of tetra in the production of CFC-11 and CFC-12. The substance flows are as follows.

Pharmaceutical industry
Solvents and heavy metals are the main substances emitted by the pharmaceutical industry to water, soil and air and released as (dangerous) waste materials. Used solvents are (partly) recycled internally by means of distilling techniques. Distillation residue, which contains solvents, is disposed of as chemical waste [Verhage 1991]. Solvents are also disposed of into both effluent and to the air. Almost all companies employ biological treatment before discharging effluent to surface water. The HHCs used in the pharmaceutical industry are methylenechloride [Ros 1989], tetrachloromethane, tetrachloroethylene, 1,1,1,-trichloroethane, trichloroethylene and chloroform [Verhage 1991]. Since 1987 the use of tetra, 1,1,1-trichloroethane and chloroform has been reduced by so much that the amounts used in 1992 were negligible [CUWVO 1993]. According to ER-1 there was a further emission of 16 tonnes of tetra to air from the pharmaceutical sector in 1990.

The production of phenylglicylchloride is a separate issue[5]. In this case a mixture of tetra and 1,2-dichloroethane is used. Each batch takes 3,000 litres of solvent (with an original use of 600 kg d,1-phenylglycine). Annual emission to the air is 178 tonnes.

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[5] Although this process is carried out at a pharmaceutical factory it is not included under the SBI code 'pharmaceutical industry'.

In all, the pharmaceutical industry emitted 194 tonnes of tetra to the air in 1990. Emissions to water are unknown but appear insignificant [CUWVO 1993]. The amount of waste is also unknown. Emission to the air is equated with consumption.

Chemical industry
Akzo Nobel uses tetra as a scrubber during the production of chlorine. ER-I registered an emission of 42 tonnes in 1990, which is equated with consumption.

Notified as waste
The National Notification Centre for Waste Substances (LMA) recorded 248 tonnes of waste tetra in 1990. It is not known which sectors were responsible for this waste but it may be assumed that some of it came from the pharmaceutical and chemical industries. N.B.: it is also likely that a quantity of tetra was disposed of in mixed batches and is therefore not reported in the notification records.

Other uses
There is a remaining item of 293 tonnes of tetra. We have assumed that half of this was emitted to air and the other half was disposed of as waste. According to Comprimo, the yarn and fibre industry emitted 80 tonnes of tetra to air in 1990 [Comprimo, 1991]

Table 25.1: Use of tetrachloromethane in 1990 (tonnes chlorine; in brackets: tonnes substance)

Target group	Consumption (tonnes)	Imp./exp. (tonnes)	Air (tonnes)	Water (tonnes)	Waste (tonnes)
Pharm.	179 (194)		179 (194)		
Chemical	39 (42)		39 (42)		
Notif. as waste	229 (248)				229 (248)
Other	270 (293)		136 (147)		135 (146)
Total:	716 (777)		353 (383)		363 (394)

3 EMISSIONS UNDER ENVISAGED POLICY

In the context of achieving the aims of the Hydrocarbons 2000 (KWS 2000) project, the emissions of volatile organic compounds, including tetra, should be sharply reduced. Companies such as Akzo Nobel Delfzijl have already taken vapour destruction installations or incinerators into operation which have led to a significant decrease in emissions of tetra to the air since 1990.

The Montreal Protocol prohibits the use of new CFCs and tetra with effect from 1 January 1996. The EU drew up a regulation to enforce this ban from 1 January 1995 (EU Regulation 3093/94). Tetra should therefore also be phased out in the Netherlands from this date. The substance is only permitted for a limited number of essential applications. These exceptions will be gradually restricted. Recycled CFCs and tetra may still be used after 1 January 1995. In effect, it is accepted that the volume of tetra present in the Netherlands on January 1 1995 will be used up.

Eventually, after implementation of envisaged policy, there will be no emission from any of the various applications. In this report we have assumed that the use of tetra in the pharmaceutical sector and for the production of aramide shall either be regarded as non-essential, or will only be possible if there is no actual emission of tetra. Table 25.2 represents this.

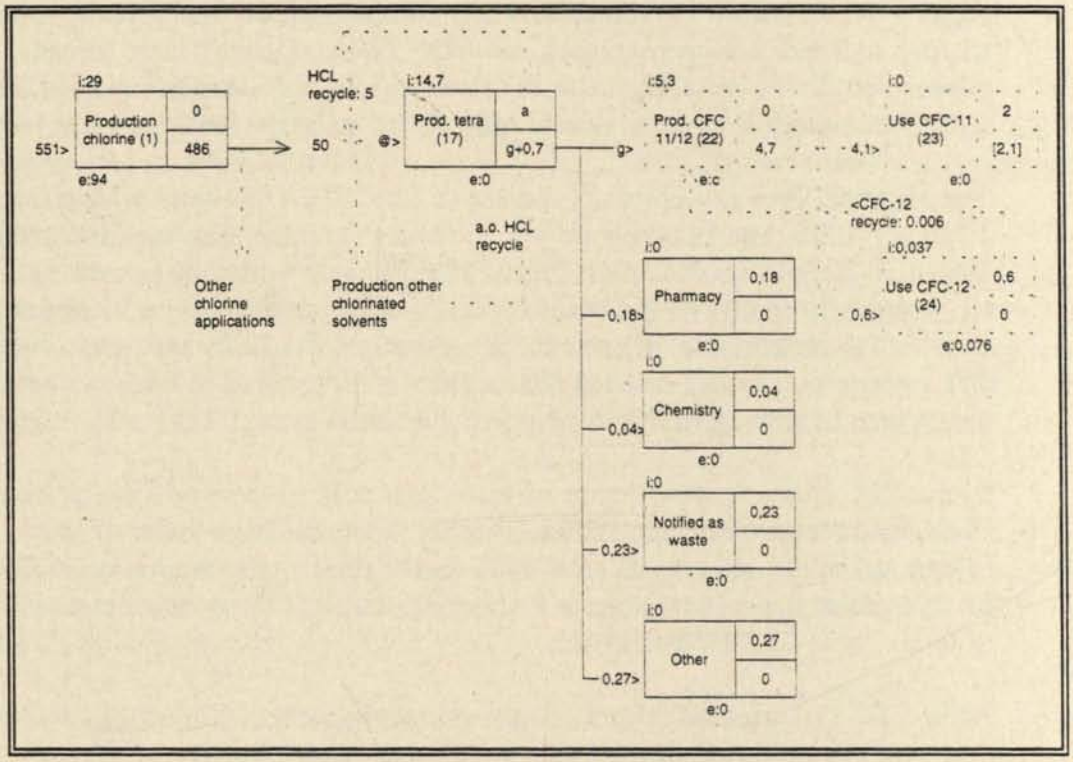
Table 25.2 Emission of tetra under envisaged policy (tonnes of chlorine; in brackets: tonnes of substance)

Target group	*Consumption (tonnes)*	*Imp./exp. (tonnes)*	*Stock form. (tonnes)*	*Air (tonnes)*	*Water (tonnes)*	*Waste (tonnes)*
Various				*0*	*0*	*0*
Total:				*0*	*0*	*0*

4 COMMENTS AND POINTS FOR DISCUSSION

None.

Figure 25.1: Substance flows in consumption applications of tetra (in kt chlorine, 1990)



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SEGMENT 26: PRODUCTION OF CFC-113 AND CFC-114

1 INTRODUCTION

DuPont de Nemours used to produce CFC-113 (1,1,2-trichloro-1,2,2-trifluoroethane) and CFC-114 (1,2-dichloro-1,1,2,2-tetrafluoroethane). The production of these substances was halted as from 1 July 1994.

The following sub-section describes the production process in more detail [Bremmer 1988, ECOTEC 1991].

2 PROCESSES

The raw materials for preparing CFC-113 and CFC-114 are perchloroethylene (PER: 1,1,2,2-tetrachloroethene), hydrogen fluoride (HF) and chlorine. In 1990 PER was imported or supplied by Akzo Nobel Delfzijl. Only imported PER has been used since Akzo Nobel stopped producing PER in 1990.

PER is converted into CFC-113 and CFC-114 by the addition of hydrogen fluoride. HCFC-123 is produced as a by-product. The reaction occurs with the aid of a catalyst. Process conditions such as temperature, pressure and the proportions of the raw materials determine which CFCs are created. A washing apparatus attached at the end of the process is used to rinse the by-product hydrogen chloride from the production stream. The separation of the various CFCs is carried out in a distilling column. Hydrogen fluoride is reintroduced to the process.

3 SUBSTANCE FLOWS AND EMISSIONS IN 1990

The following raw materials were used to produce CFC-113 and CFC-114 in 1990:

- PER (volume is confidential)
- chlorine (7.435 tonnes).

The following compounds were produced (quantities expressed in tonnes of chlorine):

- 10,277 tonnes CFC-113 and CFC-114
- 10,314 tonnes HCl (sold).

A further 943 tonnes was discharged as chloride and 212 tonnes was lost in other emissions. The amount of HCFC 123 is disregarded.

Table 26.1 presents the CBS import statistics for 1990 [CBS 1991]. The CFC action programme gives an insight into the consumption during 1990. CBS does not report export statistics for CFC-113 and CFC-114 because there is only one manufacturer in the Netherlands. Figure 26.1 summarises these figures.

Table 26.1: Production, import and export of CFC-113 and CFC-114 in 1990 (tonnes chlorine; in brackets: tonnes substance)

Substance	Production	Import [CBS 1991]	Export	Consumption [CFC Commission 1994]
CFC-113	*	235 (414)	*	679 (1.197)
CFC-114	*	26 (62)	*	41 (99)

* Confidential

For DuPont, the ER-I only gives statistics on emissions to air for a combined process 'production of freons' [ER-I 1994]. These include the emissions relating to HCFC production. Emissions of C_2 compounds are allocated to the CFC-113/114 production because these CFCs are themselves a C2 compound; emissions of C1 compounds are allocated to the production of HCFC-22.

Emissions to water reported in WIER and the ER-I are total figures for all of the DuPont processes taken together [RIZA 1994a, ER-I 1994]. They must be allocated to the production of CFC-113/114, HCFC-22 and teflon. In the absence of anything better, they have been allocated to the three processes in the ratio 40:50:10 on the basis of the global chlorine input.

The ER-I reports emissions of DCM and CFCs from other processes (such as cooling). Such emissions have not been included here but in the segments which describe the applications of DCM and CFCs.

ER-I and WIER emission figures for processes can not be published without the consent of the company concerned. In this case, since only one company in the Netherlands carries out the process, the emission figures cannot be disguised, not

even by means of aggregation. For this reason, the emission figures for the process cannot be published here.

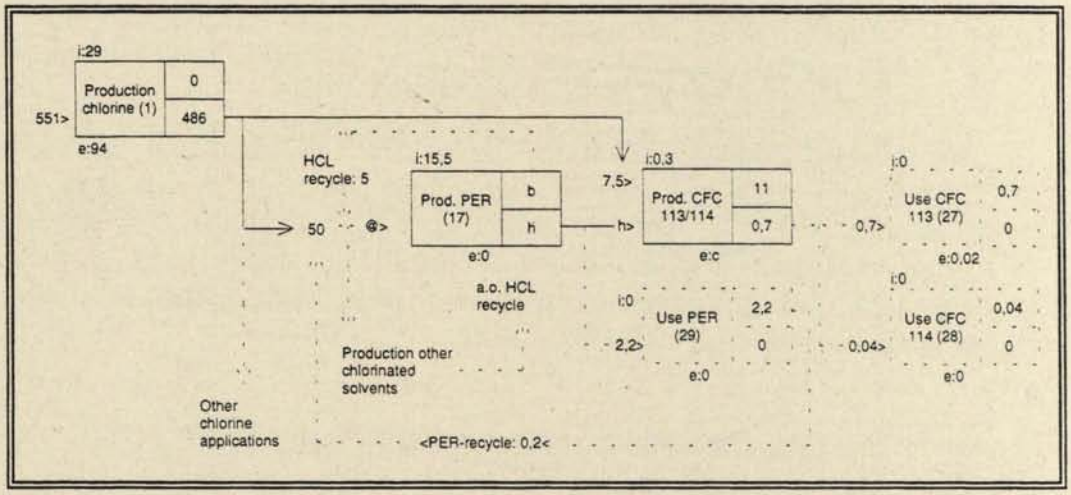
4 EMISSIONS UNDER ENVISAGED POLICY

The Montreal Protocol forbids the use of new CFCs and tetra from 1 January 1996. The EC drew up a regulation to enforce this ban as of 1 January 1995 (EC Regulation 3093/94). The production of CFC-113 and -114 is therefore not permitted after this date. In this connection, DuPont stopped production on 1 July 1994. The emissions related to this process have therefore been fixed at zero for the future situation.

5 COMMENTS AND POINTS FOR DISCUSSION

The figures in ER-I and WIER show that in 1990 the amount of chlorine measured as EOCl was about 10 times higher than the amount of chlorine which was discharged into water in the form of individually known compounds [RIZA 1994a, ER-I 1994]. This discrepancy can probably be explained by the entry 'CFC's - not further known' in the ER-I. The company was included in the AOX/EOX measuring programme carried out by RIZA in 1992. The amount of EOX was a factor of 4 lower than in 1990 [RIZA 1994b]. These figures and uncertainties are now irrelevant as production has ceased.

Figure 26.1: Substance flows in production of CFC 113 and 114 (in kt chlorine, 1990)



SEGMENT 27: CONSUMPTION APPLICATIONS OF CFC-113

1 INTRODUCTION

CFC-113 has a number of uses such as:
- degreasing agent in the mechanical and electrical engineering industry;
- dry cleaning;
- aerosols.

2 PROCESSES, SUBSTANCE FLOWS AND EMISSIONS IN 1990

According to the CFC Commission, 1197 tonnes of CFC-113 was consumed in various applications in 1990 [CFC Commission 1994]. This sub-section discusses the diverse uses in more detail.

Mechanical and electrical engineering industry
Purification of solvents is common practice in the metal products industry. Generally, aliphatic hydrocarbons (such as paraffin, turpentine and petrol) and HHCs (such as 1,1,1-trichloroethane, dichloromethane and CFC-113) are used. If solvents are too polluted, particularly with oils, dirt and fats, they are replaced and removed as hazardous waste.

From the report 'Cleaning and degreasing with HHCs in small companies' [van der Most 1993] we conclude that an estimated 683 tonnes of CFC-113 was used by the mechanical and electrical engineering sector in 1990. Of this, about 608 tonnes was emitted to air and 6.8 tonnes to water. A further 68.2 tonnes was disposed of as waste[6].

Dry cleaning
The CFC Commission estimates a total consumption of 91 tonnes of CFC-113 in 1991 in the sectors 'dry cleaning' and 'industrial textile cleaning'. We have also adopted this figure for 1990. The v.d.Most report [1993] gives a lower estimate of consumption, but probably only included the dry cleaners. The CFC commission figures, which are compiled from an annual monitoring investigation, seem to be the most reliable [CFC Commission 1994]. We used the proportions given in v.d.

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[6] The amount in the mechanical and electrical engineering industry is calculated by the total emissions to air, water and waste named in the main text of the report by v.d. Most, less the emissions for SBI 983 (laundries) listed in appendix 2

Most [1993] to divide the amounts emitted to air, water and waste. There is therefore an estimated 72 tonnes of CFC-113 emitted to air and 1 tonne to water. A further 18 tonnes approximately is disposed of as waste.

Aerosol

In 1990 an estimated 115 tonnes of CFC-113 was used in the production of aerosols. This involves use in technical/medical spray cans [CFC Commission 1994]. Due to an export surplus, 33% less spray cans are used than are produced in the Netherlands [Tukker 1993b]. For want of specific data, we have assumed that this also applies to technical/medical spray cans. This means a total use of 76 tonnes in the Netherlands. It is assumed that this amount was emitted to the air.

Other applications

There remains a volume of 308 tonnes of CFC-113 which is allocated to "Other applications". The CFC commission lists applications in this context such as medical use, the optical industry and fine metals [CFC Commission 1994]. For want of specific data the allocation of this remaining entry over the environmental media air, water and waste is calculated according to the proportions for the mechanical and electrical engineering industry.

Table 27.1: Use of CFC-113 in 1990 (tonnes of chlorine; in brackets: tonnes of substance)

Target group	Consumption (tonnes)	Imp./exp. (tonnes)	Air (tonnes)	Water (tonnes)	Waste (tonnes)
Mechanical and electrical engineering industry (degreasing)	388 (683)		345 (608)	3.9 (6.8)	38.7 (68.2)
Dry cleaning	52 (91)		41 (72)	0.6 (1)	10 (18)
Aerosols	65 (115)	- 22 (- 39)	43 (76)		
Other	175 (308)		157 (277)	1.7 (3)	16 (28)
Total:	679 (1197)	- 22 (- 39)	586 (1033)	6.1 (10.8)	64.8 (114.2)

3 EMISSIONS UNDER ENVISAGED POLICY

The Montreal Protocol forbids the use of new CFC's and tetra from 1 January 1996. The EC drew up a regulation to enforce this on 1 January 1995 (EC Regulation 3093/94). CFC-113 will therefore also be phased out in the Netherlands after this date. The substance is only permitted for a limited number of essential uses. These exceptions will be gradually restricted. Recycled CFCs and tetra may still be used after 1 January 1995. In effect, it is accepted that the amount of CFCs present in the Netherlands on 1 January 1996 will be used up.

Eventually, there will be zero emissions for all applications after implementation of envisaged policy as from 1 January 1995. This is represented in Table 27.2.

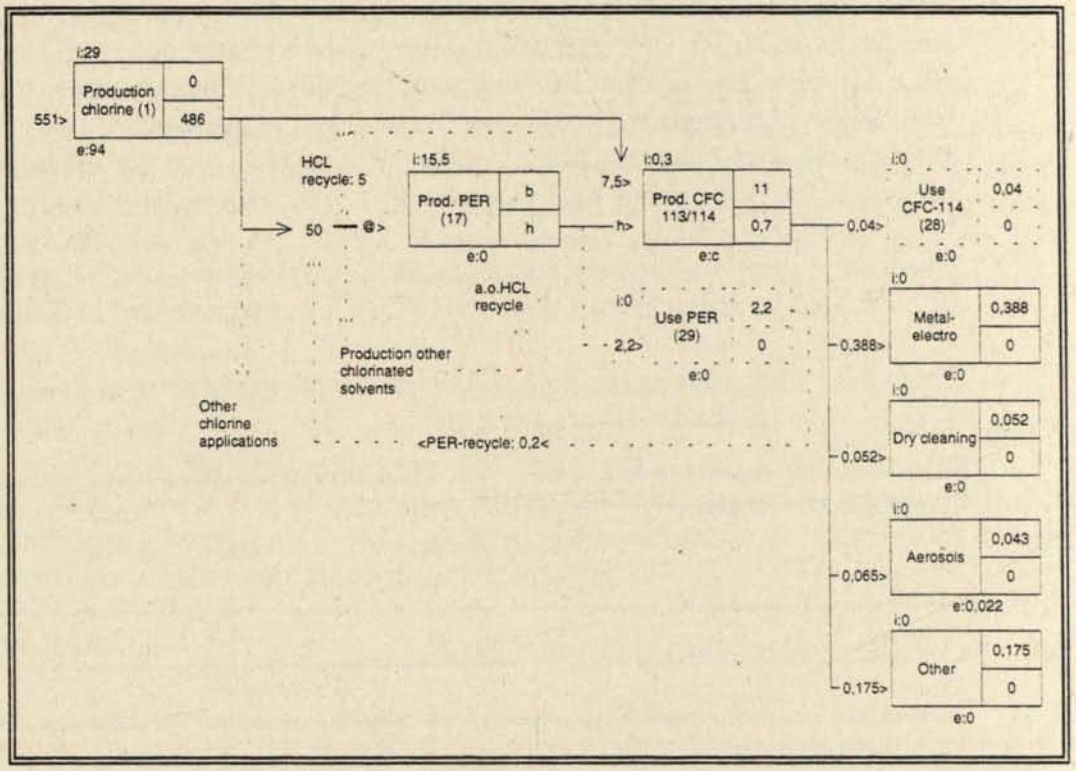
Table 27.2 Emissions of CFC-113 under envisaged policy (tonnes chlorine; in brackets: tonnes substance)

Target group	Consumption (tonnes)	Imp./exp. (tonnes)	Stock formations (tonnes)	Air (tonnes)	Water (tonnes)	Waste (tonnes)
Various				0	0	0
Total:				0	0	0

4 COMMENTS AND POINTS FOR DISCUSSION

None.

Figure 27.1: Substance flows consumption applications of CFC 113 (in kt chlorine, 1990)



SEGMENT 28: CONSUMPTION APPLICATIONS OF CFC-114

1 INTRODUCTION

CFC-114 was mainly used as a propellant in the production of synthetic foams. No other uses are known [SPIN 1993b, CFC Commission 1994].

2 PROCESSES, SUBSTANCE FLOWS AND EMISSIONS IN 1990

According to statistics from the CFC action programme around 99 tonnes of CFC-114 was used in 1990. CFC-114 was used as a propellant and not for any other purpose [CFC-Commission 1994, KPMG 1994]. It was mainly used in the production of polyethylene foam (PE). Some of the CFC-114 is emitted to air during production. The structure of PE-foam is such that all of the CFC-114 absorbed in the foam is emitted in a short time [SPIN 1993d]. Factors such as accumulation and import/export of CFC-114 are not significant in this case. We have therefore equated emissions to air with the amount consumed.

Table 28.1: Use of CFC-14 in 1990 (tonnes of chlorine; in brackets: tonnes of substance)

Target group	Consumption (tonnes)	Imp./exp. (tonnes)	Air (tonnes)	Water (tonnes)	Waste (tonnes)
Foam	44 (99)		44 (99)		
Total:	44 (99)		44 (99)		

3 EMISSIONS UNDER ENVISAGED POLICY

The Montreal Protocol forbids the use of new CFCs and tetra from 1 January 1996. The EC drew up a regulation to enforce this from 1 January 1995 (EC Regulation 3093/94). CFC-114 will therefore also be phased out in the Netherlands after this date. The substance is only permitted for a limited number of essential uses. These exceptions will be gradually restricted. Recycled CFCs and tetra may still be used after 1 January 1995. In effect, it is accepted that the amount of CFC's present in the Netherlands on 1 January 1995 will be used up.

Eventually, there will be zero emissions for all applications after implementation of envisaged policy as from 1 January 1995. This is represented in Table 28.2.

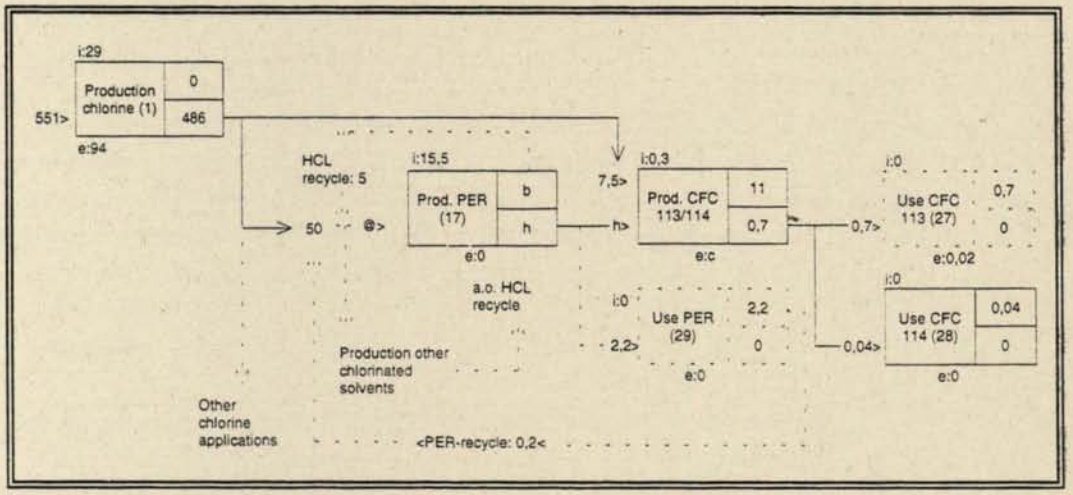
Table 28.2 Emissions of CFC-114 after envisaged policy (tonnes chlorine; in brackets: tonnes substance)

Target group	Consumption (tonnes)	Imp./exp. (tonnes)	Stock formation (tonnes)	Air (tonnes)	Water (tonnes)	Waste (tonnes)
Various				0	0	0
Total:				0	0	0

4 COMMENTS AND POINTS FOR DISCUSSION

None.

