

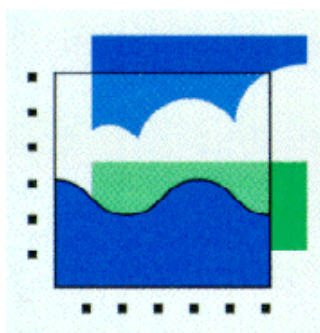
Chlorine in Western Europe

A MacTempo Case study

Summary report

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1 Objectives

1.1 General Introduction

Environmental pressure groups are campaigning for a total phase out of chlorine and its compounds, 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. Material Flow Analysis (MFA) can give discussions on environmental problems caused by material and substance flows a more factual basis (Udo de Haes et al., 1988; van der Voet 1996a; van der Voet 1996b; Baccini & Bader, 1996). In this study MFA is used to structure and aggregate information on flows of chlorine and its compounds through Western Europe, to identify problem flows and to discuss possibilities to reduce these problemflows.

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. Consumers buy chlorine 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 via bans or restrictions on the applications. 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 anthropogenic sources. Only a small fraction of these organochlorines can be identified. The uncertainties connected to the environmental impact of anthropogenic chlorine micropollutants are at present a major topic within the chlorine debate (Colborn et al., 1996).

1.4 Objectives and research questions

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.* The following subjects were treated:

- goal and systems definition
- 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
- elaboration of the problemflows from stocks of PVC and CFC in the anthroposphere
- describing possibilities to cope with the problem of chlorinated micropollutants
- discussion of policy implications and possible abatement measures

1.5 Case Study Region: Western Europe

By choosing the region one of the most important system boundaries is defined. The chosen region for the chlorine case study is Western Europe. The choice for Western Europe was based on the international context of the chlorine industry and the environmental policy and the transboundary nature of the environmental problems related to chlorine flows.

In Figure 1 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.

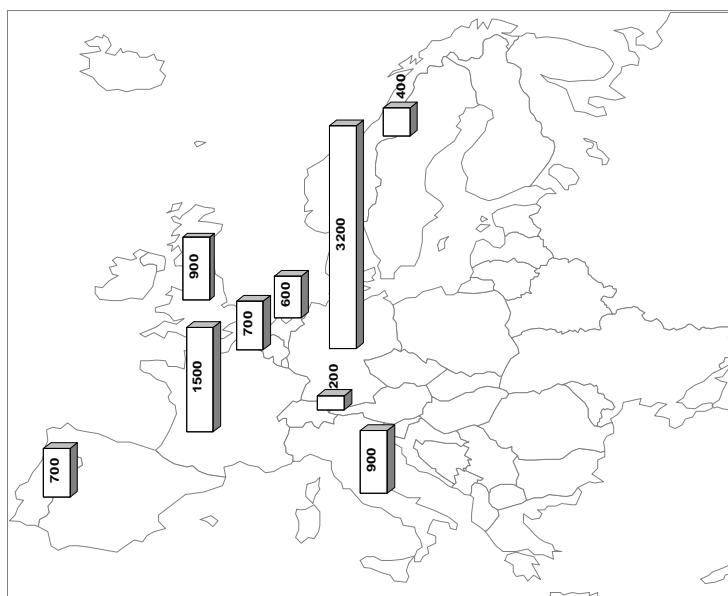


Figure 1: Chlorine production in Western Europe, 1994, kMt (Eurochlor, 1995)

2 Methodology

2.1 Selection of goods and substances

A motivation for choosing the group of chlorinated hydrocarbons as an object of this study is given in Chapter 1. All flows of elementary chlorine, chlorinated hydrocarbons and some important anthropogenic inorganic chlorine compounds are taken into account. A list of main substances in the chemical production processes is given in Figure 3. In Appendix 4a and Appendix 4b the main substances of which emissions are accounted for is given. One of the most important types of stockformation in MFA is the accumulation of substances in durable products. Examples are the use of metals in cutlery, pots and pans, and other 'normal' household products. PVC in the building sector and CFCs in refrigerators and foams were chosen to exemplify the importance of stocks in the anthroposphere on future problemflows..

2.2 Definition of processes

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.

2.3 Definition of system boundaries

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

2.4 Data sources for the European overview of chlorine flows

National and EuroStat statistics were found to be only of limited use for the chlorine case study in other cases statistical data has proven to be useful for Materials Accounting studies but previous chlorine studies on the national level showed important differences between the statistics and the data provided by the major industries (Tukker et al., 1995). Therefore data was used from earlier studies by others (Ayres & Ayres, 1996) and partly extrapolated to the Western European level from national Dutch data (Tukker et al., 1995). Import and Export data were taken from EuroStat statistics.

