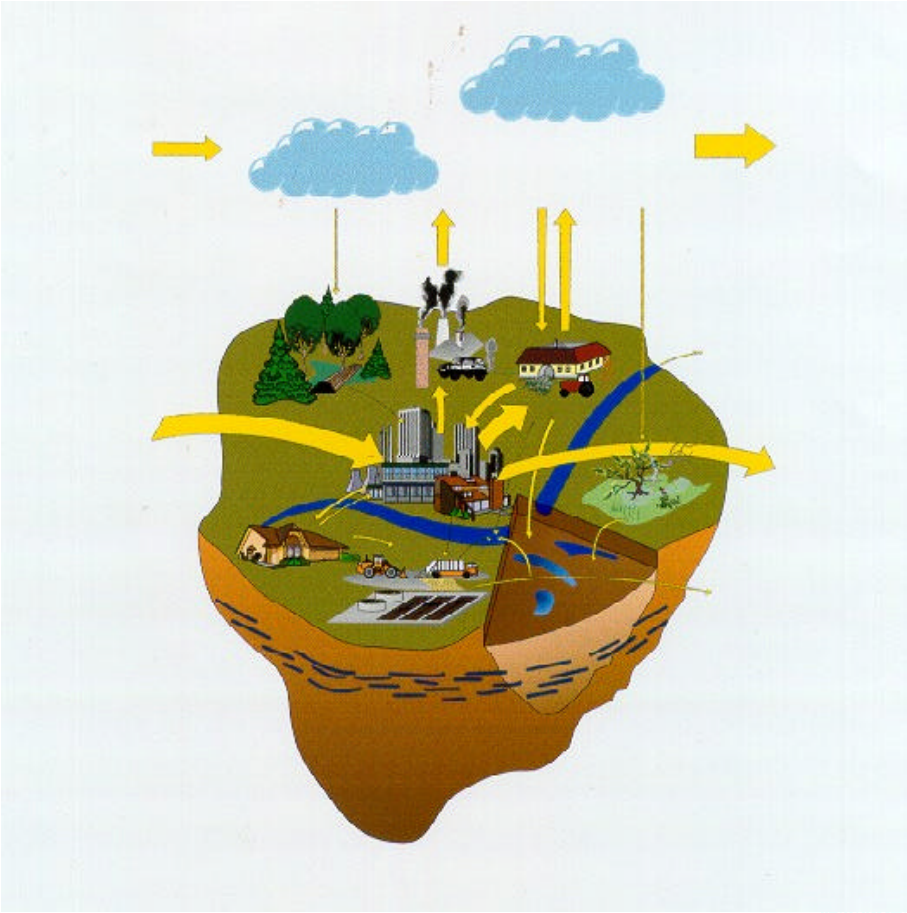
EC ENVIRONMENTAL RESEARCH PROGRAMME
Reseach Area III - Economic and Social Aspects of the Environment

Materials Accounting as a Tool for Decision Making in Environmental Policy

Case Study Report 3

Chlorine in Western Europe



Centre of Environmental Science, Leiden University

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Case Study Report 3

Chlorine in Western Europe

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1. Introduction

1.1 General Introduction

Environmental pressure groups are campaigning for chlorine and its compounds to be phased out, since they are convinced that the environmental risks are too great to be controlled. Industry argues that this is neither necessary, since the risks can be controlled, nor feasible, since 60% of the current production system makes use of chlorinated compounds. A Substance Flow Analysis (SFA) of chlorine and its compounds in Western Europe can give the discussion a more factual basis (Udo de Haes et al., 1988; van der Voet 1996a; van der Voet 1996b; Baccini & Bader, 1996).

1.2 Economic importance of chlorine and chlorinated compounds

In the anthroposphere chlorine has come a long way since it was simply a by-product of caustic production at the end of the 19th century. Today chlorine is one of the most important starting materials in the chemical industry. Worldwide production capacity is currently about 44 million tons per year (Müller, 1993). Of the 70,000 frequently used compounds, about 10% contain chlorine. Of these, 99% are organic compounds. Chlorine is bought by consumers in only a small number of recognizable applications. However, these few applications include the largest single use of chlorine: the plastic PVC, which accounts for about 34% of the use of chlorine in the EU. Some other common consumer applications are (H)CFCs in refrigerators and reactive inorganic chlorine compounds in household cleaning agents. A large number of chlorinated compounds, representing only a small amount of chlorine, are also bought by consumers incorporated in other materials such as dyes and other additives in plastics and pharmaceutical products. All other applications of chlorine occur within the chemical industry as chemical intermediates, or in other branches of industry as auxiliaries, such as chlorinated solvents. In fact, around 60% of consumer products currently contain materials whose production process at some stage involves the use of chlorine or chlorinated compounds.

1.3 Environmental problems related to chlorinated compounds

Since chlorine is of great importance to today's chemical industry, and the chemical industry is one of the key elements of Western society, it could be argued that the use of chlorine is of great importance to Western society. However, the other side of the coin is that chlorinated compounds contribute to a number of important environmental problems,

including: ozone depletion, global warming, toxicity to humans and ecosystems, acidification, smog formation, smell and production of solid waste (Berends & Stoppelenburg, 1990; International Joint Commission 1992 and 1993; Johnston & McCrea 1992; Thornton, 1991; Kleijn, 1993). Two of these problems - ozone depletion and global warming - can be related to a small group of chlorinated compounds: (H)CFCs, Halon 1211, tetrachloromethane and 1,1,1-trichloroethane. The contribution of chlorine to acidification, smog formation, smell and production of solid waste is of minor importance in comparison with other compounds. At this moment the chlorine debate focuses on the toxic effects of chlorinated compounds. From the point of view of environmental management, emissions of intentionally produced and known toxic substances such as pesticides and PCBs are relatively easy to control. Owing to the reactivity and aselectivity of active chlorine, however, unknown chlorinated compounds are produced unintentionally in small quantities as by-products: chloromicropollutants. Thousands of different organochlorines are found in sediments and biota, at least some of these coming from anthrophogenic sources. Only a small fraction of these organochlorines can be identified. The uncertainties connected to the environmental impact of anthrophogenic chlorine micropollutants are a major topic within the chlorine debate (Colborn et al., 1996).

2. Scope and Scale

2.1 Objectives and research questions for the reporting period

The main objective of the chlorine case study is *to give an overview of flows and stocks of chlorine and chlorinated compounds within the European Union (EU), to identify problemflows, to describe trends and to explore different policy measures and their results*. In this period the following subjects were treated:

- definition the chlorine debate as it is today
- the goal of the study
- definition of systemboundaries
- inventory of data:
    - flows within the industry on the basis of the literature survey
    - applications of chlorinated hydrocarbons extrapolated from national data
    - emissions extrapolated from national data
- combine these data to get a total overview of flows of chlorinated hydrocarbons through the anthroposphere from the cradle to the grave
- describing priorities for forthcoming period

2.2 Case Study Region: Western Europe

By choosing the region one of the most important systemboundaries is defined. The chosen region for the chlorine case-study is Western Europe.

2.2.1 Selection criteria

The choice for Western Europe was based on a number of arguments:

International market with multinational companies

The key-players in the chemical industry are multinational companies with plants in most European countries. Therefore possible policy measures should not only be formulated on a national level but also on the level of the EU.

Transboundary environmental problems

Most of the problems which are caused by chlorinated hydrocarbons are transboundary: global warming and ozone depletion are the best examples but also the toxicity of persistent bioaccumulating compounds is a transboundary problem.

International policy

Due to reasons of competitiveness possible policy measures should be on a supranational level. The EC is could play an important role in formulating policy regarding chlorinated hydrocarbons. The EC is already involved in regulations for specific (groups) of compounds (see paragraph 0).

2.2.2 Description of the region

The region Western Europe is formed by 17 countries of which 15 are EU member states (Table 1).

Table 1: Population, GNP and per capita GNP of Western European countries (World Factbook, 1995)

	population (est. July 1995)	GNP (billion $) (est. 1994)	GNP/capita ($)
Austria	7,986,664	139.3	17442
Belgium	10,081,880	181.5	18003
Denmark	5,199,437	103	19810
Finland	5,085,206	81.8	16086
France	58,109,160	1080.1	18587
Germany	81,337,541	1344.6	16531
Greece	10,647,511	93.7	8800
Ireland	3,550,448	49.8	14026
Italy	58,261,971	998.9	17145
Luxembourg	404,660	9.2	22735
Norway (*not EU*)	4,330,951	95.7	22097
Portugal	10,562,388	107.3	10159
Spain	39,404,348	515.8	13090
Sweden	8,821,759	163.1	18488
The Netherlands	15,452,903	275.8	17848
United Kingdom	58,295,119	1045.2	17929
Switzerland (*not EU*)	7,084,984	148.4	20946
Western Europe	**384,616,930**	**6433.2**	**16726**

The total population is 385 million (USA 264). The total GNP is 6433 billion $ (USA 6738). Norway and Switzerland are the only two countries which are not a member of the EU. The nations within Western Europe are very different in size, population, culture, modes of production etc.. These differences influence the chlorine flows in society and the emissions connected to them. In Figure 1 the differences between the different nations is illustrated by comparing the GNP per capita. A factor 2 difference can be found between the 'poorer' and the 'richer' countries.

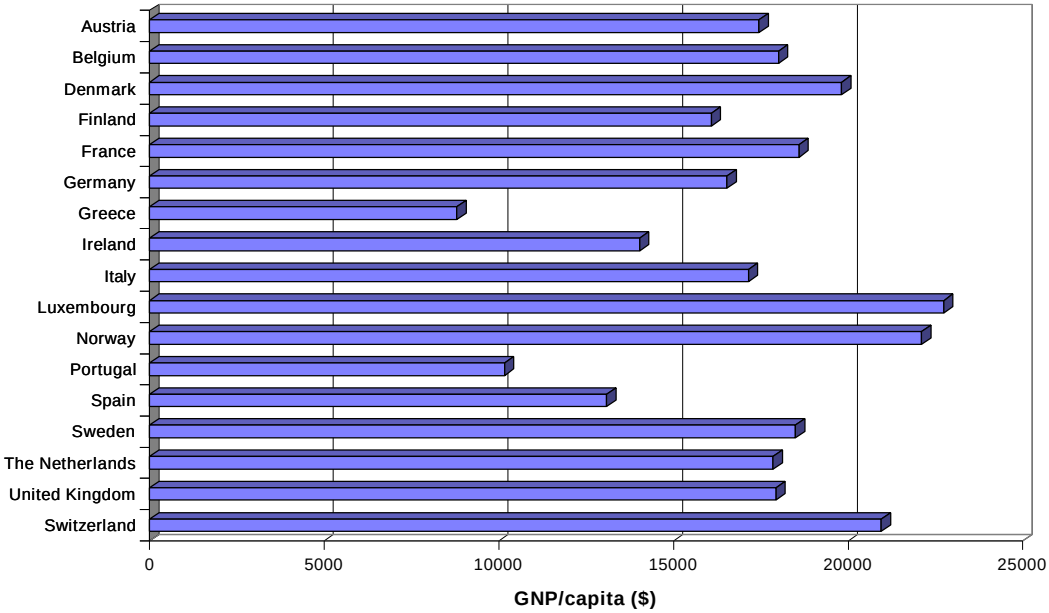

Figure 1: GNP per capita for Western European countries (World Factbook, 1995)

Western Europe has the second largest Chlor-alkali production capacity after North America (Figure 2).

In Figure 3 the distribution of the chlorine production in Western Europe is illustrated. Germany is by far the largest producer followed by France and the UK. Interesting to see is that two small countries, Belgium and the Netherlands, both have a relatively large chlorine production.

Figure 2: Chloro-alkali capacity 1991 in kMt (Datasource: Ayres & Ayres, 1996)

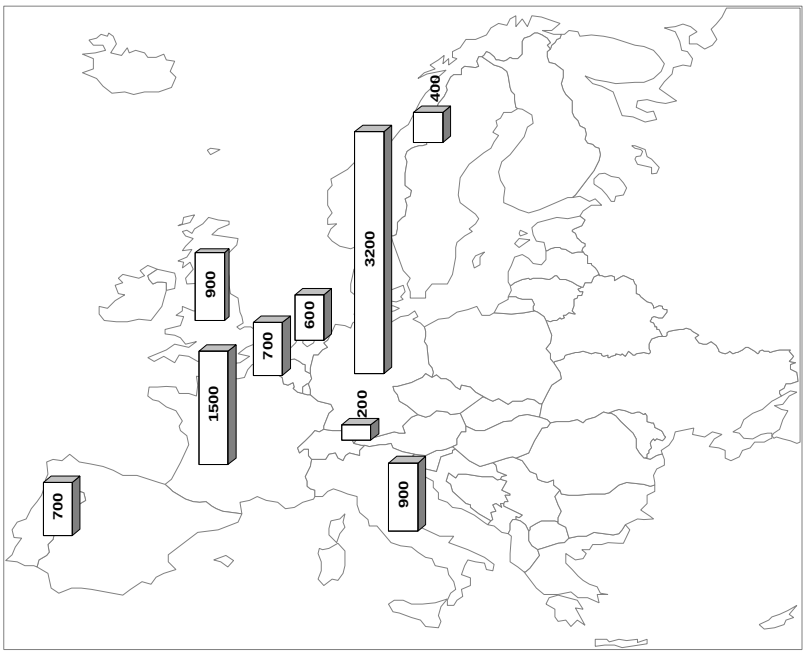

Figure 3: Chlorine Production in Western Europe, 1994, kMt (Eurochlor, 1995)

3. System Definition

3.1 Selection of goods and materials

A motivation for choosing the group of chlorinated hydrocarbons as an object of this study is given in Chapter 0. All flows of elementary chlorine, chlorinated hydrocarbons and some important anthrophogenic inorganic chlorine compounds are taken into account. Excluded from the study are flows of relatively harmless inorganic chloride (salts)in products like table salt, all kinds of foodstuffs etc. The emissions of chloride (salts) are accounted for to complete the mass balances and because these emissions can cause problems when emitted in large amounts to fresh water. A list of main substances in the chemical production processes is given in Figure 8. In Appendix 4a and Appendix 4b the main substances of which emissions are accounted for is given.

3.2 Definition of processes and subprocesses

The flows of the chlorine and its compounds are followed from the cradle to the grave: from production to destruction in waste treatment or landfill. Processes are divided in four main groups:

1. **chlorine industry**: chemical production processes in which chlorinated compounds are produced or used as feedstock (e.g. production of PVC from VCM and production of PC from phosgene);
2. **market**: the trade of chlorinated compounds from domestic and foreign producers to domestic and foreign users (e.g. dichloromethane market);
3. **applications**: the use of chlorine and its compounds (e.g. the use of DCM as a solvent in the pharmaceutical industry or the use of chlorine as a bleaching agent in pulp&paper industry) *excluding* the use as feedstock (e.g. the use of VCM as a feedstock in the PVC production);
4. **waste treatment**: e.g. incineration and landfilling of final waste.

The production processes taken into account in this study are given in Table 2. Markets exist for all chlorinated compounds which are stable enough to transport. In the model a market node is added for all substances which are produced. However, markets are most important for (semi)finished products (e.g. solvents and polymers) and for substances used as feedstock in the chemical industry (e.g. EDC). The main applications can be divided in applications of PVC and applications of chlorinated solvents and CFCs. The main application nodes are given in

Table 3. Waste Treatment represents the treatment of final waste and consists of landfill and incineration. Internal waste which is recycled within the industry and applications is excluded from this group.