Figure 28.1: Substance flows in consumption applications of CFC 114 (in kt chlorine, 1990)



SEGMENT 29: CONSUMPTION APPLICATIONS OF PERCHLOROETHYLENE

1 INTRODUCTION

Until 1994, perchloroethylene (PER) was mainly used as a raw material for producing CFC-113 and CFC-114 (see segment 26). In addition, a limited amount was used for applications which we will deal with in this segment. These applications refer to use as degreasing or cleaning agents in:

- the mechanical and electrical engineering sector;
- dry cleaning;
- printing industry.

We will explore these applications in the following sub-section.

3 PROCESSES, SUBSTANCE FLOWS AND EMISSIONS IN 1990

According to segment 17 around 2,600 tonnes of PER were used in consumption applications in the Netherlands in 1990. About 2,400 tonnes concerned "primary" PER whereas 200 tonnes were supplied via the recycling circuit (distillation). The following consumption and emission figures apply for each application:

Mechanical and electrical engineering industry
We assume that the use of perchloroethylene in the mechanical and electrical engineering industry in 1990 was around 825 tonnes. Of this, about 738 tonnes were emitted to air and 7.5 tonnes to water. A further 73.5 tonnes was disposed of as waste [van der Most 1992][5].

Dry cleaning
Around 1182 tonnes of PER were emitted to air, 15 tonnes to water and 303 tonnes disposed of with or as waste [v.d. Most 1993][7]. According to the National Notification Centre for Waste Substances [LMA] about 1,000 tonnes of PER sludge was disposed of as chemical waste, mainly by chemical laundries. According to Verhage [1991], the PER content of this sludge is about 30%, so these figures correspond closely. Almost all PER sludge is distilled.

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[7] The amount in the metal electric industry is calculated by the total emissions to air, water and waste listed in the main text of the report by v.d. Most minus the emissions for SBI 983 (laundries) named in Appendix 2

Printing industry
Studies carried out in the framework of the Target Group Consultations showed that the printing industry target group emitted 68 tonnes of perchloroethylene to air and discharged 4 tonnes with or as waste annually [Berenschot 1989]. Emissions to water are unknown. In the mechanical and electrical engineering industry and dry cleaning they amount to less than 1% of the amount used. There is no reason to assume that the situation in the printing industry is essentially different; we have therefore disregarded emissions to water in this case. In all, this gives a total consumption of 72 tonnes of PER annually.

Other applications
There is a remaining item of 203 tonnes of PER. It is uncertain where this amount is used. It is possible that various industries (for example the pharmaceutical or paint industry) use PER as a solvent. However, it must concern small amounts as various studies of the pharmaceutical and paint industries have paid no attention to PER in contrast to other HHCs [see for example Ros 1989; SPIN 1992a; CUWVO 1992]. For simplicity's sake, the emissions to water, air and waste for this remaining quantity were calculated on the basis of the ratios used for the mechanical and electrical engineering industry.

Waste disposal
Table 29.1 shows that 395.5 tonnes of PER (338.3 tonnes of chlorine) was discharged as waste. On the basis of LMA [1994] figures, one can assume that only PER sludge from dry cleaning was distilled (259 tonnes chlorine). Given a distillation yield of around 80% this means that about 200 tonnes of PER (calculated as chlorine) is recycled. The remaining 59 tonnes are discharged as distillation residue and incinerated as chemical waste, just as the other waste flows containing PER. Briefly, of the 338 tonnes of chlorine in PER waste:
- 200 tonnes are recycled;
- 138 tonnes are incinerated.

Table 29.1: Use of perchloroethylene in 1990 (tonnes of chlorine; in brackets: tonnes of substance)

Target group	Consumption	Imp./exp. (tonnes)	Air (tonnes)	Water (tonnes)	Waste (tonnes)
Mechanical and electrical engineering industry	705 (825)		631 (738)	6.4 (7.5)	62.9 (73.5)
Dry cleaning	1283 (1500)		1011 (1182)	13 (15)	259 (303)
Other	174 (203)		156 (183)	1.7 (2)	15 (15)
Graphics Industry.	62 (72)		58 (68)		3.4 (4)
Total:	2223 (2600)		1857 (2171)	21.0 (24.5)	338,2 (395,5)

3 EMISSIONS UNDER ENVISAGED POLICY

The measures established to reduce emissions for each target group as of 1 January 1995 are discussed below. On the basis of the emission situation in 1990, we estimate which emissions remain after implementation of this policy. We have disregarded changes in emissions resulting from economic growth or other autonomous developments within the target group.

Mechanical and electrical engineering industry
The 'Memorandum of Understanding for the implementation of environmental policy in the mechanical and electrical engineering industry' provides for implementation of the IMT. For 1995, 2000 and 2010 this means reductions in emissions of 50%, 90% and 99% respectively to air and 85%, 85% and 98% respectively to water. The objective for 2010 is not a concrete aim but is more of a guideline. These reduction percentages refer to the environmental impact of the sector in 1985.

The environmental impact of the mechanical and electrical engineering industry on which the memorandum of understanding is based amounted to 302 tonnes of PER emitted to air and 0.5 tonnes to water (in 1985) [IMT 1995]. However, TNO has calculated significantly higher emissions for 1990: 738 tonnes to air and 7.5 tonnes to water.

Emissions as a result of metal-degreasing could be higher than stated in IMT. A VROM survey produced an estimated emission of 538 tonnes in 1987/1988. There are quite some discrepancies between the emission statistics given by various sources. This itself indicates the measure of the uncertainty regarding the volume of PER emissions.

Analysis of the mechanical and electrical engineering industry target group shows that the DCM emissions in 1990 were roughly equal to the emissions in 1985 [Tebodin 1994] (see also segment 30). With the accelerated phasing out of chlorinated solvents in the context of the CFC action programme a temporary shift to PER (and TCE) is expected. As a result, the reduction target for PER will not be achieved in 1995. It is now assumed that the PER emissions in 1990 will remain the same as the PER emissions in 1985. Of the quantity of PER emissions calculated by TNO for 1990 it can be stated that they do not produce any discrepancies in the balances of the substance flow analysis. This means that the entire reduction of emissions has to be achieved after 1990. The assumption is therefore of PER emissions to air of 738 tonnes and to water of 7.5 tonnes in 1985 (the TNO figures). The expected emissions in the year 2000 amount to 74 tonnes PER to air and 1.1 tonnes PER to water (90% reduction from 738 tonnes and 85% reduction from 7.5 tonnes respectively).

Dry cleaning
Following the entry into force of the 'Dry Cleaners Environmental Management Decree' (as of 1 April 1990) the emissions of perchloroethylene will decline considerably. It is provided that existing installations must be closed more tightly (water seals) and that new machines must be fitted with deep cooling so that the loss of perchloroethylene can be reduced by around 80%. The emission targets for dry cleaning of 500 tonnes a year in the context of the Hydrocarbons Project 2000 (KWS 2000) has been geared to these measures [Verhagen 1991]. KWS 2000 focuses on an emission reduction objective of *at least* 50% for volatile organic substances in the year 2000 compared with 1981. Assuming a reduction of 80% with a final target of 500 tonnes in the year 2000, one can calculate back to a PER emission to air of 2,500 tonnes in 1981.

In the previous sub-section an emission to air of 1182 tonnes was calculated for 1990. This means that a reduction of almost 50% had already been achieved by 1990. With a final target of 500 tonnes in 2000, a further 60% reduction will be achieved compared with 1990. If emissions to water are reduced by the same percentages, the PER emission to water will amount to 4 tonnes in 2000. Waste contaminated with PER must be separated and disposed of in a specially equipped processing plant.

Printing industry

Emissions from the printing industry are covered by the programme for the implementation of environmental policy in the printing industry and packaging printers [VROM/KVGO, 1993]. This programme is based on a reduction of 95% in emissions to air in 1996 through the replacement of PER with non-halogenated washing out agents. The PER emissions to air will then be 3.4 tonnes in the year 2000.

Other applications

In 1990, there was an item of 203 tonnes for other PER emissions. Because the applications for which this PER was used are not known and at the same time no policy measures aimed at this item are known of, the 1990 emission figures have been retained for the year 2000.

Table 29.2 shows the emissions after the envisaged policy.

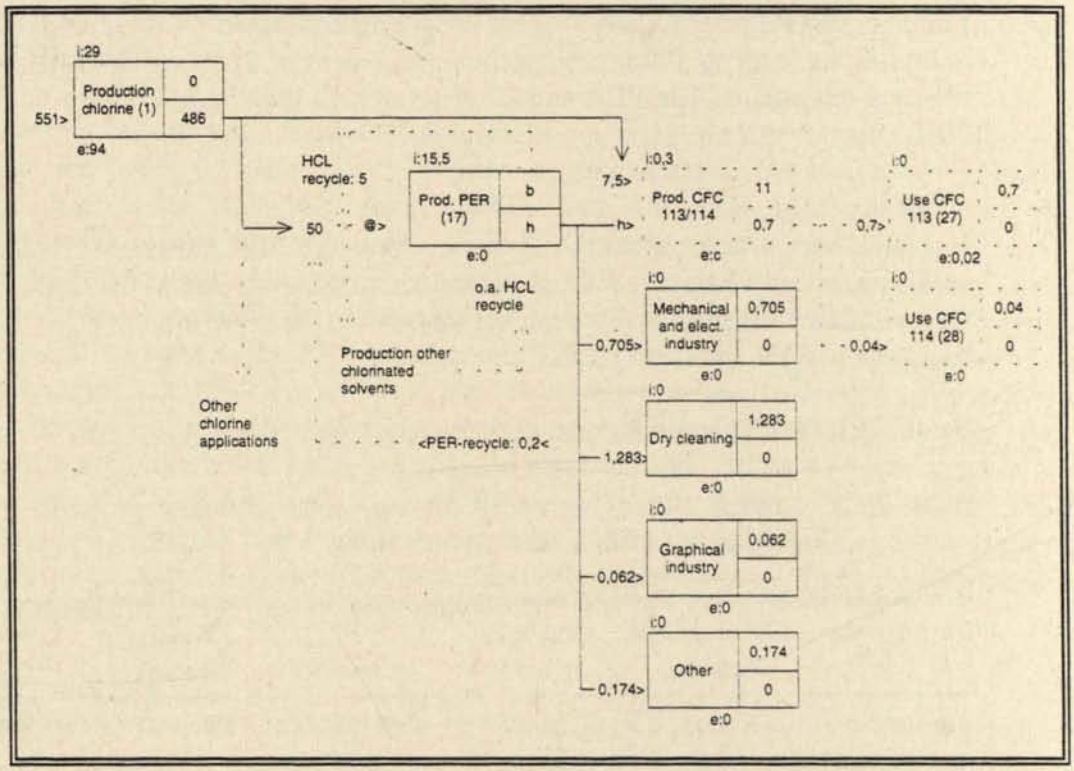
Table 29.2 Emissions of perchloroethylene after envisaged policy (tonnes chlorine; in brackets: tonnes substance)

Target group	Consumption (tonnes)	Imp./exp. (tonnes)	Air (tonnes)	Water (tonnes)	Waste (ton)
Mechanical and electrical engineering industry	p.m.	p.m.	63 (74)	0.9 (1.1)	p.m.
Dry cleaning	p.m.	p.m.	428 (500)	3.4 (4)	p.m.
Other	p.m.	p.m.	156 (183)	1.7 (2)	p.m.
Graphics ind.	p.m.	p.m.	2.9 (3.4)		p.m.
Total:	p.m.	p.m.	650 (760)	6 (7.1)	p.m.

4 COMMENTS AND POINTS FOR DISCUSSION

None.

Figure 29.1: Substance flows in consumption applications of PER (in kt chlorine, 1990)



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SEGMENT 30: CONSUMPTION APPLICATIONS OF DICHLOROMETHANE (DCM)

1 INTRODUCTION

Dichloromethane (DCM), also known as methylene chloride, is used in a range of applications. These are:

- degreasing agent in the mechanical and electrical engineering industry;
- dry cleaning;
- pharmaceutical industry;
- foodstuffs industry;
- chemical industry;
- paint removers;
- adhesive products;
- aerosols.

These applications are discussed in the following sub-section.

2 PROCESSES, SUBSTANCE FLOWS AND EMISSIONS IN 1990

According to Segment 17, the consumption of DCM amounted to 8,500 tonnes in 1990. The use and the emissions by target group are discussed below. Table 20.1 presents a summary of the use, emissions and disposal as waste. The table also shows the imports and exports of products containing DCM.

Mechanical and electrical engineering industry
According to the report 'Emissions of halogenated hydrocarbons as a result of cleaning and degreasing in small companies', in 1990 emissions of DCM to air amounted to 350 tonnes, to water 2 tonnes and 255 tonnes were disposed of in waste [Van der Most 1993]. The figures for DCM in this report related mainly to the mechanical and electrical engineering industry for which a total consumption of 607 tonnes was calculated.

Dry cleaning
Dichloromethane is used for the industrial cleaning of polishing cloths. It is estimated that this leads to emissions of 20 tonnes of dichloromethane to air [Brouwer 1994]. In the target groups mechanical and electrical engineering and pharmaceuticals the quantities emitted to air are roughly the same as the quantity disposed of with waste. On this basis, a volume of 20 tonnes of waste has been estimated for dry cleaning. This leads to a total consumption of 40 tonnes a year.

For most HHCs the emissions to water in dry cleaning are far less than 1% [V.d. Most 1993]. These emissions are disregarded here.

Pharmaceutical industry
According to ER-I the pharmaceutical industry produced emissions of 12.5 tonnes to air and 552 tonnes to water [Berdowski 1993]. These figures accord reasonably closely with those mentioned in the case study 'Dichloromethane in the pharmaceutical industry' in the 'Integrated Substance Chain Management' study by VNCI/McKinsey. McKinsey assumes disposal of 440 tonnes of DCM in waste [VNCI/McKinsey 1991]. This figure has also been maintained in this study. It follows from this that total consumption of dichloromethane was 1004.5 tonnes by the pharmaceutical industry. These are net figures: the (sizeable) internal recycling within the pharmaceutical industry has been ignored. The volume of waste is possibly underestimated: according to v.d. Steen [1991] one pharmaceutical company alone accounted for a deposit of 700 tonnes of DCM in 1988.

Coffee-roasting factories
During the production of caffeine-free coffee the caffeine is extracted from the coffee using DCM. According to the SPIN document on coffee-roasting factories, 10 tonnes of DCM are emitted to water and 35 tonnes to air in the process [SPIN 1992c]. In view of the process used (stripping) we have assumed here that no DCM is disposed of with waste or the volume is negligible. This produces a total annual consumption of 45 tonnes.

Chemical industry
The Association of Traders in Chemical Products (VHCP) conducted a survey on the consumption of various solvents as part of a monitoring project for KWS 2000 [Knoop 1993]. According to this survey, the consumption of DCM in the chemical industry amounted to around 3,700 tonnes in 1991. This figure has been rounded upward by TNO/CML to correct for the incomplete response. We have assumed consumption of 4,000 tonnes in 1990. Emissions to water are, as for the mechanical and electrical engineering industry, fixed at 0.3 %. The emission to air depends heavily on the process. Some companies emit more than 99% of the amount used to air [ER-I 1994], while in the pharmaceutical industry the figure is only 50%. In this report we have taken a ratio of 65% emission to air and 35% disposal with waste. Based on these figures, in segment 45 we have estimated a chlorine content of 30% in chemical waste reported as containing halogens. This accords with the generally accepted figures [Verhage 1991]. DCM is far and away the most important chemical waste substance containing chlorine. If a much higher, or even a lower emission of DCM to air was assumed, the balance for the quantity of chlorine in chemical waste would no longer add up. The ER-I in fact

gives a much lower emission of DCM to air. The reason for this is that the ER-I does not cover all consumption applications in the chemical industry.

Paint removers

The Dutch paint industry used over 2,200 tonnes of HHCs, mainly DCM and 1,1,1 trichloroethane in 1989 [VVVF 1989). The consumption of 1,1,1 trichloroethane in 1990 was 280 tonnes.[CFC Commission 1994]. It is assumed that the difference consists of DCM and that consumption in 1990 can be taken to be around 2,000 tonnes. This quantity accords reasonably, taking into account the incomplete response, with the sales of DCM to the paint industry according to the VHCP survey in 1991 [Knoop 1991]. DCM is used in paint removers [Slooff 1987]. Due to an import surplus 1.37 times as many paint products are used in the Netherlands as are produced [Tukker 1993b]. In the absence of more specific figures, it is assumed that this also applies to paint removers. When paint removers are used the majority of the substance is emitted to air; a limited amount (around 15%) is released as waste. These proportions are based on the HHCs information document which states that 10-20% of the paint remover used reaches the waste phase [Verhage 1991]. Around 25% of the paint products used in the Netherlands are sold in the do-it-yourself market [KPMG 1992]. In the absence of more specific figures, we have assumed that this also applies for paint removers: this gives a consumption of 685 tonnes of DCM in the do-it-yourself market. Research by RIZA shows that households release over 5 tonnes of DCM into the sewage system each year [Teurlinckx 1991]. Because paint remover is the most important product containing DCM in households in terms of volume, the emission to water of DCM in paint remover should probably be put into perspective. It involves slightly less that 1% of the quantity of DCM in paint removers used in households. This emission is disregarded here.

Rubber industry and adhesive products

The rubber processing industry alone emits 55 tonnes of dichloromethane into air [SPIN 1992f]. These are mainly emissions resulting from the use of adhesives. According to figures from KWS 2000, 3,800 tonnes of volatile organic substances are used in adhesives. Some (unknown) share of this is 1,1,1-trichloromethane and DCM. A conservative estimate puts the total consumption in adhesive products at 100 tonnes. There are no figures available for imports and exports of adhesive products. It is assumed that they are emitted for 100% to air. The estimates is low compared with the (dated) figures from the Basic Document on DCM, which gives a figure of 1,000 tonnes for consumption of DCM in adhesives in 1985 [Slooff 1987].

Aerosols

The content of a spray can consists of active substance, in solvent of otherwise, and a propellant. For certain applications solvents of the active substance and/or a pressure increaser can be added, such as dichloromethane and 1,1,1 trichloroethane. Figures from the Collective Emission Record state that the consumption of DCM in spray cans is around 200 tonnes. Taking into account an export surplus of aerosols filled in the Netherlands, only 66% of this is consumed in the Netherlands [Tukker 1993b]. It is assumed that all DCM is emitted to air.

Other consumption

There is a further item of 503.5 tonnes for 'other' uses. The same proportions as for the chemical industry are taken for the emission to water, waste and air.

Table 30.1: Use of dichloromethane in 1990 (tonnes chlorine; in brackets: tonnes substance)

Target group	Consumption	Imp./exp.	Air	Water	Waste
Mechanical and electrical engineering	507 (607)		292 (350)	1.7 (2)	213 (255)
Dry cleaning	34 (40)		17 (20)		17 (20)
Pharmaceutical industry	839 (1004.5)		461 (552)	10.4 (12.5)	367 (440)
Foodstuffs (extraction)	38 (45)		29 (35)	8.3 (10)	
Chemicals	3339 (4000)		2164 (2592)[1]	10.0 (12)	1165 (1396)[1]
Paint removers	1670 (2000)	+618 (740)	1944 (2329)		343 (411)
Adhesives	83 (100)	?	83 (100)		
Aerosols	167 (200)	- 57 (- 68)	110 (132)		
Other	421 (503.5)		273 (327)[2]	0.8 (1)	147 (176)[2]
Total:	7098 (8500)	561 (672)	5374 (6437)[3]	31.3 (37.5)	2252 (2698)[3]

1)Range of emissions to air 50-90 % : Air: 1663-2999 (1992-3592); Waste: 331-1666 (396-1996)
2)Range of emissions to air 50-90 % : Air: 210-378 (252-453); Waste: 42-210 (50-251)
3)Range of emissions to air 50-90 % : Air: 4810-6314 (5762-7563); Waste: 1312-2816 (1572-3373)

3 EMISSIONS UNDER ENVISAGED POLICY

The measures adopted to reduce emissions for each target group as of 1 January 1995 are discussed below. The emissions remaining after implementation of this policy have been estimated on the basis of the emission situation in 1990. No account has been taken of changes in emissions as a result of economic growth or other autonomous developments within the target group.

Mechanical and electrical engineering industry
The 'Memorandum of Understanding for the implementation of environmental policy in the mechanical and electrical engineering industry' provided for implementation of the IMT. For the year 2000, this means a reduction of 80% in emissions to air and of 50% to water. The objective for 2010 is not a firm objective but more a guideline (90% reduction in emission to air and 50% reduction to water). These percentages are in relation to the environmental burden of the sector in 1985. This amounted to 264 tonnes to air and 1.1 tonnes to water, according to the memorandum of understanding. For 1990 TNO reports an emission of 350 tonnes to air and 2 tonnes to water.

Both sources report similar emission quantities. From the analysis of the mechanical and electrical engineering industry target group it can be seen that the DCM emissions in 1990 are almost the same as the emissions in 1985 [Tebodin 1994]. Taking into account uncertainties in these findings, and the fact that the quantity of emissions calculated by TNO produces no discrepancies in the balances of the substance flow analysis, it is argued that the emissions in 1985 and 1990 remained the same. It is therefore assumed that emissions of DCM in 1985 were 350 tonnes to air and 2 tonnes to water (the TNO figures for 1990).
The volume of DCM emissions in the year 2000 would then be 70 tonnes to air (80% reduction) and 1 tonne to water (50% reduction).

Dry cleaning
The Dry Cleaners Environmental Management Decree has no bearing on DCM emissions. It is therefore assumed that emissions of DCM will not be reduced in dry cleaners. This is probably an underestimate of the actual situation but in the context of this study we can only base ourselves on established policy.

Pharmaceutical/Chemical industry
The Emission Record shows that emissions to air from the pharmaceutical industry were roughly halved in the period 1985-1990. The emissions to air from the chemical raw material sector increased slightly in the same period [Berdowski et al. 1993]. The sum of the emissions to air of the pharmaceutical and chemical raw material industries (SBI 29.6 and 29.4 respectively) are nevertheless significantly

lower than the DCM emissions to air based on the BMPs [FO-Industrie 1995]. It is therefore impossible to establish with any certainty the trend in emissions in the period 1985-1990.

In the preceding sub-sections, DCM emissions to air in 1990 were calculated as 552 tonnes for the pharmaceutical industry and 2,592 tonnes for the chemical industry, a total of 3,144 tonnes. The aggregate in the BMPs was based on DCM emissions to air of 2,656 tonnes in 1985. There is great uncertainty about the trend of emissions in the period 1985-19990. The BMPs cover the companies with the largest DCM emissions. The same reduction targets are sought for the companies in the chemical industry which have not drawn up a BMP. On this basis, it will be assumed that the emissions in the period 1985-1990 remained the same, so that the entire reduction target has to be achieved after 1990. The DCM emissions to air in 1995 are fixed at 3,144 tonnes. On the basis of the BMPs a reduction objective of 89% is expected, which comes down to an emission of 314 tonnes of DCM to air in the year 2000.

For the DCM emissions to water, in the last sub-section emissions were calculated to be 12.5 tonnes for the chemical industry and 12 tonnes for the pharmaceutical industry, a total of 24.5 tonnes for 1990. The aggregate in the BMPs gives an emission to water of 121 tonnes for 1985. The ER states that DCM emissions to water in the chemical raw materials industry and the pharmaceutical industry in the period 1985-1990 declined by around 80% [Berdowski et al. 1993]. This corresponds with the discrepancy to be found between the TNO figures for 1990 and the BMP figure for 1985. Assuming a DCM emission to water of 121 tonnes in 1985 and a projected emission reduction objective of 99% on the basis of the BMPs, the result is emissions of DCM to water of 1.2 tonnes in the year 2000.

Coffee-roasting factories
There is a new process for the extraction of caffeine involving water and the adsorption of caffeine to an adsorbent (active carbon). DCM is no longer used in this process. If this process is widely adopted coffee-roasting factories will no longer consume DCM [SPIN 1992c]. For the time being, however, there is no certainty about this. For the purposes of this study this cannot be regarded as established policy. For the year 2000, therefore, the same emissions as in 1990 have been taken.

Paint remover
The Ministry of VROM is preparing an Order in Council providing for a ban on the use of DCM in paint removers. The procedure will begin in June 1995 [Josephus Jitta, verbal communication, 1995]. For the time being there is no policy

with respect to DCM in paint remover. For the year 2000, therefore, we have taken the same emissions as for 1990.

