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Substance Flow Analysis for dioxins in Denmark

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Content

Preface

The issue of dioxins continues to create attention in modern society. Although significant efforts already have been and still are being invested in developing a thorough understanding of the sources and the implications of dioxin, there is still a long way to go. And new knowledge continues to push for further efforts both with respect to developments in our understanding of the toxicological aspects and recognition of new sources for emission to the environment.

The objective of this investigation has been to integrate the present knowledge of dioxins related to Denmark into the framework of substance flow analysis, aiming at obtaining a better understanding of the flow of dioxins in society.

The objective, furthermore, has been to reconsider the knowledge so far reported from Denmark (reference is made to /Jensen 95 and Jensen 97/) paying respect to the significant amount of knowledge made internationally available during the nineties, and the actual measurements available for Denmark up to the summer of 2000.

Thus the report has tried to develop a complete picture – to the extent possible – of the dioxin circulation in Denmark and have inter alia tried to develop estimates for sources like accidental fires and uses of PCP that due to a very high level of uncertainty are often not included in dioxin surveys.

The report has been financed by the Danish Environmental Protection Agency and has during its preparation been supervised by a steering committee consisting of:

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Sammenfatning og konklusioner

Denne undersøgelse har forsøgt at skabe – i det omfang dette er muligt ud fra den eksisterende viden – et opdateret og dækkende billede af omsætningen af dioxin i det danske samfund. Dannelsen af chlorerede dioxiner i Danmark i 1998-99 er estimeret til 90 – 830 g I-TEQ/år, mens emissionen til miljøet er estimeret til:

Luft:	19 - 170	g I-TEQ/år
Vand:	0,3 – 1,4	g I-TEQ/år
Jord:	1,3 - 54	g I-TEQ/år
Depoter:	38 – 420	g I-TEQ/år

Som forurening i forskellige produkter og materialer er chlorerede dioxiner tillige importeret til Danmark eller udvundet fra naturen, idet dioxiner findes i både ler, fisk, dyr og planter på grund af tidligere og nuværende forurening. Estimatet for emission af dioxiner til luft er i fornuftig overensstemmelse med det estimerede atmosfæriske nedfald på 16 - 160 g I-TEQ/år over det danske landareal.

Dannelse af dioxiner i Danmark er næsten udelukkende knyttet til forbrændingsprocesser. Begrebet forbrændingsproces dækker i denne sammenhæng enhver proces, hvor tilstedeværende organisk materiale forbrændes og omfatter processer som afbrænding af træ og halm, affaldsforbrænding, ildebrande og bål, cementfremstilling og genvinding af stål. Dannelse af dioxiner sker derfor mange steder i samfundet.

Dannelse af dioxiner afhænger i betydelig grad af de lokale proces forhold herunder råmaterialer og temperaturforløbet i røggassystemer. At estimere dannelse og emissioner handler derfor om at håndtere et virvar af usikkerheder. De store intervaller for dannelse og emissioner der er givet ovenfor afspejler den usikkerhed, der er knyttet til estimaterne.

Baggrund og formål

Denne undersøgelse er igangsat af Miljøstyrelsen i november 1999 for at opnå en bedre forståelse af transporten og omsætningen af dioxiner i det danske samfund.

De kontante formål med undersøgelsen har været at organisere den eksisterende viden om dioxiner i Danmark ved brug af værktøjet massestrømsanalyse og som led i denne proces at revurdere den viden, der indtil nu er rapporteret fra Danmark i lyset af den betydelige viden, der er gjort tilgængelig internationalt i løbet af 1990'erne.

Tidligere undersøgelser om emissionen af dioxiner i Danmark er offentliggjort i 1995 og 1997.

Undersøgelsen

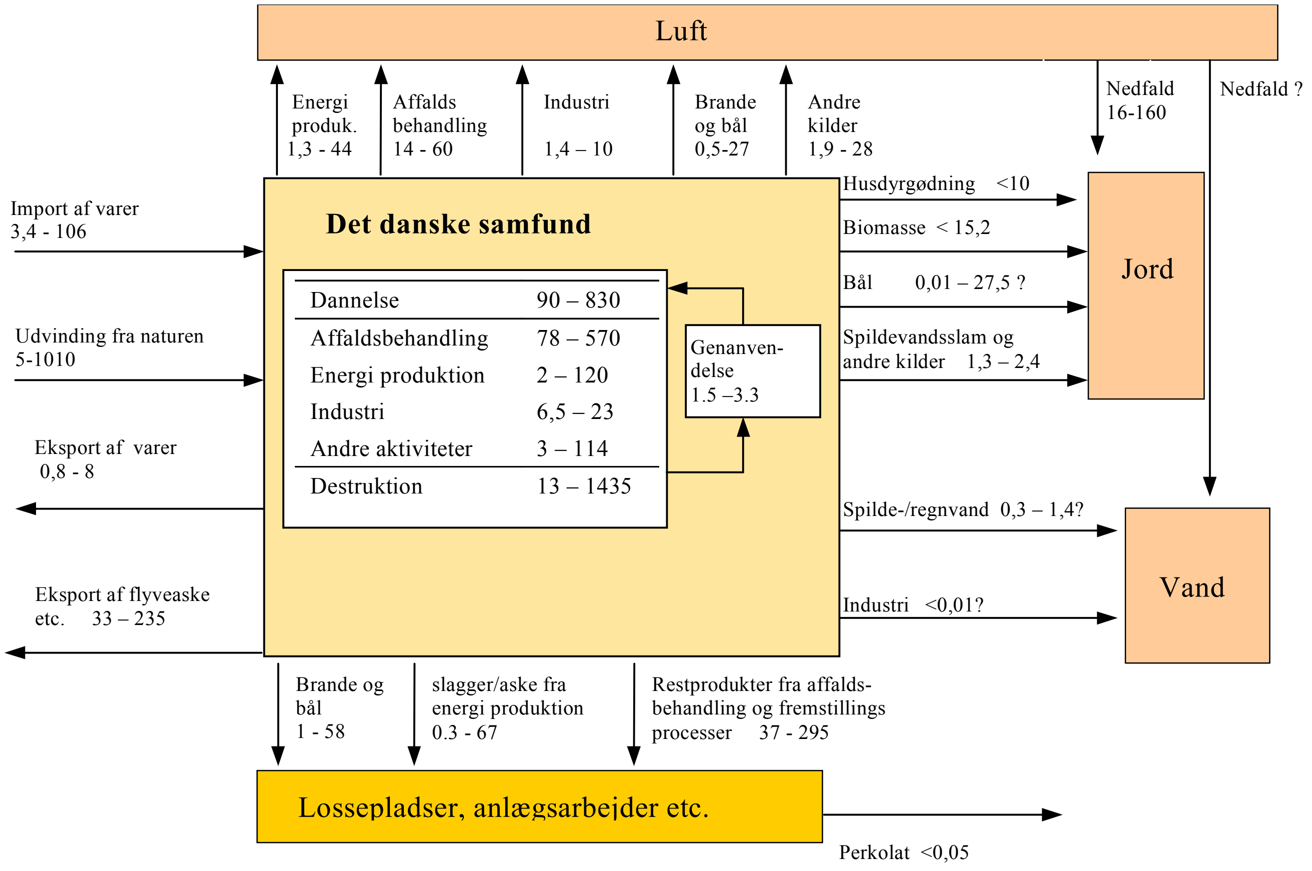
Undersøgelsen er udført i overensstemmelse med Miljøstyrelsen paradigme for massestrømsanalyser. Den viden der præsenteres her bygger på data fra Danmarks Statistik, videnskabelig litteratur, offentlige institutioner, private organisationer og virksomheder. Analysen har kontant sammenfattet al tilgængelig information for at beskrive omsætningen af dioxiner i det danske samfund.

Da dioxinanalyser er relativt dyre, er der kun foretaget et begrænset antal målinger i Danmark. Det har derfor været nødvendigt for de fleste processer at bygge på udenlandske emissionsfaktorer. Ved vurderingen og udvælgelsen af sådanne emissionsfaktorer, er det blevet anset for fagligt mere rigtigt at bruge minimum- og maksimumtal i stedet for gennemsnitstal, da gennemsnitstal generelt giver et falsk indtryk af estimaternes nøjagtighed. En tilsvarende fremgangmåde er i visse tilfælde også brugt for processer, hvor der findes danske målinger, fx. for affaldsforbrænding. Et af de problemer, som denne fremgangsmåde tager hensyn til – i det mindste delvist – er det forhold, at dioxindannelse og emissioner ved “normale” procesforhold må forventes at kunne være væsentligt forskellig fra “ikke-normale” forhold, og at “ikke-normale” forhold kan svare for en væsentlig del af den samlede dioxindannelse og -emission. De fleste målinger som er tilgængelige må antages at bygge på normale procesforhold og giver dermed ikke nødvendigvis et pålideligt billede af den samlede emission fra de enkelte anlæg.

Vigtigste konklusioner

Den foreliggende viden og vurderinger om omsætningen af chlorerede dioxiner i Danmark i 1998-99 er sammenfattet og illustreret i figur 1.

Figur 1
Balance for chlorerede dioxiner for Danmark 1998-99 (alle tal i g I-TEQ/år)



Det danske samfund modtager chlorerede dioxiner med importerede varer og med råmaterialer udvundet fra naturen. De pågældende varer er primært materialer som træ, læder og tekstiler, der er behandlet med pentachlorphenol, men også ler, papir og pap samt foderstoffer. De udvundne råmaterialer handler om ler, kaolin og lignende materialer som bruges til produktion af varer i Danmark, men også fisk, græs og husdyr, som bruges til fødevarer og foderstoffer i Danmark.

I Danmark sker en dannelse af chlorerede dioxiner ved en lang række forskellige processer. Den samlede dannelse svarer til 90-830 g I-TEQ/år. Den vigtigste kilde er affaldsforbrænding. Andre betydningsfulde kilder omfatter brug af kul og biomasse til energiproduktion, brande og bål, samt bl.a. omsmeltning af stål- og aluminiumsskrot.

Tabel 1
Estimerede emissioner/tab til miljøet og depoter i Danmark 1998-99

Aktivitet	Emission/tab (g I-TEQ/år)			
	til luft	til vand	til jord	til depoter 1)
Industriel fremstilling				
Kemisk industri 2)	?		<1?	
Cement og brændt kalk	0,045-3,5	?		
Stål- og aluminium-omsmeltning	1,3-5,6		<0,005	0,26-1,5
Andet 3)	0,07-1,0?	<0,01		<0,002?
Energiproduktion				
Fossile brændsler	0,54 –2,76			0,23 – 31?
Forbrænding af biomasse	0,73 – 41		< 15,2	0,04 – 36?
Brug af produkter				
Træ, læder og tekstiler behandlet med PCP	0,5 – 26?	0,2 4)		
Blegemidler og –processer		<0,5 4)		
Foderstoffer		?	<10	?
Diverse aktiviteter				
Brande	0,5 – 20?		?	1-30
Bål m.m.	0,03 – 6,5		0,01 – 27,5?	0,01-27,5
Trafik og andet 5)	1,4-1,9?	?	?	?
Behandling og bortskaffelse af affald				
Genvinding af kabelskrot	0,005-5			?
Kommunekemi 6)	2,2-2,7	0,000001		0,9?
Affaldsforbrænding	11-42			35-275
Lossepladser/depoter 7)	0,25-10?	<0,05?		0,4-17?
Spildevandsrensning og regnvand		0,3 – 1,4?		
Spildevandsslam	0,07-0,15		1,3	0,42-0,46
Andre aktiviteter 8)	0,08-0,2		0,01-0,07	?
Total (afrundet)	**19 – 170**	**0,3 –1,4?**	**1,3 – 54**	**38-420**

? Tal kan ikke estimeres pga. mangel på data – bør ikke overses.
x? Tal eller deltal bedømt som højst usikre.
1) Inkluderer mængder som er indeholdt i restprodukter, der bruges til anlægsarbejder.
2) Dækker fremstilling af pesticider and farmaceutica.
3) Dækker fremstilling af isoleringsmaterialer, tegl og mursten, glas, metalstøbning, varmgalvanisering, fiskeolie/-mel, kød- og benmel, grøntfoder, asfaltfremstilling og en række andre processer, som ikke kan kvantificeres.
4) Omfatter emission til spildevand. Udledning fra spildevandsrenseanlæg er angivet under "spildevandsrensning".
5) Dækker trafik, kremering og en række andre aktiviteter, der kun delvist kan kvantificeres, såsom fyrværkeri, havegrills, madlavning og andre aktiviteter.
6) Emission til luft kun gyldig for 1999. Når grænseværdien på 0.1 ng I-TEQ/Nm^3 er opfyldt for alle ovne, vil den maksimale emission være 0,09 g I-TEQ/år.
7) Emission til luft og tab til depoter beror på brand i midlertidigt oplagret brændbart affald.
8) Dækker shredderanlæg, klinisk hospitalsaffald og biologisk affaldsbehandling.

Størsteparten af den mængde chlorerede dioxiner, der dannes i Danmark emitteres til miljøet i Danmark. En mindre del vil dog blive eksporteret med restprodukter som kulflyveaske og filterstøv fra røggasrensning.

En væsentlig destruktion af chlorerede dioxiner påregnes også at finde sted i Danmark. Denne destruktion er anslået til 13 – 1435 g I-TEQ/år og omfatter dioxiner i ler o.lign, der bruges til fremstilling af tegl, mursten og andre produkter i Danmark, idet disse produkter brændes ved en temperatur, der må antages at nedbryde dioxiner. Der sker også nedbrydning af dioxiner i affald og spildevandsslam som forbrændes samt af dioxiner i flyveaske og papirslam, der bruges til cementfremstilling, idet både affaldsforbrænding, slamforbrænding og cementfremstilling må antages i væsentligt omfang at nedbryde dioxiner. Hertil kommer en ukendt dioxinmængde i specielle dioxinfiltre, som brændes i ovne ved de anlæg, hvor de har været benyttet.

En række af de anlæg, hvor der sker en destruktion af dioxiner er dog samtidig blandt de vigtigste kilder til dannelse og emission af dioxiner. Dette gælder især affaldsforbrænding, hvor der dannes og emitteres en dioxinmængde, som er væsentlig større end den mængde, der destrueres. Affaldsforbrænding er således den vigtigste kilde til dannelse og emission af dioxiner i Danmark.

Emission af chlorerede dioxiner til miljøet i Danmark omfatter emission til både luft, vand og jord samt deponering på lossepladser eller andre typer depoter, såvel slagger fra forbrændingsanlæg og kulflyveaske anvendt til anlægsarbejder. Den estimerede emission af chlorerede dioxiner til miljøet i Danmark i 1998-99 er sammenfattet i tabel 1.

Den samlede emission til luft i Danmark er estimeret til 19 - 170 g I-TEQ/år. De dominerende kilder omfatter:

- Affaldsforbrænding
- Afbrænding af biomasse i mindre enheder uden røggasrensning som brændeovne og gårdfyr - for brændeovne gælder, at rent træ næppe er det store problem, men at der tillige brændes andre materialer såsom papir, pap, mælkekartoner, behandlet træ mv. som må forventes at fremme dioxindannelse, bl.a. fordi det kan indeholde kobber (fx. som farvestof på papir), der virker som katalysator for dioxindannelse, og fordi træ (fx. fra engangspaller importeret til Danmark og brugt som brændsel) kan være behandlet med pentachlorphenol, uden at dette kan ses på træet.
- Fordampning fra træ behandlet med pentachlorphenol - det drejer sig især om konstruktionstræ brugt i perioden 1950 –1978, hvor pentachlorphenol var almindeligt anvendt til træbeskyttelse i Danmark – en del af dette træ er stadig i brug i huse etc. og må antages stadig at indeholde dioxin, som langsomt fordamper.
- Brande i bygninger, køretøjer og midlertidige depoter for brændbart affald - den foreliggende viden er meget usikker, da det er vanskeligt at foretage pålidelige målinger, men alle betingelser for dioxindannelse er normalt opfyldt.
- Omsmeltning af stål- og aluminiumsskrot.

Hertil kommer en lang række andre kilder, fx. Kommunekemi, som var en signifikant kilde i 1999, men Kommunekemi har lukket den pågældende ovn og installerer dioxinfilter.

Den samlede emission til vand i 1998-99 er estimeret til 0,3 – 1,4 g I-TEQ/år. Den dominerende kilde synes at være atmosfærisk nedfald, men congener profiler for spildevandsslam passer bedre med profiler for dioxinindholdet i tekstiler. Den foreliggende viden er for spinkel til at drage sikre konklusioner.

Den samlede emission til jord i 1998-99 er estimeret til 1,3 – 54 g I-TEQ/år. De dominerende kilder skønnes at være:

- Aske fra afbrænding af biomasse (fra brændeovne og gårdfyr), som spredes direkte på jorden.
- Rester fra diverse bål (fx. havebål, Skt. Hans bål), som efterlades og med tiden blandes med jorden.
- Husdyrgødning.

Det samlede tab til lossepladser og andre depoter er estimeret til 38 – 420 g I-TEQ/år. Restprodukter fra affaldsforbrændingsanlæg er den dominerende kilde. Hertil kommer aske fra biomassefyr, kulkraftværker og brande samt filter støv fra røggasrensning hos diverse virksomheder. Den foreliggende viden om skæbnen for dioxiner i lossepladser er meget beskeden.

Inden for affaldssektoren synes at ske en indsats for at mindske dioxinemissioner, fx. ved installation af særlige dioxinfiltre. Vurderet ud fra Stålvalseværkets eget skøn for dioxin-emissionen har denne virksomhed tilsyneladende også haft succes med at reducere emissionerne væsentligt. For andre anlæg og aktiviteter i Danmark vurderes, at der indtil nu ikke har været specielt fokus på dioxin.

Der eksisterer et lager af chlorerede dioxiner i træ tidligere behandlet med pentachlorphenol. Den nuværende størrelse af dette lager er groft skønnet til 100 – 5.000 g I-TEQ. Lageret må antages langsomt at blive mindre, dels fordi der sker en løbende udskiftning af det pågældende træ, som vil bortskaffes til forbrænding og dels pga. fordampning af dioxiner fra træet.

En anden gruppe dioxiner er de bromerede dioxiner. Der er ikke foretaget målinger for disse dioxiner i Danmark og kun relativt få målinger internationalt, bl.a. fordi de analystiske procedurer endnu ikke er færdigudviklede. Det er skønnet, at der sker en import af størrelsen 2 – 60 g I-TEQ/år til Danmark af bromerede dioxiner med plast som indeholder bromerede flammehæmmere. I det omfang, at sådant plast udsættes for brand eller videre bearbejdning, fx. omsmeltning ved genanvendelse, kan der ske en yderligere dannelse af bromerede dioxiner. Bromerede dioxiner vil formodentligt blive nedbrudt ved affaldsforbrænding, men dannelse af bromerede dioxiner samt kombinerede bromerede/chlorerede dioxiner kan ske på ny i røggasser helt parallelt til dannelse af chlorerede dioxiner.

Summary and conclusions

This study has tried to develop – to the extent possible – an updated and complete picture of the dioxin circulation in the Danish society based on the knowledge available. The formation of chlorinated dioxins in Denmark in 1998-99 has been estimated at 90 – 830 g I-TEQ/year, whereas the emissions to the environment have been estimated at:

Air:	19 – 170	g I-TEQ/year
Water:	0.3 - 1.4	g I-TEQ/year
Soil:	1.3 – 54	g I-TEQ/year
Depots:	38 – 420	g I-TEQ/year

As contaminants in various products and materials chlorinated dioxins are furthermore imported to Denmark and extracted from the nature around us, as dioxins can be found both in clay, fish, animals and vegetation due to historical and ongoing contamination. The estimate for emission of dioxins to air is in reasonable balance with the estimated atmospheric deposition on the Danish land area of 16 - 160 g I-TEQ/year.