Table 2: Production Processes in the Western European Chlorine Industry

Name	Description
chlorine	electrolysis of brine to produce Cl_2
HCl	direct production of HCl from salt (thus not as a byproduct of other chlorinated compounds)
chloromethanes	direct chlorination of methane with Cl_2 to produce dichloromethane, chloroform and tetra
CFCs	production of C1-chlorinated fluorocarbons from tetrachloromethane and HF
HCFC 22	production of HCFC 22 from chloroform and HF
methyl chloride	production of methyl chloride from HCl and methane
EDC (direct)	direct chlorination of ethene with Cl_2 to produce 1,2-dichloroethane
EDC (oxy)	oxychlorination of ethene with HCl to produce 1,2-dichloroethane
VCM	cracking of 1,2-dichloroethane to produce monochlororethene (vinyl chloride, VCM)
PVC	polymerization of VCM to produce polyvinylchloride
VDM	production of vinylidene chloride via 1,1,2-trichloroethane and 1,2-dichloroethane
ethylene amines	production of chlorine-free ethylene amines from 1,2-dichloroethane, NH_3 and NaOH
Per/Tri	production of tetrachloroethene (Per) and trichloroethene (Tri), partly from 1,2-DCE and Cl_2
1,1,1-tri	production 1,1,1-trichloroethane from vinyl chloride and Cl_2
chloroacetic acid	production of chloroacetic acid from acetic acid and Cl_2
AC	production of 3-chloropropene (allyl chloride, AC) from propene and Cl_2
ECH	production of epichlorohydrin (ECH) via dichlorohydrin from allyl chloride and hypochlorite and $Ca(OH)_2$
PO	production of Propylene Oxide via propylene chlorohydrin from propene and Cl_2
epoxy	production of epoxy resins from epichlorohydrin
glycerin	production of glycerin from epichlorohydrin
chloroprene	production of 2-chloro-1,3-butadiene (chloroprene) from 1,3-butadiene and Cl_2
phosgene	production of $COCl_2$ (phosgene) from carbon monoxide and Cl_2
chlorobenzenes	production of chlorobenzenes from benzene and Cl_2
PC	production of polycarbonate from phosgene and Bisphenol-A
TDI	production of toluene diisocyanate (TDI) from phosgene and toluene diamine
MDI	production of 4,4'-diphenylmethane diisocyanate (MDI) from phosgene and diaminodiphenylmethane (MDA)
hypo	production of hypochlorite from Cl_2 and NaOH
TiO_2	production of titanium dioxide (TiO_2)
other process chains	production of other compounds, mainly inorganic

Table 3: Applications of chlorinated substances in the Western Europe

Name	Description
Solvents/CFCs	
metals/electronics	degreasing agents in the metal and electronic industry
dry cleaning	solvent used for cleaning clothes
graphical industry	solvent in the printing ink
pharmaceutical industry	solvent in production of pharmaceutical products
foodstuffs (extraction)	solvent used to extract compounds from feedstuffs e.g. caffeine from coffee
paint remover	solvent used to remove paint or adhesives from painted surfaces
adhesives	solvent used in adhesive products
aerosols	solvents used as propellants in aerosols
paint	solvent used in paints
textile refinement	textile refinement
yarns/fibres	solvents used in the production of yarns and fibres
household/industrial cooling	(H)CFCs used in cooling equipement
foam	solvents used as blowing agent to create foams
sterilization gas	CFC-12 used as sterilization gas
(chemical) industry	other use in the chemical industry
PVC	
pipes&fittings	pipes&fittings used for distributing e.g. water and gas and collection of sewer
profiles	profiles used mainly in building applications e.g. windowframes
film&sheet	film & sheet used for coatings, glazing etc.
bottles	PVC-bottles
cables	insulating material for electricity cables
flooring	PVC-flooring, vinyl flooring
wall covering	PVC-wall covering, vinyl wall covering
hosepipe	PVC hosepipes, flexible pipes&hoses
other	other applications of PVC

3.3 Definition of systemboundaries

The chlorine case focuses on flows in anthroposphere (technosphere, physical economy) and the flows between anthroposphere and environment: extraction's and emissions. Flows and formation within the environment are not analyzed in this study although these flows have been found to significant in some specific cases (de Leer, 1993). However, where it is possible and needed the anthrophogenic flows are related to the environmental flows.

3.4 Treatment of the "Hinterland"

Flows outside of the chosen region (Western Europe) are not analyzed in this study. However, where possible and needed the relation between flows within Western Europe and flows in the rest of the world is discussed.

4. Data Collection

4.1 Use of regional/national statistics

National and EuroStat statistics are only of limited use for the chlorine case study. Import and export statistics are in principle useful although previous studies on national levels showed important differences between the statistics and the data provided by the major industries. In those studies it was concluded that the import and export statistics were less reliable as a source of information than the data provided by the industries. These problems tend to increase for national statistics even further with the disappearing of the national borders. Another problem is that statistical data is confidential when there are less than three producers of a certain good or material. Especially in smaller countries this can lead to very incomplete statistical data or strangely aggregated data. As shown in the next paragraph data was used from earlier studies and partly extrapolated to the Western European level from national Dutch data. Import and Export data were taken from EuroStat statistics.

4.2 Assessment of flows and stocks

The chlorine chain consists of lots of chemical processes and lots of different applications which are connected to lots of different emissions. The production processes are linked together as in a web: products of process A are used to produce other products in process B of which the byproducts can be used in process A again (Figure 4).

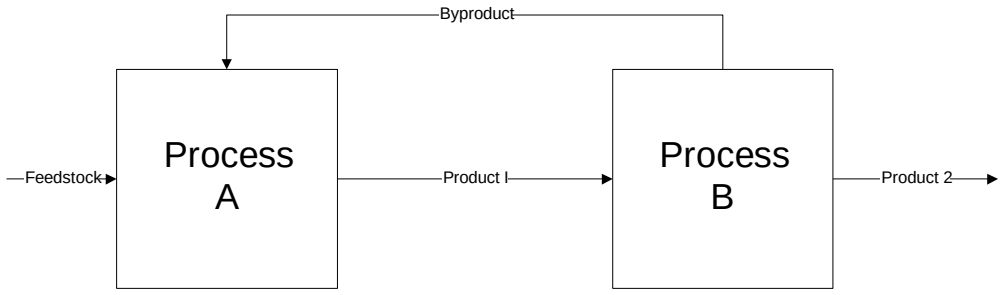

Figure 4: Production processes of the chlorine chain are interlinked via products and byproducts

Because the interlinkages makes the analysis more complicated, data from the industry and chemical knowledge about the chlorine industry is necessary. During the MAc TEmPo process Ayres & Ayres finished an study that would prove an important basis for the chlorine case (Ayres & Ayres,1996). In their report they quantified the bulkflows of chlorine and its compounds within the Western European chlorine industry. Next to these bulkflows within the industry they presented very limited data on the use and emissions

during production and application of these compounds. Ayres & Ayres based their study on a number of datasources, like Tecnon, and Euro Chlor, representing the Chlor-Alkali industry. The authors reported important gaps in the data and lots of inconsistencies when comparing different datasources. Furthermore, they criticize the chemical industry for their reluctance to publish production, consumption, trade and stockpile data. They industry reacted by supplying additional information (still marked confidential) only after a draft report had been send to them. Despite all the troubles they had the work of Ayres & Ayres proved to be an important datasource for this study.

The data of Ayres & Ayres was compared with data of other sources, mainly data given to us by EuroChlor during earlier studies.

As mentioned before the data of Ayres & Ayres is very useful for quantifying the bulkflows of chlorine and its compounds within Western Europe. In this MAc TEmPo case-study data on the applications and emissions of these compounds was largely extrapolated from a national Dutch study of TNO and RUL.CML (Tukker et al., 1995; Kleijn et al., 1997). Tukker et al. quantified around 99% of all the flows of chlorinated hydrocarbons in the Netherlands including applications, waste treatment and emissions during the whole life cycle of chlorine and its compounds.

Imports and exports are taken from EuroStat data. The total imports and exports of the EU-12 were corrected with imports and exports to individual countries to get the imports and exports for Western Europe.

4.3 Data sources for stock dynamics

As can be seen in Figure 5 around 38% of the amount of chlorine which goes to the applications is accumulated in the economic stock (1627 kMt). Around 94% of this amount (1536 kMt) is accounted for by PVC the rest is polychloroprene (synthetic rubber) and CFCs. In the future the chlorinated compounds which accumulate now in the economic stock will become waste which has to be recycled, incinerated or landfilled. Next to that the chlorinated compounds which have been accumulating in the past are emitted now. In the Dutch Chlorine Chain study (Tukker et al. 1995; Kleijn et al. 1997) it was clearly shown that the most important Dutch contribution to the depletion of the ozone layer accounted for by the emissions of CFCs from foams which were produced in the past with the aid of CFCs as blowing agents.

For the calculation of stock dynamics of PVC in durable applications data was taken from a study of PVC flows in Sweden (Tukker et al., 1996). In this study all flows of PVC and the main additives, from the cradle to the grave, were quantified for the base year 1994. To calculate the emissions of additives from the PVC-stocks estimates of the magnitude of these stocks were made. These estimated stocks were the bases for further calculations on

stock dynamics. For CFCs calculations of stock dynamics were based on world production figures (Worldwatch Institute, 1997) and rough estimations of the distribution of these CFCs over different applications.

4.4 Scaling up and Down

In this study the distribution of chlorinated compounds over the different applications and the emissions during production and applications are extrapolated from Dutch data (Tukker et al., 1995; Kleijn et al., 1997)). The Dutch emissions during the production processes were translated in emission factors on the basis of the chlorine input of the processes. These emissions factors were then multiplied by the chlorine input of these processes on a Western European level. Thus the assumption was made that the emissions related to a specific production process in the whole of Western Europe are similar to the emissions in the Netherlands (the validity of this assumption is discussed in paragraph 0). Dutch data was also used to estimate the distribution of chlorine compounds over the different types of applications. This procedure is only used for solvents and (H)CFCs. The Dutch distribution is given in Appendix 3.

4.5 Accounting of flows and stocks

By using the data on chlorine flows in the Western European chemical industry from Ayres & Ayres (1996) and Eurochlor (1995), data on emissions and applications extrapolated from the Dutch situation, EuroStat import export data and the mass balance principle an overview of chlorine flows in Western Europe has been generated.

4.6 Treatment of uncertainty

In paragraph 0 it is stated that the emissions of chlorinated compounds are extrapolated from Dutch emissions. However, during the Dutch chlorine chain study (Tukker et al., 1995) important differences in emissions were found between different companies and plants producing the same products. Moreover it is expected that the differences between chemical production plants within the Netherlands is small compared to the differences over the whole of Western Europe. As stated in paragraph 0 the differences between the countries in Western Europe in terms of GNP/capita are more than a factor 2. The differences in emissions is expected to be much bigger up to a factor 100.

The differences in emissions from the application of chlorine compounds (mostly solvents) are expected to be much less. In the Netherlands more than 80% of the consumption of solvents (excluding internal recycling) are emitted the rest ends up in chemical waste. The maximum amount of emission is therefore only 25% higher than estimated on the bases of the Dutch figures.

5. Modelling

5.1 SFINX, a computer program for substance flow analysis

The integrated analysis of all flows of a substance or group of substances in the economy and the environment of a given system has proved to be an effective instrument to support the definition of substance-specific policies. The SFINX (Substance Flow InterNodal exchange) computer program is a tool to assist in substance flow analyses (van der Voet et al., 1995a; van der Voet et al, 1995b). It can be used as a:

1. bookkeeping system: it provides a framework for sorting, processing and presenting data on a given substance or group of substances to provide an overview of the flows and accumulations of the substance or group in a specified system (generally the Netherlands) during a specified period (generally one year).
2. model: for example, to assess the effect of envisaged policies, including the shift of any problems which might result.

Each of these objectives requires the use of a clearly defined and systematic system, free of any inconsistencies, to ensure that the outcome can be verified and to ensure that analyses undertaken at different times are comparable. A complete specification of all substance flows in a system is also needed for more than elementary applications. The flows, particularly those in the economy, of some substances are extremely complex. At present RUL.CML uses the SFINX (Substance Flow InterNodal exchange) model which is still being refined. At present, SFINX

users can:

- obtain an overview of all flows of a single substance or group of substances within a delineated system;
- check the consistency and completeness of basic data;
- make estimates of any unavailable data through defined relationships within the system;
- present the data and outcome of the calculations in various formats, depending on user requirements;
- calculate the long-term effects of various assumptions such as trends and policy measures;
- identifying the ultimate origins of certain problemflows.

In future SFINX should also provide the following facilities:

- specifying links between the SFINX files of different substances;
- provide estimates of the short-term effects of certain trends or measures (dynamic operation).

5.1.1 Structure of SFINX

SFINX is written in PROLOG and runs under DOS. Substance flow models can be created one step at a time. A menu is used to specify nodes (i.e. nodes in substance flows, e.g. economic processes, agriculture as a whole, or environmental media), connections between nodes (the substance flows), to quantify known flows as tables and to specify the relationships between substance flows through formulas. The calculation of the magnitude of the substance flows is handled by a mathematical program, Mathematica, currently one of the standard programs in this field. SFINX handles the communication between itself and Mathematica.

To use SFINX as a bookkeeping program the flows are quantified using literature data, statistical information and measurement data which is entered into tables. Spreadsheet tables can be imported into SFINX. Similarly, SFINX tables can be exported to Spreadsheets.

When SFINX is used as a model it is important to ensure that substance flows are entered with their interdependencies where possible, using formulas. In this way, the substance flows within the system can be derived from the smallest possible set of basic data. The remaining fixed data should be selected with great care.

The results of the calculations can be presented in several formats. The basic output (general view) is a list of all nodes and the related substance balances of the input and output flows for each node. Users can also define special views by selecting groups of flows and creating separate lists with totals.

5.1.2 Limitations of the model

At this moment no dynamic calculations can be performed. The model is therefore not suited for scenario analysis. Furthermore the database structure of the model itself is not very well developed and will be improved during this study. As stated in paragraph 0 the stock dynamics is important for future waste treatment and for current and near future emissions of substances which were banned earlier.

5.2 Modelling stock dynamics

Until recently, MFA has concentrated mostly on flows. During the past few years, MFA researchers have realized that stocks may be equally or more important: *today's stocks are tomorrow's waste flows and emissions.* In the MAc TEmPo project a choice has been made to focus on the stocks in the anthroposphere as well.

The rule of IN = OUT is *the* most basic starting point for MFA. Although the inflows have to equal the outflows in the end (in the *steady state* situation) this might never occur in reality due to chances in regimes and flows over time. If IN > OUT the substance which is studied will accumulate and stocks will be formed within the system. If IN < OUT there will be a negative accumulation and the stocks of the system will be depleted. In MFA practice, where one year is often the base time unit, accumulation will occur if products are consumed with a lifespan longer than one year. It is important to notice that the outflow of the system can be seen as a delayed and reversed (negative) inflow. For our modeling of stocks we have chosen to adopt this approach which has been used before for example for modeling the development of buildings stocks (e.g. Gabathuler & Wüest, 1984). The stocks are then a result of the combination of inflows and outflows over the years. The time lag equals the lifespan of the products. The lifespan, although generally known as an average, will be distributed in some way: some individual products will be discarded earlier then others. To get an accurate picture of stock formation and depletion the distribution of lifespan should be know. However, empirical data on the lifespan distribution is often not available and the gathering of this empirical data can be very time-consuming. The Swedish group within the MAc TEmPo project has focussed on the gathering and estimation of data on current and past stocks of metals in the city of Stockholm. An alternative for using empirical data would be to assume a certain known lifespan distribution. In terms of Systems Theory: we use a dynamic, linear, deterministic model and assume a known impulse response derived from a discretisized normal distribution[1]. In other words we assume a linear time independent system (LTI). The outflow can thus be calculated as a combination (convolution) of the inflow signal and the lifespan distribution.

In this paper the *output = delayed input* approach described above is used to describe the economy as a system, that responds to an input of products (the *input signal*) with an equal output after a certain delay (the *output signal*). As discussed above time lag is dependent on the lifespan distribution (or disposal function) of the product. The shape of the output signal is determined by the shape of the input signal and by the transformation of this signal by the system.

We used two case studies to apply this approach: PVC in Sweden and CFCs in the world. The PVC case studies will be published in the near future (Kleijn et al., 1998). A publication of the CFC case study is planned together with the TUW.IWAG.

[1] The choice for a normal distribution is rather arbitrary. A Poisson or Weibull distribution might be more appropriate in some cases. The normal distribution was also choosen as an example of a known impulse response in the book of Baccini & Bader 1996.

6. Results

6.1 A chlorine balance for Western Europe

In Figure 5 the flows of chlorine and its compounds through Western Europe is summarized. Chlorine and its compounds are produced from chloride salts, mostly Sodium Chloride (NaCl). The NaCl is taken from either mineral deposits in the earth's crust (old sea beds) or from seawater (minor part). Around 44% (4123 kMt) of the chlorine inflow via salts is emitted again as chloride salts from production processes, applications and waste treatment. About 9 % (862 kMt) flows as HCl to other industries. The chlorine in this HCl will probably be emitted as chloride salts after use. Another 9% (829 kMt) leaves the industry as unknown products according to Ayres & Ayres (1996). A comparison of their figures with figures of Euro Chlor leads to the conclusion that this flow mainly consists of inorganic compounds which are not followed any further. The chlorine in this flow will probably be emitted as chloride salts somewhere during the use of these inorganic compounds. About 2% (214 kMt)of the inflow leaves the chlorine industry in compounds which are transformed in other parts of the chemical industry (e.g. methyl chloride, monochlorobenzene, chloro acetic acid and allyl chloride). Most of the 214 kMt will be used in the production of chlorine-free products and the chlorine will be released as chloride salts. This brings us to the conclusion that about 6000 kMt (65%) of the chloride which flows into the system is emitted again as chloride salts. Chloride is present in large concentrations in sea water (around 2%) but also in living tissues. The only environmental effect that could be linked to chloride emissions is salination when it is released in large amounts into a fresh water environment.