Adhesives and aerosols
These products are used in the plastic and rubber processing industry. The negotiations on a memorandum of understanding for the implementation of an environmental policy in this industry have not yet been concluded. For the time being there is no established policy. Here also, therefore, the figures for 1990 have been retained for the year 2000.

Other consumption
In 1990 there was an outstanding item of 503.5 tonnes of DCM, resulting in an emission of 327 tonnes to air and 1 tonne to water. The applications that caused this emission are not known nor whether there is a policy for reducing it. The same emission figures as for 1990 have therefore been taken for the year 2000.

Table 30.2 shows the emissions in the year 2000 on the basis of envisaged policy.

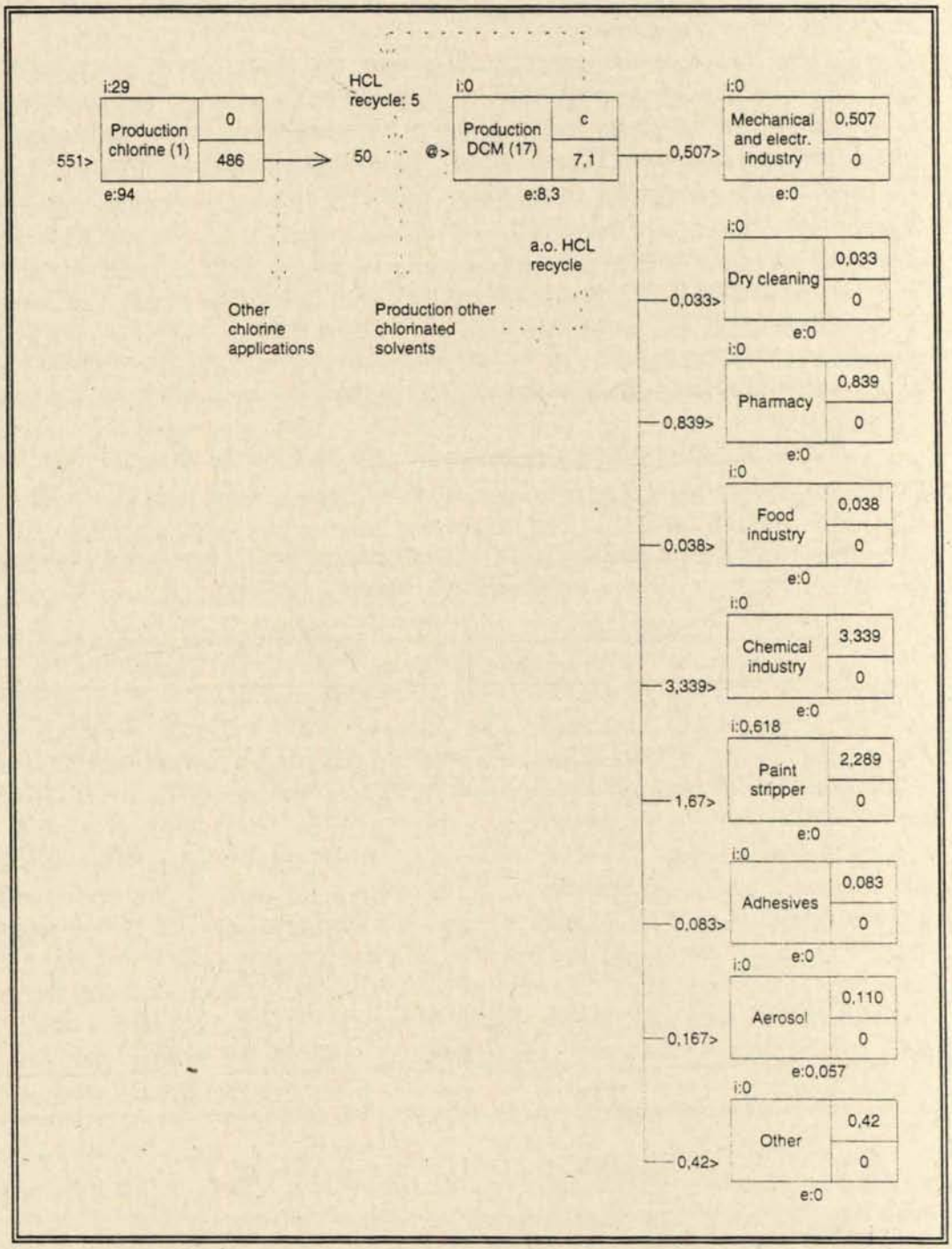
Table 30.2 Emissions of dichloromethane under envisaged policy in tonne chlorine (in brackets: tonnes DCM)

Target group	Consumption	Imp./exp.	Air	Water	Waste
Mech. and El. Engineering	p.m.	p.m.	58 (70)	0,8 (1)	p.m.
Dry cleaning	p.m.	p.m.	17 (20)		p.m.
Pharm + Chemicals	p.m.	p.m.	262 (314)	1,0 (1,2)	p.m.
Foodstuffs (extraction)	p.m.	p.m.	29 (35)	8,3 (10)	p.m.
Paint remover	p.m.	p.m.	1944 (2329)		p.m.
Adhesives	p.m.	p.m.	83 (100)		p.m.
Aerosols	p.m.	p.m.	110 (132)		p.m.
Other	p.m.	p.m.	273 (327)	0,8 (1)	p.m.
Total:	p.m.	p.m.	2776 (3327)	10,9 (13,2)	p.m.

4 COMMENTS AND POINTS FOR DISCUSSION

None.

Figure 30.1: Substance flows in consumption applications of DCM (in kt chlorine, 1990)



SEGMENT 31: CONSUMPTION APPLICATIONS OF 1,1,1-TRICHLOROETHANE

1 INTRODUCTION

1,1,1-trichloroethane (also 1,1,1-tri for short) is used in a range of applications, such as:

- degreasing agent in the metal electric industry;
- paint;
- aerosols;
- adhesives/rubber products
- solvents.

The following sub-section deals with these applications.

2 PROCESSES, SUBSTANCE FLOWS AND EMISSIONS IN 1990

1,1,1-trichloroethane is not produced in the Netherlands. It is imported from a number of countries. According to the CBS, the import surplus comes to 1,500 tonnes of 1,1,1-tri [CBS, 1991]. This figure is almost certainly too low: both the analysis presented below based on the CFC action programme and the VHCP survey show a consumption of over 5,000 tonnes a year [CFC Commission 1994, Knoop 1993]. Although distillation of 1,1,1-tri waste is expected be a factor, this can not be more than 100 and 200 tonnes in view of the volume of waste. The most likely explanation is that imports of 1,1,1-tri are classified under, for example, the CBS category 'other saturated acyclical chlorinated compounds'. This explanation is supported by the fact that in contrast to the CBS the other countries and EUROSTAT do not separately record imports and exports of 1,1,1-tri and many shipments may therefore not be imported under the CBS code number for 1,1,1-tri.

It is assumed here that the imports are equal to the consumption of 1,1,1-tri which was reported by the CFC Commission for 1990 (5,540 tonnes). In 1992 the CFC Commission for the first time reported figures broken down by target group (in a total consumption of 3,803 tonnes). Until 1992 there was an active preventive policy towards 1,1,1-tri, especially in the mechanical and electrical engineering industry in connection with the production of large volumes of waste. It is therefore assumed that the reduction in the consumption of 1,1,1-tri between 1990 and 1992 was attributable entirely to the mechanical and electrical engineering

industry. For the other applications the consumption figures for 1992 have also been adopted for 1990.

The consumption by target group in 1990 is discussed below. Table 31.1 presents a summary of the consumption, emissions and disposal as waste. The table also shows the imports and exports of products containing 1,1,1-tri.

Mechanical and electrical engineering industry and industrial cleaning
The CFC Commission reported consumption of 2,070 tonnes in 1992 for the mechanical and electrical engineering and industrial cleaning sectors. In 1992 1,737 fewer tonnes of 1,1,1-tri were consumed than in 1990 [CFC Commission 1994]. On the assumption that this reduction occurred entirely in the use as degreaser/cleaner, it follows that consumption was 3,807 tonnes. The distribution across the media air, water and waste is calculated on the basis of the ratios determined by Van der Most [1993]. V.d. Most bases his figures on a total consumption in the mechanical and electrical engineering industry around 1,000 tonnes higher than the figures adopted here. Taking those figures would, however, lead to a higher total consumption in the Netherlands than was reported by the CFC Commission. V.d. Most bases himself on the consumption figures for 1988 as estimated by Verhage [1991]. Since the CFC Commission based itself on an annual monitoring and audit conducted by KPMG, the commission's figures appear the more reliable.

Paint production
The CFC action programme reports the use of 280 tonnes in the production of paint in 1992. This figure has been retained for 1990. In connection with an import surplus, 37% more paint is used in the Netherlands than is produced [Tukker 1993b]. This leads to an excess consumption of 104 tonnes. The do-it-yourself (household) market accounts for 25% of paint sales and the professional market for 75% [KPMG 1992]. According to Verhage [1991] around 15% of the quantity of HHCs in paint are disposed of as waste. It is assumed that the remainder is emitted to air. A small portion is probably emitted to water. As with the DCM in paint remover, this can be estimated at less than 1% (see segment 22). In contrast to DCM, RIZA reports no significant releases of 1,1,1-tri by households [Teurlinckx 1993]. This is probably due to the low 1,1,1-tri consumption compared with DCM.

Aerosol
The annual consumption of 1,1,1-trichloroethane for use in aerosol packaging was 130 tonnes in 1992 [CFC Commission 1994]. This figure has also been adopted for 1990. An export surplus means that 33% fewer aerosols are used in the Netherlands than are produced [Tukker 1993b]. It is assumed that this ratio also

applies to aerosols filled with 1,1,1-tri, which produces exports of 43 tonnes and consumption of 87 tonnes in spray cans. It is assumed that it is emitted for 100% to air.

Rubber industry and adhesive products
According to the CFC Commission, 780 tonnes of 1,1,1-tri was used in adhesive products in 1992. This figure has been maintained for 1990. Imports and exports of adhesive products are not known and are disregarded. It is assumed that all the solvent is emitted to air when adhesives are used. The contribution of the rubber industry to this emission is 45 tonnes, based on the assumption that this is entirely due to adhesive products [SPIN 1992e].

Other applications
On the basis of the figures given above, there is a remaining item of 543 tonnes of 1,1,1-tri. The distribution over the environmental media water, air and waste is estimated on the basis of the distribution adopted for the mechanical and electrical engineering industry.

Table 31.1: Use of 1,1,1-trichloroethane in 1990 (tonnes chlorine; in brackets: tonnes substance)

Target group	Consumption (tonnes)	Imp./exp. (tonnes)	Air (tonnes)	Water (tonnes)	Waste (tonnes)
Mech. and Elec. Engineering	3035 (3807)		2731 (3426)	30 (38)	273 (343)
Paint	223 (280)	+ 83 (+104)	276 (346)		30 (38)
Aerosols	104 (130)	- 34 (- 43)	69 (87)		
Adhesives/rubber products	622 (780)	?	622 (780)		
Other	433 (543)		390 (489)	4 (5)	39 (49)
Total:	4417 (5540)	49 (61)	4088 (5128)	34 (43)	343 (430)

3 EMISSIONS UNDER ENVISAGED POLICY

The Montreal Protocol prohibits the use of new CFCs and tetra and 1,1,1-tri with effect from 1 January 1996. 1,1,1.-tri should therefore also be phased out in the Netherlands from this date. The substance is only permitted for a limited number

of essential applications. These exceptions will be gradually restricted. Recycled CFCs and tetra may still be used after 1 January 1995. In effect, it is accepted that the volume of tetra present in the Netherlands on January 1 1995 may be used up.

Eventually, after implementation of envisaged policy, there will be no emission from any of the various applications. Table 31.2 represents this.

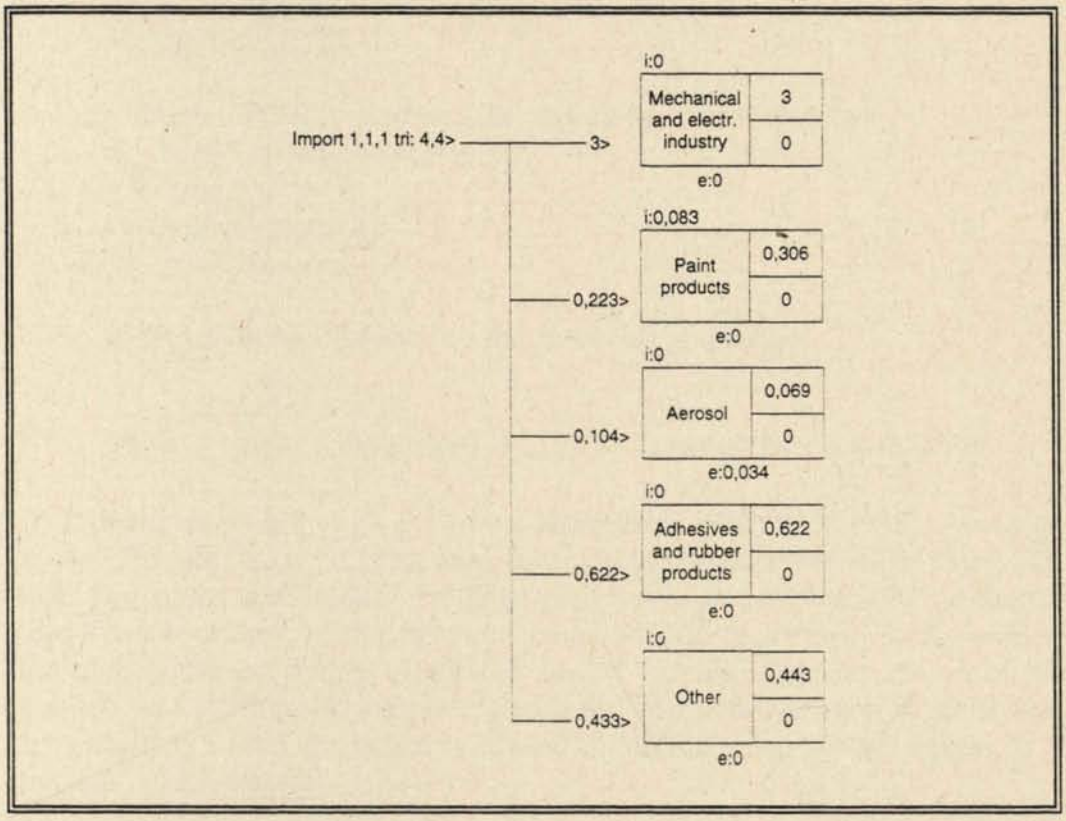
Table 31.2 Emissions of 1,1,1-trichloroethane under envisaged policy (tonnes chlorine; in brackets: tonnes substance)

Target group	Consumption (tonnes)	Imp./exp. (tonnes)	Stock formation (tonnes)	Air (tonnes)	Water (tonnes)	Waste (tonnes)
Various				0	0	0
Total:				0	0	0

4 COMMENTS AND POINTS FOR DISCUSSION

None.

Figure 31.1: Substance flows in consumption applications of 1,1,1 trichloroethane (in kt chlorine, 1990)



SEGMENT 32: CONSUMPTION APPLICATIONS OF TRICHLOROETHENE

1 INTRODUCTION

Trichloroethene (TCE) is used in a number of sectors, including:
- metal electric (as degreasing agent);
- dry cleaning;
- pharmaceutical industry;
- textile refinement.

These applications are discussed in the following sub-section.

2 PROCESSES, SUBSTANCE FLOWS AND EMISSIONS IN 1990

Trichloroethene is not produced in the Netherlands [Bremmer 1988]. According to the CBS, the import surplus was over 850 tonnes in 1990 [CBS 1991]. The estimates for the consumption by target group are discussed below. This analysis produced a consumption of 926 tonnes, which accords reasonably closely with the consumption to be derived from the import surplus. Changes in stocks and inaccuracies are the most logical explanations for the discrepancy in the figures. For simplicity's sake, the figure calculated for consumption has been taken to be the same as the imports.

Mechanical and electrical engineering industry
The report 'Cleaning and degreasing with HHCs in small companies' states that the mechanical and electrical engineering industry emits 629 tonnes of trichloroethene to air, 5.2 tonnes to water and disposes of 52.7 tonnes as waste [V.d. Most 1993]. This gives a total consumption of 687 tonnes.

Dry cleaning
The volume of trichloroethene used in dry cleaning is around 14 tonnes [v.d. Most 1993]. In the use of trichloroethene for dry cleaning an estimated 11 tonnes is emitted to air and 0.15 tonnes to water. A further 3.3 tonnes is disposed of in or as waste.

Pharmaceutical industry
The ER-I recorded an emission of 21 tonnes of trichloroethene to air and 1.7 tonnes to water for the 6 major pharmaceutical firms in the Netherlands [Berdowski 1993]. The volume of waste is not known. In the absence of better statistics, as with the mechanical and electrical engineering industry the volume

of waste has been estimated at around 10% of the emission to air (2.3 tonnes). This gives a total consumption of 25 tonnes. A much higher percentage of waste appears unlikely since this would further increase the total consumption and increase the deviation from the CBS import figures even further.

Textile refinement
Figures from ER-I show that one textile refinement company emitted around 150 tonnes of trichloroethene to air and 50 tonnes to water in 1990 [Berdowski 1993]. The volume of waste is not known and has been disregarded. On the basis of these figures, the consumption is estimated at 200 tonnes.

Table 32.1: Use of trichloroethene in 1990 (tonnes chlorine; in brackets: tonnes substance)

Target group	Consumption	Imp./exp.	Air	Water	Waste
Mech. and Elec. Engineering	556 (687)		509 (629)	4,2 (5,2)	42,7 (52,7)
Dry cleaning	11 (14)		9 (11)	0,12 (0,15)	2,7 (3,3)
Pharm.	20 (25)		17 (21)	1,4 (1,7)	1,9 (2,3)
Textile refinement	162 (200)		121 (150)	40 (50)	p.m.
Total:	750 (926)		657 (811)	46,2 (57,1)	47,2 (58,3)

3 EMISSIONS UNDER ENVISAGED POLICY

The measures adopted to reduce emissions for each target group as of 1 January 1995 are discussed below. The emissions remaining after implementation of this policy have been estimated on the basis of the emission situation in 1990. No account has been taken of changes in emissions as a result of economic growth or other autonomous developments within the target group.

Mechanical and electrical engineering industry
The 'Memorandum of Understanding for the implementation of environmental policy in the mechanical and electrical engineering industry' provided for the implementation of the IMT. For 1995 and the year 2000 this means a reduction of 50% in emissions to air and of 75% in emissions to water. The objective for 2010 is not a firm objective but more a guideline (50% reduction in emissions to air and 95% reduction in emissions to water). These percentages are in relation to

the environmental impact by the sector in 1985. According to the memorandum of understanding this was 338 tonnes to air (emissions to water are not reported). In the preceding sub-section emissions of 629 tonnes to air and 5.2 tonnes to water were taken for 1990.

The analysis of the mechanical and electrical engineering industry target group shows that the DCM emissions in 1990 were roughly the same as in 1985 [Tebodin 1994] (see also segment 30). With the accelerated phasing out of chlorinated solvents in the context of the CFC action programme a temporary switch over to TCE (and PER) is expected. This will mean that the reduction objective for TCE in 1995 will not be achieved. It is now assumed that the TCE emissions in 1990 are the same as the TCE emissions in 1985. This means that the entire reduction in emissions must be achieved after 1990.

Taking into account uncertainties in these findings and the fact that the volume of emissions calculated in the preceding sub-section do not produce any discrepancies in the balances of the substance flow analysis, it is argued that the emissions in 1985 and 1990 remained the same and an emission of 629 tonnes to air and 5.2 tonnes to water are taken for 1985 (figures for 1990 from the previous sub-section). On the basis of the reduction percentages agreed in the IMT the expected emissions in the year 2000 would then be 315 tonnes to air and 1.3 tonnes to water.

Dry cleaning
The Dry Cleaners Environmental Management Decree has no bearing on the DCM emissions. It is therefore assumed that emissions from dry cleaners will not be reduced. This is probably an underestimate of the actual situation but this study is based only on established policy.

Pharmaceutical industry
The ER-I shows that TCE emissions to air remained stable or even slightly increased in the period 1985-1990 [Berdowski et al. 1993]. On this basis it is assumed that emissions in 1985 were the same as the emissions in 1990: according to the previous sub-section 21 tonnes of TCE to air and 1.7 tonnes of TCE to water.

The companies in the pharmaceutical industry have signed the 'Memorandum of Understanding for the implementation of environmental policy in the chemical industry' and have drawn up a BMP. The BMPs are based on reductions of 72% in emissions to air and 86% to water [FO-Industrie 1995]. The expected emission in the year 2000 would then amount to 6 tonnes of TCE to air and 0.2 tonnes to water.

Textile refinement

The 'Memorandum of Understanding for the implementation of environmental policy in the textile and carpet industry' reports an emission to air of 216.5 tonnes and an emission to water of 33.3 tonnes in 1985. The ER reports an emission of 150 tonnes to air and 50 tonnes to water for 1991. These emissions declined sharply in 1992: The ER reports an emission of 25 tonnes to air and 1.3 tonnes to water in that year [Berdowski et al. 1993]. Because there is otherwise no known established policy it is assumed that the emissions in the year 2000 will be the same as in 1992 as reported by the ER (25 tonnes to air and 1.3 tonnes to water).

Table 32.2 shows the emissions under the envisaged policy.

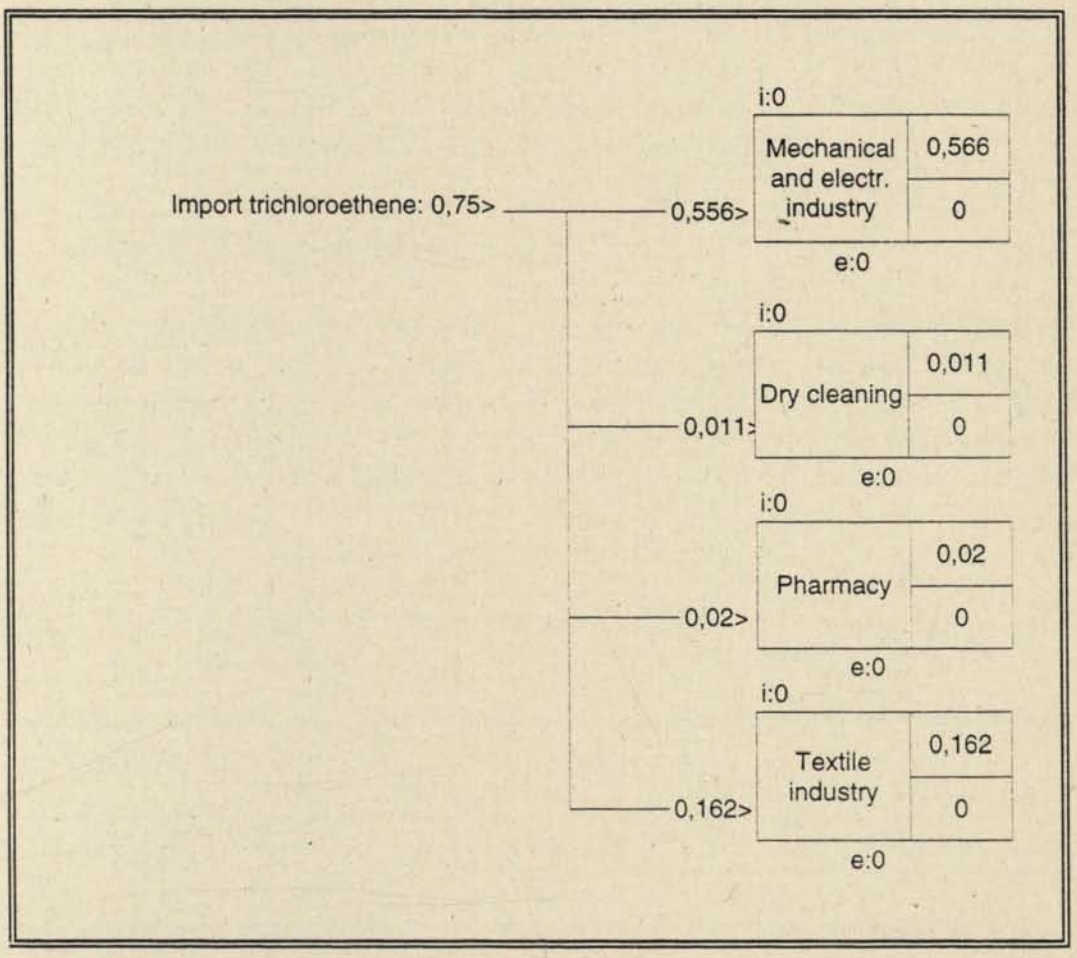
Table 32.2 Emissions of trichloroethene under established policy in tonnes chlorine (in brackets: tonnes DCM).