Formation of dioxins in Denmark is almost entirely related to combustion processes. Combustion process is in this context used for any process leading to combustion of organic matter present, including processes such as wood and straw burning, waste incineration, fires, cement manufacturing and steel reclamation. Formation of dioxins is thus widespread in the society.

Formation of dioxins is highly influenced by local process conditions including raw materials and temperature pattern in flue gas emission systems. Estimating formation and emissions is a matter of dealing with a host of uncertainties. The large ranges of formation and emissions stated above reflect the uncertainties related to the estimates.

Background and objectives

This study has been initiated by the Danish EPA in November 1999 in order to improve the existing understanding of the circulation of dioxins in the Danish society.

The objectives of the study have been to integrate the present knowledge of dioxins related to Denmark into the frame work of substance flow analysis and as part of this process to reconsider the knowledge so far reported from Denmark paying respect to the significant amount of knowledge made internationally available during the nineties.

Previous studies on emissions of dioxins in Denmark have been published in 1995 and 1997.

The study

This study has been carried out in accordance with the paradigm of substance flow analysis of the Danish Environmental Protection Agency. The knowledge presented is based on data from Statistics Denmark, the literature, and public institutions as well as from private organisation and companies. In the analysis, all the information has been held together to describe the flow of dioxins through the Danish society.

As dioxin analyses are relatively costly, the number of measurements available to Danish plants is limited. It has thus been necessary for most processes to rely on emission factors developed abroad. In adopting such figures it has been assumed more correct to use minimum and maximum figures instead of average figures, as average figures generally give a false impression of the accuracy of the estimates presented. The same approach has in some cases been adopted also for processes for which Danish measurements actually exist, e.g. for municipal waste incineration. One of the problems addressed by this approach – at least partly – is the fact that dioxin formation and emission may differ considerably from "normal" process conditions to "deviating" process conditions, and that deviating process conditions could contribute significantly to the total dioxin formation and emission. Most measurements available should be assumed to reflect normal process conditions and do not necessarily give a reliable picture of the total emission from the individual plants.

Main conclusions

The main conclusions of the study are:

- The total Danish formation of chlorinated dioxins in 1998-99 is estimated at 90 – 830 g I-TEQ/year. The dominant source is municipal waste incineration. Other significant sources also include coal and biomass combustion and fires, both accidental fires and others. Most chlorinated dioxins formed by processes in Denmark are emitted to the environment. A minor part is exported with residues like coal fly ash and filter dust from Denmark.

- Denmark also receives chlorinated dioxins by products imported to Denmark and by raw materials extracted from nature. The import by products is estimated at 3.4 – 106 g I-TEQ/year and is partly related to import of products like wood, leather and textiles treated by pentachlorophenol (PCP) abroad, as chlorinated dioxins are contaminants in PCP. Chlorinated dioxins are also imported with products like clay, paper/cardboard and feedstuff. Raw materials extracted from nature in Denmark accounts for 5 - 1010 g I-TEQ/year dominantly in clay but also in fish, grass and animals used for food and feedstuff.

- The total Danish emission of chlorinated dioxins to air in 1998-99 is estimated at 19-170 g I-TEQ/year. The dominant sources include municipal waste incineration, biomass combustion in small units without flue gas cleaning like wood stoves and farm boilers, evaporation from PCP-treated wood in use in Denmark, fires, steel and aluminium reclamation. Other sources of emission that could be significant are cable scrap reclamation, lime and cement manufacturing, traffic and landfills that in this context cover fires in temporary depots for combustible waste. In 1999 incineration of chemical waste was a significant source as well, but the contribution from this source is likely to be heavily reduced in 2000 due to redesign of kilns and installation of dioxin filters.

- The total Danish emission to water in 1998-99 is estimated at 0.3 – 1.4 g I-TEQ/year. The dominant source seems to be atmospheric deposition, but congener profiles for sewage sludge correspond better to textiles than to atmospheric deposition. The knowledge is limited, and any definite conclusions on this issue should be taken as premature.

- The total direct emission of chlorinated dioxins to the soil environment is estimated at 1.3-54 g I-TEQ/year. The dominant sources are deemed to be ash from biomass combustion in wood stoves and farm boilers applied directly to soil, residues from miscellaneous fires (garden fires, bonfires etc.) not removed from the place of the fire and by time mixed into soil, and manure from domestic animals applied to farmland.

- The total quantity of chlorinated dioxins directed to landfills and other types of depots in Denmark is estimated at 38 – 420 g I-TEQ/year. Again municipal waste incineration stands out as the dominant source. However, neither residues from coal combustion, biomass combustion nor fires should be overlooked.

- Apart from steel reclamation and waste incineration, no specific trend in dioxin emissions should be noted. The Danish steel reclamation plant has based on the company's own estimate of dioxin emission apparently succeeded in reducing emissions considerably, whereas Danish waste incineration plants are in the process of speeding up installations of special dioxin filters. For other plants and activities the focus on dioxin emissions in Denmark has so far been limited.

- A significant destruction of chlorinated dioxins corresponding to 13 – 1465 g I-TEQ/year is assumed to take place. The destruction is related to high temperature manufacturing of products based on clay, besides that thermal waste treatment like incineration of municipal waste and sewage sludge are believed to destroy – more or less – the dioxins present in the waste materials treated. It should be stressed that recycling of materials like coal fly ash and paper sludge for cement manufacturing also should imply destruction of the dioxins present in the recycled materials due to the temperatures involved by cement manufacturing. To this an unknown amount of dioxins in special dioxin filters burned in the ovens/kilns at the plant, from where they were used can be added.

- It must be recognised that the plants effective in destruction of dioxins at the same time may belong to the dominant sources of dioxin formation. For municipal waste incineration the overall picture is that the amount of dioxins emitted by flue gas and incineration residues is significantly higher than the amount assumed to be destroyed. Municipal waste incineration should be regarded as the most important source for dioxin formation and emission in Denmark.

- A stock of chlorinated dioxins in the Danish society exists in the form of dioxins in PCP-treated wood. The stock is mainly due to the widespread use of PCP as wood preservative that took place in Denmark from 1950 to 1978. By 1999 the size of this stock was roughly estimated at 100 – 5,000 g I-TEQ. The stock should be assumed slowly decreasing due to replacement of the wood in question as well as evaporation of dioxins from the wood, as the use of PCP in Denmark is now banned. The wood replaced is assumed directed to incineration.

- Another group of dioxins is the brominated dioxins. No measurements for brominated dioxins have been undertaken in Denmark and only relatively few internationally, as analytical procedures are still in the process of being developed. Denmark is importing an estimated 2 – 60 g I-TEQ/year of brominated dioxins as contaminants in plastics containing brominated flame retardants. To the extent such plastics are exposed to accidental fires or further processing, e.g. recycling, further formation of brominated dioxins may take place. Brominated dioxins in plastics are likely to be destroyed by waste incineration, but formation of brominated dioxins as well as mixed brominated/chlorinated dioxins may take place by flue gas cleaning and emission processes parallel to formation of chlorinated dioxins.

1 Introduction

1.1 What are dioxins?

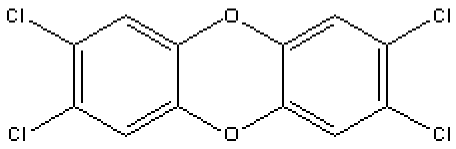
The phrase "dioxins" is typically used as a short designation of two groups of tri-cyclic, halogenated, organic compounds, of which some chlorinated compounds have turned out to be extremely toxic.

The first group covers the polychlorinated dibenzo-p-dioxins (PCDDs) and the polybrominated dibenzo-*p*-dioxins (PBDDs). As the number of halogen substituents may range from one to eight, the sub-group of chlorinated dioxins as well as the sub-group of brominated dioxins consist of 75 members or congeners, as they are named in this report.

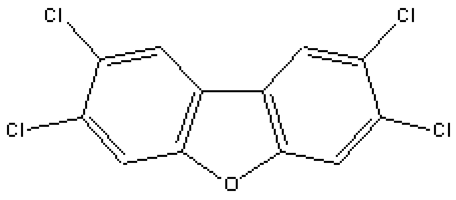
The second group covers the dioxin-like "furans" or more precisely the polychlorinated dibenzofurans (PCDFs) and the polybrominated dibenzofurans (PBDFs). Again the number of halogens may range from one to eight bringing the number of congeners for the sub-group of PCDFs as well as for the sub-group of PBDFs up to 135.

To these groups of substances should be added the large groups of mixed brominated/chlorinated dibenzo-*p*-dioxins (PXDDs) and dibenzofurans (PXDFs) that consist of 1550 respectively 3050 different congeners /IPCS 1998/.

The chemical structure of dioxins and furans are shown in figure 1.1 below.



2,3,7,8-TCDD



2,3,7,8-TCDF

Figure 1.1 Chemical structure of 2,3,7,8-TCDD and 2,3,7,8-TCDF

1.2 Formation of dioxins

The mechanisms for formation of chlorinated dioxins may - based mainly on /Ballschmiter 1996/ (partly adjusted based on /Dam-Johansen, 1996/ and other sources) - be divided in:

Thermal formation that may be subdivided into "de novo synthesis" and formation from precursors:

- "De novo synthesis" means formation of dioxins from its basic elements - carbon, hydrogen, oxygen and chlorine - taking place at temperatures between approximately 250 and 500°C on catalytic active surfaces. In particular copper compounds are regarded as effective catalysts.

- Formation from precursors means formation of dioxins from chlorinated organic compounds, such as chlorinated phenols. Similarly, these reactions may take place at temperatures between approximately 250 and 500°C on catalytic active surfaces, but also spontaneously at the relevant temperatures.

Chemical reactions at lower temperatures:

- Chemical reactions below 300°C:
  Such reactions are relevant only to processes involving specific chemical compounds regarded as precursors for dioxin formation. Typical examples include halogenation of phenols and manufacturing of other chemical compounds from halogenated phenols.

- Photochemical reactions:
  Exposure of dioxin precursors to UV-light may lead to dioxin formation. Relevant precursors in this context may include halogenated phenols and benzenes as well as polyhalogenated biphenyls and polyhalogenated diphenylethers.

- Exposure of organic matters to active chlorine:
  Formation of dioxins by use of active chlorine for bleaching and other purposes seems to be possible. Dioxin formation has been observed by use of chlorine as bleaching agents in pulp and paper manufacturing and by use of chlorine for disinfecting, e.g. drinking water, but also in cork production (reference is made to section 2.7). Dioxin formation has also been observed by chlor-alkali processes using graphite electrodes. The mechanisms behind this kind of dioxin formation are not well known, but could be direct chlorination of natural non-halogenated dioxins. Also chlorine releasing compounds, such as hypochlorits are known to contain dioxins in small amounts (reference is made to section 2.1.3)

- Biological formation:
  Formation of dioxins by biological processes from precursors - at least from chlorophenols - seems to be possible. Dioxin formation from chlorophenols has been observed at composting processes.

Based on the list of mechanisms for dioxin formation presented here, it may be assumed, that:

Formation of dioxins may take place at any combustion process based on natural organic materials including fossil fuels. This is due to the fact that chlorine and catalytic active substances such as copper are essential elements that will be present at least as traces in all kind of natural organic materials (but not necessarily in industrially manufactured chemical compounds). Larger quantities of chlorine, organic materials and catalyst should be expected to increase the amount of dioxins generated. Attention should be paid to a number of recycling processes involving metals, glass etc. that may lead to combustion of organic materials present like paint, plastic and dirt.

Other processes taking place above 250°C may develop dioxins in case precursors or organic matter as well as chlorine, oxygen and an appropriate catalyst are present. As organic matter could be present almost everywhere, at least as contamination, attention should be paid to all processes utilising halogenated compounds and taking place at relevant temperature levels. In reality only measuring may confirm or disconfirm formation of dioxins.

Whereas dioxins are likely to be decomposed at very high temperatures (above 800-1000°C) assuming adequate residence time at this temperature level, formation of dioxins may take place again at lower temperatures in the flue gas or on active surfaces by "de novo synthesis". This sets the focus on all kinds of high temperature processes. The source of chlorine or bromine could be the material itself, assuming it contains such halogens that may be released to air during the process, or it could be the fuel. Attention should be paid to it that materials like clay and lime are sedimentary materials that naturally contains chlorine in the form of salts (chlorides), and that very small amounts of chlorine is needed to account for the content incorporated in dioxins.

For all thermal processes the presence of precursors may be anticipated to increase the probability of dioxin formation, and may reduce the need for catalytically active surfaces. All processes involving chlorination of organic compounds or at which active chlorine is present together with organic matter may be regarded as potential sources of dioxin formation at temperatures below 250 °C. Again only measurements may show whether dioxin formation actually takes place.

Photochemical and biological formation may be processes relevant to formation of dioxins in nature and by treatment of organic waste.

For all industrial and natural processes creating dioxins, it would be logical to expect dioxins to be present in all products or materials created by the process to the extent such products or materials actually contain organic matter. Accordingly, it would be logical to expect that all residues from combustion processes creating dioxins also contain dioxins. In case dioxins are created by the process of plastic manufacturing, also industrial products containing plastics should be expected to contain dioxins (has been confirmed for both brominated dioxins /IPCS 1998/ and chlorinated dioxins /Carroll et al 1999 quoted by Greenpeace 2000/). On the other hand glass and metals containing virtually no organic matter should not be expected to contain dioxins.

1.3 Toxicity equivalency factors for dioxins

Dioxins are always found in samples as a mixture of various congeners. The most toxic of the chlorinated dioxins is 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). The toxicity of other chlorinated dioxins is estimated relatively to 2,3,7,8-TCDD. Today only congeners with chlorine atoms in the 2,3,7,8-positions are considered to have toxic properties as TCDD.

Over the years a number of toxicity equivalency factor systems have been developed. The dominating system during the nineties has been the international system that was developed by a NATO-working group in the late eighties. This system replaced more or less the German UBA-system from 1985, the Nordic system from 1988 as well as older systems developed by USEPA.

Recently in 1998 a new system was developed and published by WHO /UNEP 1999/. This system gives in contrast to previous systems separate toxicity equivalency factors for humans/mammals, fish and birds. In table 1.1 the factors for the WHO, the Nordic, the German and the international system are listed.

It should be noted that the Nordic and the International systems are almost identical, whereas the German system as a very early system also assign toxicity to non-2,3,7,8-congeners. The new WHO-system differs strongly in the assessment of pentachloro- and octachlorodioxins.

The knowledge of brominated dioxins is less developed. On an interim basis WHO suggests that the current toxicity equivalency factors for chlorinated dioxins are also applied to brominated dioxins /IPCS 1998/.

In this report the international system will be used, mainly because most data reported follow this system.

Table 1.1
Important toxicity equivalency factor systems for dioxins

Congener	WHO 1998	Nordic 1988	German 1985	International 1989
	WHO-TEF 1)	**Nordic-TEF 2)**	**BGA-TEF 2)**	**I-TEF 2)**
2,3,7,8-TCDD	1	1	1	1
Other TCDDs	0	0	0,01	0
1,2,3,7,8-PeCDD	1	0,5	0,1	0,5
Other PeCDDs	0	0	0,01	0
1 2,3,4,7,8-HxCDD	0,1	0,1	0,1	0,1
1,2,3,6,7,8-HxCDD	0,1	0,1	0,1	0,1
1,2,3,7,8,9-HxCDD	0,1	0,1	0,1	0,1
Other HxCDDs	0	0	0,01	0
1,2,3,4,6,7,8-HpCDD	0,01	0,01	0,01	0,01
Other HpCDDs	0	0	0,001	0
OCDD	0,0001	0,001	0,001	0,001
2,3,7,8-TCDF	0,1	0,1	0,1	0,1
Other TCDFs	0	0	0,01	0
1,2,3,7,8-PeCDF	0,05	0,01	0,1	0,05
2,3,4,7,8-PeCDF	0,5	0,5	0,1	0,5
Other PeCDFs	0	0	0,001	0
1 2,3,4,7,8-HxCDF	0,1	0,1	0,01	0,1
1,2,3,6,7,8-HxCDF	0,1	0,1	0,01	0,1
2,3,4,6,7,8-HxCDF	0,1	0,1	0,01	0,1
1,2,3,7,8,9-HxCDF	0,1	0,1	0,01	0,1
Other HxCDFs	0	0	0,0001	0
1,2,3,4,6,7,8-HpCDF	0,01	0,01	0,01	0,01
1,2,3,4,7,8,9-HpCDF	0,01	0,01	0,01	0,01
Other HpCDFs	0	0	0,00001	0
OCDF	0,0001	0,001	0	0,001

1) The TEF-values stated cover exposure to humans and mammals. Separate and slightly different TEF-values have been stated for fish and birds /UNEP 1999/.

2) From /Jensen 1997/.

1.4 Properties and degradation of dioxins

Based on /Jones & Sewart 1997/, the properties of chlorinated dioxins may be briefly described as follows:

- Dioxins are non-polar, poorly water soluble, lipophilic and stable chemicals.
- Solubility in water decreases with increasing level of chlorination. E.g. the solubility of 2,3,7,8-TCDD is in the order of 20 ng/l, whereas the solubility of OCDD is about three orders of magnitude lower.
- The octanol-water partition coefficient (log K_{ow}) increases with chlorination and ranges from 6.80 for 2,3,7,8-TCDD to 8.20 for OCDD. These values are among the highest reported for environmental organic contaminants and means that dioxins will have a high affinity for organic matter, fats and oils.
- Dioxins are generally stable in the presence of strong acids and bases and remains stable at temperatures below 750^{o}C.

Degradation mechanisms should be expected to include thermal, photochemical and biological degradation. Photo-degradation has been shown to favour the 2,3,7,8-positions for PCDFs and the 1,4,6,9-positions for PCDDs, leading to a decrease of 2,3,7,8-PCDF congeners and an increase in 2,3,7,8-PCDD congeners /Jones & Sewart 1997/. Biological reactions in sediments are believed to cause a dechlorination of higher chlorinated dioxins like OCDD thereby transforming these into 2,3,7,8-TCDD and lower chlorinated dioxins /Albrecht et al 1999/.

However, all degradation processes apart from thermal degradation should be expected to be extremely slow. Preliminary estimates of degradation half-lives in nature indicate half lives in water and sediments ranging from around 30 years to around 200 years /Sinkkonen 1998/. In soil, it is generally accepted, that the half-life of 2,3,7,8-TCDD and other congeners is in the order of 10 years, which however may be due to physical loss processes like volatilisation, leaching of particles, oils and surfactants rather than degradation /Jones & Sewart 1997/. The fact, that dioxins have been detected in natural clay (reference is made to section 2.2.1) shows that dioxins have the ability under appropriate conditions to persist for thousands and maybe even millions of years.

A natural conclusion to be made based on this knowledge is that the fate of dioxins in industrial and residual products will depend strongly on the fate of the product itself. Logically it should be assumed that:

1. Dioxins integrated in products are likely not be degraded during the useful life of products.
2. A significant potential for circulation of dioxins between the technosphere and the environment exists.

Furthermore, attention should be paid to the risk that dioxins with a high number of chlorine or bromine atoms like octachlorodibenzo-*p*-dioxin that are relatively non-toxic, in nature or landfills should be degraded to the more toxic hepta-, hexa-, penta- or tetrachlorinated dioxins.