The main single product in the chlorine chain is without any doubt PVC. In terms of chlorine flows it overshadows the sum of all other products. Around 18% of the chloride input (1536 kMt) accumulates in the anthropospheric stock as PVC in products with a long life span such as pipes and building materials. Another 8% ends up as PVC in landfills. In total we now accounted for 91 % of the chloride inputs. The remaining 9% is mainly emitted during applications and production (694 kMt, 7%), accumulated in anthropospheric stock in other polymers and CFCs (91 kMt, 1%) and exported (122 kMt, 1%).

The import and export stated here only reflects the import and export of compounds which are not used as feedstock for the chemical industry. Again PVC-powder and half products are most important: import 360 kMt and export 332 kMt . This leaves 45 kMt import and 195 kMt export for the other products.

Of the 1496 kMt of other products which flow to the applications about 42% (625 kMt) is inorganic: chlorine and hypochlorite. Another 47% (710 kMt) is accounted for by

organochlorine solvents. The remaining 11% (161 kMt) is present in (H)CFCs, polychloroprene and EDC (used as a scavenger). The chlorine and hypochlorite will be transformed to chloride(salts) during the application. The solvents will largely (70% -100%) be emitted (mainly to air) and partly end-up in chemical waste. The emissions and waste generation from solvents are taken from Dutch data (Tukker et al., 1995) which can be found in Appendix 3. A specification of the emissions during production, (also extrapolated from the Dutch data) can be found in Appendix 4a and Appendix 4b.

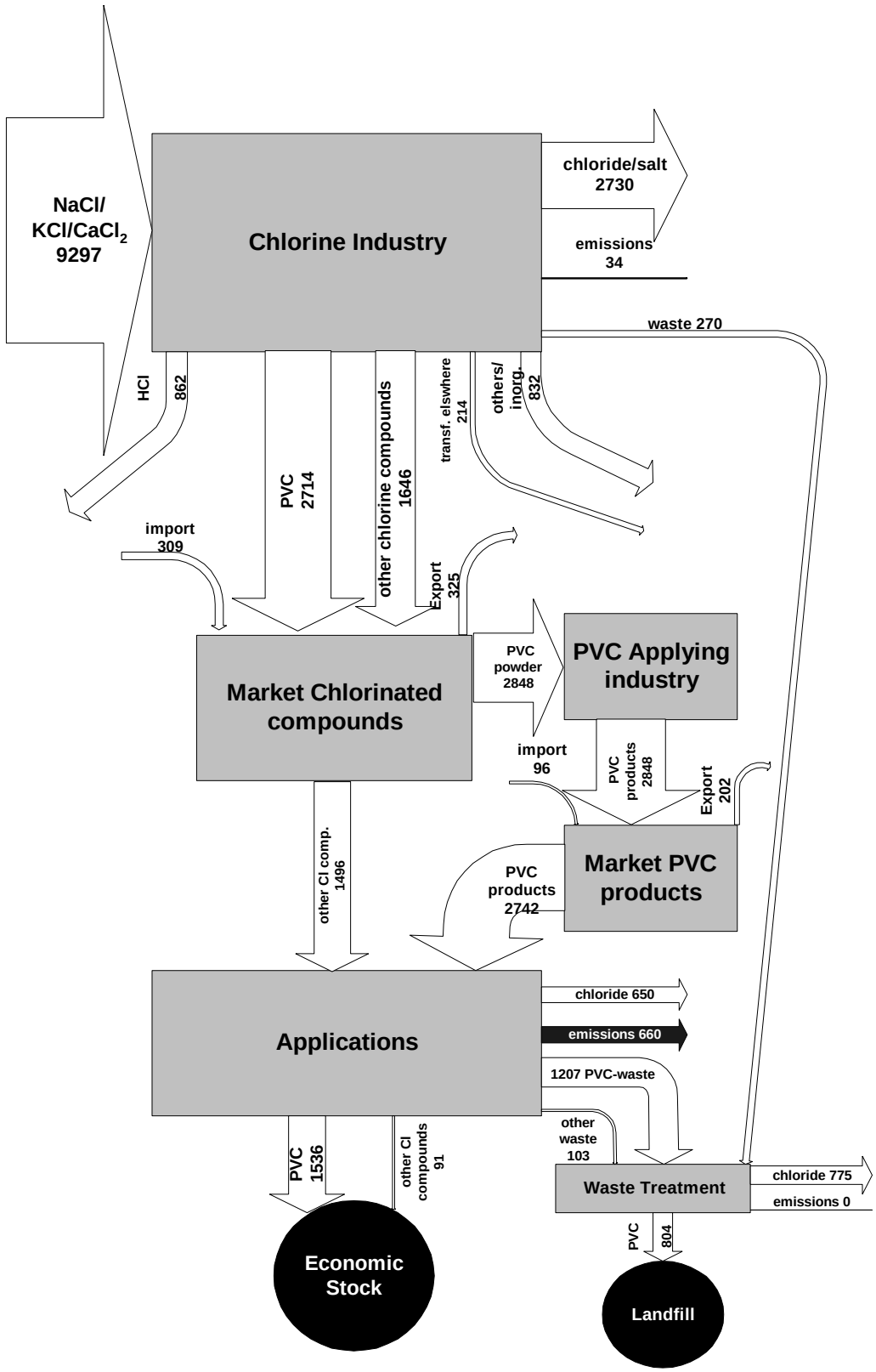

Figure 5: A chlorine balance for Western Europe, 1992 (kMt Cl). More detailed quantitative information can be found in Appendix 2.

6.2 Chlorine in the chemical industry

A chlorine balance for the Western European chemical industry is given in Figure 6. An Input-Output table of the WE chlorine industry is given in Appendix 5. By far the most important chlorine feedstock is ordinary table salt (NaCl) from mineral deposits. Around 30% of the chloride which flows into the industry in salts is emitted to the environment as chloride salts, mostly after temporary having been incorporated in chlorinated hydrocarbons. Somewhat less than 55% is incorporated in chlorinated hydrocarbon products other than HCl. Another 10% is used in other industries as HCl and some 5% is used directly as elementary chlorine in the pulp&paper industry and in water treatment.

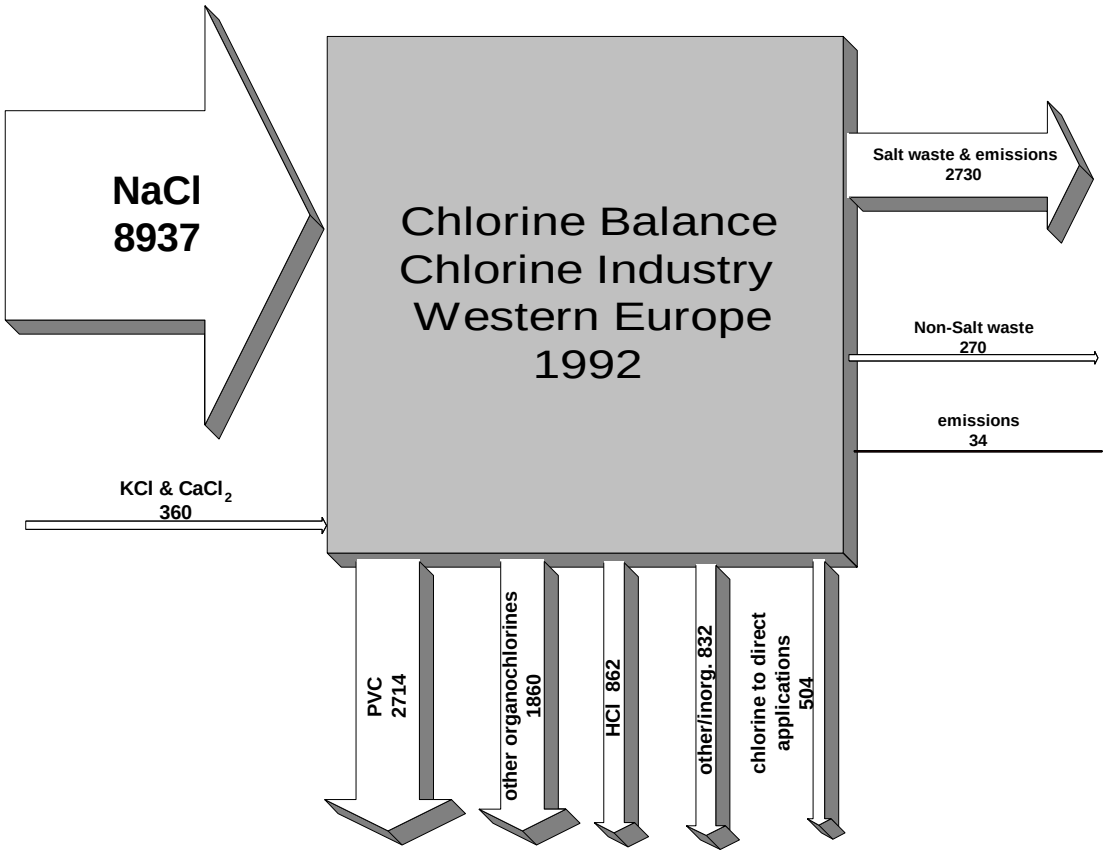

Figure 6: A chlorine balance for the Western European chlorine industry for 1992 based on Ayres & Ayres 1996 (kMt Cl)

In Figure 7 the differences in chlorine end-use between Western Europe and the world average is illustrated. The biggest difference occurs in the use of chlorine as a bleaching agent in the pulp&paper industry. Western Europe uses 7% less chlorine is this applications than the world average. On the other hand relatively more chlorine is used in Western Europe in the production Propylene Oxide and phosgene (an intermediate in the production of polycarbonate and PUR-foams).

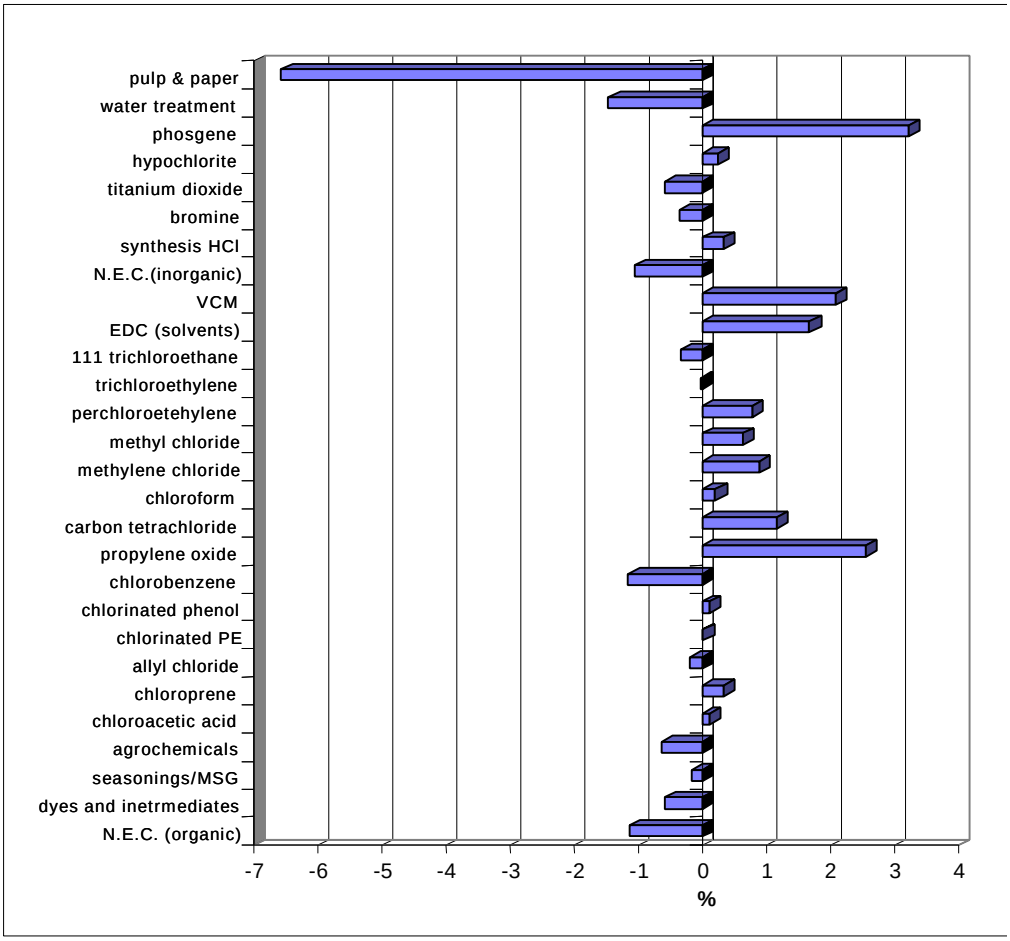

Figure 7: A comparison of the end-use of chlorine in Western Europe with the end-use of chlorine in the world for 1992. In % extra chlorine use in Western Europe (based on Ayres & Ayres 1996).

6.3 The backbone of the chlorine industry in Western Europe

In Figure 8 the backbone of the chlorine industry in Western Europe is given. Next to the direct applications of chlorine there are 7 important vertebrae in the backbone which represent the non-chlorine part which is combined with chlorine or HCl to produce chlorinated compounds. More than half of the net inflow is used in the C2 (ethane, ethene) vertebra. About 14% is used in the C3 (propane, propene) vertebra and about 8% in the C1 (methane). Around 3% is used for a reaction with CO to form phosgene and around 2% to react with caustic (NaOH) to form hypochlorite. Minor amounts are used as input for C4 (butane, butene) and aromatics. Another 19% is used in the production of other compounds, mainly inorganics

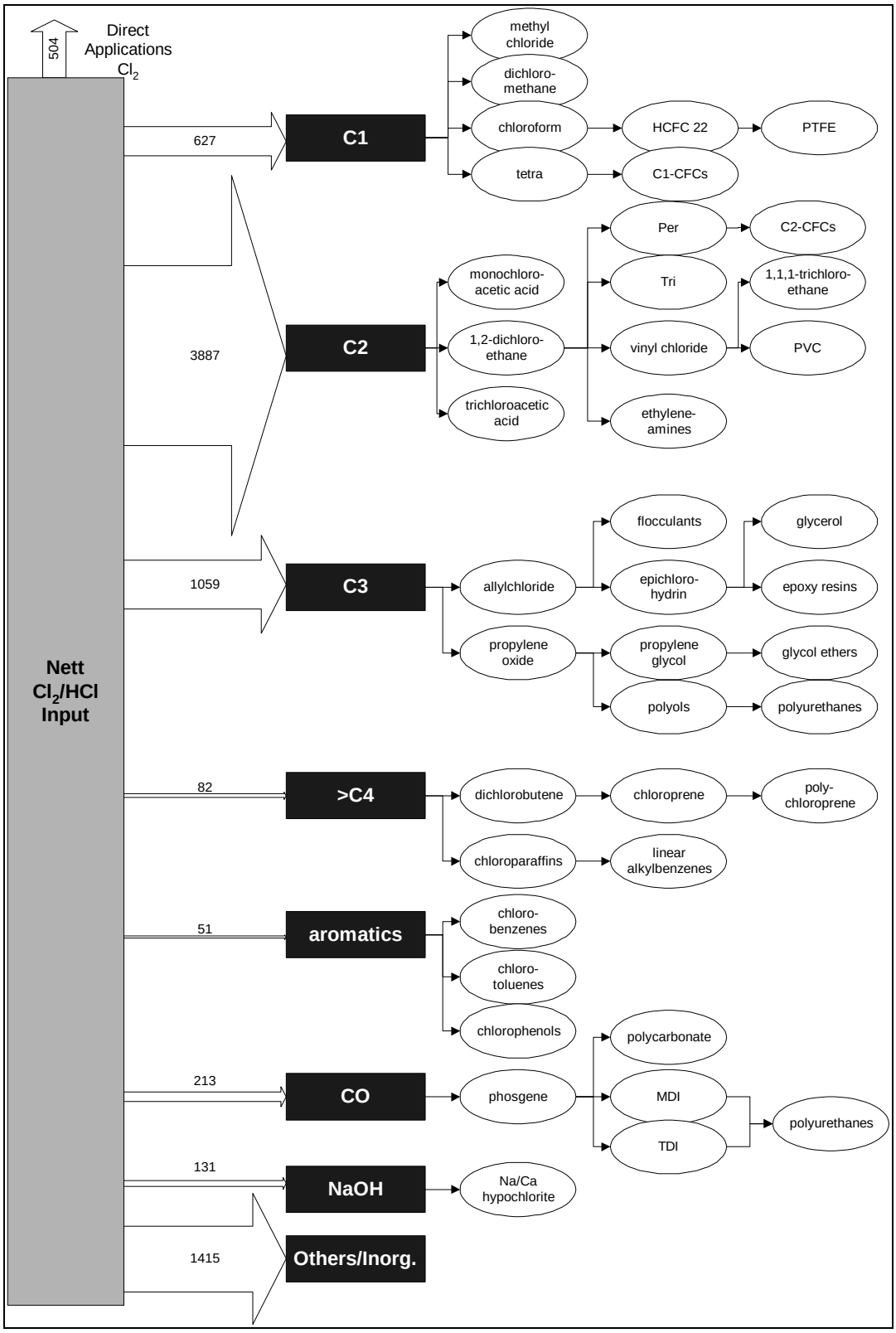

Figure 8: The Backbone of the Western European Chlorine Industry, black rectangles represent non-chlorine part which is combined with HCl or Cl_2 to produce chlorinated compounds. The chlorine input is calculated by adding the Cl_2 input and the HCl input and subtracting the HCl formation (quantities based on Ayres & Ayres 1996).