Target group	Consumption	Imp./exp.	Air	Water	Waste
Mech. and Elec. Engineering	p.m.	p.m.	255 (315)	1,1 (1,3)	p.m.
Dry cleaning	p.m.	p.m.	9 (11)	0,12 (0,15)	p.m.
Pharmaceutical	p.m.	p.m.	5 (6)	0,2 (0,2)	p.m.
Textile refinement	p.m.	p.m.	20 (25)	1,1 (1,3)	p.m.
Total:	p.m.	p.m.	289 (357)	2,5 (3,0)	p.m.

4 COMMENTS AND POINTS FOR DISCUSSION

None.

Figure 32.1: Substance flows in consumption applications of trichloroethene (in kt chlorine, 1990)



SEGMENT 33: CONSUMPTION APPLICATIONS OF CFC-115

1 INTRODUCTION

CFC-115 is used especially as a cooling agent in industrial cooling plants. Other applications have little significance [CFC Commission 1994].

2 PROCESSES AND SUBSTANCE FLOWS

Around 105 tonnes of CFC-115 was consumed in total in 1990 [CFC Commission, 1994]. The entire amount is imported; it is not produced in the Netherlands. As far as in known CFC-115 is only used as a cooling agent in industrial cooling plants. The consumption of cooling agent can be equated with the replacement of losses due to leaks. It is therefore assumed that the consumption is emitted for 100% to air.

Table 33.1: Use of CFC-115 in 1990 (tonnes chlorine in brackets: tonnes substance)

Target group	Consumption (tonnes)	Air (tonnes)	Water (tonnes)	Waste (tonnes)
Industrial cooling	24 (105)	24 (105)		
Total:	24 (105)	24 (105)		

3 EMISSIONS UNDER ENVISAGED POLICY

The Montreal Protocol prohibits the use of new CFCs and tetra with effect from 1 January 1996. The EU drew up a regulation to enforce this ban from 1 January 1995 (EU Regulation 3093/94). CFC-115 should therefore also be phased out in the Netherlands from this date. The substance may then only be used for a limited number of essential applications. These exceptions will be gradually restricted. Recycled CFCs and tetra may still be used after 1 January 1995. In effect, it is accepted that the volume of tetra present in the Netherlands on January 1 1995 will be used up.

Eventually there will be zero emissions from all the applications after implementation of the policy adopted as of 1 January 1995. This is shown in Table 33.2.

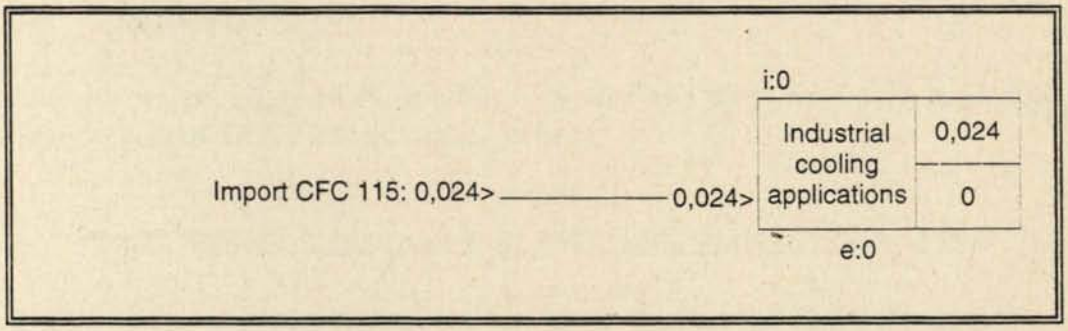
Table 33.2 Emissions of CFC-115 under envisaged policy (tonnes chlorine; in brackets: tonnes substance)

Target group	Consumption (tonnes)	Imp./exp. (tonnes)	Stock formation (tonnes)	Air (tonnes)	Water (tonnes)	Waste (tonnes)
Various				0	0	0
Total:				0	0	0

4 COMMENTS AND POINTS FOR DISCUSSION

None.

Figure 33.1: Substance flows in consumption applications of CFC 115 (in kt chlorine, 1990)



SEGMENT 34: CONSUMPTION APPLICATIONS OF HCFC-142b

1 INTRODUCTION

As far as we are aware HCFC-142b is only used as a propellant in the production of styrofoam at DOW Benelux in Terneuzen.

2 PROCESSES, SUBSTANCE FLOWS AND EMISSIONS IN 1990

DOW Benelux reported consumption of 1,016 tonnes of HCFC-142b in 1990 to TNO/CML [DOW 1994]. This quantity corresponds closely with the total Dutch consumption of 1,023 tonnes reported by the CFC Commission [1994][8]. For simplicity's sake the DOW figures have been taken as the total Dutch consumption. HCFC-142b is not produced in the Netherlands. The entire domestic consumption is imported.

Some of the HCFC is emitted to air during production. As with hard PUR the remainder is absorbed into the cell structure (see segment 23 on consumption applications of CFC-11). This involves periods of 50 to 80 years. The HCFC-142b in foam therefore accumulates in society. Since HCFC-142b was only introduced at the end of the 1980s the emission from the quantity already accumulated in society has been ignored. Imports and exports of styrofoam containing HCFC-142b have been disregarded in the absence of statistics. Table 34.1 shows consumption and emissions as reported by DOW Benelux.

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[8] Figures for 1990 from the 1993 Annual Report of the CFC Commission. In the annual report for 1990 (published in 1991) the CFC Commission refers to a higher consumption. According to those involved in preparing the annual report it was sometimes found in hindsight that the figures received when researching the earliest annual reports were not entirely accurate. These figures were therefore corrected in later reports [KPMG 1994]. We have therefore adoped the figures for 1990 from the most recent annual report.

Table 34.1: Use of HCFC-142b in 1990 (tonnes chlorine; in brackets: tonnes substance)

Target group	Consumption (tonnes)	Imp./exp. (tonnes)	Stock formation(tonnes)	Air (tonnes)	Water (tonnes)	Waste (tonnes)
Styrofoam	359 (1016)	p.m.	273 (773)	86 (243)		
Hist. foam emission	nil			nil		
Total:	359 (1016)		273 (773)	86 (243)		

3 EMISSIONS UNDER ENVISAGED POLICY

In December 1995 the European Commission published a new integrated regulation covering substances that deplete the ozone layer (PbEC 3093/94), which includes HCFCs for which the European Union has included provisions for reductions which go further than the reductions agreed in the Montreal Protocol. The regulation is based on a phased reduction in the use of CFCs in relation to the reference year 1989. If the proposed regulation is approved without change, emissions must be reduced by 100% by the year 2015.

The measure is one which will only be realised in the medium term. It is, however, established policy which is no longer open to discussion. We therefore chose to regard the situation after implementation of this policy as the future situation and not a point in time when HCFCs are still being used. There will ultimately be zero emissions for all applications after implementation of the policy established as of 1 January 1995. This is shown in Table 34.2.

Table 34.2 Emission of HCFC-142b under envisaged policy (tonnes chlorine; in brackets: tonnes substance)

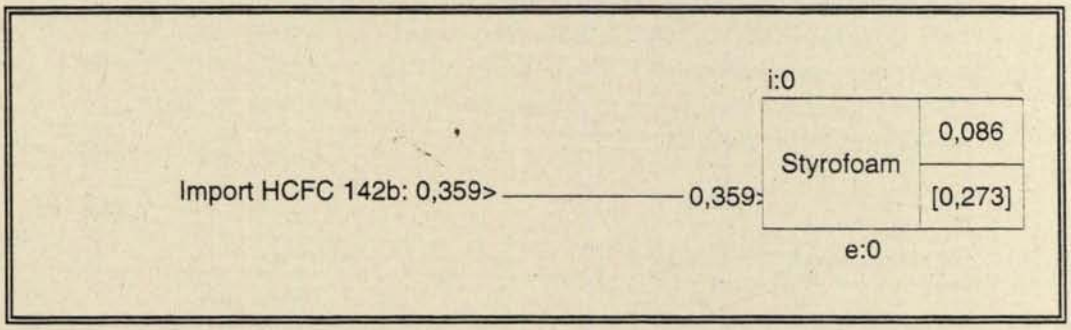
Target group	Consumption (tonnes)	Imp./exp. (tonnes)	Stock formation (tonnes)	Air (tonnes)	Water (tonnes)	Waste (tonnes)
Various				0	0	0
Total:				0	0	0

In contrast to CFC-11, we have not taken account of emissions of HCFC-142b accumulated in the foam in society. HCFC-142b was only introduced as a propellant at the end of the 1980s; the accumulated volume in the year 2015 will probably be small compared with the quantity of accumulated CFC-11. Since the ozone depleting effects (ODP) of HCFC-142b is significantly smaller than that of CFC-11 it seems justifiable to ignore historical emissions of HCFC-142b compared with those from CFC-11.

4 COMMENTS AND POINTS FOR DISCUSSION

None.

Figure 34.1: Substance flows in consumption applications of HCFC 142b (in kt chlorine, 1990)



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SEGMENT 35: PRODUCTION AND USE OF VINYLIDENECHLORIDE

1 INTRODUCTION

Until 1992 DOW Benelux produced vinylidenechloride from 1,1,2-trichloroethane. The steps in the process for this product are described in the following sub-section. The description is based on the SPIN document for the process [SPIN 1993b].

2 PROCESSES

In a continuous process under the influence of 20% sodium hydroxide and at 95-100°C and at 4-5 bar pressure the raw material 1,1,2-trichloroethane reacts to 1,1-dichloroethene (vinylidenechloride, VDCM). The reaction is as follows:

(1) $CHCl_2$-CH_2Cl + NaOH ----> CCl_2= CH_2 + H_2O + NaCl

The conversion rate ranges from 80 to 90%. The exhaust of the reactor consists (besides raw material and product) of water, NaCl and cis/trans dichloroethene (by-product: 0.5%). After drying, 1,1-dichloroethene, cis/trans dichloroethene and 1,1,2-trichloroethane are separated. The 1,1,2-trichloroethane is recycled and cis/trans dichloroethene is stored and incinerated. The 1,1-dichloroethene is shipped out. Water and NaCl (salt) are released via a stripper.

3 SUBSTANCE FLOWS AND EMISSIONS IN 1990

Dow Benelux imported around 5,600 tonnes of 1,1,2-trichloroethene in 1990 for the production of VCDM, which corresponds with around 4,400 tonnes of chlorine. This quantity more or less completely covers all the imports of 'Other saturated hydrocarbons' reported by the CBS (No. 290319009) [CBS 1991]. Around 4,000 tonnes of VCDM is produced from this amount, corresponding with some 2,900 tonnes of chlorine. The entire volume is exported. Around 1,500 tonnes of chlorine is released as chloride (salt).

Table 35.1 shows the emissions to water and air. The figures were provided by DOW Benelux. Emissions to air are significantly lower than the figures recorded in the ER-I. This is because the consequences of measures to curb emissions were not yet incorporated in the ER-I. These involve the installation of a condensation unit in the waste gas exhaust and the removal of the condensate to an incinerator [ER-I 1994, DOW 1994].

The list of emissions to water accords with the figures in WIER and ER-I. A bottleneck is that these emissions are combined figures for the whole plant: the VDCM production, the production of ethyleneamines and a number of other processes in which no compounds containing chlorine are used. Emissions were allocated to individual processes as follows. The emissions to water which are included in WIER for trichloroethene, tetrachloroethene, trichloroethane, tetra and chloroform are allocated to the production of VDCM since according to the SPIN document and ER-I figures for emissions to air these substances are released during the production of VDCM. According to DOW Benelux's statements EOCl is released during the VDCM process, the ethyleneamine process and other processes roughly in the proportions 40:30:30. The volume of EOCl included in WIER was allocated to the various processes on this basis [RIZA 1994a].

4 EMISSIONS UNDER ENVISAGED POLICY

The production of VDCM was halted in 1992. The emissions relating to this process are therefore fixed at zero for the future situation.

5 COMMENTS AND POINTS FOR DISCUSSION

The company was included in the AOX-EOX measurement programme conducted by RIZA in mid-1992 [RIZA 1994b]. The volume of chlorine measured as EOX and AOX was a factor of 5 to 8 higher than the quantity of chlorine which was released to water in the form of individually registered compounds. The reasons for this could be: measurement errors, (e.g. inorganic) chlorine which was incorrectly identified with EOX/AOX or emissions of organic chlorine compounds which are not measured individually.

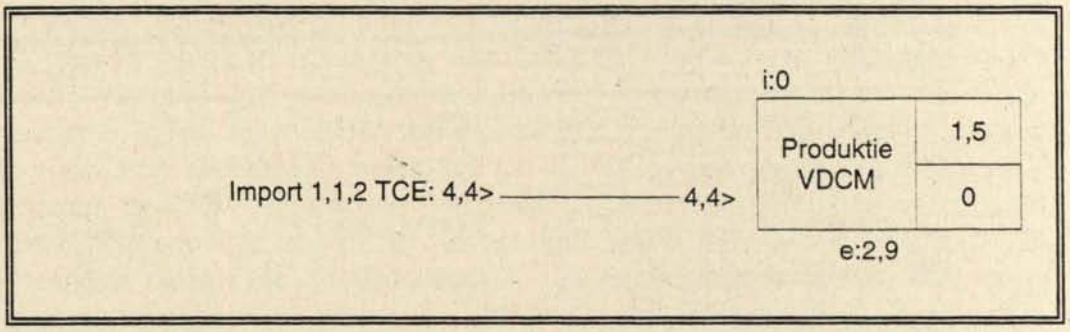
The uncertainties in emission figures and uncertainties introduced by the allocation of water emissions are no longer relevant since production has been halted.

Table 35.1 Emissions to water and air during the production of VDCM in 1990 (kg chlorine; in brackets: kg substance.)

Compound	Air	Water
1,1 dichloroethene	1,034 (1,413)	
trans 1,2 dichloroethene	56 (76)	
1,1,2 trichloroethane	1,433 (1,796)	66 (83)
other chlorinated HCs	1,077 (1,436)	
trichloroethene		2 (2)
tetrachloroethene (PER)		4 (5)
tetra		12 (13)
chloroform		14 (16)
chlorine	4	
HCl	3 (3)	
EOCl		431*
Total chlorine: 4,038	3,607	431*

* Chlorine in EOCl overlaps with chlorine in individual compounds

Figure 35.1: Substance flows in production of VDCM (in kt chlorine, 1990)



SEGMENT 36: PRODUCTION PROCESSES WITH AROMATIC CHLORINE COMPOUNDS

1 INTRODUCTION

Apart from a number of pesticides no aromatic chlorine compounds are produced in the Netherlands [Slooff 1991]. Up to the beginning of 1990 hexachlorobenzene was released as waste from Akzo Nobel's PER/TET factory. The flow was processed entirely abroad. Since this production has been terminated this flow is otherwise ignored.

The quantities and applications are discussed below. The text is largely based on information from various companies, figures from ER-I for 1990 and the Chlorobenzenes Criterion Document [Slooff 1991] (reference years 1987 and 1989). Chlorobenzenes and chlorotoluenes are also released as unintentional by-products during other production processes. These are not dealt with here but are included as emissions under the relevant process.

This segment covers the processes during which chlorine aromates are converted in the production process. The consumption applications are discussed in segment 37. For the sake of clarity, sub-section 2 of this segment does discuss the entire import and consumption of chlorine aromates.

2 PROCESSES AND SUBSTANCE FLOWS IN 1990

2.1 INTRODUCTION

According to the CBS, 1,691 tonnes of monochlorobenzene (MCB) and 1,2 and 1,4 dichlorobenzene were imported to the Netherlands in 1990. Exports amounted to 471 tonnes, which gives a domestic consumption of around 1,200 tonnes [CBS 1991]. Chlorotoluenes, other aromatic chlorinated compounds and the other chlorobenzenes are recorded in a joint category 'other halogenated derivatives of aromatic hydrocarbons'. The volume involved is around 9,000 tonnes.

Chlorobenzenes are used in the pesticides industry, pharmaceuticals, other industry and small-scale consumers (households and industry). Chlorotoluenes are used in the production of pesticides and benzylalcohol. Various aromatic chlorine compounds were also used in 1990 in the pesticides and specialty division of Shell. These applications have been or will be halted, according to Shell. They are therefore otherwise disregarded.

The distribution by substance by area of application is shown in Table 36.1.

Table 36.1: Use of chlorobenzenes in 1990 (in tonnes chlorine; in brackets: tonnes substance)

Substance	Total	Pesticides	Pharmacy	Other ind.	Small-scale use
MCB	323 (1.024)	241 (764)[a]	32 (100)[a]	50 (160)[b]	
1,2 DCB	14 (30)		14 (30)[b]		
1,4 DCB	48 (100)				48 (100)[b]
Total	*385 (1154)* [1]				
1,3 DCB	160 (332)	160 (332)[a]			
1,2,4 TCB en Dichlorotoluene	464 (1.006)	464 (1.006)[a]			
Benzylchloride	1596 (5.700)			1596 (5.700)[a]	
Various Shell	400[2] (1.000)				
Unknown	385[2] (962)				
Total	*3.005 (9.000)*[3]				

[1] To be compared with import-export balance of CBS of 1,200 tonnes o- en p-chlorobenzene

[2] Based on 40 % chlorine

[3] To be compared with import-export balance of CBS of 9,000 tonnes other halogenated aromates

[a] Segment 36: application in production processes

[b] Segment 37: consumption applications

Very small quantities of 1,2,4 trichlorobenzene (TCB; < 500 kg) were used as a carrier in the textile industry in 1990. This application will be entirely phased out around 1995 and has been otherwise ignored [Schwartz 1993]. Possible imports of traces of TCB in imported clothing were disregarded. Chlorobenzenes are not used in wood preservation or (chemical) dry cleaning [Slooff 1991].

2.2 *Pesticides production*

Three manufacturers of pesticides use organic chlorine compounds in their production, either as raw materials or as a solvent.

a: Production of organotin compounds
Monochlorobenzene (MCB) is used in the production of organotin compounds. The current volume is not essentially different from that referred to in the Basic document on chlorobenzenes [Slooff 1991; Tel. inf. 1994]. MCB reacts with magnesium to a Grignard reagent. Further reaction produce triphenyltin (chlorine-free). All the chlorine escapes as chloride (salt) and is released into salt water. ER-I and WIER record no emissions of chlorinated compounds. The company was included in the AOX/EOX measurement programme conducted by RIZA in mid-1992. The quantity of EOX was below the detection limit; a very low level of AOX was found [RIZA 1994b].

b: Production of tetradiphon
The raw materials for the manufacture of tetradiphon are 1,2,4-trichlorobenzene (1,2,4 TCB) and monochlorobenzene (MCB). The first step is to convert 1,2,4 trichlorobenzene by means of chlorosulphones (HSO_3Cl) to the intermediate product 2,4,5-trichlorobenzenesulphonylchloride. In a following reaction 2,4,5-triclorobenzenesulphonyl reacts with monochlorobenzene to produce the end product 2,4,4,5-tetrachlorodiphenylsulphon (tetra-difon).

The producer supplied the volumes of raw material and the product. They do not differ essentially from those mentioned in the Basic Document on chlorobenzenes [Slooff 1991]. Emissions to air were taken from the ER-I. WIER does not record any releases to water which can be allocated to this process. The Basic document refers to a maximum emission of 5 kg of MCB a year to water. It is assumed that the remaining chlorine is released as waste. The LMA recorded a sizeable flow of halogenated waste from this company which is incinerated at AVR. According to ER-C, tetradiphon is not used in The Netherlands so the entire output is regarded as exports [ER-C 1994]. The company was not included in the AOX/EOX measurement programme conducted by RIZA in mid-1992. The EOCl emission was registered in WIER but since 1990 amounts to no more than a few kilos a year [RIZA 1994a].

c: Production of dichlobenil
Dichlobenil is produced by converting 2,6-dichlorobenzaldehyde ($C_7H_4Cl_2$) to oxide form followed by dehydration. The LMA has recorded a sizeable flow of halogenated waste from this company which is incinerated at AVR. Most of the product is exported. According to ER-C, 1 tonne of active substance is used in the

Netherlands. Emissions are taken from the ER-I. WIER does not record any releases which can be allocated to this process. The company was not included in the AOX/EOX measurement programme conducted by RIZA in mid-1992. The EOCl emission is included in WIER but since 1990 has amounted to no more than a few kilos a year [RIZA 1994b].

d: Shell specialties
The SPIN document on Shell Chemie refers to a large number of processes in the agrochemical and specialty division in which chlorobenzenes, anilines and toluenes are used. The basic document on chlorobenzenes mentions the use of 332 tonnes of dichlorobenzene as a raw material for chlorophenvinvos.

The division concerned has since been hived off by Shell and is being phased out. According to Shell such compounds will no longer be used by Shell in the future. For the purposes of this study they are therefore not followed any further. Because it would have been too time-consuming for Shell to find exact figures, we have made do with a rough estimate of total consumption of 1,000 tonnes of chlorine aromates besides dichlorobenzene. With a chlorine content of 40%, this would represent 400 tonnes of chlorine. Table 36.2 presents a summary of these figures.

2.3 Pharmaceutical industry

In 1989 a pharmaceutical company used MCB as a raw material for the production of fine chemicals/medicines.

Table 36.3 shows the use of these substances according to the Basic Document on chlorobenzenes [Slooff 1991] and the distribution of emission between the environmental media. The ER-I records significantly higher emissions to air for 1988 and 1990 than the basic document [ER-I 1994, Berdowski 1993]. The emissions to air have been adjusted to take this into account; the discrepancy has been deducted from waste. It is impossible to estimate the fate of MCB and the associated chlorine which is converted into product. The company was not included in the EOX/AOX measurement programme conducted by RIZA in mid-1992.

Table 36.2: Use of chlorine aromates in production of pesticides in 1990 (in tonnes chlorine; in brackets: tonnes substance)

Pesticide/substance	Consumption	Product	Air	Water	Waste
a: Organotin		0			
- MCB	110,5 (350)		0,05		-
- Cl^- (salt)				110,5	-
b/c: Tetradiphon en Dichlobenil*		405 (989)	1 (2)		
- MCB	131 (414)		10 (31)		
- 1,2,4 TCB en Dichlorotoluene	464 (1006)		0.5 (1)	< 0,003	
- Waste					178.5
d: Specialties Shell					
- 1,3 DCB	160 (332)				
- Various	400 (1.000)				

* For reasons of confidentiality the figures for these products are aggregated.

Table 36.3: Use of chlorobenzenes in the pharmaceutical industry in 1990 (tonnes chlorine; in brackets: tonnes substance)

Substance	Quantity	Product	Air	Water	Waste
MCB	32 (100)	19 (60)	8 (25)	0.2 (0,5)	4.6 (14,5)
1,2 DCB	14 (30)		10 (20)	0.25 (0,25)	4.7 (9,75)

2.4 Other industry

Benzylchloride is used a raw material for the production of benzylalcohol. In principle all chlorine is released as chloride (salt). The company is not registered in ER-I or WIER and not regarded as a priority for the purposes of the ER or the RAP/NAP. RIZA did not include the company in the AOX/EOX measurement programme it conducted in 1992 [RIZA 1994b]. A total of 5,700 tonnes of benzylalcohol is used, corresponding to 1,598 tonnes of chlorine.