1.5 Basic assumptions for this investigation

Relation to the Danish paradigm on substance flow analysis (SFA)
This report is organised according to the Danish Paradigm for substance flow analysis (reference is made to /Lassen & Hansen 2000/). However, some adjustments to the paradigm have been necessary, as the paradigm is developed for substances used intendedly in products and causing emissions to the environment by manufacturing, use as well as disposal processes. The paradigm distinguishes between intended uses and non-intended used. Non-intended uses cover uses as a natural or anthropogenic contaminant.

By contrast, the use of dioxin can in no way - apart from laboratory purposes - be described as intended, and dioxins are by nature process related, although they may be present in products and materials contaminated by processes. Thus the choice has been made to organise the report according to processes and treat transport and fate by products as sub-items to the relevant processes.

Concepts and terminology
The SFA-methodology applied to dioxins in this report means that the following balance has to be considered:

Import + formation + extraction = export + destruction + emissions + stock building

The system considered is the Danish Society - or more precisely the technosphere within the Danish Society.

In geographical terms the system boundaries correspond to the national borders of Denmark. In temporal terms the boundary is 1 year taken as an average of 1998 and 1999, as most data utilised and in particular the statistical data describing activity levels relate to either 1998 or 1999. In case it has been necessary to use older or newer data, this is done based on the implicit assumption that such data are valid also to the period of 1998 to 1999.

Concerning the elements in the balance presented above, they should be taken as self-explaining perhaps with the exception of "stock building" that covers the change in the society's stock of the substance in question that typically addresses the presence of the substance in products in use in the society. In case of dioxins the dominant type of product seems to be wood previously treated by pentachlorophenol.

Another concept normally used in SFA is the term "consumption" that covers the input into the society by end products. For substances used intendedly in products, the consumption is a key figure, as it indicates the total turnover of the substance in the society or by the product type in question. However, for dioxins formed un-intendedly by processes and to a significant extent emitted directly to the environment, the consumption by products is in itself not a relevant indication of the total turnover and needs to be supplemented by a calculation of the total formation of dioxin in Denmark.

Data reliability
It is recognised that dioxin formation is extremely process specific. This means that the local conditions of the individual manufacturing plants etc. with respect to actual raw materials and process conditions, flue gas cleaning and in particular temperature patterns in the flue gas cleaning system and chimneys have determining significance to the amount of dioxin created.

As a consequence, most confidence is generally placed with measurements from Danish plants, no matter whether they are few and may be regarded as spot tests rather than thorough investigations. Still they represent actual conditions in Denmark with respect to raw materials and process conditions.

Second most confidence is assigned to literature data available from comprehensive reviews like the European Dioxin Inventory, as these data build on many data from different countries thus reflecting the typical variation caused by different process conditions, besides that the data presented has been reviewed by competent persons.

The lowest level of confidence is assigned to individual literature data covering one situation or country only, as these data may in worst case deviate from the true Danish figures by several orders of magnitude due to different process conditions.

Whereas these considerations have guided the overall strategy for assessment of data reliability basically a case by case assessment has been performed. In some cases, it has not been possible to be critical, as only a few data – if any – were available. In the assessment attention has also been paid to the fact that the factors determining dioxin formation may be subject to variations at the individual plants (one will typically distinguish between "normal" and "deviating" process condition, where the deviating conditions may include start up and close down operations as well as other problems occurring during operation), and one should be prepared to expect significant variations in dioxin formation also for individual plants.

Although steps have been taken to improve the existing knowledge on dioxin formation and emission in Denmark by measurements, the number of analyses available to Danish plants is still limited, and the assessment presented in this report is primarily based on literature data originating from other countries. In adopting such figures for Danish conditions it has been considered more correct to rely on minimum and maximum figures than on average figures, as it is not known to what extent the data available is representative of Danish plants, and average figures would give a false impression of the accuracy of the estimates presented. A consequence of this approach is the very high intervals of uncertainty that typically have been accepted.

Brominated dioxins

Measurements on brominated dioxins and in particular congener specific measurements are relatively few. This reflects the fact that analytical procedures are still in the process of being developed /Vikelsøe 2000/. It has therefore not been possible to assess the turnover of these substances in Denmark. However, an attempt has been made to estimate the consumption of brominated dioxins present in goods due to the use of brominated flame retardants. The estimate shows that the turnover of brominated dioxins most likely is significant, and it can only be recommended to devote efforts to improve the general knowledge of this issue, and in particular to develop analytical procedures that would allow quantification and evaluation of the relevant flows.

Destruction of dioxins

Destruction of dioxins is an issue normally not addressed by dioxin inventories, but anyhow relevant to include in a substance flow analysis. Destruction of dioxins in a modern society will primarily be related to incineration and other high temperature processes at which dioxins will be exposed to temperatures of 800-1000ºC or above for an adequate period of time. However, only little knowledge seems to be available on the exact rate of destruction by different processes.

For municipal waste incineration /UNEP 1999/ states that incomplete destruction or transformation of dioxins present in the incoming waste is not relevant to consider as a source for dioxin emission from modern incineration plants. Several studies quoted in /Dam-Johansen 1996/ indicate efficient destruction of dioxins by waste incineration although exact destruction rates are not stated apart from a few laboratory investigations resulting in complete destruction. Danish investigations show that the destruction rate for phthalates by municipal waste incineration is likely to be better than 99.8% /Hoffman 1996/ which may in this context indicate that also other organic compounds like e.g. dioxins may be destroyed with an destruction rate close to 100%.

Based on this knowledge it is in this report assumed that dioxins directed to modern waste incineration plants and other high temperature plants operating at temperatures around 1000ºC or above like brickworks and cement manufacturing plants will be destroyed at a destruction rate close to 100%. The calculations have in reality been based on a destruction rate of 100%. It is emphasised that the destruction rate will most likely never be exactly 100%, and so far it is not possible to say whether the destruction rate of the individual plant will be down to 99% or even further below, as the destruction rate should be expected to depend on plant design as well as conditions of operation. Thus, the assumption of complete dioxin destruction by high-temperature processes used in this report should be taken as an indication that such processes should generally be expected to result in a significant destruction of dioxins, but not as a documentation that complete dioxin destruction will always be obtained by any high-temperature process.

2 Formation and turnover by industrial activities

2.1 Chemicals

Manufacturing of chemicals in Denmark is dominated by pharmaceuticals, pesticides, cleaning agents and food additives. Only few manufacturing processes utilise temperatures above 200°C and involve an intended presence of halogens, such as chlorine. Based on contact to the relevant Danish companies, it seems that the dominant potential process for dioxin formation in Danish chemical industries would be elimination of gases vented from manufacturing processes by high-temperature burning (800-1000°C). This process is relevant to one pesticide manufacturing company and one pharmaceutical company. To the best of knowledge, the use of chlorine for industrial processes in Denmark is dominated by 3 major companies including the two companies mentioned above. The third company in question deals with vitamin manufacturing and is discussed in section 2.8.
There are no indications of potential dioxin formation in Danish industries involved in manufacturing of cleaning agents or food additives.

2.1.1 Pesticide manufacturing

The pesticide manufacturing company uses chlorine in the production, and the air is before emission burned in a ceramic filter at 800-850°C. In 1991 the dioxin emission was measured to 1 ng total dioxin/Nm^3 corresponding to a total emission of 0.4-0.5 g total dioxin per year. No information regarding congener patterns and TEQ is available. No recordings of collected filter dust have been made, as the quantity is assumed marginal.

The company furthermore practices combustion of wastewater and flash drying of sludge. Air emission from combustion of wastewater has been shown in 1995 to contain < 1 pg N-TEQ/ Nm^3 equalling an emission of < 90 µg N-TEQ per year. Drying of sludge from production processes takes place in a flash drier by 750-900°C warm air heated by burning of natural gas. The air passes a filter bag at about 130°C. Filter dust is returned to the sludge that after drying is utilised for agricultural purposes. No measurements of dioxin in air emission nor dried sludge have been carried out. No knowledge from similar processes abroad is available. The airflow is approx. 80 million Nm^3/year, but in absence of actual measurements it is not possible to make an estimate of the emission to air from the process. It is not possible either based on the existing knowledge to assess the potential amount of dioxin directed to farmland with sludge.

The present knowledge may be summarised to the following: Some emission of dioxins takes place to air besides that dioxins are applied to farmland by sludge or directed to landfills as filter dust. As the existing measurements are incomplete and old, and thus may not be reliable, it is not possible to quantify the emissions in question.

2.1.2 Manufacturing of pharmaceuticals

The pharmaceutical company uses chlorine in the production, and the off-gases are before emission burned in a sand filter at 900-1000°C. No measurements of dioxin emission have been undertaken. The airflow through the filter is approx. 600 million Nm^3/year. Again no recordings of collected filter dust have been made, as the quantity is assumed marginal. In absence of actual measurements it is not possible to make estimates of the emission to air or the amount of dioxins directed to landfill as filter dust.

2.1.3 Chemical products

It is known, that a number of chemical products may contain dioxins:

Bleaching agents
Bleaching agents containing hypochlorite salts may contain 5 pg I-TEQ/litre /Jensen 1997/. The use of hypochlorite and similar chemicals in Denmark is dominated by sodium and potassium hypochlorite, and the consumption of sodium and potassium hypochlorite in the middle of the eighties has been estimated at around 15,000 tonnes/year /Danish EPA 1989/. Assuming that the consumption of bleaching agents has remained unchanged, the consumption of dioxins may be roughly estimated at <1 mg I-TEQ/year. This consumption will primarily end in wastewater.

Pesticides
Dioxin has been registered in a number of pesticides and other pesticides are suspected to contain dioxins due to formation during manufacture. The relevant pesticides are listed in /Costner 1999/ and /Jensen 95/. Of these pesticides the following were used in Denmark in 1998 /Bekæmpelsesmiddelstatistik 1998/:

Table 2.1
Danish consumption of pesticides confirmed or suspected to contain dioxins

Common name	**Consumption in Denmark 1998 kg active substance**
Bromoxynil	80,192
Chlorfenvinphos	89
Chlorothalonil	25,070
2,4-D	0
Dicamba	3,183
Dichlorprop	302
Dichlor-P	4,347
Diflubenzuron	392
Diuron	27,370
Imazalil	12,389
Linuron	8,019
MCPA	159,444
Mechlorprop	19,413
Mechlorprop-p	1,269
Paclobutrazol	23
Tetradifon	5
Total	**341,507**

Investigations of the content of dioxins in pesticides sold in Denmark are scarce. In Danish investigations from 1987 (quoted in /Jensen 95/) the dioxin content of dichlorprop was measured to 0.35 µg I-TEQ/kg, whereas the dioxin content of MCPA and mechlorprop was determined to 0 µg I-TEQ/kg, as only non-toxic congeners were present in MCPA and mechlorprop.

Assuming that other pesticides than MCPA and mechlorprop would have the same dioxin content as dichlorprop, the consumption of dioxin with pesticides in Denmark in 1998 may roughly be calculated to 56 mg I-TEQ. Thus, it seems realistic to accept despite all uncertainties related to lack of complete and updated information, that the real consumption of dioxin with pesticides in 1998 in Denmark was less than 1 g I-TEQ. This consumption will primarily end in soil.

Brominated flame retardants
Brominated flame retardants are suspected to be a significant source for brominated dioxins. Brominated dioxins occur in the commercial brominated flame redardants and are furthermore created by manufacturing and other processing (inclusive recycling) of plastic products based on flameretarded resins /IPCS 1998/. Brominated dioxins are also formed by burning of plastic products containing brominated flame retardants /IPCS 1998/.

Brominated flame retardants form a diverse group of compounds and the dioxin content is highly varying among the specific compounds. According to the IPCS review, the highest levels of PBDDs/PBDFs are found in materials flame retarded with PBDEs (polybrominated diphenyl ethers) exceeding the dioxin levels of other polymer/flame retardants systems by several orders of magnitude. The levels of PBDDs/PBDFs in polymers with PBDEs were in the range of several thousands mg/tonne. The review, however, does not give any information on the dioxin congener patterns of the specific polymer/flame retardants systems. Other information, however, indicates that the content of the toxic congeners in polymers is significantly higher in polymers flame retarded with PBDE. The German Dioxin Ordinance specifies the maximum allowable concentration of a number of 2,3,7,8-substituted PBDDs/PBDFs in products marketed in Germany. As a consequence of the ordinance, PBBs (polybrominated biphenyls) and PBDEs have been replaced by other flame retardants in the German industry, because the dioxin content of the PBDE containing polymers often exceeded the maximum allowable (ZVEI 1988). Until July 1999 the Ordinance prohibited any product containing more than 10 mg/tonne ppb of the sum of four congeners: 2,3,7,8 TBDD; 2,3,7,8 TBDF; 1,2,3,7,8 PeBDD and 2,3,4,7,8 PeBDF whereas the sum of eight other congeners was not to exceed 60 mg/tonne (ppb). By July 1999, the limits were lowered to 1 and 5 ppb, respectively. In terms of toxicity equivalence factors, the actual requirements of the German Dioxin Ordinance correspond to a maximum of less than 2 mg I-TEQ/tonne for the 12 congeners, whereas the requirement before July 1999 corresponded to <20 mg I-TEQ/tonne.

About 90% of the consumption of BFRs with finished products in Denmark are imported, and the flame retardants used in products on the Danish market are most probably the same as in products marketed in Germany.

The present knowledge of the occurrence and formation of brominated dioxins in flame retardants and in flame retarded plastics does, however, not allow for trustworthy detailed calculations on the formation or consumption of brominated dioxins in Denmark. But it is possible to present a rough screening-like calculation appropriate for indicating the relevant order of magnitude for the consumption of brominated dioxins with plastics in Denmark. This calculation is based on the following facts and assumptions:

- The total consumption of brominated flame retardants in plastics in Denmark has been estimated at 340-730 tonnes for 1997, of which PBDEs and PBBs counted for 30-120 and 1-7 tonnes, respectively. Printed circuit boards counted for 130-230 tonnes and housing of electronic and electrical appliances and machines counted for 80-140 tonnes /Lassen & Løkke 1999/.
- The concentration of flame retardant in finished plastic products varies between 1% and 15% with the lowest concentration found in building materials and the highest in printed circuit boards /Lassen & Løkke 1999/. Assuming an average concentration of 10%, the total quantity of flame retarded plastics in Denmark may be estimated at 3,400-7,300 tonnes in 1997. The consumption of plastic flame retarded with PBDEs and PBBs can roughly be estimated at 300-1,300 tonnes. This may be an underestimate of the actual quantity, which however, is appropriate for the following calculations.
- Concentrations of brominated dioxins found in casings and circuit boards for electrical appliances with unknown polymer/flame retardant system corresponded to I-TEQ values for casings in the range of 0 - 37 mg I-TEQ/tonnes and for circuit boards in the range of 0 - 6.6 mg I-TEQ/tonnes (based on data from /IPCS 1998/ assuming similar toxicity factors for brominated congeners as for chlorinated congeners). It is likely that the high end of the ranges represent polymers containing PBDEs or PBBs, which may be used for both applications, but this assumption cannot be confirmed.

Assuming that the presence of brominated dioxins in plastics is mainly related to the use of PBDEs and PPBs, and that plastics containing these flame retardants (300 - 1,300 tonnes) will contain brominated dioxins in the range of 6.6 - 37 mg I/TEQ/tonne, whereas plastics with other brominated flame retardants will contain less than 2 mg I-TEQ/tonne, the consumption of brominated dioxins by flame retarded plastic products in Denmark can be estimated at 2 - 60 g I-TEQ/year.

The present knowledge does not allow for quantification of the further fate and transport of brominated dioxins in the Danish society. On a qualitative level the further fate and transport may be briefly outlined as follows:

- Part of the content of brominated dioxins in plastics will be released, as dust or vapours to the rooms in which the appliances/machinery are placed, used or dismantled.
- To the extent the flame retarded plastics are exposed to accidental fires or further processing, e.g. recycling operations, further formation of brominated dioxins may take place.
- To the extent the flame retarded plastics are directed to waste incineration plants, the dioxins present in the materials are likely to decompose at high temperatures, but formation of brominated dioxins as well as mixed brominated/chlorinated dioxins may further take place in the colder part of the plant such as the boiler zone or the flue gas cleaning system etc. parallel to the experiences of chlorinated dioxins presented in section 5.2.1.

Other chemical products
Dioxins have been detected in PVC, ethylene dichloride and hydrogen chloride /Carroll et al 1999 quoted by Greenpeace 2000/ and dyestuffs /Jensen 1997/. It is deemed likely that dioxins will be present in other products containing chlorine. However, the knowledge available does not allow an estimate of the consumption of dioxins and the release to the environment in Denmark to be made.

2.2 Materials manufactured by high-temperature processes

Manufacturing of materials by high-temperature processes in Denmark includes:

- Insulation materials based on clay
- Manufacturing of insulation materials based on glass and other mineral fibres
- Tiles and bricks
- Cement
- Lime
- Other materials.

However, it is now clear that dioxins are not only generated by manufacturing processes. Dioxins must be assumed also to be present in the raw materials.

2.2.1 Raw materials

An investigation of 33 samples of natural clay of various origin (mainly kaolin-clay) has revealed a median content of dioxin of 154 ng I-TEQ/kg dry matter with a variation of 3.9-1132 ng I-TEQ/kg dry matter /Jobst & Aldag 2000/. Parallel to this analysis of kaolin-clay, moler and other materials used as binders in feedstuff in Denmark have shown dioxin content of normally 10-400 pg I-TEQ/kg at 88% dry matter /Plantedirektoratet 2000/. A single sample, however, was measured to 16738 pg I-TEQ/kg at 88% dry matter /Plantedirektoratet 2000/. For moler originating from Denmark was on 5 samples measured an average of 139 pgI-TEQ/kg with a variation of 90-173 pg I-TEQ/kg at 88% dry matter /Plantedirektoratet 2000/. It should be noted that EU has established a threshold for dioxin in kaolin-clay for feedstuff of 500 pg WHO-TEQ/kg /Plantedirektoratet 2000/, meaning that the Danish investigations described above for kaolin etc. can only be taken as representative to materials used for feedstuff and not for clay in general.

The origin of the dioxin measured is not known, but may be volcanic eruptions or natural fires in ancient times. It must be assumed that other clay deposits in Denmark and internationally may contain dioxin in small concentrations, although no knowledge of the actual concentrations is available. In the following the concentrations reported above are used for estimating the consumption of dioxin with clay-like raw materials used for manufacturing of construction materials etc. No knowledge exists and no estimate is made regarding the content of dioxin in raw materials like lime and chalk.

Quantities of raw materials

Based on the Danish manufacturing and trade statistics /Danmarks Statistik 1999a and 1999b/, Danish production, import and export of the relevant commodity items in 1998 is summarised as stated in table 2.2 below.

Table 2.2
Statistical data for clay-like raw materials

Item	Production (tonnes)	Import (tonnes)	Export (tonnes)	Supply (tonnes)
Kaolin	0	17300	170	17100
Kaolin-clay	0	2900	1300	1600
Bentonite	7300 [1]	24500	3600	28200
Clay- others	16 [2]	10900	1700	9200
Moler	50000 [1]	7900	48400 [1]	9500

[1] Figures estimated based on value

[2] Figure does not include extraction for own production of items like tiles and bricks. The total figure should likely be in the range of 900,000 tonnes (reference is made to section 2.2.3).

Dioxin balance

Assuming dioxin concentrations as follows

- Kaolin: As "clay-others"
- Kaolin-clay: 0,1 – 1100 ng I-TEQ/kg dry matter
- Bentonite: As "clay-others"
- Clay - others: 154 ng I-TEQ/kg dry matter (variation 4 - 1100 ng)
- Moler: 100-200 pg I-TEQ/kg dry matter

The dioxin balance for clay-like raw materials can be calculated as stated in table 2.3.