6.4 Production and consumption of chlorine and its compounds

6.4.1 Total chlorine inflow and outflow in the vertebrae of the chlorine backbone

In Figure 9 the net chlorine inflow (via chlorine/HCl) of the vertebrae in the chlorine industry is related to the chlorine outflow in products. From this figure it is clear that not all of the chlorine which flows in comes out with the products. The main products from the production of C3-derivates are chlorine-free: epoxyresins and propylene oxide. All products which are produced with the aid of phosgene (produced from CO) are chlorine-free (polyurethane's and polycarbonate). In the production of C2-derivates 320 kMt of chloride is released during the production of the chlorine-free ethyleneamines. The products in the category Others/Inorganic are probably mainly inorganic and not followed any further.

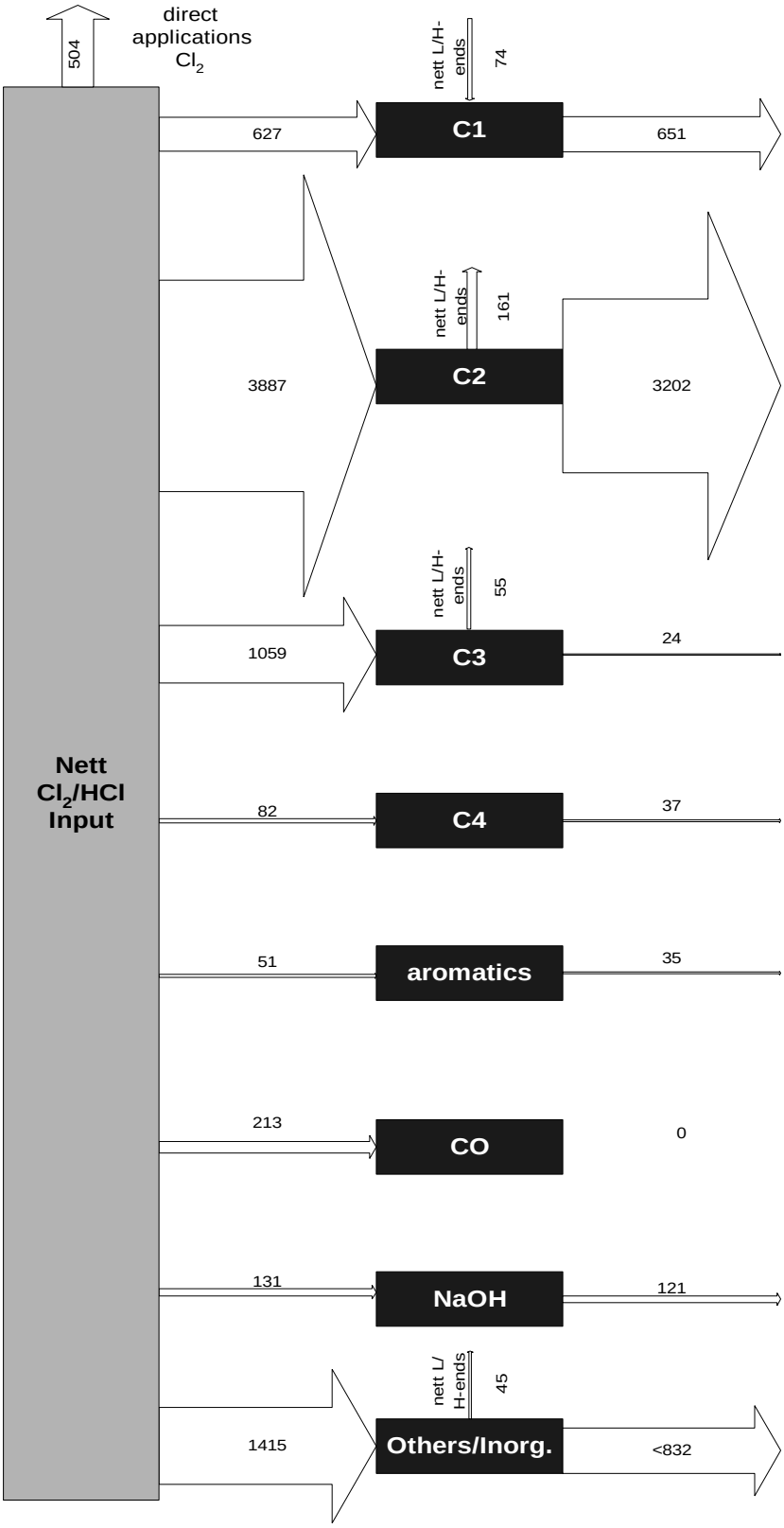

Figure 9: Net Chlorine/HCl inflow in the Vertebrae of the chlorine backbone (kMt Cl)

6.4.2 Production and use of elementary chlorine (Cl_2)

6.4.2.1 Production of elementary chlorine (Cl_2)

Chlorine is produced by the electrolysis of brine: a solution of common salt, NaCl. In the electrolysis electricity is used to separate the sodium and chlorine. In the brine sodium is present as Na^+ and chlorine is present as Cl^- (chloride). At one electrode of the cell chlorine gas (Cl_2) is produced from chloride at the other electrode water is split to form hydrogen gas (H_2) and hydroxide (OH^-) which forms the new anion for the sodium. The electrolyze therefore generates three products from the brine: hydrogen gas, chlorine gas and caustic soda:

$$NaCl + H2O \rightarrow NaOH + Cl_2 + ½ H_2$$

Three different types of electrolytic cells are used in Europe: amalgam, diaphragm and membrane. Because both amalgam and diaphragm cells have important environmental drawbacks, mercury and asbestos emissions respectively, the membrane cells are preferred from an environmental perspective. The raw brine taken directly from the deposits contains next to sodium also calcium and magnesium. In the amalgam process this is not a problem but in the membrane process calcium and magnesium must be separated first.

According to Ayres & Ayres (Ayres & Ayres, 1996) different sources give different figures for the production and end-use of Chlorine in Europe. For 1992 Tecnon reported a production of 8760 kMt while Euro Chlor reported 8610 kMt (Euro Chlor 1995). Ayres and Ayres assume that the Euro Chlor data is more reliable than the Tecnon data but give no reasoning for this assumption. Figure 10 illustrates the mass balance of the production of chlorine in Western Europe.

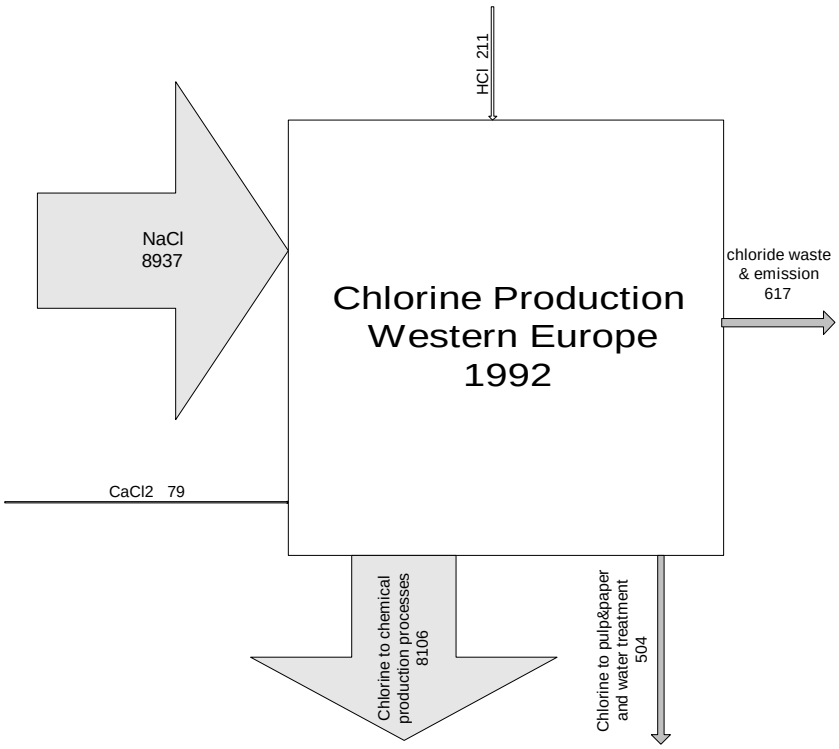

Figure 10: A chlorine balance for the production of chlorine in Western Europe, 1992 based on Ayres & Ayres, 1996 (kMt Cl)

About 93% of the chloride that flows in as chloride salts and HCl is converted to chlorine of which 94% is used in chemical production processes while the remaining 6% is used directly as bleaching agent in the pulp&paper industry and water treatment. The remaining 7% is emitted, mainly as chloride salts.

6.4.2.2 Use of elementary chlorine (Cl_2)

In Figure 11 the use of chlorine is given. More than 94% of the produced Chlorine is used as basic material in the chemical industry to produce other compounds. The remaining 6 % percent of the chlorine is used in direct applications. An explanation of the abbreviations used in the figure are given in Table 2.

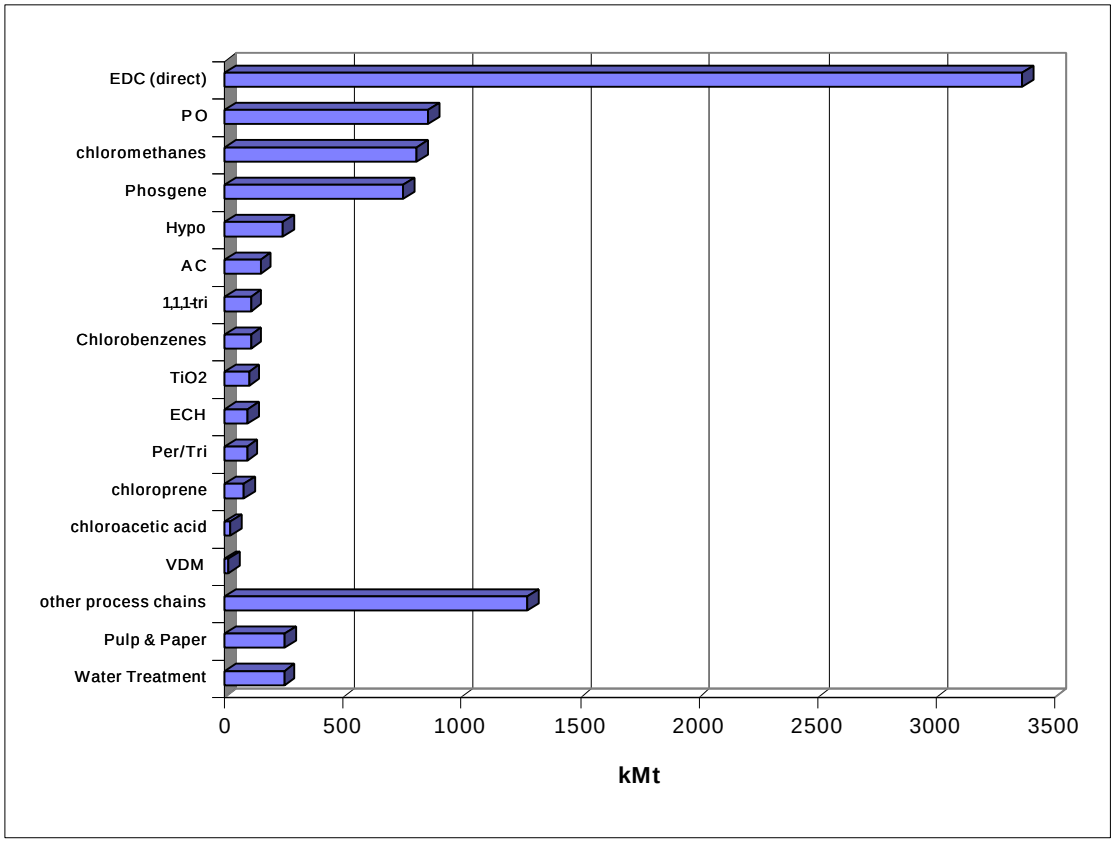

Figure 11: The use of Chlorine in Western Europe in 1992 (based on Ayres & Ayres, 1996)

About 3% of the produced chlorine (251 kMt) is used in water treatment and another 3 % (253 kMt) as a bleaching agent in the pulp & paper industry.

About 39 % of the produced chlorine (3360 kMt) is used for the production of 1,2-dichloroethane (EDC) via direct chlorination[2]. By far the most important use of EDC is the production of polyvinylchloride (PVC) via vinyl chloride monomer (VCM).

Almost 10 % of the chlorine (859 kMt) is used for the production of propylene oxide (PO). PO is an intermediate product in the chemical industry and is used to produce a several products.

More than 9% (809 kMt) is used in the production of chloromethanes: dichloromethane (DCM), trichloromethane (chloroform) and tetrachloromethane (tetra)[3]. DCM is used mainly as a solvent. Chloroform is used to produce HCFC 22 and as a solvent. Tetra is used to produce CFCs, as a solvent.

[2] This is only about half of the total amount of EDC which is produced. The other half is produced via oxychlorination with HCl as source of chlorine.

[3] Monochloromethane (methyl chloride) is produced with HCl as source of chlorine.

Almost 9% (755 kMt) is used for the production of phosgene which is used to produce three main products:

- polycarbonate (PC): a polymer used mostly as synthetic glass in glazing, bottles etc.;
- toluene diisocyanate (TDI): an intermediate in the production of polyurethane's which are used in numerous applications varying from adhesive and lacquers to cogs;
- methylene diphenyl diisocyanate (MDI): another intermediate in the production of polyurethane's.

Almost 3% (246 kMt) is used to produce hypochlorite (hypo) which is used in water treatment, as a disinfection agent in households and in several industrial processes as a bleaching and oxidation agent.

About 2 % (153 kMt) is used to produce allyl chloride (AC) of which 90% is used to produce epichlorohydrin (ECH), an intermediate in the production of epoxyresins. Epoxyresins are used as adhesives, lacquers and coatings.

More than 2 % (207 kMt) is used in the production of solvents like tetrachloroethene (PER), trichloroethene (TRI) and 1,1,1-trichloroethane (1,1,1-tri).

Another 5% (440 kMt) is the following applications:

- production of chlorobenzenes (112 kMt) used as intermediates in the chemical industry and as disinfectants
- production of titanium dioxide (TiO_2) (104 kMt), a white pigment
- production of epichlorohydrin (ECH) (97 kMt), an intermediate in the production of epoxyresins (used in adhesives, lacquers and coatings)
- production of 2-chlorobutadiene (chloroprene) (82 kMt), the monomer of artificial rubber: polychloroprene.
- production of chloroacetic acid (27 kMt), an intermediate in the production of herbicides (MCPA and MCPP), modified starch and modified cellulose
- production of 1,1-dichloroethene (VDM) (18 kMt)

In total 8610 kMt of chlorine was produced in Western Europe. Of this 7333 kMt are accounted for by direct applications and by use in the chemical industry. This leaves 1278 kMt (14%) unaccounted for. Ayres & Ayres (1996) give an elaborate overview of problems they encountered closing the mass balance of the chlorine chain and possible explanations

for the differences. It is assumed that the remaining 1278 kMt of chlorine flows to *other chains and processes*.