Table 36.4: Use in other industry in 1990 (tonnes chlorine; in brackets: tonnes substance)

Substance	Quantity	Recycling	Air	Water	Waste
Benzylchloride	1596 (5700)	-		1596 [1]	

[1] Release as chloride (salt)

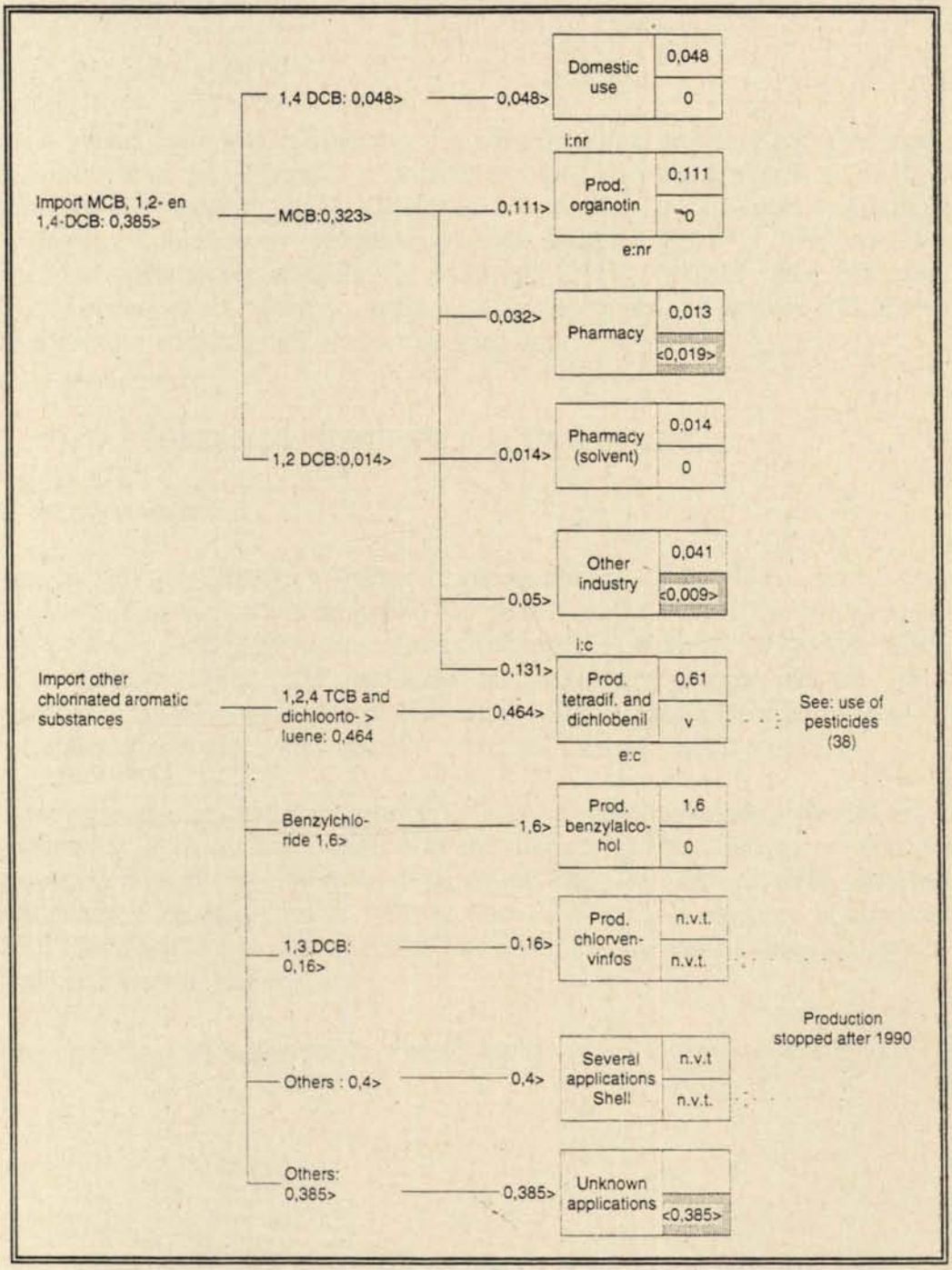
3 EMISSIONS UNDER ENVISAGED POLICY

The emissions from the processes in this segment make no essential contribution to the score on the environmental themes for the situations in 1990. For simplicity's sake, the emission figures for 1990 are also used for the analysis of the situation arising after implementation of the environmental policy established as of 1 January 1995.

4 COMMENTS AND POINTS FOR DISCUSSION

Figure 36.1 describes the substance flows in this segment. To clarify the balances, it also includes the quantities used in the consumption applications (segment 37).

Figure 36.1: Substance flows in production with and consumption of chlorinated aromats (in kt chlorine, 1990)



SEGMENT 37: CONSUMPTION PROCESSES WITH AROMATIC CHLORINE COMPOUNDS

1 INTRODUCTION

This segment deals with the processes in which chlorine aromates are consumed. Their uses as a raw material in production are discussed in segment 37. The quantities and applications are discussed below. The text is largely based on information from various companies, figures from the ER-I for 1990 and the Criterion document for chlorobenzenes [Slooff 1991] (reference years 1987 and 1989). For the sake of clarity, sub-section 2 of this segment describes all imports and the entire consumption of chlorine aromates.

2 PROCESSES AND SUBSTANCE FLOWS IN 1990

2.1 Introduction

According to the CBS, 1,691 tonnes of monochlorobenzene (MCB) and 1,2 and 1,4 dichlorobenzene were imported to the Netherlands in 1990. Exports amounted to 471 tonnes, which gives a domestic consumption of around 1,200 tonnes [CBS 1991]. Chlorotoluenes, other aromatic chlorinated compounds and the other chlorobenzenes are classified in a joint category 'other halogenated derivatives of aromatic hydrocarbons'. This quantity involved is around 9,000 tonnes.

Chlorobenzenes are used in the pesticides industry, pharmaceuticals, other industry and small-scale consumers (households and industry). Chlorotoluenes are used in the production of pesticides and benzylalcohol. Various aromatic chlorine compounds were also used in 1990 in the pesticides and specialty division of Shell. These applications have been or will be halted, according to Shell. They are therefore otherwise disregarded.

The distribution by substance by area of application is shown in Table 37.1.

Table 37.1: Use of chlorobenzenes in 1990 (in tonnes chlorine; in brackets: tonnes substance)

Substance	Total	Pesticides	Pharmaceu-tical	Other ind.	Small-scale use
MCB	323 (1.024)	241 (764)[a]	32 (100)[a]	50 (160)[b]	
1,2 DCB	14 (30)		14 (30)[b]		
1,4 DCB	48 (100)				48 (100)[b]
Total	*385 (1154)* [1]				
1,3 DCB	160 (332)	160 (332)[a]			
1,2,4 TCB and Dichlorotoluene	464 (1.006)	464 (1.006)[a]			
Benzylchloride	1596 (5.700)			1596 (5.700)[a]	
Various Shell	400[2] (1.000)				
Unknown	385[2] (962)				
Total	*3.005 (9.000)*[3]				

[1] To be compared with import-export balance of CBS of 1,200 tonnes o- en p-chlorobenzene

[2] Based on 40 % chlorine

[3] To be compared with import-export balance of CBS of 9.000 tonnes other halogenated aromates

[a] Segment 36: application in production processes

[b] Segment 37: consumption applications

2.2 *Pharmaceutical industry*

1,2 DCB is used in the pharmaceutical industry as a solvent. Table 37.2 shows the consumption according to the chlorobenzenes basic document [Slooff 1991] and the distribution of emissions between environmental media. The ER-I records significantly higher emissions to air for 1988 and 1990 than the basic document [ER-I 1994, Berdowski 1993]. The emissions to air have been adjusted to take this into account: the discrepancy has been deducted from waste. It is impossible to estimate the fate of MCB and the associated chlorine which is converted into product. The company was not included in the EOX/AOX measurement programme conducted by RIZA in mid-1992.

Table 37.2: Use of chlorobenzenes in the pharmaceutical industry in 1990 in consumption applications (tonnes chlorine; in brackets: tonnes substance)

Substance	Quantity	Product	Air	Water	Waste
1,2 DCB	14 (30)		10 (20)	0.25 (0,25)	4.7 (9,75)

2.3 Other industry

MCB is used as a solvent in the production of isocyanates. According to Slooff [1991], the application and emissions in 1987 were divided as shown in the table below. There are no signs that the situation changed essentially after 1987. Around 0.1 tonnes of MCB are included as an impurity in the isocyanate (10-50 mg/kg). The ER-I reports no emissions other than a release of chloride (salt) to water. The company was not registered in WIER but was included in the AOX/EOX measurement programme conducted by RIZA in mid-1992. The quantity of EOX was a number of times, and the quantity of AOX over ten times greater than the quantity of chlorine released in the form of MCB [RIZA 1994b] .

Table 37.3 Use in other industry in 1990 (in tonnes chlorine; in brackets: tonnes substance)

Substance	Quantity	Recycled	Air	Water	Waste
MCB	50 (160)	9 (30)	25 (80)	0.02 (0,05)	16 (50)

2.4 Small-scale consumption

According to the Basic document on chlorobenzenes [Slooff 1991], in 1987 around 327 tonnes of 1,4 DCB were used as deodorant in air fresheners and toilet blocks. Emissions of dichlorobenzenes occur into all environmental media, most of it air. The use of 1,4-DCB as pesticide is banned under the Pesticides Act. Prohibiting the use of the substance in other applications, such as toilet blocks, was considered but no such ban was implemented.

The volume of 1,4-DCB has declined sharply to 100 tonnes in 1989 [Slooff 1989]. It is assumed that the figure for 1989 can also be taken for 1990. The distribution

of emissions is estimated on the basis of the distribution compiled for 1987 [Slooff 1991]. This is shown in table 37.4.

On the basis of measurements, RIZA estimates the release of 1,4 DCB into sewage by households at over 5 tonnes a year in the period 1984-1987 [Teurlinckx 1991]. Since 75% of toilet fresheners are used outside the home (offices, catering, public facilities) this figure corresponds closely with the total for 'Decomposition in sewage plant' and 'Release to water' in Table 37.4. The Basic document states that an advertising campaign for air fresheners could lead to a rise in the volume of 1,4-DCB unless the government steps in.

Table 37.4: Applications of 1,4 DCB in 1990 (in tonnes chlorine; in brackets: tonnes substance).

Quantity	Decomposition in sewage plant	Air	Water	Waste
48 (100)	6.8 (14)	38 (80)	0.5 (1)	2.1 (5)

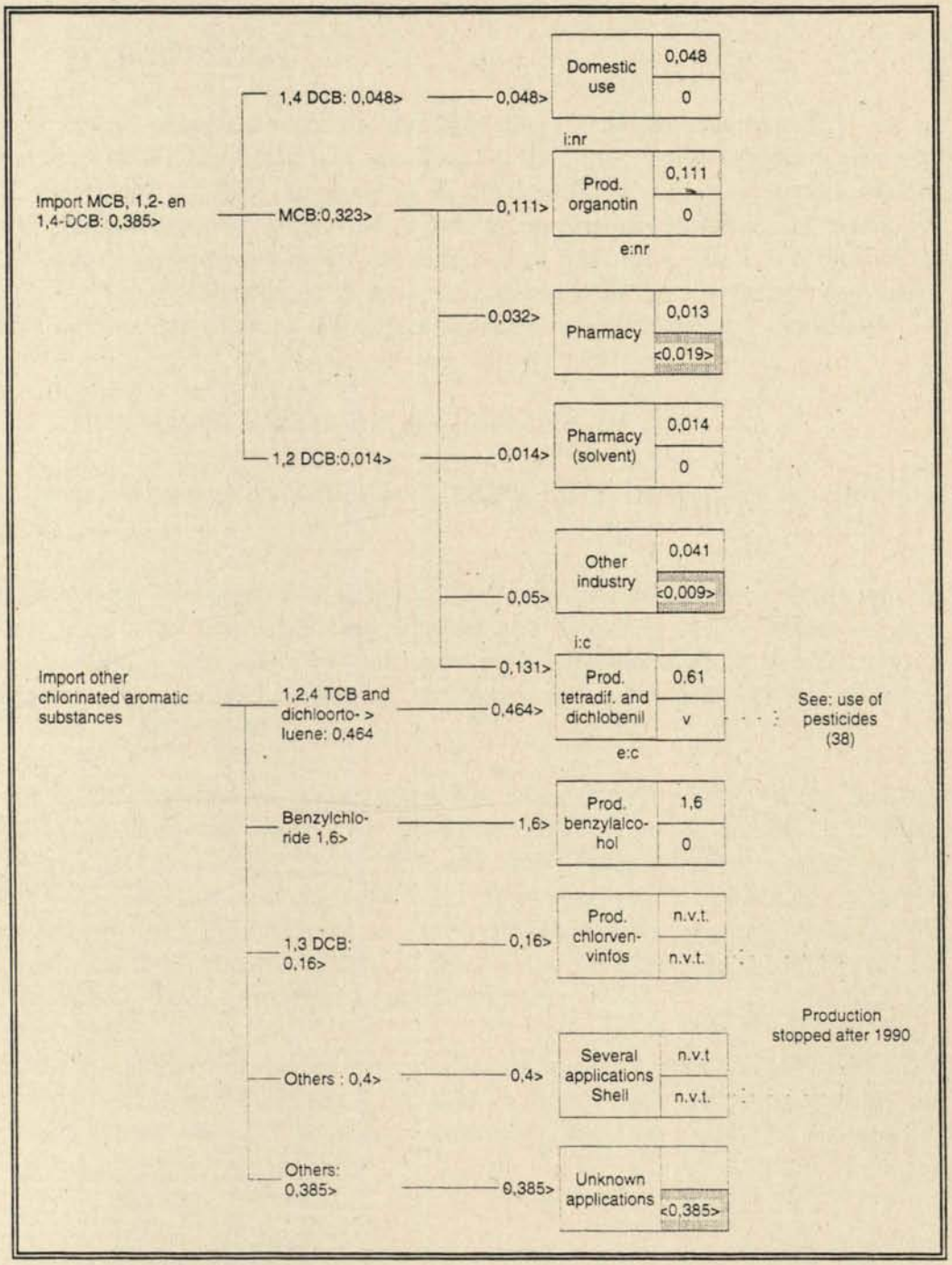
3 EMISSIONS UNDER ENVISAGED POLICY

The emissions from the processes in this segment make no essential contribution to the scores on the environmental themes for the situation in 1990. For simplicity's sake, the emission figures for 1990 have also been taken for the situation arising after implementation of the policy established as of 1 January 1995.

4 COMMENTS AND POINTS FOR DISCUSSION

Figure 37.1 provides a summary of the substance flows in this segment. For the sake of clarity, in the balances the quantities used in the applications during production are also included (Segment 36).

Figure 37.1: Substance flows in production with and consumption of chlorinated aromats (in kt chlorine, 1990)



SEGMENT 38: USE OF AGRICULTURAL AND NON-AGRICULTURAL PESTICIDES

1 INTRODUCTION

Some of the pesticides used in the Netherlands contain chlorine. The use of pesticides in the Netherlands is regulated by the Pesticides Act 1962. Under this act, the Board for the Approval of Pesticides (CTB) which is responsible for enforcing the approval policy for pesticides. In this sense, the use of pesticides represents a 'permitted' leak for the purposes of this study. The use of pesticides has, however, been included in order to contrast it in the assessment with other leaks in the chlorine chain. Pesticides are used in agriculture and elsewhere.

2 PROCESSES AND SUBSTANCE FLOWS IN 1990

All pesticides, except dichloropropene, MCPA and dichlobenil are imported from abroad.

Pesticides are generally classified according to their application: in agriculture or elsewhere. In the latter case, they are used as a biocide in cooling water and as a decontaminant. The use of sodium hypochlorite for this purpose is dealt with in segment 40. The consumption of dichloropropene as a soil decontaminant is included in this segment.

Figures for consumption in agriculture are taken from the ER-C which contains figures based on the Multi-Year Plan for Crop Protection (MJP-GA) [VROM 1991, ER-C 1994]. Wherever possible, the NEFYTO has also been used a source. NEFYTO publishes annual aggregated sales figures for quantities of active substance [NEFYTO 1993]. In so far NEFYTO publishes figures for individual compounds they are used instead of those from the ER-C. Table 38.3 gives the consumption figures in tonnes of active substance.

Figures for sales of pesticides outside agriculture are reported annually to VROM by the VNCI [VROM 1994b]. In view of the duty of confidentiality they are not published here. They are however incorporated in the assessment of emissions.

3 EMISSIONS UNDER ENVISAGED POLICY

The Multi-year Plan for Crop Protection prescribes targets with regard to crop protection in Dutch agriculture and horticulture for the period 1990-2000. The two underlying objectives of the plan are:

- reduction of the structural dependence on the use of chemical agents in crop protection;
- substantial reduction in the use of chemical agents.

The principal task set out in the plan is to translate the main points of the Integrated Policy Document on Agriculture (SNL) into concrete measures. The SNL formulates a quantitative objective with respect to total consumption of chemical pesticides: a reduction of at least 50% by the year 2000. Each sector must draw up plans to achieve - if possible - a reduction of 80% in 1985 levels for the overall use of soil decontaminants by the year 2000.

The Multi-year Plan for Crop Protection proposes a reduction, averaged over all sectors, of around 37.5% in consumption in 1995 compared with 1990, rising to 56% in the year 2000 compared with the annual consumption in the period 1984-1998. Table 38.1 shows the estimated annual consumption during this period.

Table 38.1: Estimated annual consumption of pesticides in the period 1984-1988

Type of agent	Estimated consumption under MJP-G (10^3 kg active substance)
Soil decontaminants	12.910
Insecticides/araricides/fungicides/other	4.309
Herbicides	3.537
Total (rounded off)	21.000

The following targets for reductions in consumption of the various categories of crop protection agents have been calculated (see Table 38.2).

Table 38.2: Reduction percentages for pesticides in the MJP-G

Type of agent	1995	2000
Soil decontaminants	45%	68%
Soil treatment agents	28%	42%
Herbicides	28%	40%
Insecticides, fungicides + other	25%	39%

In this chlorine chain study the figures which form the basis of the Multi-Year Plan for Crop Protection have been used to estimate the situation regarding their use in 1990. The targets prescribed in the Multi-year plan can therefore be applied directly to the figures adopted here for 1990. To calculate the situation after implementation of the envisaged policy, these emissions have been reduced by the percentages shown in Table 38.2.

Table 38.3 shows the effects of the policy formulated in the Multi-year Crop Protection Plan on emissions of pesticides containing chlorine in agriculture. An important assumption in this is that the reductions will be equally divided over the various pesticides. In practice, the rates of reduction will in fact differ for each pesticide.

The Multi-year Plan for non-agricultural Pesticides sets out government policy for non-agricultural pesticides. In a progress report in February 1994 [VROM/DWL 1994a] however, there is no mention of concrete objectives for emission reductions. In this study, therefore, no account has been taken of a possible reduction in emissions after implementation of the envisaged policy.

3 COMMENTS AND POINTS FOR DISCUSSION

In this study, in the assessment of emissions it is assumed that around 1% of the quantity of a pesticide is emitted to water and contributes to the score on aquatic ecotoxicity. The remainder is assumed to be emitted into the soil and to contribute to the score on terrestrial ecotoxicity. This assumption has been derived from the assumptions adopted in the Uniform System of Evaluation of Substances (USES). The number of classification factors for terrestrial ecotoxicity in the LCA method is very limited, so the LCA score on this themes is unsatisfactory.

Assessments made in the context of the approval policy are more specific. Depending on the application, it is assumed that 0.1 - 10% of the dosage of the pesticide is emitted to water via drift. The remainder is assumed to be partly emitted to the soil; the quantity depends on the interception by the crop. The number of toxicity tests relating to the terrestrial ecosystem is currently fairly limited (rain worms, nitrification, mammals). Tests are being developed for other soil organisms (springtails, spiders).

Table 38.3: Emissions of agricultural pesticides in 1990 and after implementation of envisaged policy (quantities in tonnes)

Name	Quantity 1990	Fraction Chlorine	Chlorine 1990	Reduction % 2000	Chlorine 2000
HERBICIDES					
Dichlorophenoxyacetic acid, 2,4-	6,48	0,32	2,07	40	1,24
Chlorotoluron	135,13	0,17	22,97	40	13,78
Linuron	22,00	0,29	6,38	40	3,83
Monolinuron	14,21	0,17	2,42	40	1,45
Chloroprofam	47,00	0,17	7,99	40	4,79
Simazine	105,46	0,18	18,98	40	11,39
Tri-allate	35,00	0,35	12,25	40	7,35
Atrazine	172,00	0,16	27,52	40	16,51
Biphenox	0,88	0,21	0,18	40	0,11
Chlorobromuron	0,51	0,12	0,06	40	0,04
Chloromequat	157,51	0,29	45,68	40	27,41
Cyanazine	35,42	0,15	5,31	40	3,19
Dichlobenil	1,03	0,41	0,42	40	0,25
Diuron	14,93	0,30	4,48	40	2,69
Ethefon	15,38	0,25	3,85	40	2,31
Fluroxypyr	9,75	0,28	2,73	40	1,64
MCPA	249,00	0,18	44,82	40	26,89
Mecoprop-p	275,00	0,13	35,75	40	21,45
Metazachlorine	13,10	0,13	1,70	40	1,02
Metolachlorine	56,50	0,13	7,35	40	4,41
Metoxuron	17,44	0,16	2,79	40	1,67
Propachlorine	71,00	0,17	12,07	40	7,24
Propazine	40,66	0,15	6,10	40	3,66
Propyzamide	4,73	0,28	1,32	40	0,79
Pyridate	16,13	0,09	1,45	40	0,87
Total			276,65		276,65

FUNGICIDES					
Vinchlozolin	109,17	0,25	27,29	39	16,65
Tolclophos-methyl	117,58	0,24	28,22	39	17,21
Tolylfluanide	236,39	0,20	47,28	39	28,84
Tridimephon	0,33	0,12	0,04	39	0,02
Triadimenol	6,76	0,12	0,81	39	0,49
Triforine	2,34	0,49	1,15	39	0,70
Anilazin	202,69	0,39	79,05	39	48,22
Captan	370,00	0,35	129,50	39	79,00
Chlorothalonyl	59,60	0,53	31,59	39	19,27
Dichlofluanide	0,08	0,21	0,02	39	0,01
Etridiazool	15,78	0,43	6,79	39	4,14
Fenarimol	0,52	0,21	0,11	39	0,07
Iprodion	247,77	0,22	54,51	39	33,25
Penconazool	0,72	0,25	0,18	39	0,11
Pencycuron	4,62	0,11	0,51	39	0,31
Prochloraz	65,50	0,28	18,34	39	11,19
Procymidon	8,70	0,25	2,18	39	1,33
Propiconazool	12,13	0,21	2,55	39	1,55
Quintozene	27,12	0,60	16,27	39	9,93
Total			446,37		446,37
INSECTICIDES					
Lindane	19,00	0,73	13,87	39	8,46
Dichlorvos	38,00	0,32	12,16	39	7,42
Trichlorphon	1,60	0,41	0,66	39	0,40
Chlofentezine	6,67	0,23	1,53	39	0,94
Hexythizox	31,91	0,10	3,19	39	1,95
Chlorophenvinphos	10,08	0,30	3,02	39	1,84
Chloorpyriphos	86,10	0,30	25,83	39	15,76
Cypermethrine	0,27	0,17	0,05	39	0,03
Dicophol	3,02	0,48	1,45	39	0,88
Dienochlorine	57,46	0,75	43,10	39	26,29
Diflubezuron	2,01	0,23	0,46	39	0,28
Fenvalerate	1,43	0,08	0,11	39	0,07
Heptenophos	5,74	0,14	0,80	39	0,49
Permethrine	4,63	0,18	0,83	39	0,51
Total			107,07		107,07
SOIL DECONTAMINANTS					
dichloropropene	2700,00	0,33	891,00	68	285,12

SEGMENT 39: APPLICATION OF OTHER IMPORTED ORGANIC CHLORINE COMPOUNDS

1 INTRODUCTION

Besides the organic chlorine compounds covered by the other substance documents, a number of others are imported. These are discussed in this segment.

2 PROCESSES AND SUBSTANCE FLOWS IN 1990

The import figures for chlorine compounds are based on the annual statistics for foreign trade 1990 from the CBS [CBS 1991]. Imports of most of the chlorinated compounds are already discounted in the other substance documents. This substance document deals with imports of those chlorinated compounds registered by the CBS which are not covered by the other substance documents. Imports and exports of inorganic chlorine compounds, such as HCl, PCl_3 and $SOCl_2$ have been ignored because they fall outside the scope of this study; inorganic compounds were generally not followed. Furthermore, the net imports of these substances amount to less than one kilotonne [CBS 1991].

The CBS records imports of the following organic chlorine compounds:

- chloromethane and chloroethane;
- 1,2 chloropropane and chlorobutane;
- chlorophenols;
- acyclical compounds with two of more halogens (excluding CFCs);
- chloroparaffins and polyethyleneglycoles.

None of these substances is produced in the Netherlands. The CBS sometimes aggregates import figures for a number of compounds. The CBS can not break the figures down further for reasons of confidentiality, nor can it name the importing companies [CBS 1994b].