During the MacTempo process Ayres & Ayres finished a study that would prove an important basis for the chlorine case (Ayres & Ayres, 1996). In their report they quantified the bulk flows of chlorine and its compounds within the Western European chlorine industry. Next to these bulk flows 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 data sources, like Tecnon and Euro Chlor, representing the Chlor-Alkali industry. The authors reported important gaps in the data and many inconsistencies when comparing different data sources. Despite all the troubles they had the work of Ayres & Ayres proved to be an important data source for this study. The data of Ayres & Ayres was compared with data of other sources, mainly data provided by EuroChlor.

Data on the applications and emissions of these compounds was largely extrapolated from a national Dutch study of TNO and 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.

2.5 Data sources for stock dynamics

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.

2.6 Modelling substance flows

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 both as a bookkeeping system and a model. One general rule of mass balances is that the mass inputs of a process equal the mass outputs. This rule is of course derived from the 18th century Lavoisier's *law of conservation of mass*. SFINX is based on Lavoisier's law and can mathematically be described as a static/steady state model based on linear equations.

At present, SFINX users can:

- obtain an overview of all flows and accumulations 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.

At this moment no dynamic calculations can be performed. The model is therefore not suited for scenario analysis. Stock dynamics is important for future waste treatment and for current and future emissions of substances, which were banned earlier. In paragraph 2.7 a method is described to include stock dynamics in MFA.

2.7 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 MacTempo 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 changes 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 modelling of stocks we have chosen to adopt this approach which has been used before for example for modelling

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 than others. To get an accurate picture of stock formation and depletion the distribution of lifespan should be known. 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 MacTempo 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 discretized normal distribution¹. 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 (3.3) and CFCs in the (3.4). 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 IWAS.

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 chosen as an example of a known impulse response in the book of Baccini & Bader 1996.