Table 2.3
Dioxin balance for clay-like raw materials

Item	Production (mg I-TEQ)	Import (mg I-TEQ)	Export (mg I-TEQ)	Supply (mg I-TEQ)
Kaolin	0	2700 (69 – 19000)	26 (0.7 - 200)	2600 (68 – 18800)
Kaolin-clay	0	0.3 - 3200	0.1 - 1400	0.2 – 1800
Bentonite	1100 (29 - 8000)	3800 (98 – 27000)	600 (14 - 4000)	4300 (113 – 31000)
Clay- others	2 (0.06 – 18) [1]	1700 (44 – 12000)	260 (7 - 1900)	1400 (37 – 10100)
Moler	5 – 10	0.8 - 1.6	4.8 - 9.7	1 - 1.9
Total	**1100 (30 - 8000)**	**8200 (200 – 61000)**	**900 (30 - 7500)**	**8300 (200 – 62000)**

[1] Figure does not include dioxin in clay extracted for own production of other items like tiles and bricks. The total production should correspond to a figure of 140,000 (3,600 - 990,000) mg I-TEQ.

The balance indicates, despite the substantial uncertainties related to the calculations that the flow of dioxin with clay-like raw materials should be considered significant.

However, apart from the quantities used as feedstuff additives, paper manufacturing and for decoration or educational purposes all clay-like materials in their further life cycle will undergo a burning process at high temperatures likely to destroy most if not all of dioxins present in the materials. The hypothesis has been presented that dioxins present in clay might partly evaporate during the heating process prior to the burning /Ferrario & Byrne 2000 quoted by Greenpeace 2000/. No precise knowledge is, however, available concerning the significance of such evaporation on the emission of dioxins from clay-based manufacturing processes and the extent to which this potential source of dioxins has been considered by the measurements from clay-based manufacturing activities referred in the following section. It is noted that the existing measurements of air emission from clay-based manufacturing processes do not support the hypothesis (reference is made to section 2.2.2 and 2.2.3) that evaporation of dioxins from clay is a significant source for release of dioxins to the environment. Is should be noted, that no measurements of the dioxin content in clay based end products like tile and bricks exist. Thus it is not known, whether some of the dioxin present in the raw materials may survive the heating process and be present in the end products.

Regarding feedstuff and paper product, the content of dioxins in such products is assessed in section 2.4.4 and 2.7.2 respectively.

Regarding clay for decoration and educational purposes, no exact figures of the consumption are available. Assuming as a rough estimate that between 10 and 50% of the supply of "clay-others" stated in table 2.2 corresponding to approx. 900 – 4600 tonnes is used for decoration and educational purposes, the dioxin consumption for these purposes may be roughly estimated at 0.004 – 5 g I-TEQ/year. Clay used for these purposes should be expected to be disposed of partly to household waste directed to incineration and partly to inert waste directed to land-filling.

2.2.2 Clay-based insulation materials

Clay-based insulation materials are manufactured by one Danish company only. Clay is burned at a high temperature in a rotary kiln, in which the materials are heated by warm air. The emission into air contains around 13% O_2 (because of massive surplus of air) and is cleaned by passing an electrostatic filter. The temperature in the filter is around 200°C. Clay naturally contains organic matter and chloride, including traces of dioxin (reference is made to section 2.2.1).

Plant activity
Filter-dust is re-circulated into the rotary kiln. Thus no filter dusts for disposal are generated. Production volume figures are confidential.

Dioxin formation and disposal
No measurements of dioxin formation have been carried out by the company. Based on information from the company on air emission volumes and assuming emission rates equal to tile- and brick-working (reference is made to German investigations reported in the European Dioxin Inventory /Landesumweltamt Nordrhein-Westfalen 1997/), the air emission may be estimated (best estimate) at around 0.009 g I-TEQ per year and most likely within the range of 0.0006 - 0.24 g I-TEQ/year.

2.2.3 Tile and bricks based on clay

There are 3 major and about 22 smaller tile and brickworks in Denmark. They use tunnel kilns, where the materials are heated by warm air. The maximum temperature is 1,000-1,050°C that decreases through the tunnel. At the point of emission, the air temperature is in the range of 150-200°C. The content of oxygen in the air stream varies within 10 and 12% in the heating zone and 15 and18% at the point of emission. Only two of the works have filters. Apart from the natural organic matter in clay, sawdust (about 1%) is added to the clay for yellow bricks (Murværkscentralen 2000). Dioxin formation has been confirmed by foreign investigations (see below).

Plant activity
According to the statistics the total production of clay based tiles and bricks in Denmark in 1998 added up to approximately 450 million pieces /Danmarks Statistik 1999b/. Assuming an average weight of approx. 2 kg/piece the total production volume in 1998 may be estimated at approx. 900,000 tonnes/year.

Dioxin formation and disposal
No measurements of dioxin formation have been carried out in Denmark. Based on German investigations the European Dioxin Inventory calculated an emission factor of emission to air of 0.018 µg I-TEQ/ton of material and a variation of 0.001 – 0.23 µg I-TEQ/ton (Landesumweltamt Nordrhein-Westfalen 1997), whereas no figures for filter dust from air cleaning are available.

Based on these figures the turnover of dioxins by tile and brick manufacturing in Denmark may be estimated as follows:

Emission to air:	0.016 g (0.001 - 0.2 g) I-TEQ/year
Residues for disposal:	Assumed insignificant

2.2.4 Cement

Cement is manufactured by one plant only in Denmark. The plant operates 7 kilns, of which 3 including the largest is used for grey cement and the rest for white cement. The raw materials for grey cement are sand, chalk and fly ash from power stations, whereas chalk, sand, kaolin and spent catalyst is used for white cement. Cement manufacturing typically involves temperatures up to around 1500°C.

The largest kiln is heated by a mixture of petcoke, coal and industrial waste including plastic (non-PVC) and sludge from paper manufacturing and textiles from tyres. Waste containing more than 0.1% chlorine is not accepted. The air emission from this kiln is cleaned in an electrostatic filter at 130°C before directed to the chimney. Coal and oil only heat the other grey kilns, and the off-gases are cleaned by an electrostatic filter at around 250°C. The air emission from the 4 kilns used for white cement is cleaned first in an electrostatic filter at around 300°C and afterwards by a scrubber.

Plant activity:
Based on information from the company a total of approx. 2.4 million tonnes of cement were manufactured in 1999.

In the largest kiln approx. 1.5 million tonnes cement with airflow of 3150-3500 million Nm^3/year was manufactured. In the other kilns together was manufactured approx. 0.9 million tonnes cement with airflow of around 3200 million Nm^3/year, and a discharge of cleaned scrubber water of approx. 400,000m^3 water/year.

Filter dust from electrostatic filters is recycled into the largest kiln. Scrubber water is cleaned and the content of solids used for gypsum manufacturing.

Dioxin formation and disposal
Measurements of dioxin emission to air from the large kiln have shown values of <0.6-2.7 pg I-TEQ/Nm^3 equalling an emission of 0-9.5 mg I-TEQ/year. The figures reflect normal operation, and should thus be representative of 98-99% of the total production time. No measurements have been undertaken for the other kilns and scrubber water. Assuming the air emission level for the large kiln to be valid also to the other kilns the total emission to air should be expected not to exceed 18 mg I-TEQ/year. However, the higher temperature over the filter for the smaller kilns indicates that dioxin formation from these kilns may likely be higher besides that the emission depends on the efficiency of the scrubber that is unknown with respect to dioxin.

The European Dioxin inventory assumes a default emission factor for emission to air of 0.15 µg I-TEQ/tonnes of cement and min.-max. figures of 0.05 - 5 µg I-TEQ/tonnes

/Landesumweltamt Nordrhein-Westfalen 1997/. The maximum figure should, however, be considered debatable, as it could well relate to old literature values describing co-combustion with industrial waste. Therefore, the choice has been made in this assessment and based on the information available in the European inventory to accept a maximum factor of 1µg I-TEQ/tonnes. For a production volume of 2.4 million tonnes these emission factors equal a total emission to air of 360 mg I-TEQ/year (120 - 2400 mg I-TEQ/year). For a production volume of 0.9 million tonnes corresponding to the production of the smaller kilns only, the emission factors similarly equal an emission to air of 135 mg I-TEQ/year (45-900 mg I-TEQ/year).

The best possible estimate is assumed to be based on the company's own measurements with respect to the largest kiln, and using the above described emission factors for the smaller kilns. This approach corresponds to a total emission to air of 45 - 920 mg I-TEQ/year.

No data on the content of dioxin in scrubber water and gypsum are available. Scrubber water is disposed of as wastewater.

2.2.5 Lime

Burned lime is produced by one company in Denmark. The process takes place in a rotary kiln at 1200 - 1250°C for 2-3 hours (1-2% oxygen at the end of the kiln). The air from this process is used in a cyclone pre-heater at about 700°C. From here the air flows into another cyclone (about 400°C) before it passes through an electrostatic filter and out the chimney at about 280°C. The oxygen concentration through these last processes is 8-9%. Dust collected in the electrostatic filter and the other cyclone is included in products for flue gas treating e.g. by municipal waste incineration plants. The goods pass the cyclone pre-heater, before it goes into the rotary kiln. From here it goes into a cooler, where the temperature of the goods declines from about 1000°C to about 175°C in one hour. The sources for heating are fuel oil, natural gas and coke. Lime is made from limestone, which being a sedimentary material naturally contains chloride and traces of copper and organic materials. Dioxin formation has been confirmed by measurements at foreign plants.

Plant activity
In 1998 approx. 90,000 tonnes of burned lime was produced /Danmarks Statistik 1999b/.

Dioxin formation and disposal
Measurement of dioxin emission to air is planned to be carried out in the summer of 2000. The result is, however, not yet available.

European measurements indicate emission factors in the range of 0,01-29µg I-TEQ/ton /Landesumweltamt Nordrhein-Westfalen 1997/. Based on these emission factors the current Danish emission may be estimated at 0.9 – 2,600 mg I-TEQ/year.

No precise figure for the amount of filter dust collected and sold as flue gas treatment material is available. Based on English data (reference is made to /Dyke et al 1997/) a quantity of around 2700 tonnes/year may be estimated. The same reference /Dyke et al 1997/ also presents figures of 0.001 – 30 ng I-TEQ/kg for the content of dioxin in the filter dust. Assuming these figures to be valid also to the Danish plant the total amount of dioxin collected and sold with filter dust can be estimated at < 0.08 g I-TEQ/year.

Other comments
In 1999 control measurements revealed that lime used in citrus pulp pellets imported to Europe from Brazil to be used as feedstuff was heavily contaminated by dioxins. Further investigations disclosed that the lime used in the actual case was not natural lime, but a waste product from chemical manufacturing /Malish et al 1999/

2.2.6 Other materials

Other materials cover:

- Insulation materials based on mineral fibres like glass wool and rock wool.
- Glass for other purposes
- China and ceramics

In Denmark 4 companies operating in total 6-7 plants are manufacturing such materials. Glass products and in particular ceramics are furthermore manufactured by a number of small arts and crafts workshops. It should be noted that for some of the companies the raw materials used in the production are partly secondary materials. This is e.g. the case for glass wool and container glass manufacturing.

Activity in Denmark
Based on statistics /Danmarks Statistik 1999b/ and other relevant sources the yearly activity in Denmark can be summarised as follows:

Insulation materials:	Approx. 150.000 tonnes
Glass for other purposes:	Approx. 600.000 tonnes
China and ceramics except tiles and bricks:	Approx. 4.400 tonnes

Dioxin formation and disposal
None of the companies involved have measured for dioxin in air emission or residues. The European Dioxin Inventory (section on Germany) and UNEP give air emission factors for glass in the range of 0.005 – 0.032 µg I-TEQ/tonnes of material /Landesumweltamt Nordrhein-Westfalen 1997; UNEP 1999/. No emission factors are available with respect to insulation materials and china/ceramics, but it is assumed that the factor for glass reflects the correct order of magnitude also for these materials. No figures are available for filter dust from air cleaning operations.

Based on these figures the turnover of dioxins by other high-temperature materials in Denmark may be estimated as follows:

Emission to air:	0.004 - 0.024 g I-TEQ/year
Residues for disposal:	Assessment not possible.

2.3 Metal manufacturing

Metal manufacturing in Denmark is limited to:

- Metal casting based on iron, steel, copper, lead, aluminium and other metals
- Welding, soldering and similar further processing of cast products or metals delivered as plates, sheets etc.
- Surface protection by hot-dip galvanising, electrolytic galvanising etc.
- Reclamation of steel and aluminium by melting operations.

Furthermore, hard metal products are manufactured in Denmark, and the use of laser cutting in manufacturing is expanding.

The assessment presented in the following is focused on metal casting, hot-dip galvanising and metal reclamation, as they are the only Danish metal manufacturing operations so far believed to develop significant quantities of dioxin. It should, however, be noted that dioxin formation by welding and soldering and similar processes has been documented /Menzel et al 1996 and Menzel et al 1998 quoted by Greenpeace 2000/

2.3.1 Metal casting

Metal casting in Denmark is mainly related to the metals iron, copper, aluminium and lead.

Iron casting takes place at around 12-15 plants, and the process conditions will typically be as follows: The iron is mixed with carbon (3-3.5%), silicone and other alloying elements and is melted by electricity. Whereas the temperature of the iron in the melting zone is around 1,300-1,400°C, the air temperature in the melting chamber will normally be around 200°C. The air is renewed continually before being cleaned by a bag filter at a temperature level of 30-40°C. The melted iron is poured into casting moulds made out of sand, bentonite, water and coke. The sand used for casting moulds is normally of inland origin, but may occasionally also come from beaches. To the extent the sand is of marine origin it may contain chloride. The raw material may be scrap iron, but without paint, galvanisation or other kind of surface treatment.

Casting of copper and aluminium and alloys of these metals takes place at approx. 50 plants, whereas lead casting is dominated by 2 larger Danish companies manufacturing batteries and electrical cables. However, a number of smaller companies involved in manufacturing of yacht keels, roof plates and fishing equipment are also active in field of lead casting. No efforts have been invested to obtain further details of manufacturing processes.

Activity
The activity related to iron casting can, based on information from a number of companies, be outlined as follows: The total production comes up to approx. 75,000 tonnes of iron per year. The amount of filter dust generated by the melting process can be estimated at approx. 200 t/year. Approx. ¾ of this quantity is exported, whereas the rest is directed to Kommunekemi as chemical waste. Casting mould and other waste products counts for a waste quantity of the same size as the amount of iron produced, that is to say around 75,000 tonnes per year and is either landfilled or reused for other purposes /Lemkow et al 1992; Danish EPA 2000e/.

For other metals the material consumption for casting processes is /Lassen et al 1996; Lassen & Hansen 1996; Hansen et al 1999/:

Copper/copper alloys:	Approx. 1500 tonnes/year (1992-data)
Aluminium/aluminium alloys:	Approx. 6000 tonnes/year (1994-data)
Lead/lead alloys:	4000-5000 tonnes/year (1996-data)

Dioxin formation and disposal
For one iron casting company dioxin emission to air was measured in 1999. The production volume for this company equals approx. 20% of the total Danish production. The production is based on scrap iron. Process air and ventilation is mixed before being emitted through a bag filter. The emission factor was determined to 0.411 µg I-TEQ/ton of material /Fyns Amt 2000/. This may be compared to air emission factors given by UNEP for electrical iron and steel foundries of 0.032µg I-TEQ/ton of material /UNEP 1999/. Based on local conditions, the Danish measurement is considered a better estimate than the UNEP value.

For other activities no measurements of dioxin formation have been carried out in Denmark. The European Dioxin Inventory (section on Germany) gives air emission factors for smelting of copper and copper alloys in the range of 0.0008 – 0.84 µg I-TEQ/ton of material and for other non-ferrous metals (tin, cobalt, chromium, nickel, silver, zinc and aluminium) in the range of 0.15-2.4 µg I-TEQ/ton of material /Landesumweltamt Nordrhein-Westfalen 1997/.

Based on these figures the emission of dioxin to air by metal casting in Denmark may be estimated at 0.032 – 0.060 g I-TEQ/year. No knowledge of dioxin content of filter dust from flue gas cleaning and other waste products seems to be available. It is not known whether any dioxin formation takes place in the casting moulds during the process.

2.3.2 Hot-dip galvanising

About 15 companies in Denmark carry out hot-dip galvanising. First the iron is cleaned for organic pollution by the use of tensides, HCl and occasionally also sand blasting. Then the iron is treated with NH_3Cl and afterwards dried, before it is drawn through a zinc-bath of a temperature of 450°C. Despite the efforts to remove organic matter, it is known that the ash layer typically formed on the surface of the zinc-bath will contain organic matter. One company found 6-13% organic matter in this ash. This makes dioxin formation likely. Dioxin formation has been confirmed by measurements abroad.

Plant activity
Based on information from Danish companies, the total production can be estimated at approx. 100,000 tonnes galvanised product per year, whereas the air emission comes up to approx. 33,000 Nm^3/tonnes product.

Generation of filter dust from air cleaning varies, as some plants have no cleaning facilities at all (emission of 50mg dust/Nm^3), whereas larger plants generally are equipped with bag filters allowing an air emission of less than 0.5 mg dust/Nm^3. It is known that one major company produces 8-10 tonnes of filterdust per year. The quantity of filter dust generated may thus be assumed to be somewhat between 20 and 165 tonnes/year.

Filter dust is directed to land-filling or temporarily stored.

Dioxin formation and disposal
No measurements of dioxin formation have been carried out in Denmark. The European Dioxin Inventory (section on Germany) gives air emission factors for hot-dip galvanising plants in the range of 0.007 – 0.132 ng I-TEQ/m^3, whereas the content of dioxins in filter dust is in the range of 2.15-9.6 ng I-TEQ/kg /Landesumweltamt Nordrhein-Westfalen 1997/.

Based on these figures the turnover of dioxins by hot-dip galvanising in Denmark may be estimated as follows:

Emission to air:	0.023 – 0.44 g I-TEQ/year
Filter dust landfilled/stored:	< 0.002 g I-TEQ/year

It is not known whether the air emission factors quoted above include emission with dust in case no cleaning of off-gases is employed. If not, the air emission may be higher than calculated. However, the figures for dioxins collected with filter dust seem to indicate that emission of dioxins with emission of dust may be insignificant.

2.3.3 Steel reclamation

In Denmark one company only carries out reclamation of iron and steel scrap. The scrap is melted in an electric arc furnaces at around 1,600°C. The raw steel bars produced will later after re-heating be processed into plates, bars and other profiles. The air passes a filter bag at about 80°C. Due to the high temperatures and the fact that the scrap received will contain residues of organic materials as well as copper dioxin formation due to "de novo synthesis" is likely. It is generally accepted that dioxin formation depends strongly on operation conditions, such as the temperature in the flue gas cleaning system and the extent to which scrap is preheated /Det Danske Stålvalseværk A/S 2000b; Landesumweltamt Nordrhein-Westfalen 1997/.

Plant activity
Based on information from the company, the activity of the plant can be summarised as follows (1998-figures - /Det Danske Stålvalseværk 1999; Det Danske Stålvalseværk A/S 2000a/):

Scrap	approx. 850,000 tonnes/year
Raw steel production	800,000 tonnes/year
Filter dust exported (own estimate)	10,000 tonnes/year
Production waste to Kommunekemi	1,118 tonnes/year
Reused production waste, excluding filter dust	approx. 90,000 tonnes/year
Production waste deposited within the plant area	approx. 29,000 tonnes/year

Of the total production waste, slag from the kiln constitutes about 47%. Slag is reused for asphalt. Other ways of recycling are iron oxide, ferrosilicium, sludge to be used in cement manufacturing etc. /Det Danske Stålvalseværk A/S 1999/. Filter dust is exported to Spain via Germany for recovery of zinc etc.