From the ER-I, the LMA and WIER we tried to discover who emitted these substances. We also tried to find out which companies used these substances through telephone conversations with chemical traders. Apart from a consumption of 300 tonnes of chloroethane as propellant and the use of halons, this activities produced no result. Given the limited volume of chlorine involved in this segment no further effort was made to trace the sources.

Table 39.1 provides an insight into the quantities imported and the emissions. The purpose and emissions are only known for chloroethane and the halons. There remains a quantity of 4,213 tonnes of compounds, the purpose of which was not discovered. If it is assumed - pessimistically - that 75% of the compounds are chlorinated compounds, this means that around 3,000 tonnes of chlorine was not traced.

Table 39.1: Other import flows and uses in 1990 (in tonnes substances)

Substance group (CBS category)	Consumption	Air	Other	Unknown
Chloromethane and -ethane	1.675	140[1]	160 accumulation	1.375
1,2 dichloropropane and butanes	1.404		-	1.404
Acyclical compounds with 2 or more different halogens[2]	382	212	170 chlorine-free	-
Chlorophenols	49		-	49
Chloroparaffins and polyethyleneglycoles[3]	1,385		p.m.	1.385- p.m.
Total	4.895	352	330	84.213[4]

1) 300 tonnes of chloroethene used; 140 tonnes to air, 160 tonnes accumulation
2) 212 tonnes Halon-1211 (chlorine-containing) emission to air; 170 tonnes Halon-1301 (chlorine-free)
3) Partly chlorine-free compounds
4) In the case of (a high estimate) a chlorine content of 75%, this in effect means around 3,000 tonnes of chlorine that was not traced.

Chloromethane and chloroethane

In 1990 DOW Benelux used around 300 tonnes of chloroethane as propellant in the production of styrofoam [Dow Benelux 1994, ER-I 1994]. Of this, around 45% was emitted directly during production of the foam; the remainder accumulates in the styrofoam in society [DOW 1994, SPIN 1993c]. The destination of 1,375 tonnes of chloroethane and chloromethane was not discovered. This quantity was allocated to "unknown applications".

Acyclical compounds with 2 or more different halogens
According to the CBS 413 tonnes of acyclical compounds with two of more different halogens are imported. These are probably not (H)CFCs because the CBS records those separately. According to the CFC Commission [1994], 212 tonnes of halon-1211 (CBr_2ClF) and 170 tonnes of halon 1301 (CBr_3F) were used in the Netherlands in 1990. Only halon 1211 contains chlorine. It can be assumed that the entire quantity is emitted to air [VROM 1994]. The volume of chlorine-free halon-1301 falls outside the scope of this chlorine chain study.

3 EMISSIONS UNDER ENVISAGED POLICY

In December 1995 the European Commission issued a new integrated regulation concerning substances which deplete the ozone layer (PbEC 3093/94), which also covered halons. Halons are being phased out under both the new and the old regulations. In the Netherlands no (new) halons may be used since 1 January 1994. The existing stocks may be used up; only halons which are recovered through recycling may still be used. In the medium term these measure will in fact lead to zero emissions of halons; this has therefore been taken as the future situation in this study. We were unable to gain an impression of the quantity of accumulated halons in society which can be used up through recycling. In the absence of statistics, no estimate was made therefore.

The emissions in the other situation referred to in Table 39.1 have been taken over unchanged for the future situation.

4 COMMENTS AND POINTS FOR DISCUSSION

There is no information about most individual substances; they are recorded as a combined group by the CBS. It is therefore impossible to properly convert quantity of substance into quantity of chlorine per substance (group) in Table 39.1. In contrast to the other segments, therefore, no detailed substance flow chart is included here.

SEGMENT 40: PRODUCTION OF HYPOCHLORITE

1 INTRODUCTION

Sodium hypochlorite is produced from chlorine and caustic soda [SPIN 1993b]. Aqueous sodium hypochlorite, better known as chlorine bleaching soda, is used as:

- cleaning agent (domestic, institutional and industrial);
- disinfectant (swimming pool water and drinking water);
- anti-fouling agent (cooling water).

The major Dutch manufacturers are Akzo Nobel and Solvay. General Electric also produces hypochlorite on a small scale. In addition, hypochlorite is imported and exported [CBS 1991]. In a RIVM study on the chlorination of swimming pool water, Chemproha of Zwijndrecht and Molenchemie of Wormerveer were also named as important suppliers besides Akzo Nobel and Solvay [Versteegh 1992].

2 PROCESSES

Under well-defined conditions relating to temperature, pressure and materials, chlorine bleaching soda is produced by dissolving chlorine in caustic soda. Impurities such as heavy metals hasten the decomposition of hypochlorite so rigid demands are made on the purity of the raw materials used. Chlorine-polluted air is produced at various stages of chlorine production. This chlorine is destroyed by caustic soda; it results in a product used internally by the manufacturer [SPIN 1993B; Akzo Nobel 1994]. Normal trade quality hypochlorite contains about 150 g of active chlorine per litre, which represents 13.5 percent of the weight [Versteegh 1992].

3 SUBSTANCE FLOWS AND EMISSIONS IN 1990

Figures from Akzo Nobel, Solvay and GEP show that 14,165 tonnes of hypochlorite (calculated as chlorine) is produced in the Netherlands.

According to the CBS [1991], 15,102 tonnes of hypochlorite was exported in 1990 and 10,928 tonnes imported. The CBS figures refer to the amount of aqueous solution of sodium hypochlorite. It is assumed that this was of normal commercial

quality containing an average of 13.5% of active chlorine. Calculated on the basis of chlorine this means imports of 1,475 tonnes and exports of 2,039 tonnes.

Judging from these figures, an estimated 13,600 tonnes of hypochlorite, expressed as chlorine, is consumed in the country. Figure 40.1 presents a substance flow diagram.

The most important emission during the production of hypochlorite is the quantity of chlorine remaining in the air which is discharged into the atmosphere. Emission figures are taken from the ER, in so far as they are recorded under the process 'production of hypochlorite' [ER -I 1994]. At Akzo Nobel, Solvay and GEP the production of hypochlorite takes place at the same location as several other activities. The emission figures to water from the ER and WIER are combined figures for all these processes. For simplicity's sake, no emissions to water have been allocated to the production of hypochlorite. Table 40.1 presents a summary of emissions. For reasons of confidentiality, the figures are not broken down by individual company.

Table 40.1: Emissions containing chlorine to water and air during the production of hypochlorite in 1990 (kg chlorine; in brackets: kg substance)

Compound	Air	Water
Chlorine	1607	

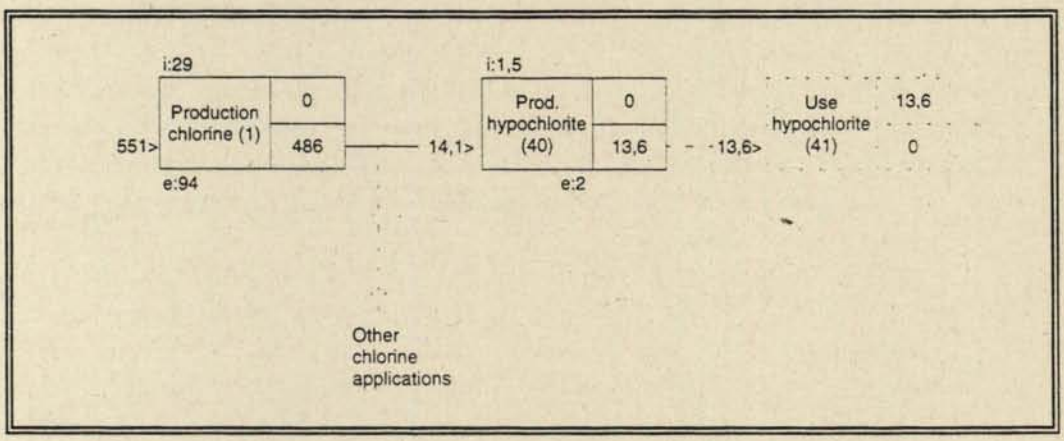
4 EMISSIONS UNDER ENVISAGED POLICY

The emissions from the processes in this segment made no significant contribution to the score on environmental themes for the situation in 1990. For simplicity's sake, the emission figures for 1990 have also been adopted for the assessment of the situation arising after implementation of envisaged policy from 1 January 1995.

5 COMMENTS AND POINTS FOR DISCUSSION

The production of hypochlorite can be seen as an 'extension' of the production of chlorine. The allocation of the residual emission is therefore open to discussion. In this case the emission is attributed to hypochlorite.

Figure 40.1: Substance flows in production of hypochlorite (in kt chlorine, 1990)



SEGMENT 41: CONSUMPTION APPLICATIONS OF HYPOCHLORITE

1 INTRODUCTION

Hypochlorite is used as a disinfectant in households, industry, swimming pools and drinking water supplies [Berends, 1990]. As described in segment 40 an estimated 13,600 tonnes of hypochlorite was used in the Netherlands in 1990. All of the figures here are calculated as chlorine, unless otherwise stated.

2 PROCESSES

2.1 Introduction

Hypochlorite is generally used as a disinfectant. The following reactions occur in water:

$$NaOCl + H_2O \rightleftharpoons HOCl + NaOH$$
$$HOCl \rightleftharpoons OCl^- + H^+$$

and if hydrochloric acid is present:

$$HOCl + HCl \rightleftharpoons Cl_2 + H_2O.$$

The hypochlorite ion, hypochloric acid and chlorine together form the "free available chlorine". The proportions of these compounds depends on the pH, temperature and ion-strength of the solution.

Some of the hypochlorite will decompose during use, depending on the amount and type of substances to be oxidized. In raw effluent, for example, a decomposition of more than 90% occurs within a few minutes [ODWM 1989]. Any chlorine present is hereby largely transformed into chloride. A number of other reactions also occur. With inorganic and organic nitrogen components (mono)chloroamines can be formed. These are gradually broken down. Finally, slow chlorination reactions of organic compounds can take place, during which incorporation of chlorine arises. This in fact results in an 'emission' of organic chlorine compounds. Attention was drawn to this problem when it emerged that chlorinated drinking water could contain chloroform and other haloforms due to reaction with the humic and fulvine acids present in the surface water [ODWM 1989]. It is difficult to quantify the amounts of such by-products. In this study we use estimates from [ODWM 1989] and the Criterion Document on chloroform [Balfoort 1987]. This

literature refers to chloroform as the most important by-product. The assessment is limited to this substance. It was impossible to strive for completeness within the scope of this study. The following sub-sections describe in more detail the consumption and possible emissions for each application. In assessing the emissions we did not consider the quantity of emissions *possibly* occurring and conversion into organic chlorine compounds referred to.

2.2 *Households*

Households used 3,900 tonnes of hypochlorite in 1988. This amount was more than halved at the beginning of the nineties by lowering the concentration of hypochlorite in domestic bleaches. Figures from the Dutch Union of Detergent Producers (NVZ) show that by 1990 consumption was already only 2,000 tonnes of chlorine [NVZ 1994]. The figure fell to 1,200 tonnes by 1993.

Around two-thirds of this volume is used to clean toilets. The remainder is used for general cleaning of floors, tiles, baths and kitchen sink-units. Chlorination of organic substance is particularly likely when water which is 'almost' drinkable reacts with the above-mentioned humus and fulvine acids. Once in the sewer the free chlorine will mainly react with other reductors to become, for example chloroamines. It is estimated that in negative circumstances between 0.1 and 0.2 tonnes of trihalomethanes could be formed [ODWM 1989].

According to a study by the RIZA a diffuse emission of chloroform to water occurs via households. On the basis of measurements during the period 1984 to 1987 an annual load of 2.3 tonnes was calculated in household effluent [Teurlinckx 1991]. This figure must be interpreted cautiously. The emission figures are possibly outdated. It was immediately after the period when the measurements were taken that the amount of chlorine in consumption applications and the consumption of hypochlorite was substantially reduced. Without new measurements and closer research we cannot quantify the size and the sources of emissions of chloroform to water from households.

Following an extensive study, the European trade association FIFE assumes a 1% rate of conversion from NaOCl to AOX [FIFE, 1993]. If 2,000 tonnes of hypochlorite are used by households this would lead to a load of 20 tonnes of AOX annually. The trihalomethanes content in AOX is under 30%; depending on the particular application of hypochlorite, AOX is estimated to contain a fraction of 10-20% of chloroform [FIFE 1993]. This results in an emission of chloroform which, in terms of size, corresponds with the measurements by the RIZA, but is ten times higher than the estimate by ODWM [1989]. According to FIFE, an

estimated 60% of the AOX in a sewage works. The FIFE figures therefore give us 8 tonnes of AOX emitted annually to surface water as a direct result of the hypochlorite used in households. To compare: RIZA estimates the total AOX discharge from households in the Netherlands to sewers at 50 tonnes annually and the emission to surface water from industrial sources at 40 tonnes annually [RIZA 1994b and 1994c]. FIFE computes that, on account of dilution in the sewer, naturally occurring AOX and the AOX already present as pollution in surface water, AOX from household hypochlorite increases the concentration by less than 2% [FIFE 1993].

2.3 Cooling water

In 1988 1,200 tonnes of hypochlorite was used in processing and cooling water (calculated as chlorine) [ODWM, 1989]. In [VROM/DWL 1994a] a figure of 6,000 to 7,000 tonnes is reported for 1992. If this latter figure refers to normal commercial quality hypochlorite in aqueous form (about 135 g/l) then there is a reasonable correspondence between the two sets of statistics. In practice, the use of cooling water is probably higher because some of the active chlorine used in industry is also used to disinfect cooling water. A detailed survey in 1994 produced a figure of around 1,900 tonnes [VROM, 1995]. The hypochlorite is used to prevent the growth of bacteria. This produces around an estimated 0.2 tonnes of chloroform, according to the Chloroform Criterion Document [Balfoort 1987]. There are no known estimates of other by-products. We assume that all chlorine in the remainder is released as chloride.

2.4 Drinking water

Chlorination of drinking water is used to further disinfect drinking water. It is also used, if required, to combat bacterial pollution in the distribution system. The use of chlorine in the drinking water sector has fallen sharply over the past 15 years. In 1976, 2,100 tonnes was used [VROM/DWL 1994a]; in 1988 the amount was estimated at around 900 tonnes [ODWM 1989]. Figures for the beginning of the nineties are somewhat lower [VROM/DWL 1994a]. We have assumed a total consumption of 800 tonnes in 1990.

Dutch tap water contains 0 - 25 ug/l chloroform [VROM/DWL 1994a]. Around 220 million cubic meters of drinking water is supplied each year [ODWM 1989]. This could represent between 0 and 5 tonnes of chloroform. The Criterion document estimated more than 7 tonnes in 1981. The disinfection of drinking

water with hypochlorite was cited as the major cause of chloroform pollution in drinking water [Balfoort 1987].

2.5 *Water in swimming pools*

The use of sodium hypochlorite in swimming pools is compulsory by law. The "Hygiene and safety in swimming pools Decree" (Stb. 1984, 470) governs the level of freely available chlorine in swimming water [VROM/DWL 1994a]. Around 3,700 tonnes of active chlorine was used in 1988 [ODWM 1989]. This should have been reduced by half by the early nineties [VROM/DWL 1994a]. We assume around 2,700 tonnes for 1990. As mentioned earlier, chloroamines and chloroform are produced by the use of hypochlorite. According to the Criterion document, the standard amount used in the mid-eighties produced around 2 - 2.5 tonnes of chloroform as a by-product [Balfoort 1987].

2.6 *Industrial applications and miscellaneous uses*

According to [ODWM 1989] around 4,500 tonnes of hypochlorite was used for industrial applications in 1988. Figures received from two starch manufacturers indicate that more than half of this amount was used as an oxidation agent in the starch industry. RIZA measured high EOX content in the effluent of such companies [RIZA 1994b]. This figure probably includes an amount used to disinfect cooling water: a survey by VROM [1995] gives a figure of 1,900 tonnes of active chlorine in 1994 in cooling water, whereas the figure in sub-section 2.3 is only 1,200 tonnes.

Akzo Nobel does not sell all the hypochlorite it produces, but keeps some for its own use [Akzo Nobel 1994]. Hypochlorite is further used as a disinfectant for effluent, including effluent from communal sewage works. These two items together have been fixed at 2,400 tonnes.

3 SUBSTANCE FLOWS AND EMISSIONS IN 1990

Table 41.1 shows the use of hypochlorite broken down by type of application. The emissions that occur are also given. For simplicity's sake, we have used the figures for 1988 also for 1990 in the case of sewage works, industrial applications and treatment of cooling water.

In principle, almost all chlorine discharged to water is converted into chloride, apart from possible conversions into organohalogens. The estimates of the quantities given in the table are indicative. Figure 41.1 presents a substance flow diagram.

Table 41.1: Applications of hypochlorite in 1990 (in tonnes of chlorine)

Application	Quantity
Households	2,000
Cooling water	1,200
Drinking water	800
Swimming pool water	2,700
Industry *	4,500*
Various	2,400
Total	13,600

* The use in industry probably includes a quantity of cooling water. For 1994 VROM [1995] gives a figure of 1,900 tonnes active chlorine in cooling water.

Table 41.2 gives a list of notifications of organic chlorine formation through the use of hypochlorite. It would take further study to quantify emissions which (possibly) relate to the use of hypochlorite.

Table 41.2: Notification of trihalomethanes in applications of hypochlorite

Application	Notification of formation of trihalomethanes or EOX/AOX
Households	Teurlinckx [1991], FIFE [1993]
Cooling water	Criterion document chloroform [Balfoort 1987]
Drinking water	Criterion document chloroform [Balfoort 1987]
Swimming pool water	Criterion document chloroform [Balfoort 1987]
Industry	EOX/AOX measurement programme RIZA [1994b]

4 SUBSTANCE FLOWS AND EMISSIONS UNDER ENVISAGED POLICY

4.1 Households

Chlorine bleaching soda was officially permitted in 1989 (Regulation on admissibility of sodium hypochlorite, no. 684786, Government Gazette 118) for uses including swimming pools and public meeting places. However, a proviso was added that this permission would be restricted or even withdrawn if alternatives became available. In 1986, around 3,900 tonnes of chlorine was used as an active agent in chlorine bleaching soda. This was reduced to around 2,000 tonnes in 1990. According to estimates by the manufacturers, lowering the concentration led to consumption of 1,200 tonnes in 1993 [NVZ 1994]; it is estimated that the AOX emissions to water would then amount to only 4.8 tonnes.

4.2 Drinking water

In recent decades the use of chlorine to disinfect drinking water fell from 2,100 tonnes in 1976 to 500 - 800 tonnes at the start of the nineties. Chlorine is now mainly used for further disinfecting drinking water prepared from surface water, and is a 'stand-by' for combatting bacterial pollution in the distribution system [VROM/DWL, 1994]. There is no known alternative for these applications. At present there are no plans for a supplementary policy.

4.3 *Water in swimming pools*

Chlorine bleaching soda was officially permitted in 1989 (Regulation on approval of sodium hypochlorite, no. 684786, Government Gazette 118) for uses including swimming pools and public meeting places. However, a proviso was added that this permission would be restricted or even withdrawn if alternatives became available. The "Hygiene and safety in swimming pools Decree" (Stb. 1984, 470) actually makes the use of chlorine in swimming pools compulsory. An estimated 25,000 tonnes of sodium hypochlorite was used in 1988. According to the branch organization VHCP, consumption in 1993 amounted to approximately 1,500 to 1,800 tonnes [VROM, 1995]. However, this amount depends on the outside temperature and the intensity with which the swimming water is used. Policy with regard to using hypochlorite in swimming pools is being formulated in the framework of the Multi-year Plan for non-agricultural Pesticides (MJP-H). Because the MJP-H is still under discussion, we have, for the time being, adopted the figures from 1990 for the future situation.

4.4 *Industry*

Hypochlorite is added to industrial cooling and processing water to combat the growth of micro-organisms. Efforts to curb the use of undesirable pesticides fall within two frameworks. The Pesticides Act 1962 governs their approval, while discharges during local use require a license under the Pollution of Surface Waters Act (Wvo). An attempt will be made to systematically combine both approaches within the framework of the MJP-H.

4.5 *Conclusions*

We expect that household use will decline to 1,200 tonnes of active substance as a result of autonomous developments. The use of chlorine to disinfect drinking water will probably stabilize at the present level. We are not aware of any alternatives for further disinfection or the "stand-by" application in the distribution system. More efficient utilization will result in a decrease in the amount used in swimming pools to an unknown minimum level. Investigations are already underway which should show whether there are alternatives for the use of chlorine in swimming pools and whether the environmental impact of these alternatives is preferable to that of chlorine. Policy with regard to using hypochlorite in swimming pools and cooling water is in preparation within the framework of the Multi-year Plan for non- agricultural Pesticides (MJP-H). Because the MJP-H is still under discussion, we have, for the time being, used the figures for 1990 also

for the future scenario. Developments in industrial use of hypochlorite are still unclear.

As in the 1990 situation, we do not give any quantitative emission figures in this case.

Table 41.3: Applications of hypochlorite as of mid-1995 (in tonnes chlorine)

Application	Quantity
Households	1,200
Cooling water	1,200
Drinking water	800
Swimming pool water	2,700*
Industry	4,500**
Various	2,400
Total	12,800

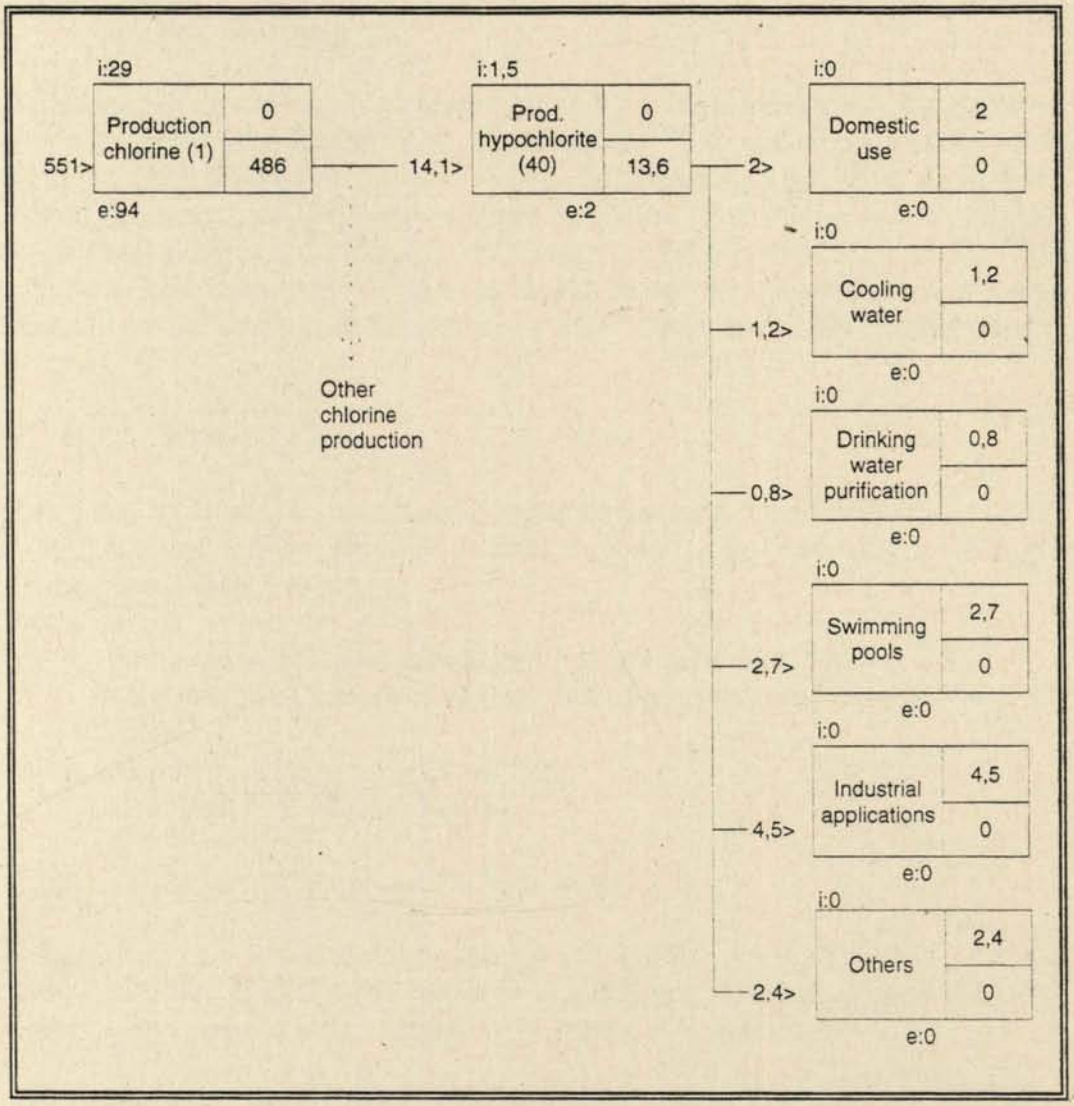
* In practice lower; depends however on outdoor and intensity of use of the swimming pool water

** Including an unknown quantity used in cooling water. According to VROM [1995] the total use in cooling water in 1994 was around 1,900 tonnes active chlorine.