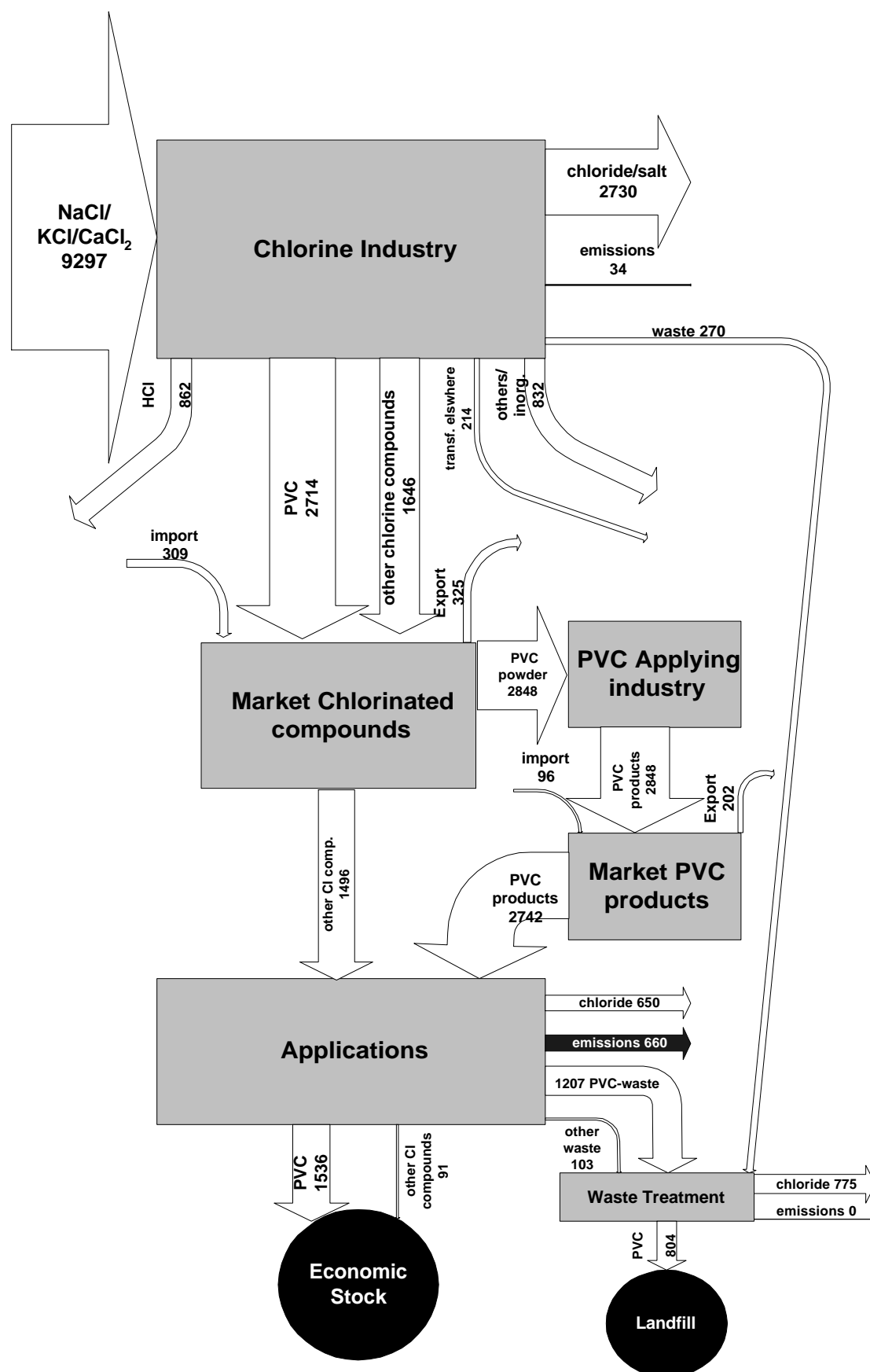


Figure 2: A chlorine balance for Western Europe, 1992 (kMt Cl).