Dioxin formation and disposal

The dioxin emission to air from this plant is of importance though the level of emission may be subject for discussion. The company itself has estimated the present dioxin emission to air at 1.5 g N-TEQ/year. This estimate is based on a number of measurements (more than 15) undertaken from 1991 to 1995. These showed dioxin contents in the flue gas after bag filter corresponding to an average of 1770 ± 510 ng N-TEQ/ton scrap (90% confidence interval), with a minimum of 60 ng N-TEQ/ton and a maximum of 3760 ng N-TEQ/ton scrap. Each of the measurements was covering 2-5 batches, the duration of one batch being in the range of 90-100 minutes with a varying dioxin emission throughout the process /Det Danske Stålvalseværk 2000a/. Based on these data, it would be correct to estimate the emission to air as within the range of 1.1 – 1.9 g N-TEQ/year.

Previously an estimate of air emission of 7.5 g N-TEQ/year has been made /Jensen, A.A. 1997/. This estimate was, however, based on 3 measurements only, of which two were done under deviating operation conditions, the duration of which is limited to less than 5% of the total time of operation. These measurements, furthermore, each lasted for no more than 1 hour. /Det Danske Stålvalseværk A/S 2000a; Det Danske Stålvalseværk A/S 2000c/. Thus the choice has been made by the authors to accept the company's own estimate reported in the section above as more reliable. New measurements are planned to November 2000.

The results from the 2 measurements done under deviating operation conditions would equal a yearly emission to air of approx. 10 g N-TEQ. Assuming that deviating operating conditions exist for up to 5% of the total operation time, and that the emission to air would otherwise be within the range of 1.1 – 1.9 g N-TEQ/year, it can be calculated that deviating operation conditions might cause an increase of the emission of up to 0.4 g N-TEQ/year. It should thus be considered fair to adjust the estimate of air emission of dioxins to 1.1 – 2.3 g N-TEQ/year.

These data can be compared with data from the European Dioxin inventory, that assumes a typical emission factor for emission to air for electric furnace steel plants of 1 µg I-TEQ/ton scrap and minimum/maximum values of 0.2 - 5.0 µg I-TEQ/ton (Landesumweltamt Nordrhein-Westfalen 1997). Based on these emissions factors the emission from the Danish plant can be estimated at 0.2 – 4.3 I-TEQ/year that is at the same level as the company estimate assuming that the Nordic TEQ can be taken as equal to the International TEQ. However, it should be noted that the emission factors chosen in the European Dioxin Inventory may well be regarded as a rather optimistic interpretation of the data available, meaning that the inventory seems to have given more weight to low German emission factors than to higher values from other countries.

Based on these data and assuming that the Nordic TEQ can be taken as equal to the International TEQ, an emission to air of 1.1 – 2.3 g I-TEQ/year is here accepted as the best estimate.

Measurements at the plant have, furthermore, shown that on average 82% of the dioxin content of the air flow before the filter was removed by the filter /Det Danske Stålvalseværk A/S 2000b/. The quantity of dioxin exported by export of filter dust may thus be estimated at 5.0 – 10.5 g I-TEQ/year.

No measurements of the content of dioxins in other production residues have been undertaken. Also no measurements from other countries or other plants are available. For blast furnace slag values of 0.001-0.18 µg N-TEQ/t slag has been given (Swedish data quoted in /Dyke et al 1997/). Assuming these values to be valid also to other production residues from steel reclamation in Denmark, and assuming that I-TEQ is equal to N-TEQ, the amount of dioxin deposited or used for asphalt, cement etc. may be roughly be estimated as:

Deposited: < 5 mg I-TEQ/year
Used for asphalt, cement etc.: < 16 mg I-TEQ/year

It is emphasised that these estimates are very uncertain, and should only be regarded as a preliminary first assessment of the potential dioxin flow by these routes.

No information exists indicating that release of dioxin by wastewater emissions from electric arc furnaces in steel reclamation should be significant. The emission by wastewater is consequently assessed as zero. As this assessment is not supported by actual measurements, it must be regarded as uncertain.

2.3.4 Aluminium reclamation

In Denmark one company only carries out reclamation of aluminium scrap. Aluminium scrap received at the plant is melted in a salt bath composed of mainly KCl and $NaCl$ to protect the metal from being directly exposed to the natural gas flame used for heating. The company policy is not to accept scrap significantly polluted by grease, oil, plastics or other sorts of organic materials. However, organic matter will be present in the processed materials and can hardly be avoided. As the melting point for aluminium is around 660ºC dioxin formation should be assumed likely.

Plant activity
Based on information from the company, the activity of the plant can be summarised as follows (1998-figures /Gotthard Aluminium 1999/):

Total production: approx. 33,000 tonnes/year
Air flow from melting process: 29,600 Nm^3/h
Salt slag to landfill: 7,600 tonnes/year
Filterdust to landfill: 360 tonnes/year
No discharge of industrial wastewater took place.

Dioxin formation and disposal
No measurements of dioxin formation have so far been carried out by the company. The local authorities are, however, in the process of initiating measurements. The European Dioxin inventory assumes a default emission factor for emission to air of 22 µg I-TEQ/ton of aluminium and min./max. factors of 5 - 100 µg I-TEQ/ton /Landesumweltamt Nordrhein-Westfalen 1997/, whereas a British study /Dyke et al 1997/ assumes the following figures for residues:

Slag	11µg I-TEQ/t
Filter dust	480-4000 µg I-TEQ/ton

Based on these figures the turnover of dioxins by aluminium reclamation in Denmark may be estimated as follows:

Emission to air: 0.7 g (0.17 - 3.3 g) I-TEQ/year
Landfilled with filter dust: 0.26 - 1.5 g I-TEQ/year
Discharged with wastewater: 0

2.4 Feedstuff

Feedstuff will contain dioxins mainly due to the content of dioxins in raw materials. Only a few manufacturing processes should be suspected to develop dioxins, as the process temperatures involved seldom will exceed 200ºC. The manufacturing processes relevant to consider include:

- Production of fish oil and meal
- Production of meat meal
- Green feed drying

It is noted that biological formation of dioxins from precursors may take place at temperatures below 200ºC. Whether or not other feedstuff manufacturing processes for this reason should be suspected to develop dioxins is, however, difficult to say, as no precise knowledge is available.

2.4.1 Fish oil and meal

There are four plants in Denmark of varying size. No production processes exceed 200ºC. However, process off-gases are burned at 850 – 1000ºC.

Two techniques for burning of off-gases are employed. One is heating in one second at 850ºC. The air passes through a ceramic filter both before and after the heating. This ensures fast cooling of the air the temperature of which is lowered to about 110ºC, when it leaves the ceramics. From here the air passes through a scrubber with seawater. In the other process the air (that either is filtered through a bag filter or through a scrubber) passes the boiler at 1000ºC, before it flows unfiltered out of the chimney at about 150ºC.

The raw materials (fish) will contain dioxin and organochlorine contaminants due to the general contamination of the marine environment. Furthermore, the possibility exists that the burning of off-gases will lead to dioxin formation by the “de novo synthesis” or by formation from precursors.

Plant activity
Based on data from a major Danish company the activity of the fish oil and meal sector in Denmark is estimated as follows:
Consumption of raw materials: Approx. 1.2 million tonnes/year
Air flow through ceramic filters: Approx. 300 million Nm^3/year
Air flow through boiler: Approx. 500 million Nm^3/year
Discharge of scrubber water: Approx. 18 million m^3/year

Dioxin formation and disposal
No measurements of dioxin in air emission are yet available. However, the local authorities have made samplings, and the results are awaited.

Several measurements of dioxin content in products are available. According to the industry the dioxin content of the raw materials is recovered in the products, indicating no net uptake or liberation of dioxin. The Danish consumption of dioxins with fish oil and meal is discussed in section 2.5.4.

One plant has measured (January 2000) a dioxin concentration in the scrubber water of <0.6 pg I-TEQ/l. Assuming this figure to be applicable to the total discharge of scrubber water, the total dioxin emission to sea can be estimated at <0.01 g I-TEQ/year.

2.4.2 Meat and bone meal

There are 4 plants for production of meat and bone meal based on dead animals and other animal residues in Denmark. Information exists from one company operating 3 of these plants covering round 75% of the total production of meat and bone meal in Denmark. In 2 of the plants the production process involves a spray drying process at around 230ºC, in which the warm air is re-circulated through the heating chamber and directly exposed to the flame. Spraying is e.g. used for processing of blood-based products. The third plant, in order to minimise smell from manufacturing processes, operates a treatment unit in which offgases before emission is treated by burning at 850ºC.

The raw materials will contain dioxin due to the content of dioxin in feedstuff (reference is made to section 2.5.4). Furthermore, the possibility exists that the spray drying and the smell elimination processes will lead to dioxin formation by the “*de novo* synthesis”.

Plant activity
The total production of meat and bone products in Denmark can be estimated at around

350,000 tonnes/year. As the Danish consumption is registered to 126,000 tonnes/year (reference is made to table 2.4) around 224,000 tonnes/year or around 64% of the Danish production must be assumed exported. The airflow exposed to burning before emission from the relevant plant comes up to approx. 530 million Nm^3/year.

Dioxin formation and disposal
No measurements of dioxin emission to air exist neither from Denmark nor literature. Measurements by the companies of dioxin content in products reported concentrations varying between 19 pg I-TEQ/kg dry matter for meat residues to 1,540 pg I-TEQ/kg for the fat fraction. Meat meal manufactured without spray drying had a dioxin content of 36-260 pg I-TEQ/kg dry matter, whereas the dioxin content in a product from the spray drier was only 19 pg I-TEQ/kg dry matter /Andreasen 2000/. Thus, it seems unlikely that significant dioxin formation takes place by the spray drying process.

Based on the data available, it is assumed likely that air emission of dioxin related to spray drying is mainly related to burning of fossil fuels and will be covered by the estimates made in section 3.1 and 3.2. However, no data are available with respect to burning of offgases, and it is not possible to assess the dioxin emission caused by this operation.

The content of dioxin in manufactured products can based on the figures stated above be estimated at 0.007 – 0.54 g I-TEQ/year, of which 0.004 – 0.35 I-TEQ/year is being exported.

2.4.3 Green feed drying

12-15 plants for green feed drying exist in Denmark. The drying process is based on warm air having a temperature of 500-700ºC. Most of the existing plants use a technology, by which part of the warm air is recycled via the heating chamber, where it is directly exposed to the flame. The energy source will typically be natural gas, but in a few cases the energy source is coke or fuel oil. The dry grass is typically separated from the air by a cyclone that typically is the only kind of air cleaning equipment employed /Mogensen 2000/. The grass will contain dioxin due to atmospheric deposition. However, it cannot be ruled out that the drying process in itself will lead to dioxin formation by the “de novo synthesis”.

Plant activity
Danish companies estimate the total production of dried green feed in Denmark at around 150,000-200,000 t/year.

Dioxin formation and disposal
No measurements of dioxin emission have been undertaken in Denmark. The European dioxin inventory (section on Germany) gives an emission factor for emission to air of 0.1µg (min./max. 0.02 - 0.21) I-TEQ/t material (Landesumweltamt Nordrhein-Westfalen 1997). Assuming these figures to be valid also to Danish plants, the emission of dioxin to air can be estimated at 0.02 (0.004 – 0.04) g I-TEQ/year.

The European dioxin inventory gives no information of the energy source used. It should be noted that the emissions factor stated above is close to the emissions factor adopted for burning of natural gas itself (reference is made to section 3.2). This may well indicate that the source of dioxin actually is the combustion process and not dioxin from the grass or the drying process.

Measurements of grass pills and meal (11 samples) showed an average of 263 pg I-TEQ/kg product (88% dry matter) and min./max. values of 111/1097 pg I-TEQ/kg product (88% dry matter) /Plantedirektoratet 1999b/. The total amount of dioxin contained in the Danish production of grass pills and meal can thus be estimated at approx. 0.05 g I-TEQ/year.

2.4.4 Feedstuff products

The quantity of dioxins in feedstuff consumed in Denmark has been estimated in table 2.4. This estimate is mainly based on literature values for dioxin content in relevant feedstuff categories. The estimate includes intake with grass consumed by animals directly in the fields in the summer season or as silage and hay in stables during the winter season. Most of the categories listed in table 2.4 should be characterised as secondary sources or circulation of nature. This covers fish products, grass, cereals, straw and grass pills etc. Oil cakes and meal, however, is generally based on import, whereas meat and bone meal as well as milk products should be characterised as recycling within the agricultural sector.

It is emphasised that the estimates should be regarded as rough estimates aimed at indicating the relevant order of magnitude for the dioxin flows taking place. It is outside the scope of this substance flow analysis to undertake a detailed analysis of the dioxin flow within the agricultural sector in Denmark.

A significant part of the estimated consumption should be expected to be recycled to farmland by manure. No exact knowledge of the amount of dioxins in question is available. As a rough estimate the quantity is here estimated at less than 10 g I-TEQ/year taking into account that feedstuff for trout farming may partly end up in the trouts produced as well as sludge being directed to landfills, whereas feedstuff for pets partly ends up in waste. No attempt has been made in this report to assess the metabolism of dioxin in domestic animals and fish. A significant part of the Danish production of trouts is exported.

Table 2.4
Consumption of dioxins with feedstuff - estimate based mainly on literature values from Europe.

Category	**Consumption 1997/98 1000 t 1)**	**Assumed dioxin content pg I-TEQ/kg 2)**		**Consumption of dioxin g/year**		
			Comments	Min.	Max.	Average
Fish meal, fish silage and wastel	1048	1.000 - 8.000	pg/kg fish, mainly based on herrings	1.0	8.4	4.7
Grass, silage, hay, root crops	26519	10 – 60	pg TEQ/kg product based on vegetables	0.27	1.6	0.94
Cereal products	6246	20	pg/kg product	0.12	0.12	0.12
Oil cakes and oil meal	2229	10 – 170	pg/kg product based on vegetables and vegetable fat	0.02	0.38	0.2
Straw	1797	10 – 60	Assumed similar to grass, silage, hay etc.	0.02	0.11	0.06
Other vegetable feeding stuff 3)	733	10 – 170	Assumed similar to oil cakes and meal	0.007	0.12	0.06
Meat and bone meal	126	19 – 1540	pg/kg product	0.002	0.19	0.1
Grass pills and grass meal etc.	131	100 – 400	pg/kg product	0.01	0.05	0.03
Milk products 4)	9	490	pg/kg fat	0.004	0.004	0.004
Sum				**1.5**	**11.0**	**6.2**

1) Consumption figures from /Danmarks Statistik 1999c/.

2) Figures are estimates based on samples reported from Belgium, Denmark, Finland, France, Germany, Italy, Netherlands, Norway, Sweden and United Kingdom from the period 1990 - 1999 and reported by EU /EU 2000/ as well as samples reported by the Danish Plant Directorate /Plantedirektoratet 1999b/. For meat and bone meal the figures are based on data from Danish companies.

3) Include mash, draff, yeast, molasses, tapioka and citrus meal etc.

4) Consumption calculated as milk fat based on 125,000 tonnes whole milk with 4% fat and 1208,000 tonnes other milk products (primarily whey) with 0.3% fat.

Air deposition of dioxin could well be the dominant source of dioxin to the agricultural sector in Denmark. However, air deposition has not been measured in Denmark. In Europe deposition data is only available from Belgium, Germany and United Kingdom. The most recent data have been summarised in table 2.5. Agricultural areas in Denmark equal 26,720 km^2 /Danmarks Statistik 1999c/. Assuming a deposition rate of 1 – 10 pg I-TEQ/m² per day (as for Hamburg – rural/background areas), the total deposition of dioxin on Danish agricultural areas may be estimated at approx. 10 – 100 g I-TEQ/year. It is noted that calculations on long-range transport of dioxins/furans reported in 1999 indicates a deposition rate of 250 pg I-TEQ/ m² per year on the Danish land area /Torp 2000/. This deposition rate equals a total deposition on Danish agricultural areas of around 7 g I-TEQ/year.

Table 2.5
Air deposition of dioxins in Europe 1)

Country	Year	Urban/industrial areas pg I-TEQ/m² per day	Rural/background areas pg I-TEQ/m² per day
Belgium	1996 – 1997	0.9 - 12.0	0.7 - 3.1
Germany			
- Hamburg	1995		1 - 10
- Thuringia	1993 – 1997	29 (3 – 464)	
- Rheinland-Palantinate	1993 – 1994	9 (0.5 – 24)	
United Kingdom			
- Hazelrigg	1993		81 (0 – 517)
- Bolsover	1992 – 1993	25 (2 – 118)	
- London	1993	8 (1 – 33)	
- Manchester	1993	28 (11 – 59)	

1) From /Fiedler H. 1999/. Only the newest data have been quoted.

2.5 Food products

Similar to feedstuff food products will contain dioxins mainly due to the content of dioxins in raw materials. No manufacturing processes should be suspected to develop dioxins, as the process temperatures involved seldom will exceed 200°C. The experience available for spray drying processes (reference is made to section 2.4.2) does not give evidence regarding spray drying as a dioxin generating process.

The quantity of dioxins in food products consumed in Denmark has been estimated in table 2.6. This estimate is mainly based on literature values for dioxin content in relevant food product groups. It is emphasised that the estimates should be regarded as rough estimates aimed at indicating the relevant order of magnitude for the dioxin flows taking place. It is outside the scope of this substance flow analysis to undertake a detailed analysis of the human intake of dioxins in Denmark, and the figures presented in table 2.6 are not aimed at that kind of discussion.

It is noted, that the estimate of 0.26 g I-TEQ/year (min./max. values of 0.06 – 0.44) with food products presented in table 2.6 is in good agreement with the most recent estimate of human intake of 1.5 pg WHO-TEQ/kg body weight per day in Denmark developed by the Ministry for Agriculture, Food Products and fishery /Fødevaredirektoratet & Plantedirektoratet 1999/. Assuming a total Danish population of 5.2 million citizens and an average body weight of 70 kg, the estimate of 1.5 pg WHO-TEQ/kg body weight per day corresponds to a total human dioxin intake of 0.2 g WHO-TEQ/year.

All of the product groups listed in table 2.6 should be characterised as secondary sources or circulation of nature. It has not been tried to estimate the exchanges taking place to and from other countries by import and export of food products.

A significant part of the estimated consumption should be expected to end up in sewage. A part will also end up as domestic waste and be disposed of either by waste incineration or by biological waste treatment.

Table 2.6
Consumption of dioxins with food products - estimate based mainly on literature values from Europe.

Product group	**Consump-tion 1997/98 1000 t 1)**	**Fat % 2)**	**Assumed dioxin content pg I-TEQ/kg 3)**		**Consumption of dioxins g/year**		
				comments	min	Max	average
whole milk, junket, yoghurt	546.6	3	490	pg/kg fat			0.008
skimmed and buttermilk	113.6	0,3	490	pg/kg fat			0.0002
Cream	50.4	20	490	pg/kg fat			0.005
Butter	9.8	85	490	pg/kg fat			0.004
Cheese	86.8	25	490	pg/kg fat			0.011
Milk products (sum)	807.2						0.028
Margarine	51.1	85	260 - 1510	pg/kg fat	0.011	0.066	0.039
Cereals	506.9		20	pg/kg			0.010
Fruit and vegetables	590		10 - 60	pg/kg	0.008	0.048	0.028
Fish	20		100 - 8000	pg/kg	0.002	0.160	0.081
Eggs	85.9	10	460 - 2670	pg/kg fat	0.004	0.023	0.013
Meat	568	10	200 - 2000	pg/kg fat	0.011	0.113	0.062
Sum	**2660**				**0.06**	**0.44**	**0.26**

1) Consumption figures for the listed product groups have been taken from /Danmarks Statistik 1999c/. However, consumption of fruit and vegetables is estimated as 0.403kg fruit and vegetables/Dane/day and 5.2 million Danes, whereas consumption of fish is estimated as 10 g/day/Dane and 5.2 million Danes /Fødevaredirektoratet & Plantedirektoratet 1999/.