5 COMMENTS AND POINTS FOR DISCUSSION

The above analysis of by-products is of necessity incomplete and very approximate. We have not quantified or assessed the creation of by-products. Further study would be needed to quantify the emissions and effects relating to the use of hypochlorite. If the use of hypochlorite is selected for phase two, we recommend that more attention be given to a comparison with alternatives. A popular argument, particularly in industrial circles, is that the chlorination of drinking water has not actually led to any noticeable effects on health.

Figure 41.1: Substance flows in consumption applications of hypochlorite (in kt chlorine, 1990)



SEGMENT 42: PRODUCTION OF TITANIUMDIOXIDE

1 INTRODUCTION

Titaniumdioxide pigment is manufactured in the Netherlands by Kemira Pigments B.V. (formerly TDF Tiofine B.V.) in Rozenburg. The production capacity totals 45,000 tonnes of titaniumdioxide, which is sold mainly to the paint, plastics and paper industries. In 1990, the company switched from the so-called sulphate production process to the more eco-friendly chloride production process. The principal motivation was to reduce acid and heavy metal discharges to water as directed by the Directorate-General for Public Works and Water Management.

2 PROCESSES

Basic raw materials for the chloride production process are titanium ore, paraffin cokes, chlorine and oxygen. The production process can be roughly divided into four phases [SPIN 1992d]:

- preliminary treatment of titanium ore and calcinated paraffin cokes;
- chlorination of ore/cokes mixture and subsequent purification of the $TiCl_4$ formed;
- oxidation of purified $TiCl_4$ to TiO_2;
- after-treatment of raw pigment.

Figure 42.1 presents this process schematically.

As a preliminary treatment, the supplied ore is dried in a tumble-dryer. $TiCl_4$ is produced in the chlorination reactor by reducing the titanium ore with the aid of chlorine and paraffin cokes according to the following reaction:

(1) $3\ TiO_2 + 4\ C + 6\ Cl_2 \dashrightarrow 3\ TiCl_4 + 2\ CO + 2\ CO_2$

The chlorine is completely used up during its passage through the chlorination bed of the reactor. Ore and cokes are continually added to maintain the correct composition of the reaction mixture. In addition to the reaction products, the mixture which leaves the reactor contains metal chlorides, traces of Cl_2, HCl, COS and particles of ore and cokes. Purification takes place in a cyclone, followed by a condensation column and a final treatment reactor.

The purified $TiCl_4$ is converted to TiO_2 by means of oxygen. Chlorine gas is thereby created according to the following reaction:

(2) $TiCl_4 + O_2 \text{ -----} \blacktriangleright TiO_2 + 2\ Cl_2$

The mixture formed in the oxidation reactor contains TiO_2 in solid form. For this reason, the reaction mixture is brought to a solid form separator where TiO_2 and gasses are separated. The gasses are purified and returned to the chlorination reactor. In principle, there are no emissions to the outside air.

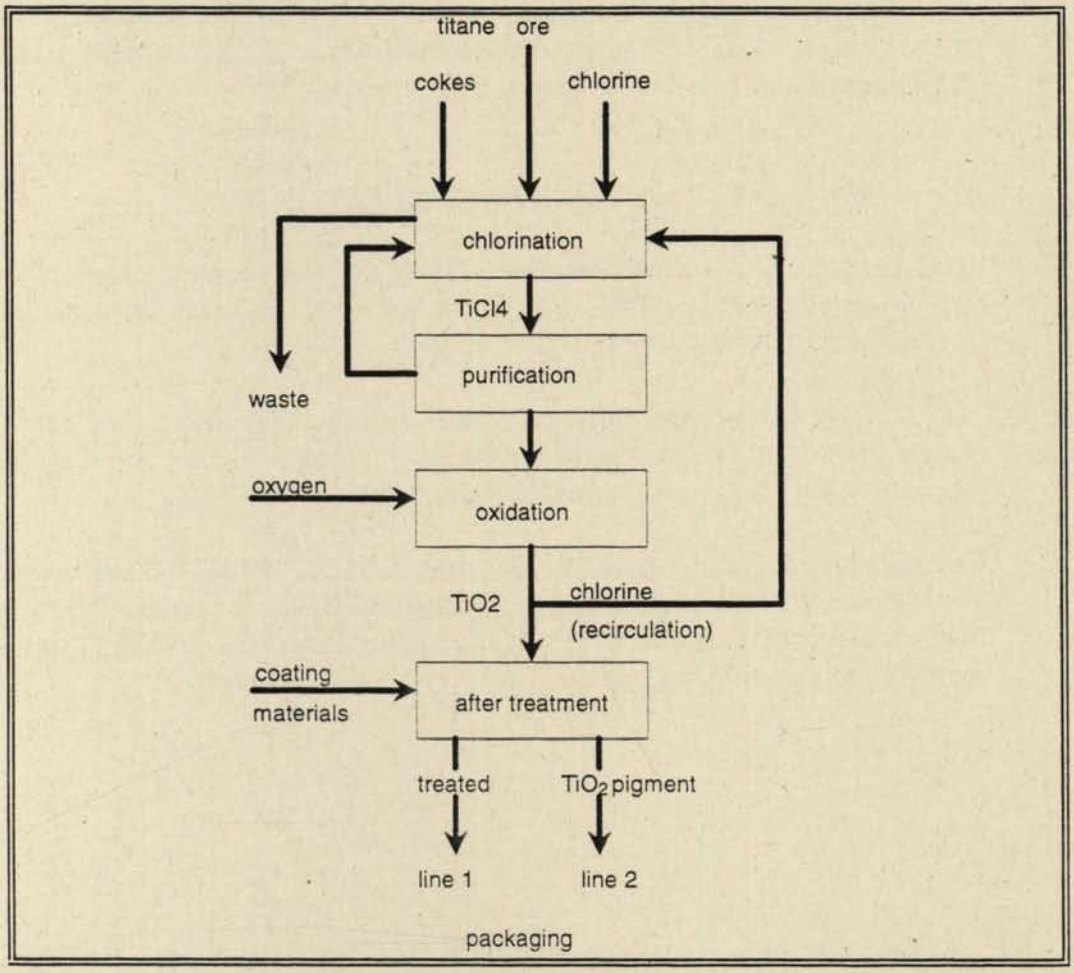
3 SUBSTANCE FLOWS AND EMISSIONS IN 1990

Almost all of the chlorine used is discharged in the form of chloride (salt). The company has supplied a chlorine balance for 1993. Because a new plant had started up in was impossible to give an exact balance for 1990. For this reason, TNO has estimated the actual consumption in 1990 from various data. In 1990, Akzo Nobel used 19,340 tonnes of chlorine in inorganic applications, 6,000 tonnes of which was supplied to third parties. Partly based on figures from [ZMF 1991] this amount is broken down into 2,000 tonnes for titanium dioxide production and 4,000 tonnes for the production of iron and tin chloride (segment 40). The balance for 1990 is estimated on the basis of the relative figures for 1993.

Table 42.1: Estimate of chlorine balance for TiO_2 production in 1990 (in tonnes of chlorine)

Substance	In	Out
Chlorine	2.000	
Chlorides	347	
Chloride (water)		2.200
Chloride (waste)		145
Emissions to air (Cl-)		2
Total	2.347	2.347

Figure 42.1 *Schematic presentation of the production of titanium pigment following the chloride process*



Emissions are taken from the ER-I. As regards compounds containing chlorine, the company is not a priority company for the purposes of the RAP/NAP and is not included in WIER [RIZA 1994a].

4 EMISSIONS UNDER ENVISAGED POLICY

Emissions from processes in this segment made no essential contribution to the scores on environmental themes in the 1990 situation. For simplicity's sake, the emissions for 1990 were also used for the analysis of the situation arising after implementation of envisaged policy as of 1 January 1995.

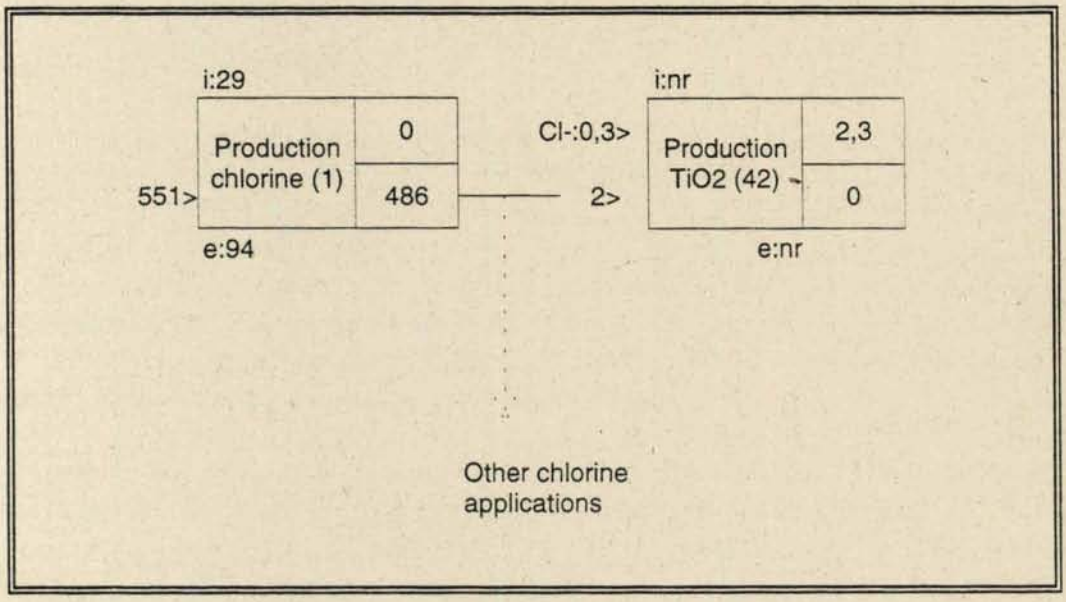
5 COMMENTS AND POINTS FOR DISCUSSION

The company was included in the AOX/EOX measurement programme which RIZA carried out in mid-1992. The amount of AOX was below the detection level; a small amount of EOX was registered [RIZA 1994b].

The chlorine balance and emission figures over the first years are of a provisional nature due to the switch to a new production process. Figures for 1990 therefore do not (so far) convey a representative situation.

Emission figures at the process level from ER-I and WIER cannot be published without the consent of the company concerned. Since in this case the process is only carried out at one company in the Netherlands the emission figures cannot be disguised even by aggregation.

Figure 42.1: Substance flows in production of titaniumdioxide (in kt chlorine, 1990)



SEGMENT 43: PRODUCTION OF OTHER INORGANIC CHLORINE COMPOUNDS

1 INTRODUCTION

A limited amount of chlorine is directly converted into hydrochloric acid by the three chlorine manufacturers in the Netherlands. This does *not* refer to hydrochloric acid which is released as a by-product through the use of chlorine or compounds containing chlorine in a range of processes (see other substance documents), but to specifically produced, chemically pure quality hydrochloric acid. Additionally, chlorine was used for various other inorganic applications, such as the production of iron chloride (Philips) and tin chloride (Billiton Arnhem). In these cases chlorine is also converted into inorganic form (chloride).

In theory, this study did not trace inorganic chlorine compounds. We have only included this segment to close the balance in the segment on chlorine.

2 PROCESSES, SUBSTANCE FLOWS AND EMISSIONS IN 1990

According to reports from the three chlorine manufacturers in the Netherlands, 14,608 tonnes of chlorine was converted directly into hydrochloric acid in 1990. The figure given by Akzo Nobel is an estimate. Akzo Nobel gave a total figure for the amount of chlorine which it used for inorganic applications, indicating at the same time the amount used to make hypochlorite and diverse salts. According to Akzo Nobel, the remainder was used to produce hydrochloric acid [Akzo Nobel 1994a].

About 4,000 tonnes of chlorine was used to make other inorganic compounds. This relates specifically to the production of iron chloride and tin chloride at Philips and Billiton. We assume that all chlorine is converted into a product. Almost negligible amounts are used for other applications such as regeneration of catalytic convertors.

Emissions related to these processes were taken from the ER-I. They are summarised in Table 43.1. For reasons of confidentiality the figures are not broken down by individual company.

Table 43.1: Emissions to water and air during the production of hydrochloric acid, iron chloride and tin chloride in 1990 (kg chlorine; in brackets: kg substance)

Compound	Air	Water
Chlorine	709	
Metal chloride	589[1]	
Total chlorine	1298	

[1] Type of metal chloride not given for reasons of confidentiality

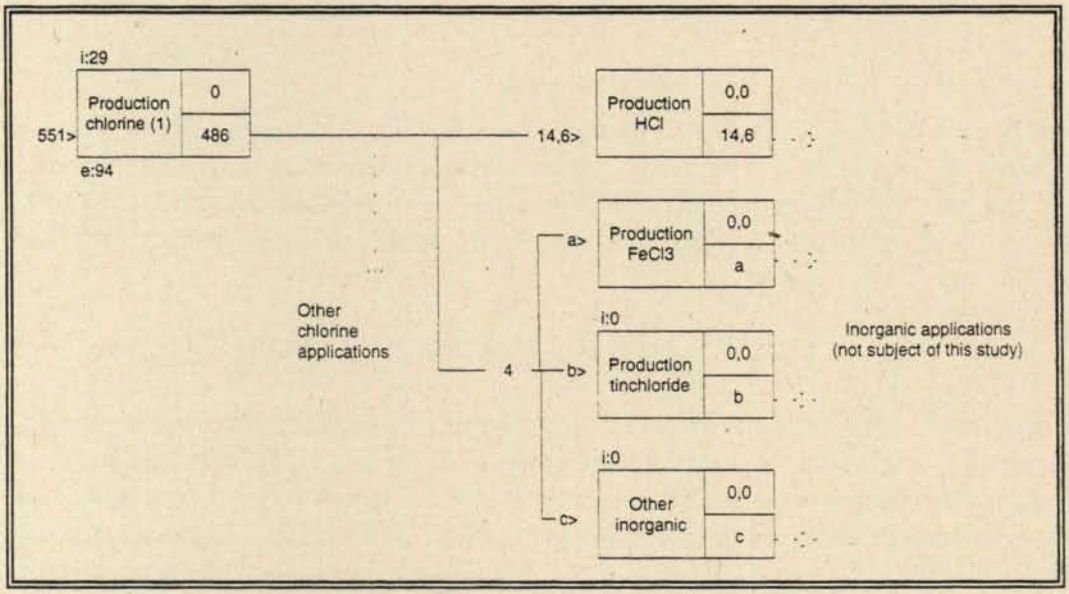
3 EMISSIONS UNDER ENVISAGED POLICY

The emissions from the processes in this segment made no essential contribution to the score on environmental themes in 1990. For simplicity's sake, the emission figures for 1990 are also used for the assessment of the situation arising after implementation of envisaged policy as of 1 January 1995.

4 COMMENTS AND POINTS FOR DISCUSSION

None.

Figure 43.1: Substance flows in production of other inorganic chlorine compounds (in kt chlorine, 1990)



SEGMENT 44: DIFFUSE SOURCES OF DIOXINS, PCBs AND PENTACHLOROPHENOL

1 INTRODUCTION

In so far as the emissions from substances belong to a chain they are treated in the other substance documents. However, some sources of emissions of dioxins (TCDD), pentachlorophenol (PCP) and polychlorobiphenyls (PCBs) can not be linked to a chlorine chain. These are treated separately in this segment.

2 PROCESSES AND SUBSTANCE FLOWS

Investigations by Bremmer et al. and Raad et al. surveyed the sources of emissions of PCBs and dioxins [Bremmer 1994, Raad 1993]. These are summarised in Table 44.1. The dioxin figures refer to 1991. For simplicity's sake, we assumed that they do not essentially differ from those in 1990. A number of these sources are discussed below.

Used up oil
(Used up) oil can contain organically-bound chlorine. These are generally pollutants containing halogenated solvents. The Chemical Substances Act sets out requirements regarding the maximum EOCl (1,000 mg/kg) and PCB (0,5 mg/kg per congener) content per congener. Around 60,000 tonnes of used up oil is disposed of annually [Stap 1993]. If all this oil was polluted to the normal extent it would mean that 60 tonnes of chlorine is discarded with oil annually. Incineration produces dioxins. The emission is estimated in [Bremmer 1994] on the basis of measurements. The possible emissions of PCBs are calculated in [Raad 1993]. In this case it is (pessimistically) assumed that PCBs are always present in oil to just below standard level. We take it that the PCBs are partly destroyed during incineration and partly evaporate (but are not formed). The figure in table 44.1 is calculated on this basis.

Incineration of timber
Timber incineration leads to dioxin formation. The source is the chloride which is present in timber. Similar diffuse, sometimes inorganic, chlorine sources are a factor in asphalt, coal incineration, sintering processes and the metal industry. In none of these cases can the dioxin emission be clearly linked to an organic chlorine source of significant volume.

Historic stock of pentachlorophenol
The timber preserving agent pentachlorophenol (PCP) contains dioxin as a contaminant. It is now banned in the Netherlands and imports of timber contaminated with PCP are virtually non-existent, according to Bremmer [1994]. However, there is an historic stock which emits PCP and dioxins and the half-lives thereof are taken into account when calculating the annual emission of dioxins. PCP evaporates more rapidly than dioxins. Based on figures for PCP consumption in the Netherlands, we can roughly estimate that of the total volume of 1,176 tonnes of PCP consumed in the Netherlands around 400 tonnes was extant in 1990. Based on a half-life of 15 years this results in a diffuse emission of PCP of more than 20 tonnes annually [Bremmer 1994].

On the basis of measurements carried out between 1984 and 1987, RIZA reports a PCP emission to water from households of more than 300 kg [Teurlinckx 1989]. Research into the occurrence of black-listed substances in North Brabant [HWB 1989] suggests that diffuse emissions from companies which discharge into the sewer are in the same order of magnitude. These emissions are possibly due to the historical consumption of PCP. It is also possible that the figure of 300 kg is out of date and, since PCP use is now prohibited, does not reflect the actual situation.

Spillage and leakage from transformers containing PCB
There are still a number of large capacitors and transformers in the Netherlands which contain PCBs. These closed applications in existing situations are permitted until the year 2005. It is estimated that around 60 kg of PCBs are emitted annually due to spillage and leakage during maintenance of transformers [Raad 1993].

Table 44.1: Diffuse emissions of dioxins, PCP and PCBs to air in 1990

Activity	g TEQ TCDD	tonnes PCP	tonnes total PCB
Waste incineration	see segment 46		
Chemical waste incineration	see segment 46		
Incineration of landfill gas e.e.	see segment 46		
Cable incineration	see segment 46		
Incineration of hospital waste	see segment 46		
Asphalt installations	0.3		-
Oil incineration	1.0		0.010
Coal burning	3.7		
Wood burning	12		
Crematoria	0.2		
Various high temperature processes	2.7		
Traffic	see segment 7		0
Sintering processes	26		
Metal industry	4		
Chemical production processes	see other segments		
Emissions from historical stock of wood treated with PCP	25	20	
Spills and leaks from PCB-containing transformers and capacitors			0.060

3 EMISSIONS UNDER ENVISAGED POLICY

Stringent source-specific measures are to be taken before the year 2000 for almost all sources of emission of dioxins. Attempts will be made to inform the public and so prevent individuals from burning wood which has been treated with PCP. It is expected that wood treated with PCP will be the largest source of emissions of dioxin in the year 2000 (20 g TEQ TCDD), followed by incineration of timber (9 g TEQ TCDD). Emissions caused by sintering processes will be reduced to 3 g TEQ TCDD [Bremmer 1994, de Koning 1993].

PCP is still released from the historic stock of PCP-treated timber. The annual emission of PCP is calculated on the basis of half-lives. In the year 2000, the stock of PCP in the Netherlands will still be around 300 tonnes. Based on a half-life of 15 years, this gives a diffuse emission of PCP of 14 tonnes in the year 2000 [Bremmer 1994].

New applications of PCBs will be prohibited in the Netherlands after the year 2005 (PCT, chloroethene, PCB Decree, Chemical Substances Act, Government Gazette 1993, 42). Closed applications must be phased out by 2005 [VROM 1993a]. Limited, diffuse pollution from PCBs can be expected to diminish further in the future.

Table 44.2: Emission of dioxins, PCP and PCBs to air under envisaged policy

Activity	g TEQ TCDD	tonnes PCP	tonnes total PCB
Waste incineration	see segment 46		
Chemical waste incineration	see segment 46		
Incineration of landfill gas e.e.	see segment 46		
Cable incineration	see segment 46		
Incineration of hospital waste	see segment 46		
Asphalt installations	0.3		-
Oil burning	1.0		0.010
Coal burning	3.7		
Wood burning	9		
Crematoria	0.2		
Various high temperature processes	2.7		
Traffic	see segment 7		0
Sintering processes	3		
Metal industry	4		
Chemical production processes	see other segments		
Emissions from historical stock of wood treated with PCP	20	14	
Spillage and leaks from PCB-containing transformers and capacitors			0

It should be noted that incineration plants are subject to stringent requirements with regard to emissions. However, virtually no policy has been formulated for the smaller sources of dioxins, PCPs and PCBs. Table 44.2 presents the emissions in the year 2000 under envisaged policy.

4 COMMENTS AND POINTS FOR DISCUSSION

Waste incineration was the most important source of dioxin emissions in 1990 (see segment 46). In some cases, the sources discussed here bear no relation to the chlorine chemical sector. Incineration of timber is one such example. However, we have nonetheless included such sources in order to make a relative comparison with sources which are linked to the chlorine chemical sector.

SEGMENT 45: TRANSPORT AND STORAGE OR TRANSHIPMENT

1 PROCESSES

The Netherlands is a transhipment centre for a large number of products. Many companies in Rotterdam provide storage or transhipment facilities for bulk chemicals (including those containing chlorine). An unknown quantity of these substances is transhipped. The substances are therefore not included in the CBS import and export statistics and are not actually part of the chlorine chain in the Netherlands. Important storage and transhipment companies include Paktank Botlek, Broere Rotterdam, Panocean Rotterdam, Tank Terminal Rotterdam, DOW Rotterdam and Van Ommeren/Matex Botlek and Europoort.

Means of transport, especially ships, are cleaned by specialized companies. The relevant processors of waste substances from shipping contribute to the emission of EOCl to surface water. Inadequate reporting and illegal discharges are also factors in shipping. Furthermore, it is not easy to link these emissions to product flows. However, these activities do result in significant emissions. Processors of waste products from shipping and tank cleaning companies include AVB/Booy Rotterdam, Tankcleaning Rotterdam/TCR and Tankcleaning Amsterdam TCA.

No meaningful allocation of emissions to processes or consumption applications is possible, largely due to the transhipment of substances. For this reason they are included in a separate segment.

2 SUBSTANCE FLOWS AND EMISSIONS IN 1990

ER-I and WIER report diverse emissions from tank transhipment companies and from processors of waste from shipping. Table 45.1 summarises the emissions. For reasons of confidentiality, the figures are not allocated to individual companies.