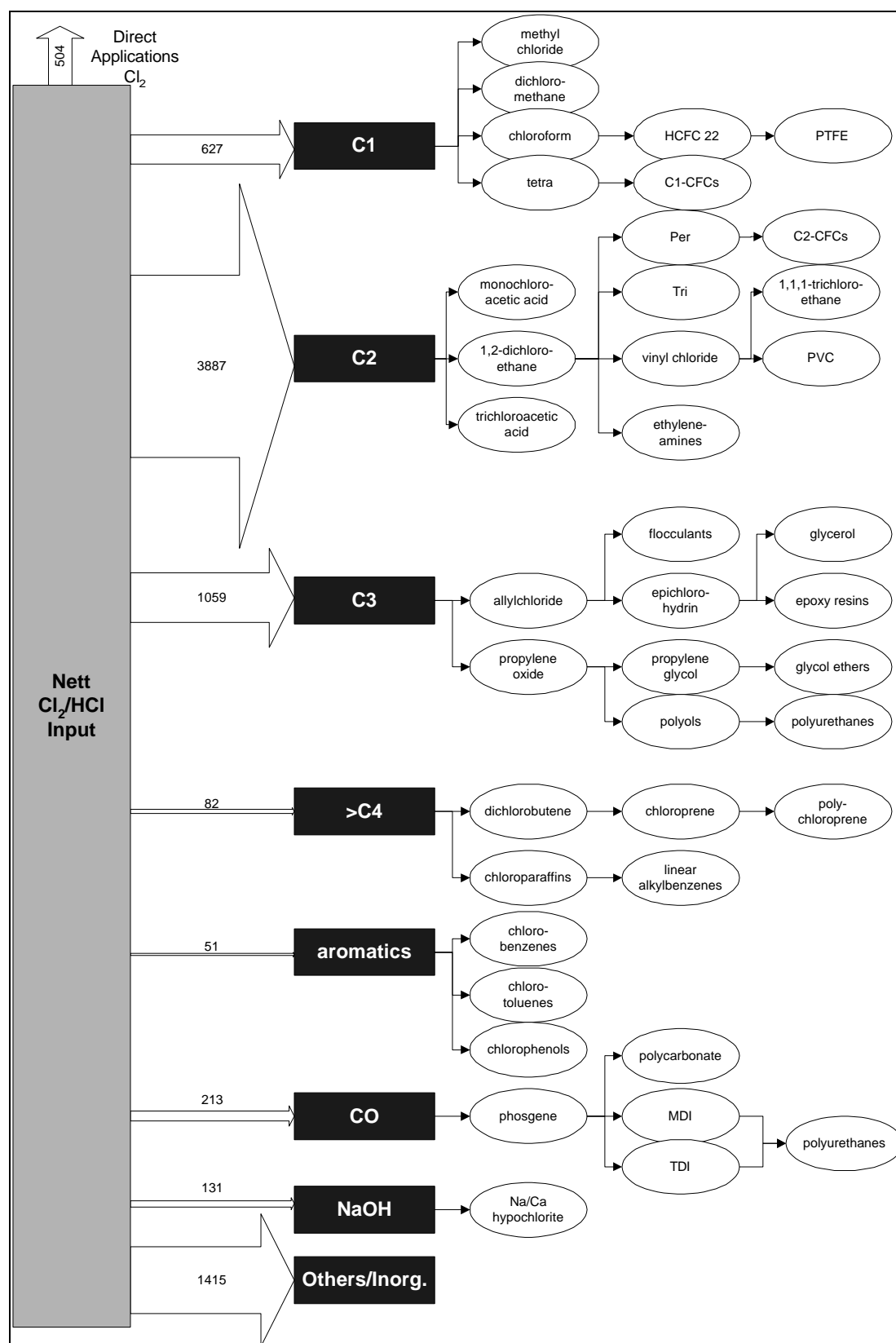


Figure 3: The Backbone of the Western European Chlorine Industry, black rectangles represent non-chlorine part which is combined with HCl or Cl_2 to produce chlorinated compounds. The chlorine input is calculated by adding the Cl_2 input and the HCl input and subtracting the HCl formation (quantities based on Ayres & Ayres 1996).

3 Main results obtained

3.1 A chlorine balance for Western Europe

In Figure 2 the flows of chlorine and its compounds through Western Europe is summarized. 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 hydrocarbons as products other than HCl. PVC is by far the most important single product of the chlorine industry. Another 10% are used in other industries as HCl and some 5% are used directly as elementary chlorine in the pulp&paper industry and in water treatment.

3.2 The backbone of the chlorine flows in Western Europe

In Figure 3 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% are used in the C3 (propane, propene) vertebra and about 8% in the C1 (methane). Around 3% are 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% are used in the production of other compounds, mainly inorganics

3.2.1 Production and use of elementary chlorine (Cl₂)

Chlorine is produced by the electrolysis of brine: a solution of common salt, NaCl. Eurochlor reported a production of 8610 kMt (Ayres & Ayres, 1996). 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.

In Figure 4 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 are used in direct applications. An explanation of the abbreviations used in the figure is given in Table 2.

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

Next to elementary chlorine there is another important chlorine feedstock that 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 is needed in some specific processes. This pure HCl is produced by mixing chlorine gas (Cl₂) with hydrogen gas (H₂), 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 5 the production and consumption of HCl is given.