6.4.3 Production and use of the second chlorine feedstock in the chemical industry: HCl

Next to elementary chlorine there is another important chlorine feedstock which is not so well known outside the chemical industry: hydrochloric acid (HCl). However, primary production of HCl does not occur except for a very small amount of very pure HCl which needed in some specific processes. This pure HCl is produced by mixing chlorine gas (Cl_2) with hydrogen gas (H_2), both produced in the production of chlorine. The rest of the HCl is produced as a byproduct of a number of important processes in the chlorine industry. There are two important sources: the production of chlorine-free products with chlorinated starting materials and the incineration of chlorinated waste. In a sense one could view the use of HCl as a chlorine feedstock as *recycling* of chlorine. The production of PVC is by far the biggest use of the HCl produced as a waste product of other production processes. Thus PVC is not only the biggest single product of the chlorine industry, it also permits the production of other products because it processes the wastes produced during their production processes. It is important to note this link between PVC and the rest of the chlorine industry when discussing policy measures focussed on (partly) banning PVC. In Figure 12the production and consumption of HCl is given.

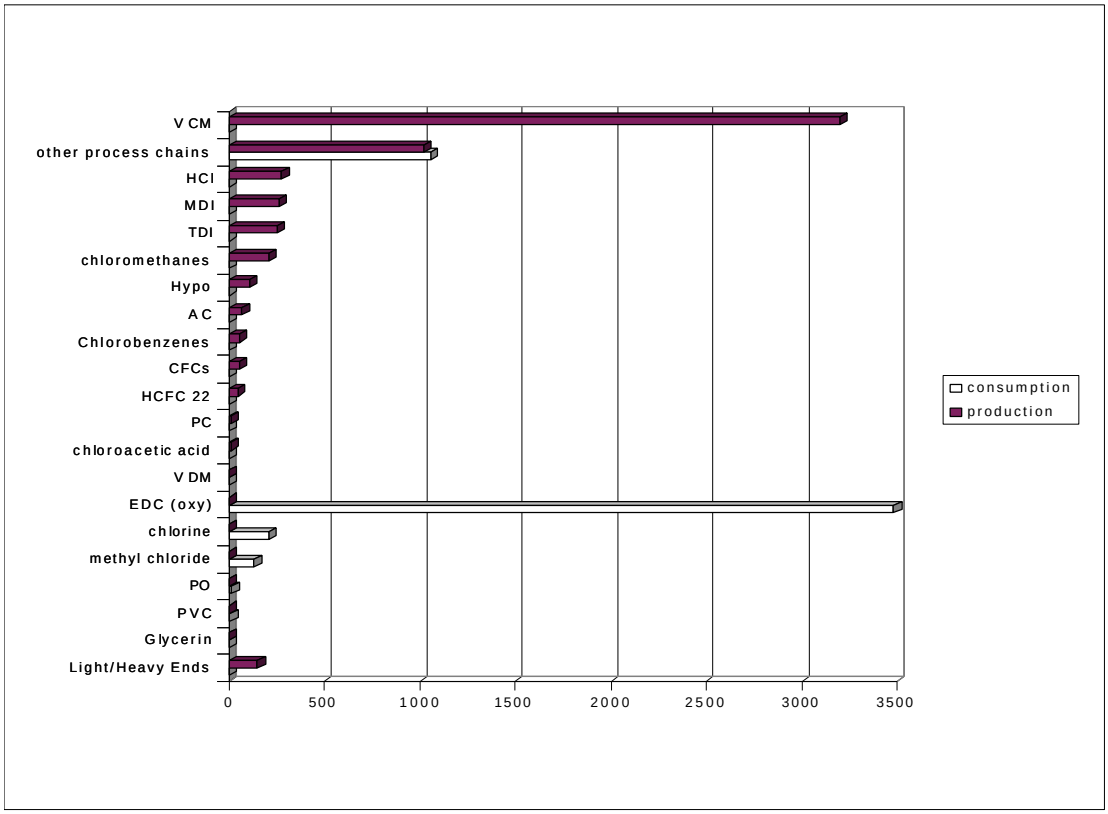

Figure 12: Production and Consumption of HCl in the Chlorine Industry in Western Europe in 1992 in kMt chlorine (based on Ayres & Ayres, 1996).

6.4.3.1 Production of HCl

According to Ayres & Ayres (1996), by far the most important source of HCl in the chemical industry is the production of VCM (feedstock for the production of PVC). When 1,2-dichloroethane (EDC) is used to produce monochloroethene (VCM) about half the chlorine incorporated in EDC is released as HCl (3196 kMt chlorine). The production of VCM from EDC accounts for more than 55% of the total formation of HCl. Other sources of HCl are the production of (all in kMt chlorine):

- potash fertilizer: 278 kMt (5%)
- MDI: 268 kMt (5%)
- TDI: 259 kMt (4%)
- chloromethanes: 213 kMt (4%)
- hypo: 115 kMt (2%)
- allyl chloride: 72 kMt (1%)
- incineration of light/heavy ends: 153 kMt (3%)
- other known sources: 199 kMt (3%)

Ayres & Ayres (1996) estimated that next to the sources mentioned above another 1054 kMt of HCl (21%) will be produced by *other chains and processes.*

6.4.3.2 Use of HCl

The most important use of HCl is the production of EDC via oxychlorination of ethene. This process accounts for more than 70% of the use in chemical (3482 kMt Cl). Other applications of HCl in the chemical industry are:

- production of chlorine: 211 kMt (4%)
- production of methyl chloride: 134 kMt (3%)
- production of propylene oxide: 17 kMt (0 %)
- production of PVC: 8 kMt (0%)
- production of glycerin: 5 kMt (0%)

Ayres & Ayres estimated that 1054 kMt (21%) was used in *other chains and processes.* The difference between the formation of HCl and the use of HCl is 863 kMt which is used in other sectors.

6.4.4 Chlorinated C1-derivates from the cradle to the grave

A chlorine balance for the C1-derivates is given in Figure 15 at the end of this Chapter. Chlorine flows into the C1-derivates production in Cl_2 ,HCl and Light and Heavy ends (waste products of chlorination processes). There is a net production of HCl and a net consumption of Light and Heavy -ends in this vertebra. Less than half of the chlorine input flows to the market in chlorinated products where net export occurs. This leaves 413 kMt chlorine in C1-derivates to be used in applications. The largest part of products consists of solvents (DCM, chloroform and tetra) and (H)CFCs. Around three quarters of the inflow will be emitted to air. The rest is partly accumulated in economic stock ((H)CFCs) and partly treated as chemical waste (solvents).

6.4.5 Chlorinated C2-derivates from the cradle to the grave

A chlorine balance for the C2-derivates is given in Figure 16 at the end of this Chapter. In terms of chlorine throughput the C2-derivates vertebra is by far the most important. Large amounts of chlorine flow into this sector in Cl_2 and HCl. There is a net consumption of HCl and a net production of Light and Heavy ends in this vertebra. Less than half of the total chlorine inflow goes to the market as chlorinated products where a small net export occurs. The most important single product is of course PVC. The other products are chlorinated solvents: 1,1,1-tri, Per and Tri. These solvents are used in applications where more than 80% is emitted to air (excluding internal recycling). The rest ends up the chemical waste and emissions to water.

PVC is used in several applications. In general the PVC can be divided into two types: rigid and flexible PVC. Rigid PVC is mostly used as a construction material and in packaging.

Flexible PVC is produced by adding large amounts (up to 50%) of plastisisers and can be used in flooring, coatings etc. A distribution of PVC over the different applications in Western Europe is given in Figure 13 and Figure 14.

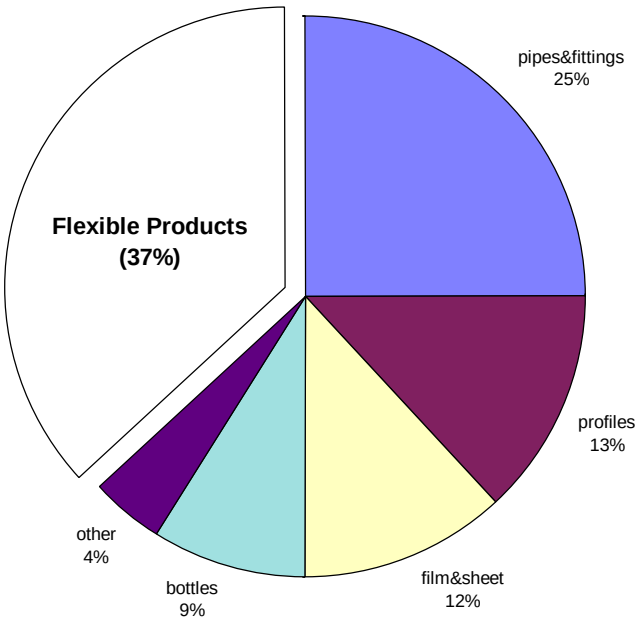

Figure 13: Applications of rigid PVC in Western Europe, (Norsk Hydro, 1992)

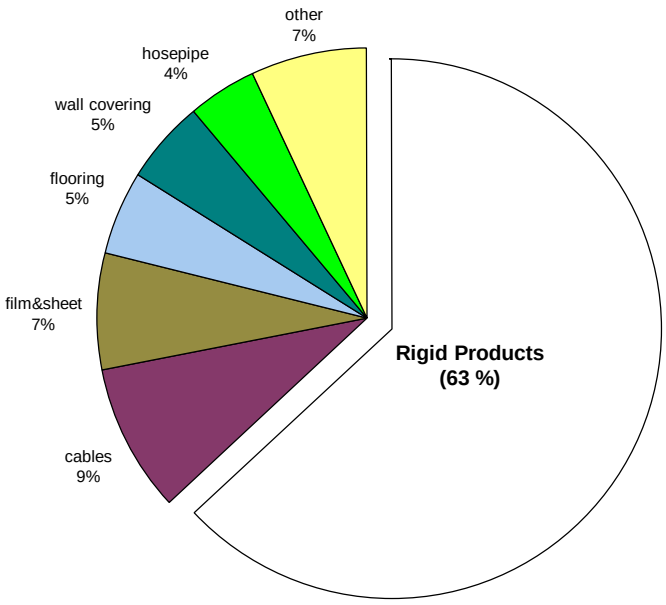

Figure 14: Applications of flexible PVC in Western Europe (Norsk Hydro, 1992)

PVC used in construction applications, especially pipes, will remain in the anthroposphere for as long the life span of the constructions (50-100 years). Applications such as wall paper and flooring have much shorter life span (less than 10 years). PVC used in packaging has a life span of less than 1 year. The PVC which is used in construction at this moment will be turned into waste after a number of decades. At this moment only minor amounts of PVC are found in building waste because the use of PVC in construction has started only a few decades ago and has risen sharply since then. Therefore an important part of the PVC that goes to applications at this moment will accumulate in the anthropospheric (economic) stock. From the PVC going into waste treatment around two third will be landfilled. One third will be incinerated (EEA, 1995), most of the chlorine ending up as chloride.

6.4.6 Chlorinated C3-derivates from the cradle to the grave

A chlorine balance for the C3-derivates is given in Figure 17 at the end of this Chapter. Chlorine flows into this sector in Cl_2 and some HCl. There is a net production of HCl and a net production of Light and Heavy ends in this vertebra. There are no chlorinated products produced in this vertebra that find their way to the applications. Most of the chlorine is transformed to chloride during the production of propylene oxide, ECH, epoxy resins and glycerin.

6.4.7 Chlorinated >C4 and higher non-cyclic derivatives from the cradle to the grave

A chlorine balance for the >C4-derivates is given in Figure 18 at the end of this Chapter. Chlorine flows into this sector as Cl_2 . There is a net production of HCl in this vertebra. Less than half of the total chlorine inflow goes to the market as chloroprene rubber where a small net import occurs. The life span of chloroprene is unknown. It is assumed that most of the chloroprene will accumulate in the anthropospheric stock.

6.4.8 Chlorinated aromatics from the cradle to the grave

A chlorine balance for the chlorinated aromatics is given in Figure 19 at the end of this Chapter. Chlorine flows into this sector as Cl_2. There is a net production of HCl in this vertebra. The produced chlorobenzenes are used in the production of pesticides, pharmaceutics, dyes etc. partly as feedstock and partly as solvent and is assumed to be transformed elsewhere.

6.4.9 Phosgene from the cradle to the grave

A chlorine balance for the phosgene-derivatives is given in Figure 19 at the end of this Chapter. Chlorine flows into this sector in Cl_2 and some HCl. Most of the chlorine which flows into this vertebra is transformed to HCl during the production of TDI and MDI

(intermediates for the production of polyurethane foams) and to chloride salt in the production of MDI and polycarbonate (PC).

6.4.10 Hypochlorite from the cradle to the grave

A chlorine balance for the hypochlorite is given in Figure 20 at the end of this Chapter. Chlorine flows into this sector in Cl_2 . Less than half of the total chlorine inflow goes to the market as hypochlorite. The other half is transformed to HCl during the production. Hypochlorite is used as a disinfectant in households, swimming pools, the preparation of drinking water, industrial cooling systems. During the use of hypochlorite it is largely transformed to chloride. Because hypochlorite is an active form of chlorine it will react with organic material and partly chlorinate this material. Formation of volatile chlorinated hydrocarbons is known to occur in swimming pools.

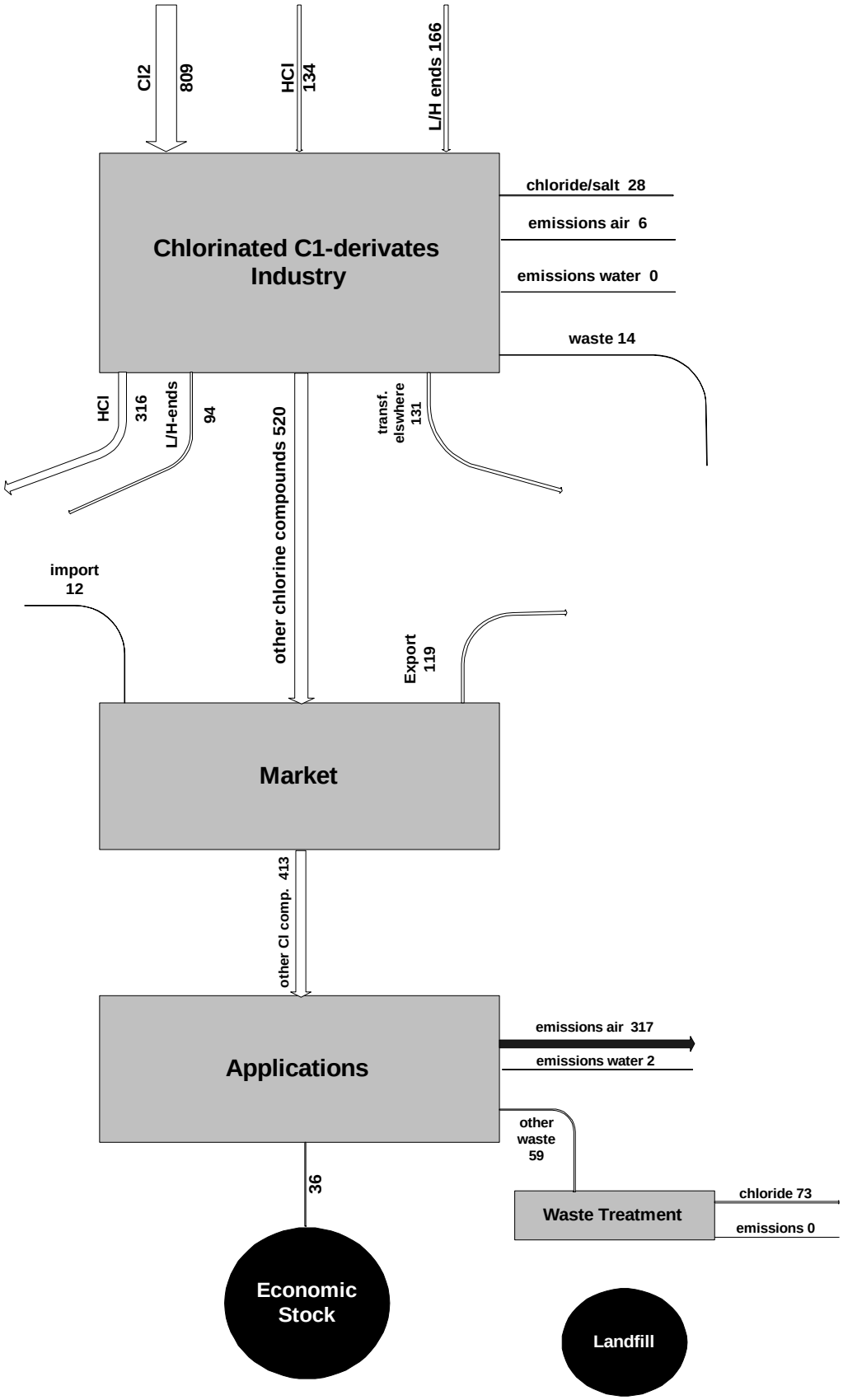

Figure 15: A chlorine balance for C1-derivates , Western Europe, 1992 (kMt Cl)