2) Estimates for content of fat in product group have been taken from /EU 2000; Fødevaredirektoratet & Plantedirektoratet 1999/.

3) Figures are estimates based on samples reported from Belgium, Denmark, Finland, France, Germany, Italy, the Netherlands, Norway, Sweden and United Kingdom from the period 1990 - 1999 and reported by EU /EU 2000/. For milk products the estimate is based solely on a Danish investigation from 1999 reported in /EU 2000/.

2.6 Pentachlorophenol

Pentachlorophenol and its derivatives are generally accepted as precursors for dioxin and will naturally contain traces of dioxin developed during the formation process of pentachlorophenol. The main derivatives of commercial interest are sodium pentachlorophenolate and pentachlorophenyl laurate. In this section the abbreviation PCP is used for pentachlorophenol as well as its main derivates.

The dioxin content of PCP depends on the formation process and primarily consists of octa-, hepta- and hexachlorinated compounds. Based on data available in /WHO 1987/ and /Christmann et al. 1989 quoted in Jensen 1995/, the dioxin content in technical PCP commercially available in the seventies and the beginning of the eighties may be roughly estimated at 0.16 – 7 mg I-TEQ/kg PCP.

It should be recognised that these figures may well be discussed with respect to whether they are representative. Analyses of samples of technical PCP commercially available in Denmark in the seventies (described in /Danish EPA 1977/) indicate that the content of dioxin in PCP used in Denmark should be in the low end of the range 0.16 – 7 mg I-TEQ/kg PCP. On the other hand the investigations of /Christmann et al. 1989 quoted in Jensen 1995/ show an average of commercial wood preservation solutions of approx. 20 mg I-TEQ/kg PCP. Other examples of high concentrations of dioxins in wood preservation solutions have also been reported /Dobbs & Grant 1981 quoted in Jensen 1995/.

Based on /Eduljee 1999/ it can be estimated that restrictions imposed by USEPA in 1987 and EU in 1991 on the content of dioxins in PCP have reduced the dioxin content to 0.11 - 4.2 mg I-TEQ/kg PCP.

PCP has been used widely for preservation and conservation purposes. Important fields of application have been and are wood preservation, leather tanning and preservation of textiles etc. The following assessment is limited to these applications, as no other applications are likely to be important in this context.

PCP has not been manufactured in Denmark, and consumption in Denmark has been based on import of chemical products and goods treated with PCP. In Denmark, restrictions on the content of dioxins in PCP was introduced in 1977 / Bylaw 582-1977/. This restriction actually functioned as a ban eliminating by and large all intended use and consumption of PCP in Denmark except for laboratory purposes and other special uses able to obtain dispensation for the general restriction. This restriction was followed by a ban in 1996 on sale of chemical substances and products containing 0.1% PCP or higher concentrations and a ban on sale, import, export and use of goods containing 5 ppm PCP or higher concentrations /Bylaw 420-1996/.

An issue essential to assessing the fate of dioxins present in products due to the use of PCP is the extent to which dioxins are likely to evaporate or otherwise migrate out of the products in question. However, no investigations addressing this issue have been found. Estimates of the relevant order of magnitude for these processes may in lack of better documentation be based on analogy considerations to PCBs used as plasticizer in joint foam for construction purposes etc. For such uses it has been estimated that 10-20% of the original PCB content would evaporate during the useful life of the product depending on the actual product and use etc. /Nisbeth & Sarofim 1972 quoted in COWIconsult 1983/. For products with lives in the range of 20-40 years, these rates of evaporation will correspond to a yearly evaporation rate of approx. 0.5% of the original content of PCB in the products.

It is noted, that /Bremmer et al 1994/ based on considerations on the physicochemical characteristics of dioxins has estimated a half-life of dioxin in wood of 150 years corresponding to an average yearly evaporation of 0.33% of the original content 0.45% calculated over quantity that remains in the wood. This estimate is based on the assessments that the half-life for PCP in wood is 15 years and that the evaporation of dioxins from wood, on average, is 10 times slower than for PCP /Bremmer et al 1994/.

Leaching of dioxins from PCP-treated poles is considered a potentially significant route for exposure in the US /Greenpeace 2000/. However, leaching from poles and other products should not be considered an issue in Denmark, as the use of PCP for many years has been banned. PCP has, furthermore, never been an important substance for treatment of wood in contact with soil, as either creosote or As-Cr-Cu compounds always have dominated this market in Denmark.

2.6.1 PCP in wood

The concern related to use of PCP as wood preservative may be focused on:

- The former use of PCP as a wood preservative in Denmark
- Current import of wood preserved by PCP

Former use of PCP as a wood preservative in Denmark
Up to 1977 PCP was widely used in Denmark for industrial wood preservation of windows and doors as well as surface preservation/priming of wood before painting. The consumption in Denmark has been estimated as follows /COWIconsult 1985/:

- Start in 1950 with around 25 tonnes PCP/year.
- Around 1960 with 100 tonnes PCP/year
- Maximum in 1972 with 250-300 tonnes PCP/year
- Decreasing to 0 tonnes per year in 1978.

Of this consumption more than 90% was used for surface preservation of wood whereas the rest was used for industrial wood preservation /COWIconsult 1985/. Assuming that the consumption has developed linearly, the total accumulated consumption can be calculated to approx. 3900 tonnes PCP.

To what extent PCP-preserved wood is still in use in Denmark there is no precise knowledge. Assuming an average life of PCP-preserved wood of around 20 years, a minimum of 10 years, a maximum of 40 years and a linearly development, the amount of wood still in use by year 2000 in Denmark should equal a PCP quantity of approx. 680 tonnes. Assuming the dioxin content of the PCP used in this period to be in the range of 0.16 – 7 mg I-TEQ/kg PCP, 680 tonnes of PCP should equal an amount of dioxin of 110 – 4800 g I-TEQ.

By now most of PCP in preserved wood still in use in Denmark would probably be evaporated /Borsholt 2000/. No precise knowledge exists as to what extent all the dioxin has evaporated as well. Assuming an evaporation of 10% of the original content over a period of 20 years (reference is made to the introduction of section 2.6) would mean that the amount of dioxin still present in wood should be in the range of 85% of the original content equalling 90 – 4100 g I-TEQ. The yearly emission would parallel to this be around 0.5 % of the original content per year. This emission rate should equal an actual emission to air in Denmark of 0.5 - 20 g I-TEQ/year.

Furthermore, dioxins will probably be present in wood directed to waste incineration in Denmark. As a rough estimate one should assume a figure in the range of 5-200 g I-TEQ/year, meaning that the stock of PCP-preserved wood remaining in the Danish society would be completely disposed of within the next 20 years.

It is emphasised that several of the assumptions stated above may be discussed, and that the results should only be considered as an indication of the relevant order of magnitude for the dioxin flows in question.

Current import of wood preserved by PCP
The European consumption of PCP (sodium-PCP) in 1996 has been estimated at 380 tonnes used dominantly in France, Portugal and Spain for anti-sap-stain control of wood used for construction and single-use pallets for transport purposes /ERM 1998/. The use of PCP for preservation of wood (and likely also anti-sap-stain control) is widespread in the US and is also used in Asian countries like Malaysia for wood types as nyatoh /ERM 1998; Henriksen 2000; Wilkinson 2000/. No information is available regarding the situation in Russia and Eastern Europe.

The import of PCP with anti-sap-stain treated wood to Denmark was for 1983 estimated at 5-25 tonnes /COWIconsult 1985/. This estimate referred to a situation, when PCP was still used for anti-sap-stain control in Finland, being traditionally a very large exporter of wood to Denmark.

Today import of PCP treated wood to Denmark is banned /Bylaw 420-1996/, and the use of PCP has for long been stopped in all the Nordic countries. The amount of wood imported to Denmark and potentially treated with PCP will not exceed 100,000 m3 corresponding to approx. 20% of the amount assumed potentially treated in 1983 /Danmarks Statistik 1999a; COWIconsult 1985/. As the direct import of wood to Denmark from countries like France, Portugal, Spain, Malaysia, the US and Canada is relatively small. The countries of concern should rather be Russia, Poland, Estonia, Latvia and Lithuania /Danmarks Statistik 1999a/.

However, no precise knowledge with respect to the use of pentachlorophenol in these countries is available.

It follows from these considerations, that the import of PCP with PCP treated wood today should be expected to be in the range of 1-10 tonnes PCP yearly. This estimate inter alia takes into account that part of the PCP used for single-use pallets in the rest of Europe also will enter Denmark with miscellaneous goods imported.

The content of dioxins in the PCP used will have changed during this period (reference is made to the beginning of section 2.6). Assuming a content of 0.11-4.2 I-TEQ/kg PCP as for the period after 1987/1991, the import of 5-25 tonnes PCP in 1983 should equal a dioxin import of 0.6 - 105 g I-TEQ/year. Similarly should an import of 1-10 tonnes PCP in 2000 equal an import of 0.11 - 42 g I-TEQ/year.

As no detailed assessment of the flow of wood and wood products in Denmark are available, the following considerations concerning the fate of the imported dioxin must be limited to a primarily qualitative assessment.

Single-use pallets imported to Denmark must be assumed dominantly to be burned shortly after the import, although a minor part may be reused for other purposes (e.g. construction of playhouses etc.) delaying its final disposal for a couple of years. It should be considered a source of dioxin to municipal incineration plants as well as to private and industrial wood stoves. For ordinary citizens they will appear untreated thereby not calling for attention when used in a wood stove for heating purposes. As a rough estimate 0.5-5 tonnes of PCP corresponding to 0.05-21 g I-TEQ is assumed to follow this route.

Other types of wood must be assumed mainly to be used for construction purposes thereby given a useful life in the range of 5-100 years depending on the actual use. For assessment purposes an average life of 20 years is assumed in the following. Again 0.5-5 tonnes of PCP corresponding to 0.05-21 g I-TEQ is assumed to follow this route.

Considering that anti-sap-stain treatment of wood is done on reasonably fresh wood and typically affects the top 1.5 mm of the wood, it seems logical to assume, that the dominant fate for the content of PCP would be emission to air by evaporation. Again, the fate of dioxins may best be predicted by assuming, that only 10% of the original content will evaporate during 20 years corresponding to an emission rate of 0.5% of the original content per year.

Assuming that the import of PCP and dioxin caused by anti-sap-stain treatment of wood has developed linearly over the years, the current dioxin emission to air may be estimated as follows:
10%*((0.5+0.05)/2 – (105+21)/2 g I-TEQ/year) = 0.03 – 6 g I-TEQ/year

Considering only imports after 1980, the amount of dioxin contained in construction wood currently directed to waste incineration may be roughly estimated at 0.1-42 g I-TEQ/year and the present stock of dioxins in wood to somewhat in the range of 4-840 g I-TEQ. Again, the possibility, that part of the wood will be combusted in private and industrial wood stoves, cannot be ruled out.

It is emphasised that the above calculations are extremely uncertain and should only be considered as an indication of the relevant order of magnitude for the dioxin flows in question.

Summary on PCP-treated wood
The estimates developed for the turnover of dioxins by preserved wood in Denmark is summarised in table 2.7.

It is noted that part of the estimated emission to air could be carried away by rainwater falling on the surface of the wood and thus be carried away as storm water. The amount in question should be expected to be included in the estimated contribution from atmospheric deposition to wastewater and storm water in Denmark (reference is made to table 5.5 in section 5.7.1).

Table 2.7
Estimated turnover of dioxins by PCP-preserved wood in Denmark

	Former use g I-TEQ/year	Current import g I-TEQ/year	Total (rounded) g I-TEQ/year
Import	0	0.11-42	0.1-42
Stock in society	90-4100	4-840	100-5000
Emission to air	0.5-20	0.03-6	0.5-26
Disposed of as combustible waste	5-200	0.1-42	5-240

2.6.2 PCP in leather

Conservation of leather with PCP ceased in Denmark by the end of 1985 /COWIconsult, 1985/. The current regulation in Denmark as well as the rest of EU does not permit import, sale and use of goods containing ≥ 5 ppm PCP.

Of 26 leather samples bought and analysed in Germany in the period 1994 - 96 6 samples exceeded the threshold of 5 ppm, whereas the average for all samples was 7 mg PCP and around 50 ng I-TEQ per kg leather /Klasmeier & McLachlan 1999/. The dominant source for dioxin in all samples seemed to be PCP. However, for a few samples the congener pattern indicated other sources as well. The trend for use of PCP for leather conservation seems to be decreasing, and today likely not more than 5% of all samples would exceed the 5 ppm limit /Klasmeier 2000/. It should be noted that PCP preservation of leather in order to be effective must allow for a content of at least 50 ppm /Frendrup 2000/.

Import of tanned leather to Denmark comes up to around 10,000 tonnes per year /Danmarks Statistik 1999a/. Assuming an average dioxin content of 50 ng I-TEQ/kg leather, this import equals an import of dioxin of approx. 0.5 g I-TEQ/year.

The fate of the imported dioxin will vary with the products in question. Due to a relatively small quantity, no effort has been invested in detailed investigations of the circulation of the imported leather, and the following description is limited to a primarily qualitative assessment.

Roughly 50 – 70% of the import covers items like footwear, gloves and bags with a relatively short lifetime. For such items one should expect the major part of the dioxin content still to be present in the items at the time of disposal which in Denmark today means waste incineration.

The remainder of the import covers mainly leather in bulk likely to be used inter alia for furniture and coats with a life of perhaps 10-20 years. For these items evaporation may take place, emitting dioxins to indoor as well as outdoor air. Again assuming that 10% of the original content will evaporate during the useful lifetime, the yearly emission to air can be estimated at less than 0.05 g I-TEQ/year, which in this context should be considered insignificant. The dominant route of disposal will again be waste incineration.

2.6.3 PCP in textiles

The main uses of PCP related to textiles seem to be:

- Preservation of so-called “Heavy duty textiles” like tents and tarpaulins for outdoor purposes.
- Preservation of cotton and textiles made of cotton for storage and sea transport.
- Conservation of fluids used for sizing of textiles.

To the best of knowledge PCP is not used for any of these purposes in Denmark today.

However, in the eighties PCP was widely used in Denmark for preservation of cotton textiles for outdoor purposes. The amount of PCP applied was typically 5-15 g PCP/kg textile and the total consumption of PCP in Denmark for this purpose was estimated at 2.5-9 t/year /COWIconsult 1985/. In Europe PCP is used today for this purpose only in the UK and mainly for military equipment /O'Neil 2000/ but to some extent also for tarpaulins, tents and similar public applications /Thomas 2000/. The consumption of PCP for this purpose in the UK in 1996 was 28 tonnes /ERM 1998/. Considering the limited consumption and the Danish ban on import of such materials, any import to Denmark of dioxins in this context is deemed insignificant.

Preservation of cotton and cotton textiles in the Far East may be done simply by spraying PCP into the closed containers in which the textile balls are stored and transported /Kemi 1997/. This way of applying PCP will naturally result in high variations in the content of PCP and dioxin to be observed in finished textile products.

A Danish investigation of dioxin and PCP content in cotton T-shirts (24 samples) showed an average of 0.35 ng N-TEQ/kg with a min.-max. range of 0.02 - 2.6 ng N-TEQ/kg textile. However, no correlation between dioxin and PCP content in the textiles was found /Vikelsøe & Johansen 1996/. German investigations (131-samples) on textiles of various materials indicate an average around 2 ng I-TEQ/kg and a min.-max. range of ~0 – 82 ng I-TEQ/kg /Klasmeier & McLachlan 1997/. In the German investigation the highest values were found in cotton textiles. As the average is highly influenced by few samples with a high level of contamination, the German study in this context is deemed the most reliable, although the Danish study may be more represenative to Danish textiles. It should be noted, that the dioxin content observed may be caused not only by the use of PCP, but could also be influenced by other sources like chlorine bleaching and dyestuffs based on chlorinated compounds like chloroanilins.

In 1998 the total import of textile products to Denmark came up to approx. 260.000 tonnes. An average content of dioxin of 2 ng I-TEQ/kg would equal a dioxin import of approx. 0.5 g I-TEQ/year.

Considering the fate of dioxins in textiles, a study referred in /Jensen 97/ estimates that 35% of the content of dioxin is removed by washing. The rest should be expected to remain in the textiles. As the useful life of textiles due to wear and tear in general is short, emission to air caused by evaporation cannot be expected to be significant. Final disposal of textiles in Denmark will be waste incineration. Thus, the fate of dioxins in imported textiles contaminated by PCP and other sources may be summarised as:

- Released to public wastewater: approx. 0.2 g I-TEQ/year
- Directed to waste incineration: approx. 0.3 g I-TEQ/year

A minor fraction will actually be collected in distillation residues from dry cleaning shops. Investigation of such residues has shown dioxin concentrations of 2-3 µg I-TEQ/kg /Fiedler 199/. However, in the overall context this route cannot be regarded as significant.

2.7 Use of chlorine for bleaching and disinfecting

2.7.1 Use in Denmark

Apart from the industrial uses of chlorine mentioned in section 2.1, chlorine and chlorinated products are widely used for bleaching and disinfecting purposes in Denmark. Bleaching operations in Denmark includes paper manufacturing, textile manufacturing and laundry, whereas disinfecting is related to water supply, cooling water, wastewater, swimming pools and several industrial processes, in particular within the food industry.

Whereas dioxin formation has been well documented with respect to the use of chlorine in the paper industry, almost no data are available for other processes involving the use of chlorine and chlorinated compounds like bleaching and disinfecting agents.

One investigation only is known to deal with dioxin formation in drinking water. Adding 0.3 g Cl_2/l to drinking water developed a dioxin amount equal to 37 pg I-TEQ/l /Rappe 89 quoted in Jensen 95/. Adding the same amount of chlorine to two times distillated water developed 8 pg I-TEQ/l, meaning that some dioxin or precursors must have been present in the gas itself.

A Russian investigation of dioxin formation by chlorination of purified wastewater from biological wastewater treatment by sodium hypochlorite reported no difference in the content of dioxins before and after chlorination /Khizbullin et al 1999/.

The consumption of chlorine and chlorinated products for bleaching and disinfecting is known with some uncertainty. Based on /Danish EPA 1989; COWI & CETOX 2000/ the consumption can be estimated as follows:

Chlorine:	500 – 1000 tonnes/year
Chlorinated compounds:	3000 – 5000 tonnes/year (primarily NaOCl)

Chlorine gas is assumed primarily to be used for bleaching of textiles and to some extent also for disinfecting of raw surface water to be used as drinking water and disinfecting of swimming pools whereas sodium hypochlorite is the main agent for cleaning and disinfecting purposes.

It should be noted, that bleaching in the paper industry in Denmark today is mainly done by hydrogen peroxide and to a lesser extent by sodium hypochlorite, and no measurements of dioxin content in wastewater and sludge from the manufacturing process are available /Dalum 2000/.