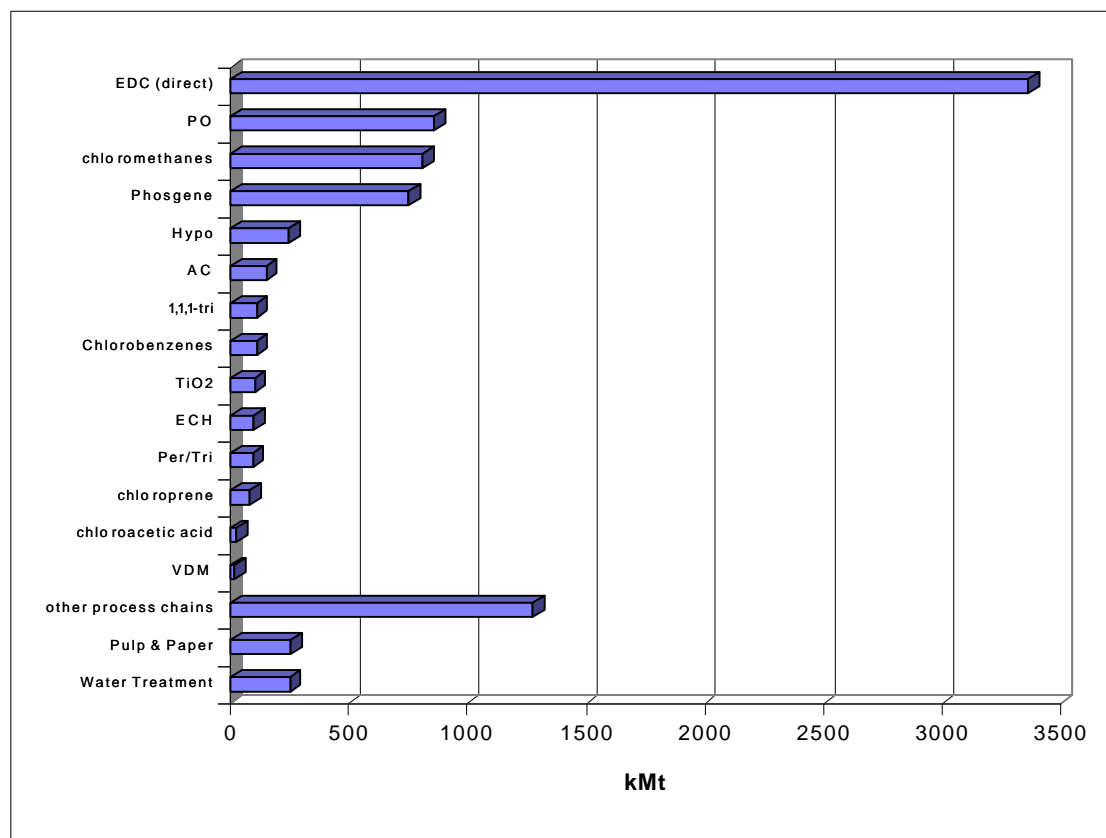


Figure 4: The use of Chlorine in Western Europe in 1992 (based on Ayres & Ayres, 1996)

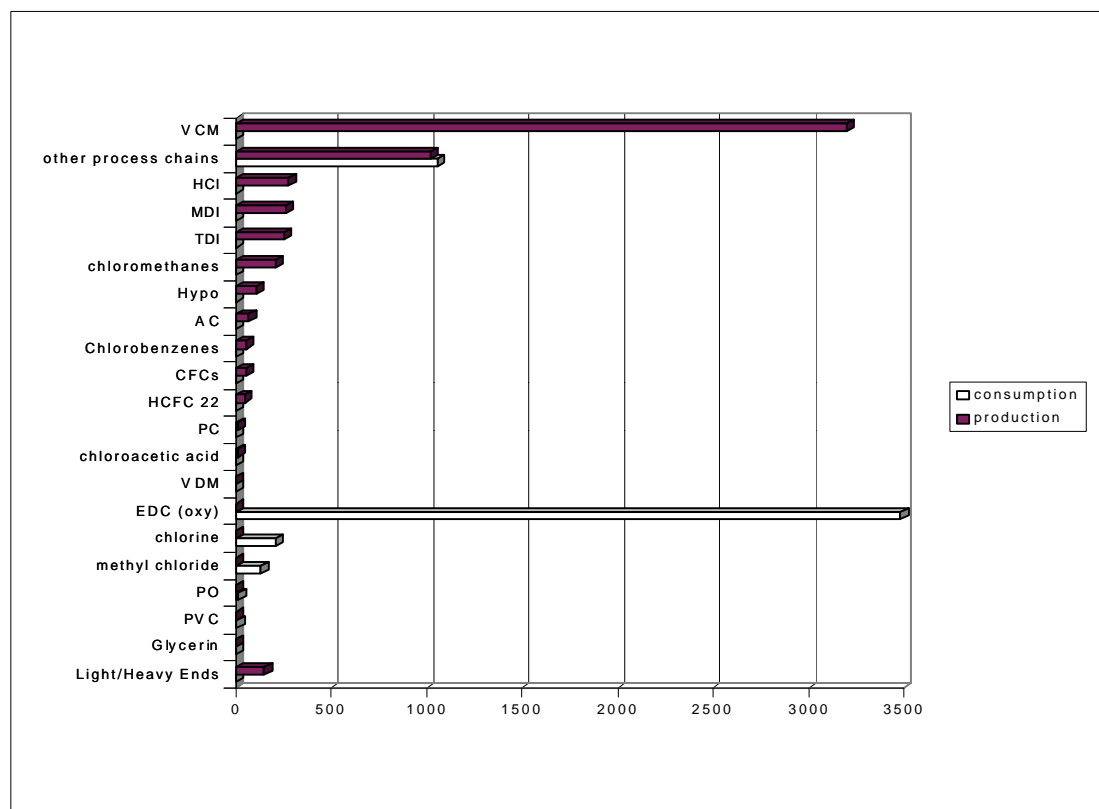


Figure 5: Production and Consumption of HCl in the Chlorine Industry in Western Europe in 1992 in kMt chlorine (based on Ayres & Ayres, 1996).

3.2.3 Chlorinated C1-derivates from the cradle to the grave

Chlorine flows into the C1-derivates production in the form of 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 stocks in the anthroposphere ((H)CFCs) and partly treated as chemical waste (solvents).

3.2.4 Chlorinated C2-derivates from the cradle to the grave

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 plastisiers and can be used in flooring, coatings etc. In Western Europe in 1992 37% of the PVC was used as flexible PVC and 63% as rigid PVC. Most important rigid applications are pipes&fittings, profiles, films&sheet and bottles. Most important flexible applications are cables, film&sheet, flooring, wall covering and hosepipe.