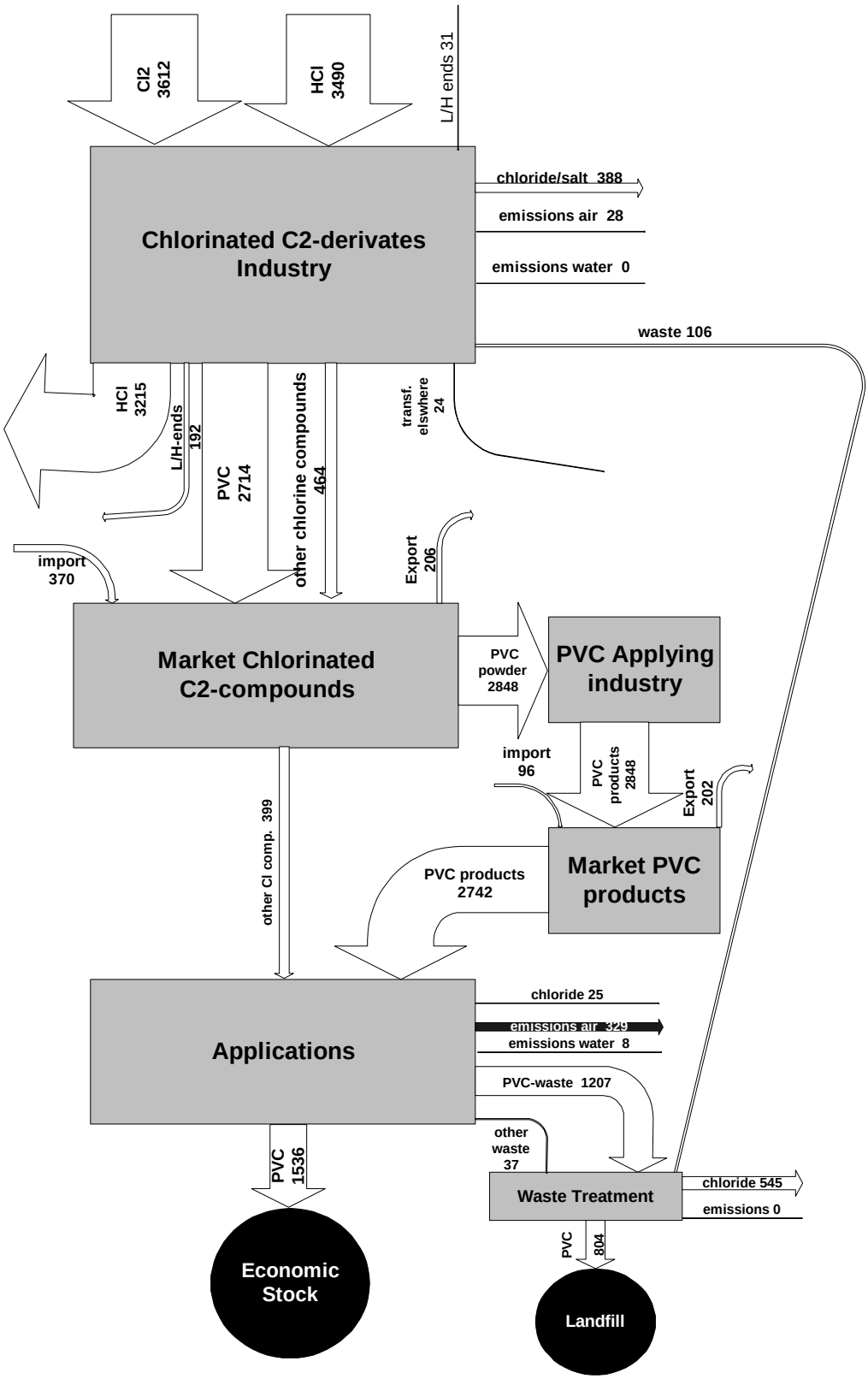

Figure 16: A chlorine balance for C2-derivates, Western Europe, 1992 (kMt Cl)

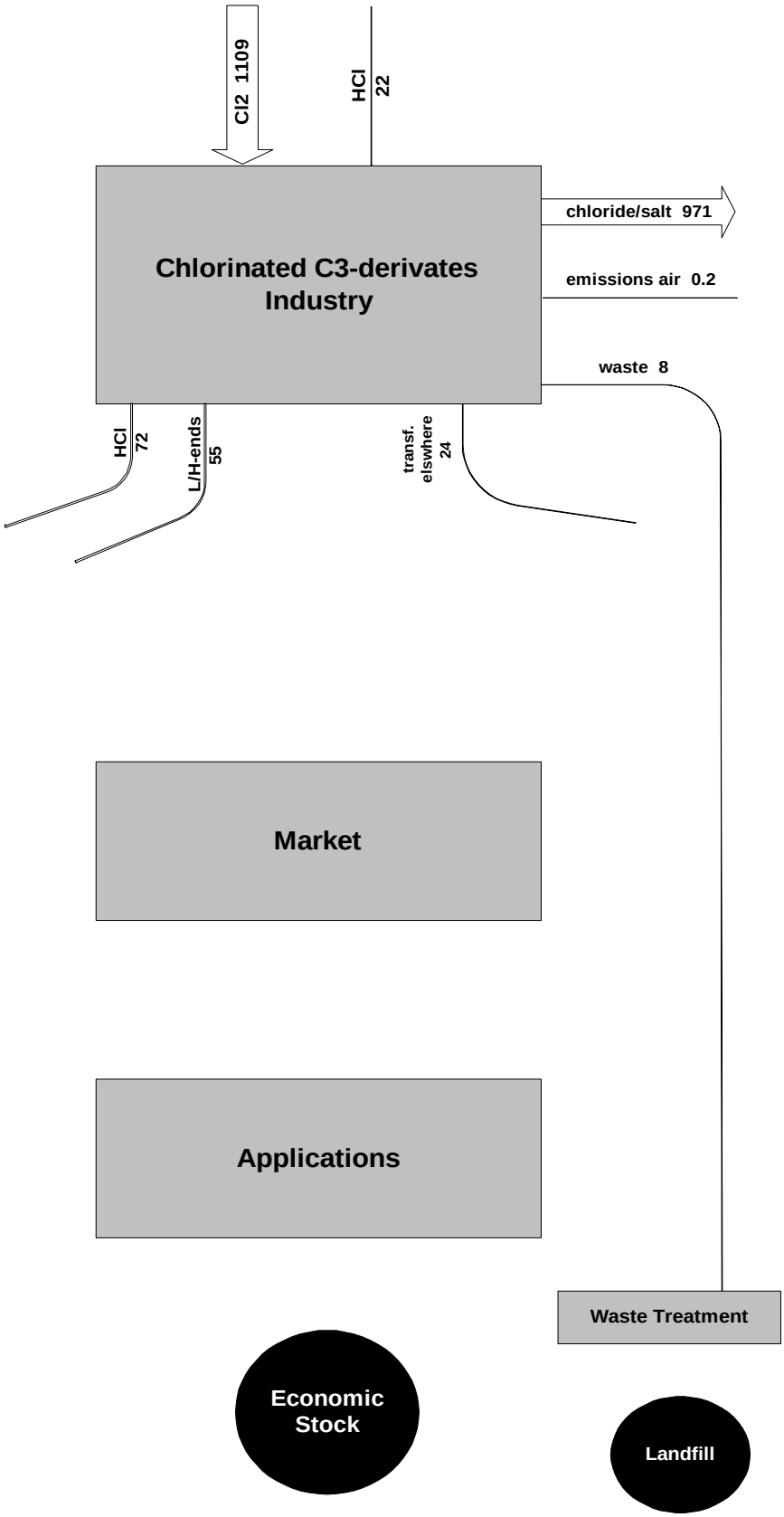

Figure 17: A chlorine balance for C3-derivates, Western Europe, 1992 (kMt Cl)

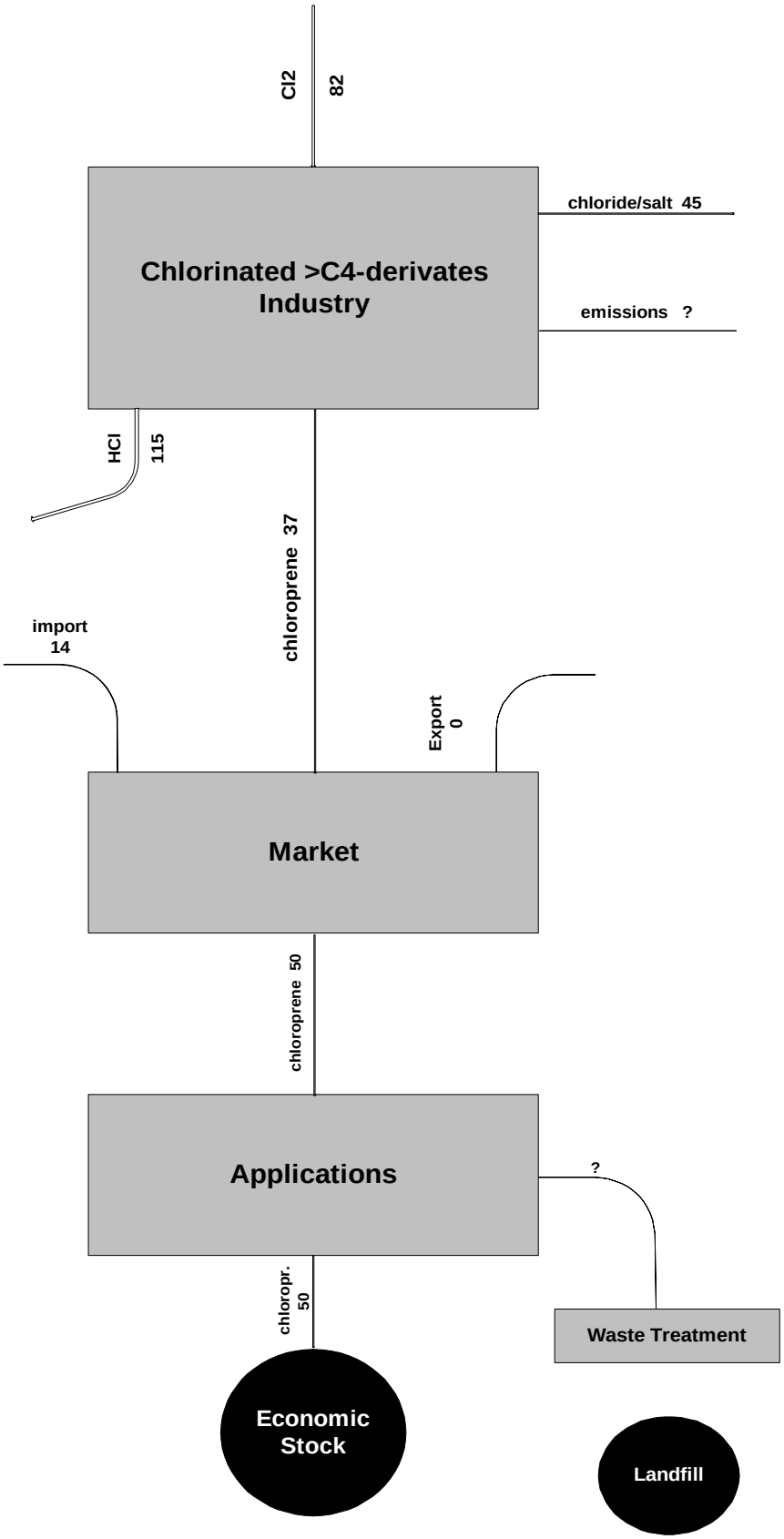

Figure 18: A chlorine balance for >C4-derivates, Western Europe, 1992 (kMt Cl)

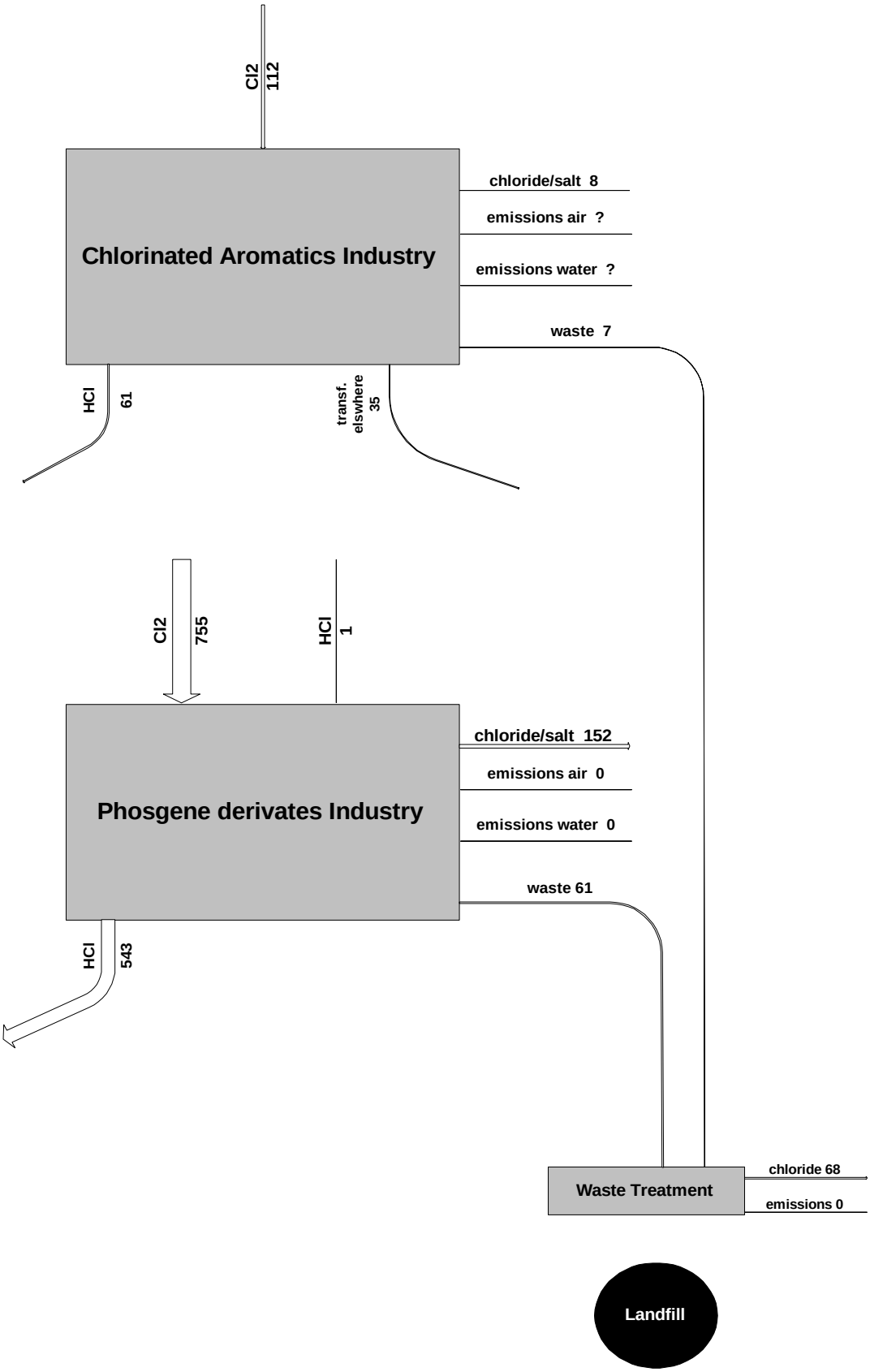

Figure 19: A chlorine balance for chlorinated aromatics and phosgene derivatives, Western Europe, 1992 (kMt Cl)