Assuming that all chlorine used for bleaching and disinfecting purposes in Denmark would develop dioxin according to measurements by Rappe (see above) the formation of dioxin may be estimated at 0.4 - 0.7 g I-TEQ/year. However, this result is questionable inter alia because:

- The dosage of 0.3 Cl_2/l is significantly above the dosages that normally will be used, e.g. in swimming pools.
- No documentation exists for formation of dioxins by the use of sodium hypochlorite and similar compounds.

As a best estimate the dioxin formation caused by the use of chlorine and chlorinated compounds for bleaching and disinfecting purposes in Denmark will here be estimated at less than 0.5 g I-TEQ/year. The fate of this dioxin will generally be discharged to the public wastewater system.

2.7.2 Bleached products (cork and paper)

This section is focused on cork and paper/carton products as textiles are assumed to be covered by the assessment made in section 3.6.3.

Cork

Cork may be bleached as well as treated with PCP. A German study /Fromberger 1991 quoted in Fiedler 1999 – no further reference/ showed a dioxin content in cork for sealing of wine bottles of 0.18-0.26 ng BGA-TEQ/kg and 12.6 ng BGA-TEQ/kg in cork-based wall covering. In case of cork sealings the congener pattern indicated bleaching as the source, whereas the congener pattern indicated use of PCP as the source with respect to the wall covering.

The quantity of cork sealings imported to Denmark comes up to approx. 350 tonnes/year, whereas import of other cork items apart from natural cork and waste comes up to around 800 tonnes/year /Danmarks Statistik 1999/.

Assuming that BGA-TEQ is equal to I-TEQ, the worst case import to Denmark of dioxins with cork may be calculated to approx. 0.01 g I-TEQ/year. The real import shall here be estimated as <0.01 I-TEQ/year. The content of dioxin should be assumed to be disposed of to waste incineration sooner or later. Although a minor emission of dioxin to air may be expected to take place from cork used as floor or wall coverings etc, this emission are probably insignificant.

Paper/cardboard

Dioxin developed by chlorine bleaching will partly be adsorbed to the paper manufactured. Furthermore, it should be expected that dioxin once formed and attached to paper fibres to some extent might remain attached also during recycling operations. Dioxins in paper may thus continue to circulate in the society for several years depending on the life of individual paper products. To this should be added that internationally PCP has also been used as a pesticide in paper manufacturing, and PCP is actually registered in paper products in concentrations op to 0.7 ppm /Maff 1997/.

No investigations of the content of dioxin in paper products have been carried out in Denmark. A German study /FLV 1993 quoted in Fiedler 1999/ investigated virgin paper as well as recycled materials. In virgin newspaper the dioxin content was generally around 1 ng I-TEQ/kg or below. In secondary paper materials dioxin content of 0.8 - 3.2 ng I-TEQ/kg was found whereas in cardboard materials and wrapping paper a content of 4.5 – 11.5 ng I-TEQ/kg was registered.

Based on these findings a rough dioxin balance for Denmark with respect to paper and cardboard materials have been established in table 2.8.

The balance should be regarded as an attempt to illustrate the relevant order of magnitude for a number of relevant dioxin flows related to paper and cardboard materials. The size of the flows indicates that some emissions to water or loss to paper sludge and other residues from paper recycling in Denmark could well take place. However, no data is available to confirm or de-confirm this hypothesis. As paper sludge in Denmark generally are re-utilised for cement manufacturing; the dioxin directed this way should be expected to be destroyed due to high temperatures of cement manufacturing.

Of the total supply of paper and cardboard in Denmark, around 50% is presently collected for recycling, whereas the rest is directed for waste incineration /Papirstatistik 1998/. Thus one would expect around 1.5-3.3 g I-TEQ/year to be directed for recycling and a similar quantity to waste incineration.

Table 2.8
Dioxin balance for paper and cardboard materials

Item	Production	Import	Export	Supply
Materials balance (tonnes/year) 1)				
Paper	110.000	450.000	60.000	500.000
Cardboard and wrapping materials	280.000	380.000	150.000	510.000
Total	390.000	830.000	210.000	1.010.000
Dioxin balance (g I-TEQ/year) 2)				
Paper	0.11 – 0.33	0.45 – 1.35	0.06 – 0.18	0.5 – 1.5
Cardboard and wrapping materials	1.4 – 2.8	1.9 – 3.8	0.75 – 1.5	2.5 – 5.1
Total	**1.5 – 3.1**	**2.2 – 4.2**	**0.8 – 1.7**	**3.0 – 6.6**

1) The figures should be taken as rounded estimates – some Danish production figures, in particular for cardboard materials, are confidential and not included. Figures are based on /Danmarks Statistik 1999a; Danmarks Statistik 1999b/.

2) For paper being a mixture of virgin and recycled materials has been assumed concentration figures of 1-3 ng I-TEQ/kg. For cardboard and wrapping materials that are dominantly secondary materials has been assumed concentration figures of 5-10 ng I-TEQ/kg.

2.8 Other industrial processes

A number of other industrial processes that may be suspected to develop dioxins exist in Denmark. The available knowledge related to these processes is presented in the following. The list of processes is not necessarily exhaustive.

Vitamin manufacturing
Vitamin manufacturing is one of the major uses of chlorine in Denmark. The manufacturing process, however, is going to be changed to a chlorine-free process by the end of 2001. No measurements for dioxins have been carried out, as the manufacturing process is not believed to generate dioxins. This assessment is based on the facts that the chlorine before being in the manufacturing process is transformed into hypochlorite, and the temperatures used in the process do not exceed 67ºC. It is thus deemed unlikely that the process will develop or cause emission of dioxins to any significant extent.

Spray drying and roasting processes
Spray drying is used in a number of manufacturing processes and in particular within the food industry on products like coffee, milk powder etc. No measurements for dioxin emission related to such industries have been carried out in Denmark. No data are to the best of knowledge available from the literature either. Spray drying processes generally takes at above 200ºC, typically by hot air recirculated through a flame fed by natural gas. The experience from spray drying of meat and bone meal (reference is made to section 3.4.2) indicates however that it is unlikely that spray drying in general will generate dioxin to any significant extent. Whether this assessment also applies to roasting processes like roasting of coffee beans etc. cannot be said. Although one would expect the formation and emission to be small, no measurements are available.

Asphalt preparation and recycling
Asphalt preparation and recycling is assumed to be a potential source of dioxin, in particular in countries doing extensive recycling and using ordinary salt (chloride) for preventing icy roads during the wintertime.

The total production of asphalt for road construction and other purposes in Denmark in 1998 came up to approx. 1,700,000 tonnes /Danmarks Statistik 1999b/, of which approx. 740,000 tonnes are recycled materials.

Recent measurements of the dioxin emission to air from a Danish asphalt mixing plant (virgin asphalt) gave an emission factor of 2.2 ng I-TEQ/tonnes products /Fyns Amt 2000/. No measurements of the emission from recycling plants from Denmark exist. From Dutch investigations an emission factor for recycling plants of 47 ng I-TEQ/tonnes of asphalt is reported. The Dutch figure is, however, likely to be an overestimate compared to Danish plants, as most Danish plants are using the so-called "cold recycling" in which only stones are heated and then mixed with the rest of the components (not preheated), whereas the Dutch plant were heating all the components.

Anyway, accepting the given figures as representing the relevant range (the high figure is only used for recycled materials), dioxin emission to air from asphalt plants in Denmark can be roughly estimated at less than 0.04 g I-TEQ/year.

Flaring
By initiation of crude oil extraction from new production wells the operators will often need to burn off (flare) the natural gas present in the oil. In order to minimise NO_x emission from the flaring operation seawater is added. Whereas natural gas in itself by burning generates dioxin in small quantities (reference is made to section 3.2), adding of seawater could make an increased dioxin emission likely. However, no measurements are to the best of knowledge available, and it is not possible to give any estimate of the emission. The source is relevant to Denmark due to the Danish oil extraction activities in the North Sea.

Oil refining
There are two oil refineries in Denmark, both of which use catalysts in the refining process. The catalysts are made of platinum on a base of aluminium oxide. The catalysts require hydrogen chloride on the surface for its operation that is obtained by adding tetrachloroethene under normal operation of the catalyst. Under normal operation the catalyst is covered by water, and formation of dioxins should not be possible. Gasses are passed through a desulphurizing installation, before it is burned off in the boiler, from where it goes out unfiltered. Whether dioxins are generated during the final burning operation is not known.

During production the platinum catalyst achieves a layer of coke. During regeneration of the catalyst the plant is closed for several days. The coke is burnt off whereas organic chlorine compounds are added. The air from this process is neutralised with NaOH in water before it goes out unfiltered. Dioxin formation by similar processes has been confirmed by investigations in Canada /Jensen 1995/. Based on information from the refineries the amount of coke burned this way can be estimated at approx. 26 tonnes/year. However, no measurements of dioxin emission have been undertaken, and no data is available to allow an estimate of the emission.

2.9 Summary

The assessments and estimates related to formation and turnover of dioxins by industrial activities in Denmark by the end of nineties and presented in sections 2.1 to 2.8 are summarised in table 2.9.

Table 2.9

Summary of formation and turnover of dioxins by industrial activities in Denmark

Activity/product	**Consumption by products**	**Formation**	**Emissions/losses (g I-TEQ/year)**				
	g I-TEQ/year	g I-TEQ/year	**to air**	**to water**	**to soil**	**to waste**	**Other routes**
Chemicals							
Pesticides 1)	< 1?	?	?		< 1?	?	
Pharmaceuticals		?	?			?	
Bleaching agents	< 0.001			< 0.001			
Brominated flame retardants 2)	2 – 60	?	?			?	?
Other chemical products	?		?	?	?	?	?
High-temperature materials							
Raw materials 3)	4 –1050					0.004-5	
Clay-based insulation materials		0.0006-0.24	0.0006-0.24				
Tiles and bricks		0.001-0.2	0.001-0.2				
Cement		0.045-0.92?	0.045-0.92	?			
Lime 4)		0.0009-2.7	0.0009-2.6				<0.08
Other Materials		0.004-0.024	0.004-0.024			?	
Metal manufacturing							
Metal casting		0.032-0.06	0.032-0.06			?	
Hot-dip galvanising		0.023-0.44	0.023-0.44			<0.002	
Steel reclamation 5)		6.1-12.8	1.1-2.3	0?		< 0.005	5.0 – 10.5
Aluminium reclama.		0.43-4.8	0.17-3.3	0		0.26-1.5	
Feedstuff							
Fish oil/meal		<0.01?	0?	<0.01			
Meat/bone meal 6)7)	0.003-0.19	?	?				0.004-0.35
Green feed drying 7)	0.05	0.004-0.04?	0.004-0.04				
Feedstuff prod. 8)	1.5-11			?	<10?	?	?
Food products	0.06-0,44			?		?	
Pentachlorophenol							
- wood	0.11- 42?		0.5-26?			5-240?	
- leather	0.5		<0.05			0.5?	
- textiles	0.5			0.2		0.3	
Chlorine bleaching							
- bleaching in DK		<0.5		<0.5			
- cork	<0.01					<0.01	
- paper/cardboard 9)	3.0-6.6			?		1.5-3.3	1.5-3.3
Other processes		<0.04?	<0.04?	?	?	?	?
Total (rounded)	12-1200?	6.5-23?	2.0-36?	0.2-0.7	<11?	7.6-250?	6.5-14?

? Figure cannot be estimated due to lack of data. The flow in question should be overlooked.
x? Figure or some of the subfigures referred to is deemed highly uncertain.
1) Reference is made to section 2.1.1 and section 2.1.3.
2) Figures refer to brominated dioxins. Toxicity equivalency factors are assumed similar to factors for chlorinated dioxins.
3) The consumption figure covers consumption with clay and clay-like raw materials used for manufacturing of insulation materials, tiles, bricks and similar items. The dominant part of this consumption is assumed to be destroyed by manufacturing processes. The indicated loss to waste covers dioxins in clay used for decoration and educational purposes.
4) The quantity stated under “other routes” covers dioxin in filter dust sold as material for flue gas cleaning operations.
5) The quantity stated under “other routes” covers dioxin in filter dust exported for zinc recovery. An estimated < 0.016 g I-TEQ will be reused in asphalt and cement manufacturing.
6) The quantity stated under “other routes” covers dioxin in meat and bone meal exported.
7) The quantity stated as “consumption by products” is also included in the consumption figure for feedstuff products.
8) The quantity stated under “emission to soil” covers land application of manure and similar waste products from animal and fish farming. As no detailed investigation of dioxin circulation within the Danish animal and fish farming sectors has been undertaken, the figure should be taken as a rough estimate only.
9) The quantity stated under “other routes” covers dioxin paper and cardboard collected for recycling.

3 Formation and turnover by energy production activities

In Denmark energy production is based on a mixture of sources, primarily coal, natural gas, oil and biomass, besides also waste incineration, wind and sun energy. This chapter focuses on fossil fuels and biomass. Emission of dioxin from combustion processes involving such materials is well documented by several studies. As no studies, to the best of knowledge, so far have indicated any natural content of dioxin in these materials, dioxin emission must be assumed entirely to be due to "de novo synthesis" during the combustion process and flue gas treatment operations.

3.1 Coal power plants

Consumption of coal and coke in Denmark in 1998 counted for approx. 235,000 TJ or approx. 9.4 million tonnes /Energistyrelsen 2000/, of which approx. 93% was used for production of electricity and heat by central power plants. The remaining was primarily used for energy supply for manufacturing purposes. Around 1100 TJ or approx. 44,000 tonnes was used for heating purposes by households, farmers or market gardens.

Coal incineration will result in around 13-15% residuals, primarily fly ash and to a lesser extent slag, bottom ash, gypsum and other desulphurization products.

Dioxin formation and disposal
Previous Danish measurements of dioxin formation by coal combustion dates back to before 1990 and did not detect dioxin /Nielsen and Blinksbjerg 1989/. In /Jensen 1997/ dioxin emission to air from coal combustion in Denmark has been estimated at 2 g I-TEQ/year corresponding to an emission factor of 0.2 µg I-TEQ/ton, whereas an estimated 40 g I-TEQ was collected and deposited as production residues. The 40 g collected as residues was estimated based on rather old measurements of total dioxin in fly ash transformed by analogy considerations to N-TEQ.

From a newly investigation in 1999 at a Danish coal power plant an emission to air of 4.7 pg I-TEQ/m^3 (n,t at 5.8% oxygen) was reported /Fyns Amt 2000/. This emission corresponds to an emission factor of 33 ng I-TEQ/ton coal. The plant in question (Fynsværket section 7) can with respect to the temperature pattern over the flue gas treatment system and dust removal in general be taken as representative to around 99% of the Danish consumption of coal for energy generation /Elsam-Projekt 2000a/.

The European Dioxin Inventory (section on Germany) gives air emission factors for electricity generation by coal power plants in the range of 1.06 - 7.01 µg I-TEQ/TJ. Assuming a conversion factor of 25 GJ/tonne of coal this equals a range of 0.027 - 0.18 µg I-TEQ/t. For residential heating the Inventory (section on Germany) states air emission factors of (Landesumweltamt Nordrhein-Westfalen 1997):

Coal:	0.83 (0.36 - 1.92) µg I-TEQ/ton
Lignite briquettes:	0.62 (0.13 - 2.92) µg I-TEQ/ton
Coke:	0.61 (0.55 - 0.68) µg I-TEQ/ton

Measurements from the Netherlands on a coal power plant and an industrial coal combustion plant gave air emission factors as follows /Bremmer et al 1994/:

Coal power plant:	0.35 µg I-TEQ/ton
Industrial plant:	1.6 µg I-TEQ/ton

Based on these figures, it seems reasonable to accept, that

- approx. 8.7 million tonnes were combusted at an emission rate of 0.033 µg I-TEQ/ton
- approx. 0.7 million tonnes were combusted at an emission rate of 0.13 - 2.92 µg I- TEQ/ton.

These assumptions result in a total emission to air of 0.4 – 2.3 g I-TEQ/year that should be regarded as below the previous estimate of 2 g I-TEQ/year.

The amount of residues from coal combustion generated in Denmark in 1998 was approx. 1.5 million tonnes of which around 10% was exported for cement manufacturing abroad, and approx. 200.000 tonnes were used for cement manufacturing in Denmark.

No measurements of dioxins in residues from Denmark exist, and literature figures are scarce. /Dyke et al 1997/ quote figures of 0.02-13.5 ng I-TEQ/kg for grate ash and 0.23-0.87 ng I-TEQ/kg for filter dust from cyclones and bag filters. The residues measured originate from industrial plants and may thus not be representative to residues from large coal power plants.

Flyash from electrostatic filters and bag filters is the dominant residue developed in Denmark. Assuming a figure of 0.2-0.9 ng I-TEQ/kg to be valid to the total amount of residues generated in Denmark, the amount of dioxins collected with these residues may be roughly estimated at 0.3 – 1.4 g I-TEQ/year. It is noted that this estimate is considerably below the previous estimate for Denmark (40 g I-TEQ – see the beginning of this section) which is due to different data sources. In recognition of that neither of the data sources likely are representative to the coal types and operating conditions found at coal power plants in Denmark today, the choice is made here to accept a range of 0.3 – 40 g I-TEQ/year as the best estimate for the dioxin amount collected with residues from coal combustion in Denmark.

Of this quantity 10 % corresponding to 0.03 – 4 g I-TEQ is exported, whereas 0.04 – 5.3 g I-TEQ is used for cement manufacturing in Denmark and the remainder directed to depot in Denmark or used for miscellaneous civil works like road construction etc.

3.2 Other fossil fuels

Other fossil fuels cover natural gas and oil products. The consumption of these energy products in Denmark in 1998 can be summarised as follows /Energistyrelsen 2000/:

Natural gas:	180,300 TJ ~ 4,520 million Nm^3
Oil products for other purposes than transport:	170,000 TJ ~ 3.95 million tonnes

Around 70% of the consumption of natural gas was used for industrial processes, power generation and other larger scale uses, whereas the remaining 30% mainly was used for residential heating /Energistyrelsen 2000/.

Dioxin formation and disposal
No measurements of dioxin emission related to combustion of oil and natural gas has been undertaken in Denmark.

The European Dioxin Inventory (section on Germany) gives air emission factors for electricity generation by natural gas in the range of 0.02 - 0.03 µg I-TEQ/TJ. Assuming a conversion factor of 40 GJ/1000 Nm^3 this equals a range of 0.0008 - 0.0012 ng I-TEQ/Nm^3. For residential heating the Inventory (section on Germany) states air emission factors of /Landesumweltamt Nordrhein-Westfalen 1997/:

Natural gas:	0.07 (0.05-0.1) ng I-TEQ/m^3
Heating oil:	0.04 (0.02 -0.09) ng I-TEQ/l

Assuming that these data are representative to the qualities and processes used in Denmark, and an average density for oil products of 0.9 kg/l can be applied, the dioxin emission to air can be estimated at:

Natural gas combustion: 0.07 - 0.14 g I-TEQ/year
Oil combustion: 0.07 - 0.32 g I-TEQ/year
Total: 0.14 - 0.46 g I-TEQ/year

No knowledge concerning the content of dioxins in soot/ash from combustion of natural gas or oil products seems to exist. The amount of soot/ash generated is, however, small. Soot/ash will be directed to landfills. Emissions to wastewater should be regarded as negligible.

3.3 Biomass

The major biomass fuels are straw and wood. There are following types of wooden fuels: firewood, forest wood chips, wood pellets, wood briquettes and wood waste, including bark.

Straw and woods are used as fuels mainly in private homes, district-heating plants and in central and de-central, combined heat and power plants (CHP).

The total energy production by biomass fuels was estimated at 33,601 TJ in 1998 (see table 3.1).