PVC used in construction applications, especially pipes, will remain in the anthroposphere for as long the lifespan of the constructions (50-100 years). Applications such as wallpaper and flooring have much shorter lifespan (less than 10 years). PVC used in packaging has a lifespan 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 stock in the anthroposphere. 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.

3.2.5 Other chlorinated compounds from the cradle to the grave

Most of the chlorine flowing into the C3 branch is transformed to chloride during the production of propylene oxide, ECH, epoxy resins and glycerin. Almost halve of the total chlorine inflow goes to the market as chloroprene rubber where a small net import occurs. The lifespan of chloroprene is unknown. It is assumed that most of the chloroprene will accumulate in the anthroposphere. Chlorobenzenes are used in the production of pesticides, pharmaceuticals, dyes etc. partly as feedstock and partly as solvent and are assumed to be transformed elsewhere. Most of the produced phosgene 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). Less than half of the amount of chlorine used to produce hypochlorite 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.

3.3 Modelling of PVC stocks in Sweden

As described in paragraph 2.7 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 modelling 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). 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 discretized normal distribution used for the lifespan
- a combination of the second model (linear increase) with a discretized normal distribution used for the lifespan

In Figure 6 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 6 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 smoothed by adding a discretized 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.

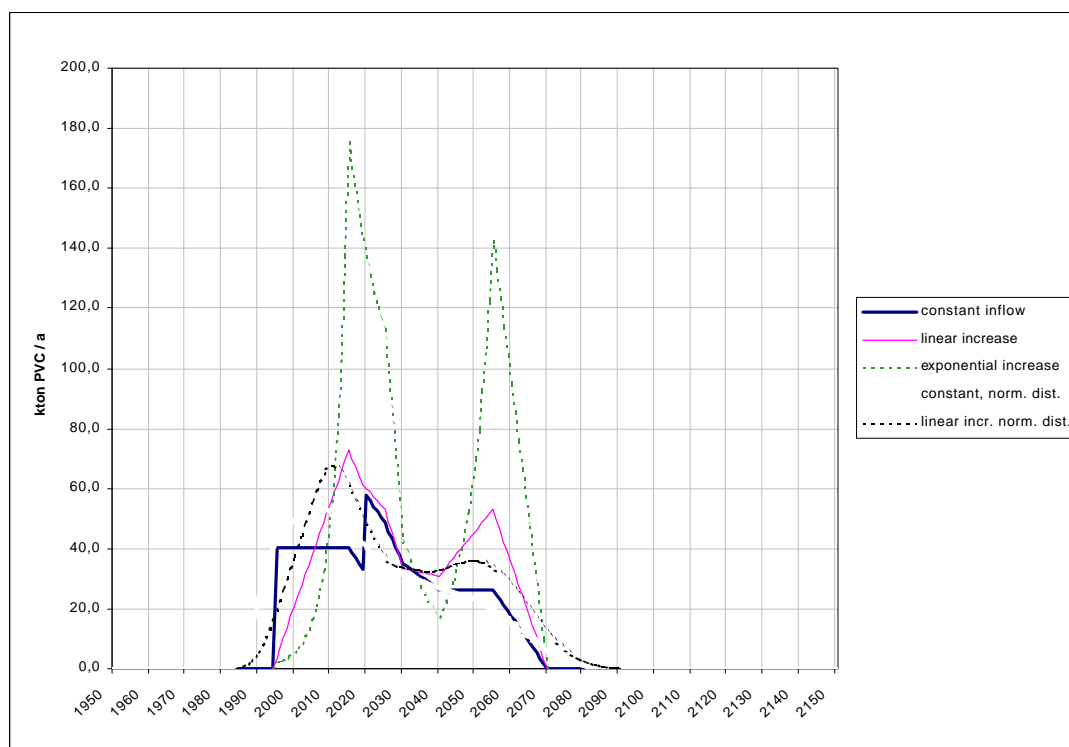


Figure 6: PVC waste flows (outflow) from pipes, cables and flooring in Sweden calculated with different models for the consumption (inflow) and different lifespan distributions