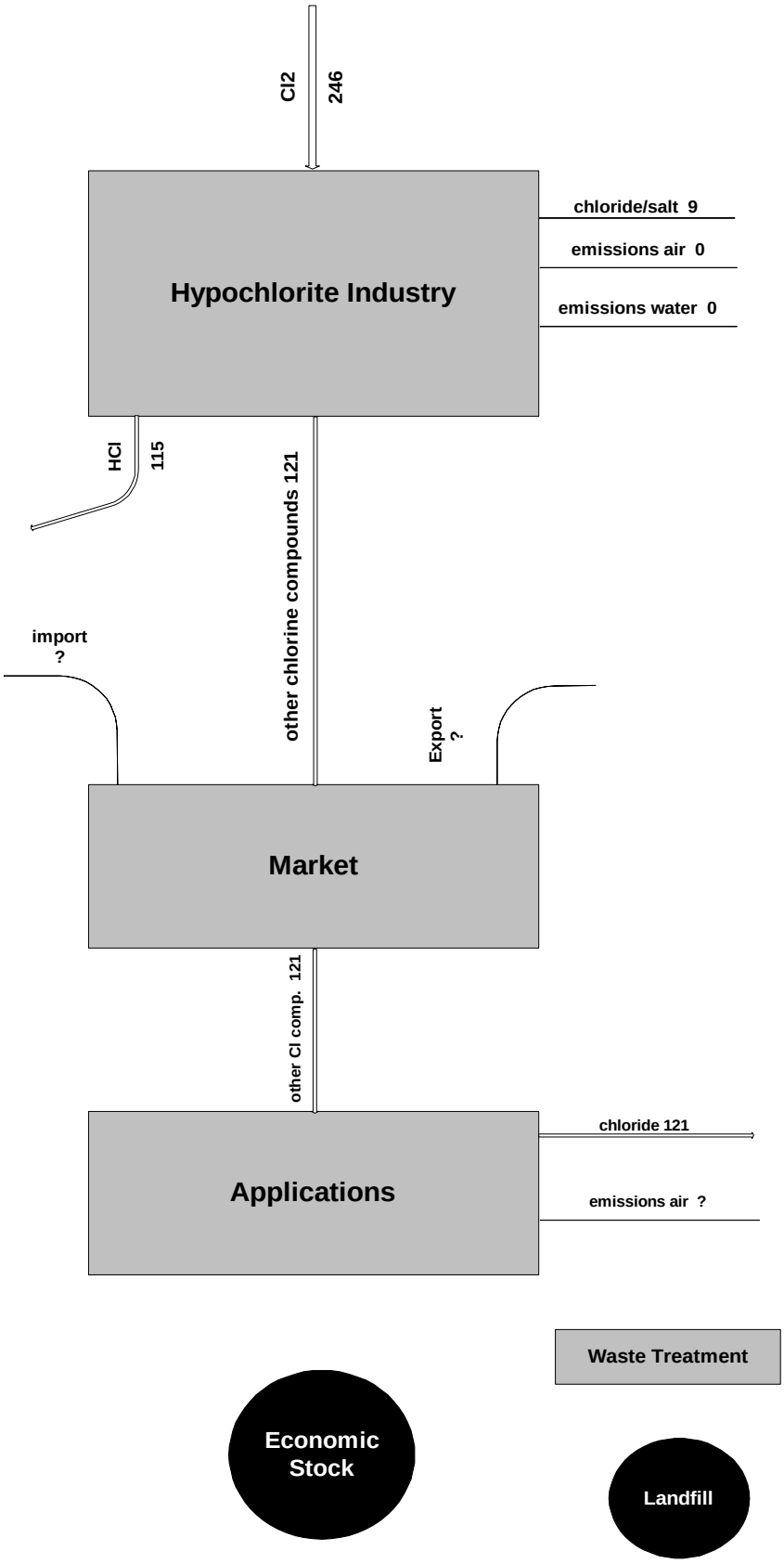

Figure 20: A chlorine balance for Hypochlorite, Western Europe, 1992 (kMt Cl)

6.5 Modeling of PVC stocks in Sweden

As described in paragraph 0 the outflow (output signal) of a material in a certain year depends on both the inflows in the years before and the lifespan distribution. In this paragraph we describe the main results of a test in which we used PVC in Sweden as an example. In this test, stock modeling was used to estimate future waste flows on the basis of a minimum amount of data. The one figure known for Swedish situation was an estimated stock in different products in 1994 (Tukker et al., 1996; Tukker et al., 1997a). This stock 1994 can be a result of different types of stock building. Five different examples are discussed in this paragraph:

- the simplest assumption would be a constant inflow since the introduction of the different products together with an exact known lifespan of these products;
- another possible inflow curve would be the result of linear increasing inflow, again combined with an exact known lifetime;
- a third possibility would be an exponential increase since the introduction of the products combined with an exact known lifespan;

To show the influence of adding a normal distribution to the lifespan a fourth and fifth model were generated:

- a combination of the first model (constant inflow) with a discretisized normal distribution used for the lifespan
- a combination of the second model (linear increase) with a dicretisized normal distribution used for the lifespan

In Figure 21 the results of the five models are shown. All outflows are a combination of the outflow of the three main products: pipes, flooring and cables. Just for the sake of this example it was assumed that the use of each of these products would linearly decrease to zero from 1995 to 2010 as a result of some phasing out policy. Because the use of every product started at a different point in time and because the lifespan is different for each product the form of the outflow curves is much more complex than one would expect on the basis of the outflow curve of every single product. From Figure 21 it can be concluded that predicted waste flows are quite similar for a constant inflow and a linearly increasing inflow. This is even more true when the curves are smoothened by adding a discretisized normal distribution for the lifespan. The exponential curve, however, gives peaks, which are very much higher than the other models. A preliminary conclusion from this exercise could be that it is important to know whether the inflow has been increasing more than linearly in the past e.g. in the case of products belonging to a fashion like certain types of PVC clothing. This may be more important than having exact time series data on past inflows.

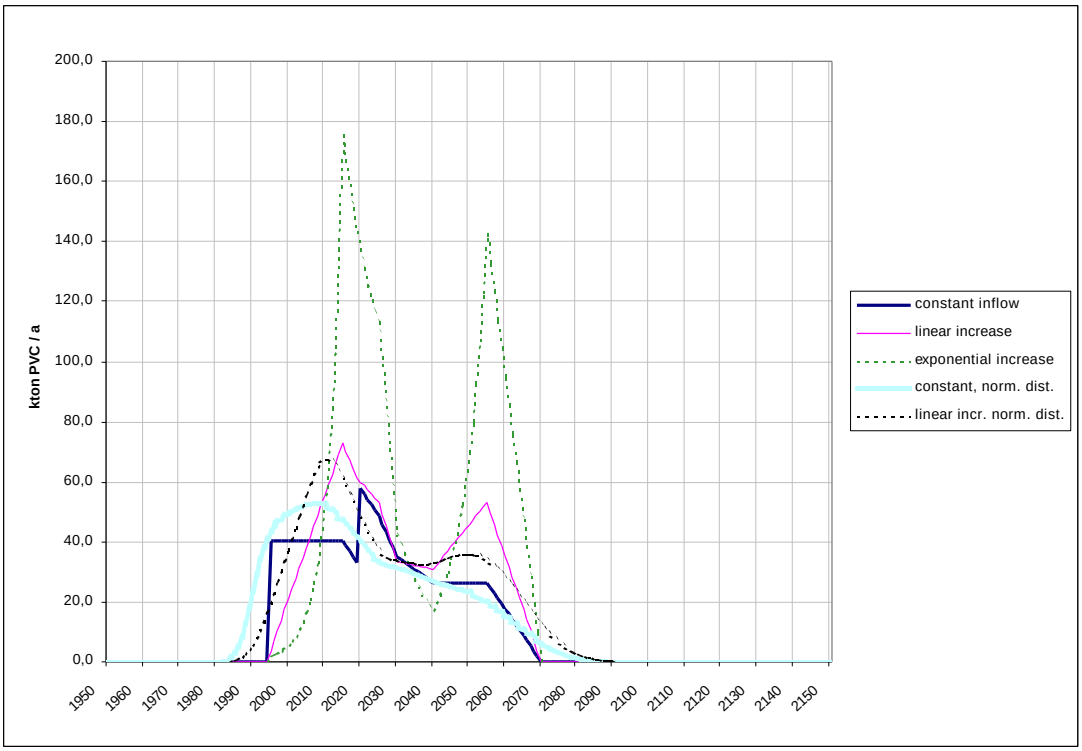

Figure 21: PVC waste flows (outflow) from pipes, cables and flooring in Sweden calculated with different models for the consumption (inflow) and different lifespan distributions

6.6 Stock modeling for CFCs in the world

CFCs have been used in a large number of applications. The best-known applications to the public are the use as propellant in spray cans and the use in refrigerators. However CFCs have also been used in the industry as solvent and cleaning agents and as a blowing agent in different types of foams. Important applications of these foams are as isolating material in the building sector and in refrigerators. In fact most of the CFCs in refrigerators are incorporated in the isolating foams. CFCs are thus only partly used in applications which immediately lead to emissions (propellants and solvents) in the other types of use there will be delayed emission. Emissions from the latter applications can be expected during the use of the products and during waste processing. Just as in the case of PVC the outflow curve (in this example emission) is dependent on the inflow curves and the lifespan distribution of the products. For CFCs in foam the situation is a little more complex because there is a diffuse emission when the foams are in use, an emission of CFCs when the products (mostly buildings) in which the foams are used are being demolished and, if the waste is landfilled, there will be a diffuse emission from the waste at these landfill sites. Thus the residence time of CFCs in the foam is not equal to the lifespan of the products.

In this example we used time series data of the production of CFCs in the world from 1950 to 1995 (Worldwatch Institute, 1996). In this database the amount used as propellant was specified. The distribution over the other applications was based on extrapolation of Dutch data. Average lifespans of the different products were estimated and a normal distribution was applied to this average lifespan.

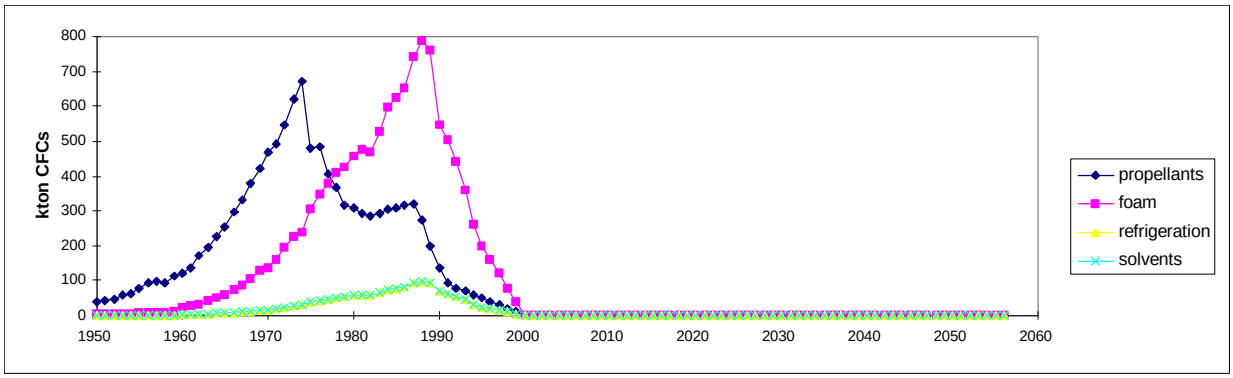

Figure 22: World use of CFCs in different applications (propellants plus total data, Worldwatch Institute, 1996; distribution over other applications calculated on the basis of Dutch data)

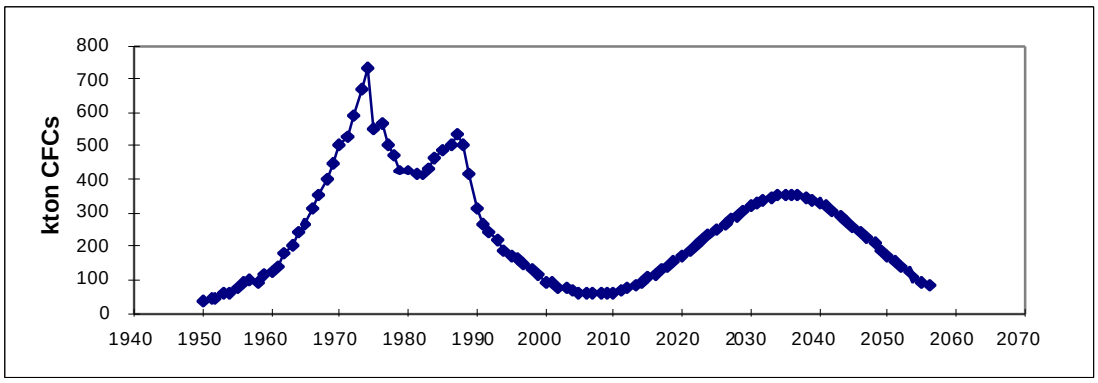

Figure 23: Calculated world emissions of CFCs

Figure 22 shows the results of the combination of the world production data, the data on use of propellants and the Dutch distribution over the other applications. Figure 23 shows the calculated total emissions of CFCs. It was assumed that the CFCs used in solvents and propellants were emitted in the same year as they were produced. The average lifespan for CFCs in refrigeration was estimated to be 10 (sd 2 years) years. In building foams it was estimated to be 50 years (sd 10 years) (a combination of lifespan of buildings and the diffuse emissions during use). The emission curve shows three peaks: one at the peak of the use of CFCs as propellants (1974), one as a combination of the starting use of CFCs in building foams and a reviving propellant use (1987) and one as a result of a delayed outflow from

foams used in the building industry (2036). This means that even after a complete phase-out we may expect a CFC emission peak, dying out only after 2050 unless additional measures are taken to avoid the emission of CFCs from insulation foam during the demolition of buildings. Although these calculations are based on a number of very rough assumptions it indicates that further research into this topic is needed. In a combined effort RUL.CML and TUW.IWAG will write a paper on this subject.

6.7 Incorporation of chlorinated micropollutants in a chlorine MFA

In the discussions around the use of chlorine and chlorinated compounds chlorinated micro-pollutants are one of the key points. When one looks at toxic compounds that pose problems at a global scale one will find that many of these compounds are chlorinated. Well-known examples are PCBs, dioxins, DDT, drins, toxaphene and chlorodane. It is important to make a distinction between three groups of compounds:

1. pesticides, which are emitted on purpose with a certain functionality
2. compounds like PCBs which have a functional use but are not emitted on purpose
3. compounds like dioxins which are emitted as byproducts of certain processes

In the last two decades the production and use of the first two types compounds have been regulated quite strictly. Most of the *old generation* organochlorine pesticides such as DDT, drins and lindane have been banned in the western world, although some of them are still used in developing countries. The production of PCBs has also been banned although there is still a large amount in use in closed applications. The emissions of dioxins have been reduced drastically in the western world due to the banning of uncontrolled burning of waste products and the installation of flue-gas treatment facilities in waste incineration plants. However, it is important to notice that although all these measures mentioned above are in active there these compounds are still found in organisms in very high concentrations (especially in arctic areas). An important question which remains is whether we are still unknowingly emitting other persistent compounds with bioaccumulating and toxic potential. In other words *are we emitting the dioxins of the future right at this moment ?*

In some publications the property of chlorine to change easily from one molecule to another (the reactivity of chlorine and its compounds) is believed to be a reason to ban chlorine as a starting material for the chlorine industry (Muir et al., 1993). The environmental movement subscribes this opinion. The chlorine industry, however, states that actions should be aimed only at those processes and products which pose a proven risk to humans or ecosystems.

One of the main knowledge gaps we found in an MFA for chlorinated substances in the Netherlands was the possible emissions of chlorinated micropollutants (Tukker et al., 1995; Kleijn et al, 1997; Tukker et al., 1997b). Well known substances like dioxins are well monitored and emissions of these compounds are therefore well known. However, not all of the AOX in effluents of processes in which chlorine is used can be explained by the emissions of known components. Thus an emission remains of unknown compounds with unknown effects. This uncertainty can be dealt with in different ways. One might start an comprehensive monitoring program focussed on identifying individual compounds in these effluents coupled to research to determine the persistency, bioaccumulative potential and toxicity of these compounds. A different approach would be to skip the step of identification and start testing the whole effluent for persistency, bioaccumulative potential and toxicity (the *total effluent* approach). Both approaches need a considerable amount of research. It is clear that identifying the thousands of different compounds in the AOX mixture is not so easy. Therefore the total effluent measurements might seem a good alternative. The problem with this latter approach is that it requires a completely new set of measurements that have to be developed via fundamental research before it can be put to practical use.

The question still remains how such a complex subject on which so little data is available can be dealt with in MFA. One way of tackling this problem would be to make a sensitivity analysis in which the toxicity of the certain known chlorinated micro-pollutants (e.g. 2,3,7,8-TCDD) are used to express toxicity for the unknown emissions. In this way worst, average and best case scenarios can be made.