Table 45.1: Emissions containing chlorine from storage and transhipment companies and cleaning companies in 1990 (kg chlorine; in brackets: kg substance)

Compound	Air	Water
1,2 EDC	21,519	1,732
Tetra	5,420	19
HHCs, not further known	12,843	
Chloroform	12,039	29
Monochlorobenzene	58	
PER	932	885
DCM	36,713	
CFC 12	1,152	
1,2 dichloropropane	2,010	
1,3 dichloropropene	4,407	
CFK 113	2,337	
1,1,1-trichloroethane	6,889	248
Trichloroethylene	4,916	270
ECH	115	
EOCl		11,247
Total chlorine	111,350	11,247[1]

1) EOCl overlaps (to a large extent) with individual compounds

3 EMISSIONS UNDER ENVISAGED POLICY

3.1 Introduction

On 1 November 1989 a covenant was concluded between the Ministry of VROM, the provinces of North and South Holland and the Association of Tank Storage and Transhipment Companies (VOTOB) which set targets for the reduction of emissions of volatile organic substances in general and of black-listed substances in particular (Hydrocarbons 2000 Project). In the covenant it was agreed that VOS

emissions which are not included in the black list should be reduced by 50% from 1985 levels. This reduction was to be achieved by 1994. A reduction of 70% by the year 2000 was agreed. As regards black-listed substances, the agreed reductions for 1994 and 2000 were 70% and 90% respectively. For the companies concerned, the covenant replaces implementation of the Hydrocarbons 2000 Project. During an evaluation of the covenant in 1994 it was established that the reduction targets had largely been met.

In addition to the independent tank storage and transhipment companies there are also dependent companies which are, however, relatively small. The licensing system imposes approximately the same reduction targets on these firms as apply to the VOTOB companies.

3.2 Measures

The measures range from the use of effective seals to various measures concerning emissions from fixed-roof tanks and loading emissions. These measures are implemented on the basis of rules laid down in the relevant permits for the companies concerned, which are in turn based on agreements in the covenant. The nature of the measures is in line with the approach taken to storage and transhipment in the chemical sector and the petrol distribution chain. Until now, the reduction has been achieved by installing internal floating covers and vapour processing units.

3.3 Conclusions

3.3.1 Emissions to air

Compared with the 1985 level emissions in 1994 were reduced by 70% and 50% for black-listed and non-black-listed substances respectively. By the year 2000 emissions can be expected to be 90% and 70% lower for these groups of substances. We have used statistics from the ER and the WIER to establish the 1990 situation. Emissions are specified for individual substances in these records. However, it emerged from the "emission reduction" plan drawn up by the VOTOB that emissions from individual substances may differ greatly from year to year because, depending on the market, the 'throughput' of a company by volume and type is totally unpredictable. This market dependency means that it is impossible to estimate emissions of individual substances. We have therefore approached the situation with regard to envisaged policy by applying the general reduction percentages to all substances emitted in 1990. In talks with VOTOB it also

emerged that no figures were available for the emission situation in 1990. In the first year of the covenant (1985) the emissions amounted to 7,591 tonnes of hydrocarbons, according to the VOTOB "Emission Reduction Plan". According to the same plan, emissions in 1988 totalled 7,049 tonnes. If we assume a linear reduction in emissions to the target for 1994, then the total emission of hydrocarbons in 1990 would amount to 5,964 tonnes. The remaining emission in the year 2000 should, according to the plan, amount to 70% of the original 7,591, which brings this to 2,277 tonnes. A further reduction of 62% compared with the estimated level in 1990 is therefore required to reach the objective by the year 2000. No individual data are available for black-listed substances. We assume that a reduction of 80% on the 1990 emission is needed for these substances.

3.3.2 Emissions to water

We found no supplementary policy on emissions to water. We therefore presumed that the emissions in the year 2000 would be the same as the 1990 emissions.

4 COMMENTS AND POINTS FOR DISCUSSION

It is generally supposed that waste from shipping is frequently disposed of and discharged illegally. According to the [Regioplan/VROM 1992] and [Tukker 1993a] between 30 and 60% of the bilge water from vessels on the inland waterways was discharged without being treated. It is virtually impossible to provide estimates for other effluent and washing water. The concentrations of possible chlorinated compounds this water contains are also an unknown factor. We can therefore give no estimate of the amount of waste containing chlorine which is discharged to water in this way. We cannot rule out the possibility that this forms a significant leak of compounds containing chlorine. In a supplement to the Multi-year Plan for hazardous waste, VROM and the provinces have formulated policy designed to improve procedures for disposing of waste [VROM 1994e].

Table 45.2: Emissions containing chlorine at storage and transhipment companies and cleaning companies under envisaged policy (kg chlorine; in brackets: kg substance)

Compound	Air	Water
1,2 EDC	4,304	1,732
Tetra	2,060	19
HHCs, not further known	4,880	
Chloroform	4,575	29
Monochlorobenzene	22	
PER	354	885
DCM	13,951	
CFK 12	438	
1,2 dichloropropane	764	
1,3 dichloropropene	1,675	
CFK 113	888	
1,1,1-trichloroethane	2,618	248
Trichloroethylene	1,868	270
ECH	23	
EOCl		11,247
Total chlorine	38,419	11,247[1]

1) EOCl overlaps (to a large extent) with individual compounds

SEGMENT 46: FINAL PROCESSING OF WASTE

1 INTRODUCTION

Several waste flows follow from the preceding segments. These can be disposed of in different ways:
- incinerated as hazardous waste;
- disposed of in landfill sites as hazardous waste;
- incinerated as household and equivalent waste;
- disposed of in landfills.

Recycling produces materials that can be used again and has therefore already been covered (where relevant) in the segments dealing with the production of various substances. This segment only deals with the final processing.

2 PROCESSES AND SUBSTANCE FLOWS

2.1 Hazardous waste

2.1.1 Volume of hazardous waste

Table 46.1 summarises the waste substances which contain chlorine already referred to in the previous documents. It refers to waste substances which have been processed externally: internal processing has been dealt with under production. According to statistics from the National Notification Centre for Waste Substances (LMA), 28,393 tonnes of waste containing halogenated hydrocarbons (HHC-waste) was processed in 1990 [LMA 1994, Stap 1994]. These figures refer not only to waste which contains chlorine but also to waste containing bromine and iodine.

Chlorine or compounds containing chlorine represent only a small percentage of the total weight of the waste containing chlorine which is reported to the LMA. Waste from pesticides consists mainly of rinsing water from formulation companies with a chlorine content of about 1% [van der Steen 1991]. Most sludge and waste flows containing oil, which are reported as waste containing HHCs, have for various reasons been contaminated with (low concentrations) of HHCs.

Table 46.1: Disposal of HHC in 1990 according to the LMA and relation to segments in this study. Amounts in tonnes.

Waste notified to LMA by substance code or company	Quantity of waste according to LMA	Percentage chlorine [v.d. Steen 1991]	Quantity chlorine (substance)	Waste from segment	Method of disposal[2]
Waste containing bromine	1,270	-	n.v.t.		Incineration AVR
Pesticide waste	1,400	<3 %	p.m.		Incineration AVR
Other sludge	1,200	< 5 % ?	p.m.		Incineration AVR
Oil-containing waste	1,400	< 5 % ?	p.m.		Incineration AVR
Deposited by Shell	9,253		2,600[1]	AC-production [8]	Incineration Akzo Nobel Export raw material
Akzo Nobel PER/Tet plant	627	ca. 30 %	230	HHC-production [17]	Export and landfill[3]
PER-sludge	1,000	ca. 30 %	200 (Dist.) 138 (Incin.)	PER [29]	Distillation, partly abroad and incineration AVR
Solvents etc., of which - HCFC-22 - CFC-11 - tetra - DCM - 1,1,1 tri - Tri - CFC 113	11,168	ca. 30 %	3,081 of which 9 (21) 2 (3) 363 (394) 2,252 (2698) 343 (430) 47 (58.3) 65 (114)	Use of HCHs segment 20-37	Incineration AVR Around 300 tonnes chlorine distillation, partly abroad
Waste from chlorinated aromates	1,075		205	Segment 37	Incineration AVR
Total	28,393				

[1] Figure for 1993 (see substance document ECH). For 1993 it is assumed that it was only given to Akzo

[2] Processing/incineration abroad disregarded in relation to incineration at AVR. On this assumption it follows from table 46.1 that around 3,400 tonnes chlorine is submitted to AVR as waste containing HHCs.

[3] No longer released since 1990.

Table 46.1 presents a comparison for each flow of the amount which is reported as *waste* to the LMA and the amount of *chlorine* that should be involved according to the figures in the segments in this study. Apart from the above-mentioned sludge, flows containing oil and waste from pesticides, this comparison shows that the chlorine content of most waste flows amounts to a weight percentage of around 30%. This figure, calculated on the basis of statistics collected in the framework of this study, accords with generally accepted figures for the chlorine content in waste containing HHCs [Verhage 1991, v.d.Steen 1991].

Around 6,000 tonnes of waste containing HHCs is processed abroad (N.B. this refers to amounts in tonnes of waste, not in tonnes of chlorine). More than 1,000 tonnes of this is distilled (particularly PER sludge); almost 1,000 tonnes is disposed of in landfills (particularly waste from PER/tetra production); more than 2,000 tonnes is used as a raw material (particularly waste from ECH production); and around 1,000 tonnes is used as a substitute fuel in cement ovens (especially sludge and waste containing oil). According to the LMA, about 22,000 tonnes is processed in the Netherlands by means of distillation (900 tonnes), incineration at Akzo Nobel (8,700 tonnes) and incineration at AVR (13,000 tonnes) [Stap 1994, Tukker 1993b]. Emissions from Akzo Nobel were already included in segment 2. Distillation is covered in segment 17. Emissions from waste treatment processes abroad fall outside the scope of this study (as are emissions relating to foreign *production* processes of imported substances). This is the consequence of choosing to examine only the Netherlands' chlorine chain. Below we describe emissions during processing in the Netherlands.

2.1.2 Incineration as hazardous waste

Table 46.1 presents the assumptions regarding the actual disposal of waste containing chlorine adopted throughout this study. We assumed that flows for incineration with a low chlorine content especially were exported because the acceptance procedures for cement ovens permit relatively little chlorine. Partly on the basis of LMA figures, we assumed that waste from chlorine aromates, solvents and (some) PER sludge was incinerated at AVR: 3,400 tonnes of chlorine, according to table 46.1. Incineration at AVR results in the conversion of chlorine to chloride. It is emitted to air in the form of HCl and to water along with the effluent from the flue gas treatment. More is landfilled with fly ash and silt. The exact proportions are not known. Another unknown factor is the proportion of chlorine in HHCs and chlorine in other waste incinerated at AVR-Chemie. It is assumed that the latter category is minimal. HCl emissions to air are taken from the ER-I [1994]. Emissions of chloride to water, fly ash and silt are calculated as balancing items.

Dioxins are produced during the incineration of hazardous waste. According to ER-I, the emission to air in 1990 amounted to around 27 g TEQ TCDD [ER-I 1994]. Emissions to water in 1991 are given by Bremmer [1994]. For simplicity's sake, we have accepted this figure for 1990. Due to the modification of the flue gas treatment to the provisions of the Order in Council on "Emissions from waste incineration plants", annual emissions will fall to 0.2 TEQ [Bremmer 1994]. Emissions of PCBs were ruled out by Raad [1993]. Table 46.2 summarises emissions of chlorine and dioxins as a result of chemical waste incineration.

Table 46.2: Destination of chlorine and emissions during incineration of hazardous waste in 1990

	Chloride	TCDD
Emission to air [1]	20 tonnes [2]	27 g
Emission to water and waste	3,380 tonnes [3]	0.8 g (water) [4] Unknown (waste)
Total	3,400 tonnes	

[1] On basis of ER-I [1994]
[2] As HCl, figures in tonnes chlorine
[3] Balancing item; figures in tonnes chlorine
[4] Figure for 1991

2.1.3 Landfill of hazardous waste

In 1990 around a hundred tonnes of waste containing HHCs was still being disposed of in landfill sites in foreign salt mines. The closure of the PER/TET factory by Akzo Nobel means that this waste is no longer released. This landfill did not cause any emissions in the Netherlands.

2.2 *Domestic and industrial waste*

2.2.1 Incineration of domestic and industrial waste in waste incineration plants (MSWIs)

In 1990 the following waste incineration plants (MSWIs) were in use in the Netherlands: AVR Rotterdam, AVI Amsterdam, GEVUDO Dordrecht, ROTEB Rotterdam, ARN Nijmegen, AVIRA Duiven and Gevulei Leiden.

PVC is the most important form of waste containing chlorine incinerated as domestic and industrial waste. According to substance document 5, the amount involved is around 17,700 tonnes of PVC annually. Taking additives into account, this represents around 8,900 tonnes of chlorine.

In addition to PVC, there are other sources of chlorine in domestic and industrial waste. According to [Nagelhout 1989], PVC accounts for 50% of the total amount of chlorine in household waste. Higher amounts are sometimes mentioned [SNM

1994]. We have stuck to the figure of 50%. We assume a total volume of 17,700 tonnes of chlorine, 8,900 tonnes of which comes from PVC.

According to [Raad 1993] 1.5 million fluorescent light fittings are discarded in the Netherlands each year. Old capacitors may still contain PCBs. This involves an estimated 7.5 tonnes of PCBs, only 2 to 3 tonnes of which are collected separately. The remaining 4 to 5 tonnes are incinerated or landfilled either as bulk household waste or as waste from construction or demolition projects.

Waste incineration produces fly ash and silt. Furthermore, in 1990 a number of Municipal Solid Waste Incinerators (MSWIs) had a wet gas washer. Treatment of the washing water resulted in effluent and flue gas treatment residue (rgr). In these flows, chlorine leaves the process almost entirely as chloride. By-products, such as dioxins, are also created. Raad [1993] gives an estimate of the emission of PCBs.

Table 46.3 summarises the substance flows and dioxin formation for the reference year 1990. For 1990 [Bremmer 1994] records the quantities of fly ash, silt and flue gas treatment residue produced. Based on the relation between the amount of waste incinerated in MSWIs in 1991 and 1990 [AOO, 1992; Bremmer, 1994], these figures are back-calculated to the reference year of the present study. The Information Document on Residual Substances in Waste Incineration Plants provides an insight into the chlorine content of the various residual substances. Along with the ER-I figures on discharges to water and air a chlorine balance was drawn up.

The balance is not entirely closed. The reasons could be:

- an inaccurate estimate of the amount of PVC waste;
- an inaccurate estimate of the proportions of PVC waste landfilled and incinerated;
- an excessive estimate of the amount of chlorine from sources other than PVC;
- an incomplete record of chloride emissions to water and air.

The discrepancy is 2,430 tonnes of (inorganic) chlorine. It is given as inorganic chlorine which did not have to be traced within the framework of this study.

The emission of hydrochloric acid can be allocated for 50% to PVC. The allocation of the emissions of dioxins poses more problems. Large amounts of chloride are present in an MSWI. A reduction in the amount of chlorine (from PVC or other inorganic salt sources in waste) has a relatively insignificant effect on dioxin formation [Smit et al., 1994]. One can therefore argue on the one hand

that the reduction of the amount of PVC is of no account and the dioxin formation in MSWIs may therefore not be attributed to PVC; on the other hand, we could use the same reasoning for the other inorganic salt sources. There are no reasons to support either a complete allocation of dioxins to PVC or a complete allocation of dioxins to other sources of chloride. In this study, the emission assessment has incorporated the entire dioxin emission from MSWIs as the worst-case scenario.

No emissions of chlorinated micropollutants other than PCBs and dioxins were included. The Environmental Impact Assessment (EIA) of the Ten-Year Programme for Waste Substances (TJP.A) also refers to an emission called 'HCB', which is translated as 'hexachlorobiphenyl' and is supposed to make a significant contribution to the score on human toxicity [AOO, 1995]. HCB generally stands for hexachlorobenzene, but this substance is listed separately in the EIA TJP. Furthermore, it is strange that the EIA also gives a total PCB content which is *lower* than the emission of hexachlorobiphenyl, one of the 209 PCB congeners. Given this conflicting information we decided not to use the figure from the Coordination Council for Waste (AOO). See sub-section four for the other substances from the EIA TJP.A.

Around 35% of MSWI fly ash was recycled in 1990, mainly as a filler for asphalt. In the same year between approximately 70-80% of AVI silt was recycled, mainly for applications in road construction. The remaining sludge and fly ash was landfilled [Tukker 1993b]

Table 46.3 Chlorine allocation and emissions from MSWIs in 1990

Emission via	Quantity(ton)	Concentration chloride[2]	Emission Cl^- (tonnes)	TEQ TCDD [Bremmer 1994]	PCB [Raad 1993]
Flue gas			6,355 [1]	510 g[1]	8 kg
Fly ash	88,700	43.7 g/kg	3,876	1,087 g	n.b.
Slag	522,000	3 g/kg	1,566	9 g	n.b.
Flue gas treatment - residue	1,000	< 10 g/kg	< 10	11 g	n.b.
Water			3,473 [1]	0.0003 g	
Discrepancies/in-accuracies			2,430		
Total			17,700		

[1] Emission according to ER-I in 1990. Emission to air occurs as HCl, emission to water as chloride (salt); figures are expressed in tonnes chlorine.

[2] See RIVM [1993]

2.2.2 Incineration of industrial waste in installations other than MSWIs

In 1990, some of the waste from hospitals was still burnt in the hospitals' own ovens. These have since been closed due to dioxin formation. According to Bremmer [1994], 2.1g TEQ-TCDD was released in this way in 1991.

Cables were also incinerated in 1990. According to [Bremmer 1994] the dioxin emission in 1991 amounted to 1.5 g TEQ. The percentage of the cables that had a PVC coating is not known. This form of waste disposal has also since been halted.

2.2.3 Landfill of domestic and industrial waste

The largest amount of chlorine in the waste phase is disposed of in landfill sites as PVC. According to segment 5, about 68,000 tonnes of PVC was landfilled in 1990, representing 34,100 tonnes of chlorine. In addition, some very small waste flows from production processes are landfilled as industrial waste. The amount involved is around 200 tons of depolymerized waste from the production of PVC (segment 3) and VC-copolymers (segment 4).

Other waste flows which may contain chlorine, particularly CFCs, are foams and refrigerators. These are also mainly landfilled and cause emissions. These emissions have already been accounted for in segments 22-35 (applications of the various CFCs).

Emissions to the environment occur due to leakage during the dumping and discharging of percolate, even after purification. The AOO assumes an emission of 0.017 mg EOCl to water and 0.0033 mg EOCl to the soil for each tonne of waste dumped at an IBC landfill site.
Judging by the amount of material landfilled in 1990 this would amount to an emission of a few hundred kilo's of EOCl to water and more than 100 kilo's to the soil. These figures have no bearing on the actual emissions in 1990 as most of the landfill sites were not then under the control of the IBC.

According to [Raad 1993], around 5,000 kilo's of PCBs is dumped. This amount is presumed to come mainly from the capacitors containing PCB which still exist and which are not collected separately. We assume that these are mainly disposed of with bulk household waste and construction and demolition waste. Incineration of landfill gas leads to the formation of a maximum of 0,3 g TEQ TCDD each year [Bremmer 1994].

There are no statistics for other compounds containing chlorine [AOO 1994].

For this study we did not trace the actual situation in 1990 with regard to emissions from Dutch landfill sites (many of which were not yet supervised by the IBC). Allocation of these emissions to landfill is also complex within the scope of this study, partly due to the fact that most originates from historical 'stocks'. We have therefore otherwise disregarded emissions related to landfill.

3 EMISSIONS UNDER ENVISAGED POLICY

3.1 Incineration of hazardous waste

When all the envisaged measures are implemented (including the Order in Council on Emission Requirements for Waste Incineration Plants) the emissions of dioxins to air from the incineration of chemical waste at the AVR will decline from 27 g I-TEQ/year in 1990 to 0.2 g I-TEQ/year [Bremmer, 1994]. No reduction targets are known for the emission of dioxins to surface water.

Table 46.4: Chlorine allocation and emissions from incineration of hazardous waste under envisaged policy

	Chloride	TCDD
Emission to air [1]	<< 20 tonnes [1]	0.2 g
Emission to water and waste	p.m. [2]	0.8 g (water) [3] Unknown (waste)
Total	3,400 ton	

[1] As HCl, figures in tonnes chlorine

[2] Unknown balancing item

[3] Figure for 1991

3.2 Incineration of domestic and industrial waste

When all the envisaged measures are implemented, the emissions of dioxins to air from the incineration of domestic and industrial waste at MSWIs will fall to between 2.5 and 4 gram TEQ/year in 2000 [Bremmer, 1994]. This plan assumes that in theory no domestic or comparable industrial waste will be disposed of in landfills in future. No reduction targets are known for the emission of dioxins to surface water. The estimate for the emissions of PCB in 1990 [Raad et al., 1993] already takes account of the effectiveness of the flue gas treatment installations. The extent to which future measures will further reduce PCB emissions is not

known. Furthermore, the emission of HCl will be reduced from more than 6,500 tonnes in 1990 to 166 tonnes under envisaged policy [AOO, 1995]. The future emission figures for dioxins and HCl take into account the planned expansion of the incineration capacity in accordance with the AOO's Ten Year Programme for Waste Substances [AOO, 1993]

In practice, the shift from landfill to incineration means that a significant share of the volume of PVC, which was still landfilled in 1990 according to segment 5, will be incinerated in future. Although the HCl (and dioxin) emissions will decline substantially, the throughflow of chlorine at MSWIs will increase significantly unless there is a supplementary policy. This is only possible if more chlorine in the form of chloride is discharged to water or is disposed of with fly ash, slags or flue gas treatment residue.

As indicated in segment 5, it is very difficult to predict exactly how much PVC will be supplied for final processing, such as landfill and waste incineration, in the future, and therefore what the future throughflow of chlorine at MSWIs will be. On the one hand, the extra release of accumulated long-cycle PVC will produce more to be disposed of; on the other hand, the recycling policy which is already being implemented could result in a reduction.

Table 46.5 Chlorine allocation and emissions from MSWIs after envisaged policy

Emission via	Quantity (tonnes)	Concentration chloride[2]	Emission Cl^-	TEQ TCDD [Bremmer 1994]	PCB [Raad 1993]
Flue gas			166 [1]	2.5 - 4 g [1]	8 kg
Fly ash	pm	pm	pm	pm	n.a
Slag	pm	pm	pm	pm	n.a.
Flue gas treatment residue	pm	pm	pm	pm	n.a.
Water			pm	0.0003 g	
Discrepancies/inaccuracies			pm		
Total			pm		

[1] Emission to air occurs as HCl, emission to water as chloride (salt); figures are expressed in tonnes chlorine

Part I of the study has already shown that PVC consumption is a priority because of the (existing) amount to be landfilled. We have therefore given no estimate of the amount of PVC entering the waste phase in the future, because this is not relevant to priority setting. The volume of PVC in the waste phase, and the quantity of chlorine which will be dumped in future with fly ash, silt and flue gas treatment residue, have, for simplicity's sake, therefore been equated with the amounts for 1990.

The HCl which was still emitted to air in 1990 will mainly be captured by flue gas treatment in the future, and then partly discharged as chloride but partly landfilled with flue gas treatment residue, which probably means that we have underestimated the future amount disposed of in landfill sites as chloride.

3.3 Incineration of industrial waste in installations other than MSWIs

The incineration of waste in hospitals' own ovens and the (legal) burning of cables has since been halted.

4 COMMENTS AND POINTS FOR DISCUSSION

Figure 46.1 gives an outline of the substance flows of chlorine compounds in the waste phase. The silts and fly ash from MSWIs are polluted with large amounts of dioxins (about 1 kilogram TEQ). No policy has been formulated for this. The silts and fly ashes are presently landfilled or recycled under controlled conditions. No reliable estimate could be made as to how these dioxins eventually end up in the environment. We therefore could not include them as emissions in this study and they do not contribute to the scores. However, the quantity of dioxins is similar to the amount which was emitted to the air in 1989. We strongly recommend looking for greater certainty about the environmental risks related to these dioxins.

The EIA TJP.A was recently finalised [AOO, 1995]. This refers to emissions of some chlorinated micropollutants at MSWIs other than the dioxins and PCBs already dealt with. We had no time to include them in the overall calculation. In future, MSWIs will, according to the AOO emission factors, emit around 3.8 kg chlorophenols, 700 gram PCP, 23 tonnes T-chl-ethene (which presumably means PER), 4 tonnes Tri-chl-eth (presumably tri) and 1,3 kg HCB (calculated as chlorine; see comment on so-called 'hexachlorobiphenyl' on page 262). Expressed in kilo's, only the emissions of HCB and chlorophenols are significant in relation to the emissions of these substances from other inventoried sources (total 0.14 kg HCB and 0 kg chlorophenols). Their relative LCA-score on human toxicity is negligible at MSWIs because of the low emissions in kilo's. Discounting T-chl-ethene and Tri-chl-eth. could well lead to an underestimation; if they actually refer to PER and tri then it would involve 10 to 15% of the future scores from MSWIs.

Figure 46.1: Substance flows in waste treatment of chlorinated substances (in kt chlorine, 1990)