3.4 Stock modelling 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.

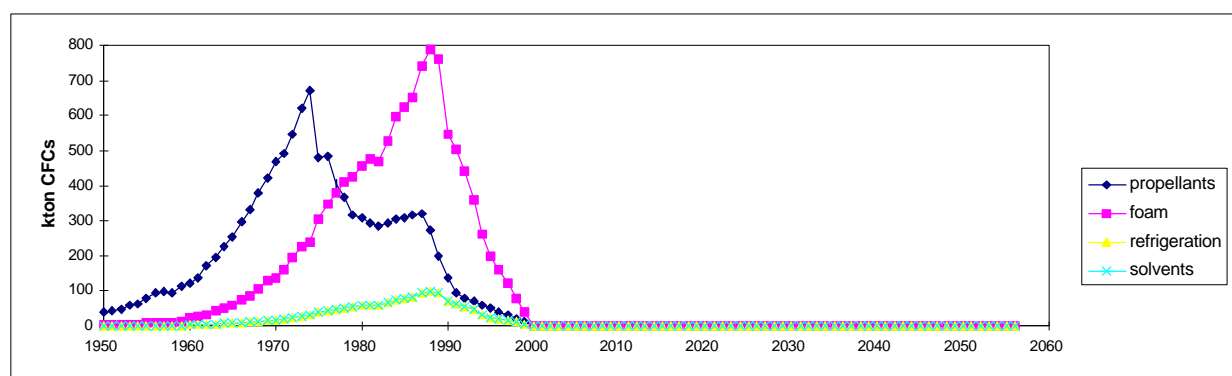


Figure 7: World use of CFCs in different applications (propellants plus total data, Worldwatch Institute, 1996; distribution over other applications calculated on the basis of Dutch data)

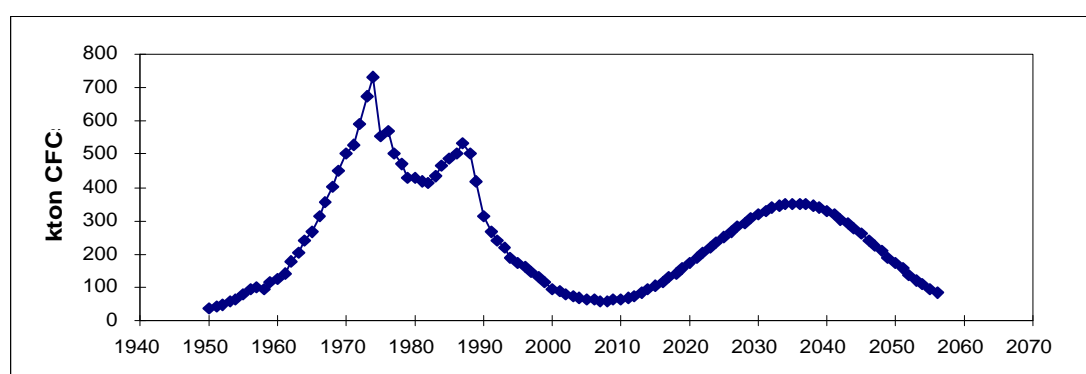


Figure 8: Calculated world emissions of CFCs

Figure 7 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 8 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 CML and IWAS will write a paper on this subject.

3.5 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). 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.

4 Consequences for implementation

4.1 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, polyurethanes 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 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 during the applications its products which should be examined further. 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. This study can be used to focuss the attention on the dirty spots in the chlorine chain.

4.2 MFA as a policy supporting instrument

The use of MFA as a policy supporting instrument can not be shown on the basis of the MacTempo case study since it has not been used yet in a policy context. However, it can be shown on the basis of previous case studies.

The Dutch Chlorine Balance (Tukker et al., 1995)

This study, carried out by the Netherlands Organization for Applied Scientific Research (TNO) and the Centre of Environmental Science Leiden (CML), was commissioned by the Dutch Ministries of Housing, Physical Planning and Environment, Economic Affairs, and Traffic, Public Works and Waterways (Tukker et al., 1995). The study lasted for a period of two years, starting in September 1993. The first phase of the study was set up as an MFA, covering about 99 % of the flows of chlorinated substances in the Netherlands. Emissions, waste generation, exports, imports, and economical transactions have been collected making use of all sources possible: the Dutch emission registration database, LCA-databases, industrial data etc. Emissions were evaluated making use of the characterization step from the LCA (Life Cycle Assessment) methodology. Emissions with toxicological effects have been additionally evaluated on the basis of actual risk assessments of the National Institute of Public Health and Environmental Protection (RIVM). This resulted in about 6 groups of priority segments of the Dutch chlorine chain, for which additional measures are being prepared. The study showed that the structural danger connected to the chlorine chain as pronounced by the

environmental groups are not supported by the present knowledge about emissions and impact assessment. However the study also indicates that important uncertainties exist that require attention, especially concerning the possible emissions of persistent bioaccumulating toxic micropollutants. At this moment CML is involved in the BITAC: an advisory commission of the Dutch Ministry of Housing, Physical Planning and Environment. The task of the BITAC is to follow and coordinate the policy actions focussed on the problemflows found in the Chlorine Balance study. Other members of the BITAC are representatives from industry, environmental movement, labor union and the Ministry of Traffic, Public Works and Waterways.