7. Conclusions

7.1 Flows and stocks of chlorine in Western Europe

In this MAc TEmPo case study an overview of flows of chlorinated compounds within Western Europe is given together with the emissions of these compounds to the environment. On the basis of earlier studies on flows of chlorine in the Western European industry and extrapolated data from national studies on applications and emissions it was possible to get a rough overview of flows of chlorinated compounds from the cradle to the grave. From this overview a number of conclusions can be drawn:

- almost half of the chloride which flows into the chlorine chain is emitted again as chloride salts during the production of chlorinated and non-chlorinated compounds, the application of chlorinated compounds and incineration of chlorinated wastes
- around 18% of the chloride inflow accumulates in the anthropospheric stock (94% PVC)
- 95% of all emissions of chlorinated hydrocarbons occur during the application phase and only 5% during production
- PVC is by far most important single application of chlorine, 65% of the total amount of chlorinated hydrocarbons that is used
- chlorinated solvents account for another 17% and the direct use of chlorine in paper&pulp industry and water treatment for some 12%
- the amount of chlorinated hydrocarbons in final waste flows is about 17% of the chloride inflow (76% PVC, 24% chemical waste from production and applications)

PVC is an important product within the chlorine industry, not only because it accounts for 65% of all chlorinated compounds which enter the applications, but also because HCl can be used to produce PVC. HCl is produced during the production non-chlorinated compounds from chlorinated starting materials (e.g. polyurethane's) and during the incineration of chlorinated compounds (e.g. wastes from processes within the chlorine industry).Thus PVC is not only the biggest single product of the chlorine industry, it also permits the production of other products because it processes the wastes produced during their production processes. It is important to note this link between PVC and the rest of the chlorine industry when discussing policy measures focussed on (partly) banning PVC.

A number of problemflows connected to methodological problems were identified and studied in more detail: emissions and waste from stocks of PVC and CFCs and emissions of chlorinated micropollutants.

From the study of stocks of PVC in Sweden it is clear that even if we stop using PVC within the next 10 years the PVC waste flows will remain until the edge of the 22nd -century. From a methodological point of view it is shown that very simple models can be used to show the importance of certain problemflows.

From the study of stocks of CFCs in the world it can be concluded that the emissions of CFCs will remain until around 2060, even if the use in developing countries would decrease just as the use in the developed countries (which seems very unlikely at this moment). It should be noted that the results for CFCs are based on first assumptions on the distribution of CFCs over different applications and on the lifetime of CFCs in different goods. Further investigation in this subject is planned together with the TUW.IWAG.

From the study of chlorinated compounds in the Netherlands it is clear that the emissions of chlorinated micro-pollutants are an important gap in the current knowledge. A number of routes to close this gap are discussed and will be further discussed within the framework of the BITAC: the steering committee assembled by the Dutch Ministry of Environment to follow the policy actions which resulted from the Dutch Chlorine chain study.

In both the Dutch Chlorine Chain study (Tukker et al, 1995; Kleijn et al., 1997), the Swedish PVC study (Tukker et al., 1996; Tukker et al., 1997) and in the MAc TEmPo case study of flows of chlorinated compounds in the Western Europe it was found that MFA can be a powerful decision supporting tool to focus a complex discussion on important problemflows. However, in every policy decision certain uncertainties will remain. MFA can be an important aid to help reduce these uncertainties by providing structured data but in the end policy makers will have to find a way to cope with remaining uncertainties. However, one might argue that making decisions in situations where there is a certain amount of uncertainty left is typically the job of policy makers and that the job of the scientists would be to minimize these uncertainties.

7.2 Policy implications of the study of European chlorine flows

In this study an overview was created of flows of chlorinated compounds in Western Europe from *the cradle to the grave*. The production of PVC is by far the most important single product in the chlorine chain. Next to that an important amount is used for the production of products which do not contain chlorine themselves like propylene oxide, polyurethane's and polycarbonate. Another important type of products are chlorinated solvents, although the use of these solvents is more and more restricted. Based on figures for the Dutch situation the biggest emissions come from the applications of chlorinated products, especially solvents. Emissions from production sites have been reduced drastically the last decades. Although the emissions from the production sites are small in terms of mass, they can still be important from an environmental point of view. There is still the possibility that unknown bioaccumulating, persistent and toxic chlorinated micropollutants

are emitted. Although MFA is better suited for quantifying bulkflows, methods should be developed to incorporate these small flows, such as indicated above. Policy makers should be aware of the large amount of interconnections between the different processes and products within the chlorine industry. One of the most important connections is that between the production of HCl as a byproduct in many processes in the chlorine industry, including the incineration of chemical waste, and the use of this HCl in the production of PVC. A ban on PVC would cause a large surplus of HCl which would become a waste product. Thereby a ban on PVC could also be the end of many other products from the chlorine industry.

The results of the examples of stock modeling for CFCs and PVC have some important policy implications. First of all it is clear that stock formation can reduce the effect of source oriented policy measures to large extent: although very strict regulations are in place to reduce the production and use of CFCs, the emissions from stocks in the anthroposphere will remain for another two decades. In the case of PVC there is much discussion going on at this moment about the possibilities to recycle PVC. However, the amount of recycling is only marginal compared to the amount of PVC still in stocks in the anthroposphere. Because recycling is only marginal at this moment it is hard to assess whether the much bigger waste flows of the future can really be handled via recycling. If we would find out in the next couple of years that PVC-recycling is not an environmental sound option for PVC waste treatment we policy measures focussed on reducing the PVC input will have effects only after 10-50 years. Another important example of how stock building can reduce the effects of policy measures is the use of PCBs. Although the production of PCBs was banned decades ago there is still a large amount of PCBs in use at this moment (mostly as cooling/insulation liquids in transformers). Policy makers should be made aware of the fact that stock formation can be an indicator for future problems.

The question whether or not a ban on the use of chlorine in the chemical industry or a part of it would be a good thing for the environment can not be answered on the basis of this study. There are still some important problems left within the chlorine industry and the applications of its products. Especially the subject of chlorinated micropollutants should be investigated. However, it is not clear that a substitution of the chlorine industry with other chemical production processes would cause less environmental problems. One of the things that should be taken into consideration when discussing a reduced input of chlorine in the chemical industry is the link between the production of chlorine and the production of caustic soda (NaOH) (Kleijn et al, 1993).

The authors believe this study can be used to focus the attention on the dirty spots in the chlorine chain.

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Appendix 1

List of used abbreviations

1,1,1-tri	1,1,1-trichloroethane
1,2-DCE	1,2-dichloroethane
AC	allyl chloride
C1	the group of hydrocarbons with 1 carbon atom (methane derivates)
C2	the group of hydrocarbons with 2 carbon atoms (ethane derivates)
C3	the group of hydrocarbons with 3 carbon atoms (propane derivates)
C4	the group of hydrocarbons with 4 carbon atoms (butane derivates)
>C4	the group of lydrocarbons with more than 4 C atoms (non cyclic)
CaCl2	calcium chloride
CFCs	chlorofluorocarbons
Cl2	elementary chlorine
CML	Centre of Environmental Science, Leiden University
CO	carbon monoxide
DCM	dichloromethane
EC	European Union
ECH	epichlorohydrin
EDC	1,2-dichloroethane
EDC(oxy)	oxychlorination production process for 1,2-dichloroethane
EDC(direct)	direct chlorination production process for 1,2-dichloroethane
EU	European Union
GNP	gross national product
HCFCs	hydrogen chlorofluorocarbons
HCl	hydrogen chloride, hydrochloric acid
hypo	hypochlorite
KCl	potassium chloride
L/H ends	Light and Heavy ends, chemical waste recycled in the chemical industry
MCPA	4-chlorine-2-methyl-phenoxyhydrochloric acid
MCPP	4-chlorine-2-methyl-phenoxypropionic acid

Appendix 1 continued

MDI	4,4'-diphenylmethane diisocyanate
NaCl	sodium chloride, common salt
NaOH	caustic soda
PC	polycarbonate
PCBs	polychlorinated biphenyls
Per	perchloroethylene
PO	propylene oxide
PTFE	polytetrafluoroethene
PUR	polyurethane's
PVC	polyvinylchloride
SFA	substance flow analysis
SFINX	substance flow internodal exchange (computer model)
TDI	toluene diisocyanate
TiO2	titanium dioxide
TNO	Netherlands Organization for Applied Scientific research
Tri	trichloroethylene
VCM	vinylchloride (monomer)
VDM	vinylidene chloride
WE	Western Europe

Appendix 2

More detailed explanation of flows in Figure 5, the chlorine balance.

NaCl/KCl/CaCl2	9297
NaCl to CL2-prod	8937
KCl to HCl prod	281
CaCl2 to Cl2 prod	79
chloride/salt	2730
from I/O table	2730
emissions	34
total air emissions	34
total water emissions	0
waste	270
+total non chloride waste&emissions	304
-total emissions	34
HCl	862
surplus HCl I/O table	862
PVC to market	2714
surplus PVC I/O table	2714
Other chlorine compounds to market	1646
DCM	195
Per	180
1,1,1-tri	158
chloroform	121
Sodium Hypochlorite	115
Tetra	104
Tri	101
CFCs	77
Chloroprene	37
EDC	25
HCFC 22	23
Calcium Hypochlorite	6
chlorine to direct applications	504
transformed elsewhere	214
Methyl Chloride	131
MCB	29
VDC	13
chloroacetic acid	11
TCP	10
Chloroethers	8
AC	6
DCB	6
others/inorganic	832
other chlorinated I/O table	829
salt as product I/O table	3
Import	405
methylene chloride	8
chloroform	2
carbon tetrachloride	1
vinyl chloride	9
trichloroethylene	8
perchloroethylene	3
trichlorofluoromethane	0.0
dichlorodifluoromethane	0.1
trichlorotrifluoroethane	0.4
dichlorotetrafluoroethane	0.0
chloropentafluoroethane	0.0
chloroprene, latex	1
chloroprene, primary	13
subtotal	45
PVC-powder	264
PVC products	96
subtotal	360
Export	527
methylene chloride	33
chloroform	38
carbon tetrachloride	24
trichloroethylene	22
perchloroethylene	54
trichlorofluoromethane	10
dichlorodifluoromethane	10
trichlorotrifluoroethane	3
dichlorotetrafluoroethane	0
chloropentafluoroethane	0
chloroprene, latex	0
chloroprene, primary	0
subtotal	195
PVC-powder	130
PVC products	202
subtotal	332

PVC to applications	2742
+PVC to market	2714
+PVC import	360
-PVC export	332

other cl. compounds to applications	1496
+other cl. compounds to market	1646
+import other cl. compounds	45
-export othrer cl. compounds	195

PVC to economic stock	1536
PVC in pipes and fittings (25%)	686
PVC in profiles (13%)	357
1/2 PVC in other rigid (0.5 * 4%)	55
PVC in cables (9%)	247
PVC in flex film and sheet (7%)	192

PVC to waste	1207
PVC in bottles (9%)	247
PVC in rigid film and sheet (12%)	329
1/2 PVC in other rigid (0.5*4 %)	55
PVC in flooring (5 %)	137
PVC in wall covering (5%)	137
PVC in hosepipe (4%)	110
PVC in other flex (7%)	192

other cl compounds to stock	86
CFCs	27
chloroprene	50
HCFC 22	8

chloride from applications	650
chlorine in direct applications	504
Na- hypochlorite	115
Ca-hypochlorite	6
1,2-dichloroethane use as scavenger	25

emissions from applications	655	
	air	water
DCM	119	0.7
Per	108	1.2
1,1,1-tri	145	1.3
Methyl Chloride	0	0.0
chloroform	84	0.2
Tetra	73	0.8
Tri	76	5.4
CFCs	26	0.0
HCFC 22	14	0.0
	646	9.5

other waste from applications	103
DCM	50
Per	20
1,1,1-tri	12
chloroform	0
Tetra	15
Tri	5
CFCs	0
HCFC 22	0

PVC to landfill	804
2/3 of PVC to waste	804

chloride from waste treatment	775
1/3 of PVC to waste (incinerated)	402
Cl in waste from chem. industry (incinerated)	270
Cl in waster from applications (incinerated)	103

Appendix 3

Emissions of different chlorinated hydrocarbons in different applications, The Netherlands, 1990

Perchloroethylene

	Air	%	Water	%	Waste	%
metals/electronics industry	738	**89.5**	7.5	**0.9**	73.5	**8.9**
dry cleaning	1182	**78.8**	15	**1.0**	303	**20.2**
graphical industry	68	**94.4**	0	**0.0**	4	**5.6**
others	183	**90.1**	2	**1.0**	15	**7.4**
	2171	**83.5**	24.5	**0.9**	395.5	**15.2**

Dichloromethane

	Air	%	Water	%	Waste	%
metals/electronics industry	350	**57.7**	2	**0.3**	255	**42.0**
dry cleaning	20	**50.0**	0	**0.0**	20	**50.0**
pharmaceutical industry	552	**55.0**	12.5	**1.2**	440	**43.8**
foodstuffs (extraction)	35	**77.8**	10	**22.2**	0	**0.0**
chemical industry	2592	**64.8**	12	**0.3**	1396	**34.9**
paint removers	2329	**85.0**	0	**0.0**	411	**15.0**
adhesives	100	**100.0**	0	**0.0**	0	**0.0**
aerosols	132	**100.0**	0	**0.0**	0	**0.0**
others	327	**64.9**	1	**0.2**	176	**35.0**
	6437	**70.2**	37.5	**0.4**	2698	**29.4**

1,1,1-Trichloroethane

	Air	%	Water	%	Waste	%
metals/electronics industry	3426	**90.0**	38	**1.0**	343	**9.0**
paint	346	**90.1**	0	**0.0**	38	**9.9**
aerosols	87	**100.0**	0	**0.0**	0	**0.0**
adhesives/rubber	780	**100.0**	0	**0.0**	0	**0.0**
others	489	**90.1**	5	**0.9**	49	**9.0**
	5128	**91.6**	43	**0.8**	430	**7.7**

Trichloroethylene

	Air	%	Water	%	Waste	%
metals/electronics industry	629	**91.6**	5.2	**0.8**	52.7	**7.7**
dry cleaning	11	**76.1**	0.15	**1.0**	3.3	**22.8**
pharmaceutical industry	21	**84.0**	1.7	**6.8**	2.3	**9.2**
textile refinement	150	**75.0**	50	**25.0**	0	**0.0**
	811	**87.5**	57.05	**6.2**	58.3	**6.3**

Chloroform

	Air	%	Water	%	Waste	%
pharmaceutical industry	1	**100.0**	0	**0.0**	0	**0.0**
yarns/fibres	115	**100.0**	0.2	**0.2**	0	**0.0**
others	0	**0.0**	0	**0.0**	0	**0.0**
	116	**99.1**	0.2	**0.2**	0	**0.0**

CFC 11 (excluding stock formation and historical emissions)

	Air	%	Water	%	Waste	%
dry cleaning	11	78.6	0.2	1.4	2.8	20.0
aerosols	63	100.0	0	0.0	0	0.0
foam	1810	36.7	0	0.0	0	0.0
cooling	143	100.0	0	0.0	0	0.0
others	127	100.0	0	0.0	0	0.0
	2154	40.8	0.2	0.0	2.8	0.1

CFC 12

	Air	%	Water	%	Waste	%
household cooling	52.4	83.3	0	0.0	10.5	16.7
industrial cooling	489	100.0	0	0.0	0	0.0
sterilisation gas	56	100.0	0	0.0	0	0.0
aerosols	253	100.0	0	0.0	0	0.0
foam	115	100.0	0	0.0	0	0.0
	965.4	98.9	0	0.0	10.5	1.1

CFC 113

	Air	%	Water	%	Waste	%
metals/electronics industry	608	89.0	6.8	1.0	68.2	10.0
dry cleaning	72	79.1	1	1.1	18	19.8
aerosols	76	100.0	0	0.0	0	0.0
others	277	89.9	3	1.0	28	9.1
	1033	89.2	10.8	0.9	114.2	9.9

CFC 114

	Air	%	Water	%	Waste	%
foam	99	100.0	0	0.0	0	0.0
	99		0		0	

CFC 115

	Air	%	Water	%	Waste	%
industrial cooling	105	**100.0**	0	**0.0**	0	**0.0**
	105		0		0	

HCFC 142b (excluding stock formation and historical emissions)

	Air	%	Water	%	Waste	%
styrofoam	243	**23.9**	0	**0.0**	0	**0.0**
	243		0		0	

HCFC 22 (excluding stock formation)

	Air	%	Water	%	Waste	%
Industrial cooling	593	**46.7**	0	**0.0**	21	**1.7**
PUR-aerosol	363	**100.0**	0	**0.0**	0	**0.0**
other aerosols	198	**100.0**	0	**0.0**	0	**0.0**
	1154	**63.0**	0	**0.0**	21	**1.1**