In the Dutch Chlorine Balance study MFA proved to be a very useful policy-supporting tool. A quantitative overview of 99% of the flows of chlorinated substances can serve as a factual starting point for further discussions on chlorine policy. Because the overview was relatively complete, problem flows could be identified and compared with each other on the basis of potential contributions to environmental problems. With the MFA links within the chlorine between different flows and processes chain have been made visible. Furthermore, gaps in the current knowledge were found which were used to focus future research efforts.

Flows of six heavy metals in the economy and environment of The Netherlands (Annema et al., 1996)

Heavy metals are since long a concern of environmental policy. In The Netherlands, standards have been set, measures have been taken and policies have been formulated for various aspects of the heavy metals problem. This study has been undertaken to provide the Dutch government with an integrative framework, wherein the various policies can be placed and the need for further measures can be identified. For six heavy metals - copper, zinc, lead, chromium, cadmium and mercury - the flows through the economy and the environment were quantified, thus providing an overview of the metals' chain from cradle to grave. These overviews have been translated into substance flow models with help of the computer tool SFINX, which have been used to calculate the origins of several specific environmental problems and calculate the effectiveness of certain possible abatement measures. It appeared that, although some problems occurred for one metal only, there were several problems concerning the group of metals as a whole due to their non-degradability. One problem is the metals accumulation in agricultural flows such as soils and manure, as a result of constant recycling. Another is the content in waste products such as sewage sludge, compost and fly ash, which makes re-use of these materials impossible. This study was one of studies on which the Dutch government has based current policies for heavy metals.

Benefits of MFA as a decision support tools

One of the most important functions of MFA is to couple environmental problem flows to anthropogene origins. In the study of heavy metals in the Netherlands SFINX static modeling was used to calculate the effectiveness of current heavy metal policy and certain alternative policy measures. In the Dutch Chlorine Balance study environmental problemflows were coupled to processes in the anthroposphere. The risks of emissions were calculated with the aid of equivalency factors expressing the potential contribution of different substances to different environmental problems. This resulted in a priority list of emissions. Furthermore, the MFA helped to focus attention of policymakers on gaps in the current knowledge.

When stock formation is included in MFA, it can be used as a tool for early recognition of future waste and emission problems. The stock modeling can be used to estimate future outflows on the basis of quantitative and qualitative information of past inflows and lifespan of different products.

Opportunities and threats

A big underdeveloped opportunity for the use of MFA as a policy-supporting instrument is the use of MFA-indicators as satellite indicators next to economic indicators in environmental reports of nations, local governments and companies. A major threat for the use of MFA is the fact that gathering data for MFA is very time consuming. If statistical data and emission inventories would be better accessible and confidentially problems would be tackled an important part of this problem would be solved.

5 Discussion & Conclusions

In this MacTempo case study an overview of flows of chlorinated compounds within the Western Europe is given together with the emissions of these compounds to the environment (more detailed information can be found in the case study report: Kleijn & van der Voet 1998). 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 IWAS.

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 MacTempo 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.

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Table 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 derivatives)
C2	the group of hydrocarbons with 2 carbon atoms (ethane derivatives)
C3	the group of hydrocarbons with 3 carbon atoms (propane derivatives)
C4	the group of hydrocarbons with 4 carbon atoms (butane derivatives)
>C4	the group of hydrocarbons with more than 4 C atoms (non cyclic)
CaCl ₂	calcium chloride
CFCs	chlorofluorocarbons
Cl ₂	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
kMt	kilo metric tonne
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
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	polyurethanes
PVC	polyvinylchloride
MFA	material flow analysis
SFINX	substance flow internodal exchange (computer model)
TDI	toluene diisocyanate
TiO ₂	titanium dioxide
TNO	Netherlands Organization for Applied Scientific research
Tri	trichloroethylene
VCM	vinylchloride (monomer)
VDM	vinylidene chloride
WE	Western Europe

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 monochloroethene (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 equipment
foam	solvents used as blowing agent to create foams
sterilisation gas	CFC-12 used as sterilisation 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