Table 3.1
Energy production in Denmark 1998 based on biomass /Energistyrelsen 2000/

Primary energy production in 1998 (TJ)	Firewood	Forest wood chips	Wood pellets	Wood waste	Straw
Private homes	8339	81	625		3447
Public service		146	365		
Industry		0	2	4728	
Agriculture and forestry		27		60	2298
District heating		2208	1986	506	3886
Industry to district heating		0	6	225	
Industrial CHP 1)				319	0
Middle-sized CHP 1)		396	34	13	2709
Large CHP power plants 1)		181		0	1014
Sum (TJ)	**8339**	**3039**	**3018**	**5851**	**13354**

1) CHP stands for Combined Heat and Power. The plants may thus generate heat as well as electricity.

An ongoing study by the Center of Biomass Technology for the Danish Energy Agency has estimated the number of biomass installations in 1998 as shown in table 3.2:

Table 3.2:
Rounded numbers of biomass installation in Denmark 1998.

Number of plants	Firewood	Forest wood chips	Wood pellets	Wood waste	Straw
Wood stoves	370,000				
Farm boilers					9000
District heating		50	40		50
Smaller stoker boilers		50	200	200	
Industrial CHP plants				5	
De-central CHP plants		5	1	1	6

Central CHP plants	1	1

The knowledge and assessments related to the different types of installations are presented in the following.

3.3.1 Wood stoves

The number of wood stoves in private homes in Denmark is estimated to be about 400,000 stoves. An investigation from the beginning of the 1990s /Houmøller 1995/ showed that 33% of the woods consumed in these stoves were good qualities of hardwood from forestry. The rest included wood from private gardens, replacement of old hedges, industrial surplus wood etc. Paper, cardboard, milk cartoons, painted and impregnated wood waste (reference is made to section 3.6.1) and perhaps also plastics are known to be used to a certain degree, but there are no available studies and therefore no precise knowledge of these partly illegal customs in Denmark. Attention should e.g. be paid to the fact that the ordinary blue colours used in newspapers, on milk packaging etc. are typically based on copper pigments. It should also be noted (see below), that the typical temperatures present in the stoves as well as the chimney belongs to the interval more or less optimal for dioxin formation.

Plant activity

Number of stoves in 1998	370,000
Total consumption of wood 1998	429,800 tonnes dry weight
Energy production	8,339 TJ
Produced ash	4,300 tonnes dry weight
Typical temperatures in combustion zone	500-800ºC
Typical temperatures in chimney	250-350ºC

No flue gas cleaning is installed for this type of equipment.

Dioxin formation and disposal

In the first Danish study /Dyrnum et al. 1990/ the total dioxin emission was estimated at 32 g N-TEQ/year with an uncertainty range of 10-50 g N-TEQ/year based on an annual wood consumption of 222,000 tonnes. The flue gas concentrations were <200 ng total dioxin/Nm^3 for hardwood, about 1000 ng total dioxin/Nm^3 for waste briquettes and about 65,000 ng total dioxin/Nm^3 for PCP-treated wood. It was assumed that burning 1kg wood would generate 8.6 Nm^3 flue gas. N-TEQ was assumed to correspond to 1.5% of total dioxin.

In a more recent Danish study /Hansen et al. 1994/ the emission concentration from burning hardwood and softwood under controlled representative conditions in commonly sold Danish wood stoves ranged 5.8-53 ng total dioxin/Nm^3 or quite similar to the previous study. The average was 12 ng total dioxin/Nm^3 or 0.18 ng N-TEQ/Nm^3. The emission factor was 1.9 µg N-TEQ/tonnes wood. The total consumption of wood for stoves was 214,000 ton/year in 1992 and based here upon the total emission was estimated at <0.4 g N-TEQ/year ± 60%. In 1995 the Danish consumption of firewood had increased to 578,231 tonnes, and the dioxin emission correspondingly to 1.1 g N-TEQ/year.

In a new Danish investigation clean birch and dried clean excess wood from manufacturing was fired in a new stove /dk-TEKNIK 2000/. The testing covered for both types of wood ordinary firing as well as night firing. Night firing covers the practice of adding a large amount of wood at one time and adjusting the air supply to a minimum in order to allow the fire to continue the night over. In all cases 6-hours sampling covering lightning as well as operation was performed. Ordinary firing gave a dioxin emission (to air) of 5.1 µg I-TEQ/tonnes wood for birch and 1.7 µg I-TEQ/tonnes wood for excess wood, whereas night firing gave emissions factors of 0.52 µg I-TEQ/tonnes wood for birch and 0.56 µg I-TEQ/tonnes wood for excess wood.

In 1993 the Swedish Environmental Protection Agency reported an emission factor for stoves of 0.13-0.3µg N-TEQ/tonnes wood burned /Swedish EPA 2000/.

In the Netherlands the emission factors for wood stoves and open wood fire places ranged 1.0-3.3 µg I-TEQ/tonnes dry clean wood and 13-29 µg I-TEQ/tonnes dry clean wood, respectively /Bremmer et al. 1994/. In Switzerland wood stoves were estimated to emit 0.77 (open door)-1.25 (closed door) µg I-TEQ/tonnes clean wood and 3,230 µg I-TEQ/tonnes household waste /Schatowitz et al 1994, quoted by Swedish EPA 2000 and US Dioxin Inventory 1998/.

In the most comprehensive German study /Bröker et al. 1992/ the emission factor for stoves burning clean wood was typically 0.71 µg I-TEQ/tonnes wood and ranged 0.53-0.94 µg I-TEQ/tonnes wood. Burning of wood at open fireplaces resulted in a lower typical value of 0.46 µg I-TEQ/tonnes wood and a range of 0.07-1.25 µg I-TEQ/tonnes wood. In another study with inclusion of 30% paper as fuel the dioxin emission concentrations raised about five times /Launhardt et al. 1996/.

The European Dioxin Inventory has assessed the existing investigations published up to the middle of the nineties (including the investigations described above) and has adopted the following default air emission factors for domestic wood combustion /Landesumweltamt Nordrhein-Westfalen 1997/:

Clean wood:	1 µg I-TEQ/ton
Slightly contaminated (without PCP):	50 µg I-TEQ/ton
Strongly contaminated (with PCP):	500 µg I-TEQ/ton

This assessment is here accepted as a reasonable illustration of the variations caused by different types of combustible materials used in wood stoves. Considering that the dominant part of the material burned in Denmark is clean wood, but that other materials to some extent will also be included, it is deemed fair to expect the overall picture to be somewhat between a clean wood situation and a slightly contaminated wood situation. An activity of approx. 430,000 tonnes/year burned and an air emission factor of 1-50 µg I-TEQ/ton equals a total air emission of 0.43 – 22 g I-TEQ/year.

Residues
No measurements of dioxin concentrations in ash and soot from wood stoves and chimneys are made in Denmark. /Dumler-Gradl et al 1993 & 1995 quoted by Dyke et al 1997/ gives figures of 75 – 500 ng I-TEQ/kg ash and 500 – 9000 ng I-TEQ/kg soot for a wood based household heating system. They also give soot values of 4 – 42000 ng I-TEQ/kg for a household heating system using a mixture of wood, coal and waste. In the last case the maximum value is related to wood burning only. The mean concentrations of dioxin in soot from various wood stoves and ovens were 1.4-3.5 µg I-TEQ/kg soot /Dumler-Gradl et al. 1995 quoted by US Dioxin Inventory 1998/. In Canada the dioxin content in soot from wood stoves was 211 ng/kg / US Dioxin Inventory 1998/.

Assuming an amount of ash of approx. 4,300 tonnes and a dioxin content of 75 – 500 ng I-TEQ/kg ash, the amount of dioxin to be disposed of with ash can be estimated at 0.32 – 2.2 g I-TEQ/year. This ash will be disposed of with other household waste or spread in gardens.

Soot from chimneys will normally be removed by the chimney sweeper. The amount of dioxin collected and disposed of in this context has not been estimated.

3.3.2 Other plants

A significant amount of other biomass combustion plants is operating in Denmark partly as a result of a Danish policy to develop the utilisation of biomass for energy generation. Generally, the materials combusted in biomass plants will be clean materials. However, it must be assumed that a number of plants will also use materials to some extent contaminated by glue, paint or plastics or perhaps disposable pallets or other types slightly contaminated by PCP. No precise knowledge on this issue is available, and it is not possible to quantify the extent to which the materials combusted are contaminated.

Plant activity

The activity of other plants for energy generation from biomass in Denmark is summarised in table 3.3. It may be noted that the activity of farm boilers has been reduced in the last 10 years, as 580,000 tonnes straw was burned at 11,000 farms in 1989.

Dioxin formation and emission factors

As the raw materials, operation conditions as well as flue gas cleaning varies between the different types of biomass combustion plants, it should be expected that dioxin formation and emission would likely vary also. However, as indicated in the following only few investigations on the different types of plants are available. The data available are presented in the following:

Concerning farm boilers for straw an early investigation by /Nielsen and Blinksbjerg 1989/ reported the very low emission concentration of 0.016 ng Eadon-TEQ/Nm^3 and an emission factor of 5 ng Eadon-TEQ/GJ. That will correspond to about 3 ng I-TEQ/GJ. The translation factor from Eadon-TEQ to I-TEQ for this source was about 0.6. In this study the dioxin emission was hundred times greater by burning straw bales than loose straw.

Table 3.3
Activity of other plants generating energy from biomass in Denmark

Plant type		Farm boilers	District heating	Smaller stoker boilers	Industrial CHP plants	De-central CHP plants	Central CHP plants
Parameter	**Unit**						
Number of plants		9,000	140	450	5		1
Total consumption – straw	Tonnes dry weight	311,000	217,100			151,300	56,600
Total consumption – wood chips	Tonnes dry weight		143,100	13,100			
Total consumption – wood pellets	Tonnes dry weight		104,400	51,100			
Total consumption – wood waste/bark	Tonnes dry weight			24,700	276,900		
Total energy production	TJ	5,745	8,697	1,725	5,372	2,709	1,014
Produced ash to landfill	Tonnes dry weight	12,800	11,100	900	2,800	6,100	2,300
Typ. temperature – combustion zone	°C	600-800	700-900	600-800	700-1000	800-1000	800-1000
Typ. temperature – chimney	°C	100-180	80-150	100-150	100-150	80-150	80-150
Flue gas cleaning		No cleaning	No information may vary	No cleaning	Likely at all plants	Likely at all plants	Yes

In a newer study /Jensen & Nielsen 1996/ three farm boilers using full bales, sliced bales and grated bales, respectively, were investigated. The emission concentrations from the two first mentioned boilers were below the detection limit (<0.02 ng N-TEQ/Nm^3). From the grated bale boiler the air emission concentration was calculated to 16 ng N-TEQ/m^3 (n, t) at 10% O_2. The airflow was about 600 m^3/h and the load was 41 kg/h, thus the emission flux was about 9.6 µg N-TEQ/h corresponding to an air emission factor of 230 µg N-TEQ/tonnes straw. As an average for all 3 plants investigated, the emission factor can be calculated to 77 µg N-TEQ/tonnes straw.

A new Danish investigation from 2000 on one farm boiler using full bales gave air emission factors of 5.3 - 9.2 µg I-TEQ/tonnes straw /dk-TEKNIK 2000/.

Concerning district heating the study of /Jensen & Nielsen 1996/ also covered three district heating plants using straw. The emission concentrations from two of them were above the detection limit (0.01 ng N-TEQ/m^3). The two plants in question can be briefly characterised as follows:

Performance:	1.6 KW/2.5 KW
Yearly consumption of straw:	2,438/4,300 tonnes
Energy production:	6,920/9,073 Gcal. (1 Gcal = 4.186 GJ)
Temperatures in flue gas:	145 ºC/176ºC,
Air flows:	3,500/4,500 m^3/h
Measured dioxin levels:	0.01/0.44 ng N-TEQ/m^3 (n, t) at 10% O_2,

All three plants had cyclone and bag filters installed.

Based on these few data, emission factors of an average 1.7µg N-TEQ/ton and min./max. factors of 0 and 5 µg N-TEQ/ton can be calculated for straw at district heaters with flue gas cleaning.

A new Danish investigation from December 1999 on a straw based district heating plant (6.3 MW) equipped with cyclone and bag filter for flue gas cleaning gave air emission factors of 17 -22 ng I-TEQ/ton straw /dk-TEKNIK 2000/. The temperature of the flue gas over the filter ranged from 110 to120ºC.The investigation was based on 3 samplings, each lasting for 6 hours.

Combustion of wood chips (dry excess wood from furniture manufacturing) and crushed chipboards (inclusive glue, plastic or paper coating and misc. additives) in a district heating plant (6.3 MW) was investigated in summer 2000 /dk-TEKNIK 2000/. The plant was equipped with electrostatic filter for flue gas cleaning, and the temperature over the filter ranged within 110 - 120ºC. For each type of fuel 4 samplings each lasting 6 hours were undertaken. However, 2 out of the total 8 samplings were later assessed as contaminated. For wood chips the air emission factors for the remaining 3 samplings were determined as 15, 18 and 39 ng I-TEQ/ton chips respectively, whereas the factors for crushed chipboards were determined as 17, 21 and 33 ng I-TEQ/ton chipboard /dk-TEKNIK 2000/.

One Danish investigation for small stoker boilers based on wood pellets is available. The investigation was carried out on a new boiler using 6 hours' sampling. The dioxin emission (to air) reported ranged within 0.21- 0.53 µg I-TEQ/ton pellets /dk-TEKNIK 2000/.

Measurements of dioxin emission from 3 Danish central or de-central CHP-plants were undertaken in autumn 1999. From each plant 3 measurements of 2 hours representing normal operation were undertaken. The fuel was mainly straw, but 2 of the plants also used wood chips. Based on energy content wood chips counted for up to 35% of the fuel consumption. The flue gas temperatures ranged between 99 and 129ºC. All plants are undertaking flue gas cleaning by electrostatic filter (1 plant) or bag filter (2 plants). The dust emission of all plants is 10 mg/ Nm^3 or below. The dioxin concentrations reported range between 0.4 and 5.3 pg I-TEQ/Nm^3 /ELSAMprojekt 2000b/. Assuming 10 Nm^3/kg of straw or chips, emission factors of 4 – 53 ng I-TEQ/ton can be calculated.

For stokers burning wood slightly contaminated by glue, PUR and other kinds of plastics and operating cyclones for flue gas cleaning Dutch investigations / Bremmer et al. 1994/ reports air emission factors of 3-8 µg I-TEQ/ton wood with a best estimate of 5 µg I-TEQ/ton wood.

For industrial wood combustion including combustion in boilers, gas turbines and stationary engines the European Dioxin Inventory – section on Germany - reports air emission factors of 1 – 500 µg I-TEQ/TJ for clean wood and 0.75 – 6,200 µg I-TEQ/TJ for contaminated wood /Landesumweltamt Nordrhein-Westfalen 1997/. Assuming a conversion factor of 20 GJ/ton wood these emission factors can be expressed as 0.02 – 10 µg I-TEQ/ton wood for clean wood and 0.015 – 125 µg I-TEQ/ton contaminated wood.

The European Dioxin Inventory /Landesumweltamt Nordrhein-Westfalen 1997/ – section on United Kingdom – reports air emission factors of 17 – 50 µg I-TEQ/ton for straw burning. These factors are partly based on /Nielsen and Blinksbjerg 1989/ referred above. Furthermore is reported air emission factors of 1-2 µg I-TEQ/ton for clean wood burning and 9 – 19 µg I-TEQ/ton for burning of treated wood.

The US air emission factors for various industrial wood-fired boilers were between 0.5-1.3 µg I-TEQ/tonnes. Regarding burning of wood stored in seawater the emission factor raised to 17 µg I-TEQ/tonnes (EPA draft report 1998).

Based on these data the following air emission factors are adopted for the current situation in Denmark:

Straw burning – no flue gas cleaning: 1 – 50 µg I-TEQ/ton
Straw burning – flue gas cleaning: 0.004 - 2 µg I-TEQ/ton
Wood burning – no flue gas cleaning: 0.2 – 10 µg I-TEQ/ton
Wood burning – flue gas cleaning: 0.01 – 5 µg I-TEQ/ton

These factors are deemed appropriate for assessing the total emission in Denmark, but it may well be the case that the emission for some biomass plants will be outside the range stated. The factors are argued as follows:

For straw burning without flue gas cleaning which mainly addresses farm boilers the emission factors reflect the actual Danish experience as described above. For straw burning with flue gas cleaning, one is considering partly CHP plants and partly district heating plants. Again the emission factors reflect the actual Danish experience as described above.

Wood burning without flue gas cleaning deals with small stoker boilers operated by small companies and individuals and fired with pellets, chips and for some boilers also crushed chipboards and larger pieces of wood. The emission factors adopted are partly based on the Danish measurement described above and recognise that the dominant type of fuel will be wood pellets, but do also pay respect to the possibility that part of the chips or wood otherwise used could be contaminated.

Wood burning with flue gas cleaning is relevant to district heating plants and CHP plants, in particular industrial CHP plants. The flue gas cleaning facilities relevant will be cyclones or bag filters and to a lesser extent electrostatic filters, whereas real dioxin filters are not assumed to be used. Generally district heating plants will be designed and operated to maximise heat extraction, and the temperature of the flue gas over the filter will typically be close to 100ºC and will certainly not exceed 200ºC. The same applies to most CHP plants. Furthermore, the plants should be expected to be in control of the materials burned. It has not been investigated to what extent district heating plants have permission to burn contaminated materials. However, as burning of materials classified as waste (e.g. chipboards) is financially less attractive due to the Danish waste fee system, it seems fair to assume that this practise is not widespread for district heating plants. Industrial CHP plants will be designed to burn wood waste from the manufacturing activities that may include chipboards, sawdust, bark etc. but occasionally also other materials like paper depending on the design of the individual plant /dk-TEKNIK 2000/. The emission factors adopted reflects the few Danish measurements described above besides paying respect to the possibility that combustion of contaminated materials could take place to a limited extent.

Combustion of biomass and air emission of dioxin can based on table 4.3 and the emission factors adopted above be summarised as follows:

Straw burning – no flue gas cleaning: 311,000 tonnes ~ 0.3 - 15 g I-TEQ/year
Straw burning – flue gas cleaning: 425,000 tonnes ~ 0.002 - 0.9 g I-TEQ/year
Wood burning – no flue gas cleaning: 88,900 tonnes ~ 0.02 – 0.9 g I-TEQ/year
Wood burning – flue gas cleaning: 524,400 tonnes ~ 0.005 – 2.6 g I-TEQ/year

The total emission of dioxins to air from biomass combustion plants in Denmark can thus be estimated at 0.3 – 19 g I-TEQ/year.

It is noted that the air emission of dioxins from combustion of biomass (other sources than wood stoves) in Denmark in a previous report /Jensen, 1997/ has been estimated at 0.07-6.6 g I-TEQ/year (straw burning) and 0.25 g I-TEQ/year (wood burning).

Residues
No measurements of the content of dioxins in residues from biomass combustion have so far been carried out in Denmark. The international data available are presented in the following:

The only study available on residues from straw combustion is a UK study concerning a whole bale straw combustor from which a concentration of 10 ng I-TEQ/kg grate ash was reported /Dykes et al. 1997/. The concentration was considered very low and caused by a high temperature and long residence time on the grate causing destruction of dioxins. As an estimate for assessing the situation in the UK covering both good and poor combustors was adopted the range of 10 – 500 ng I-TEQ/kg ash /Dykes et al. 1997/.

On wood a few studies are available:
Burning of natural wood in different wood combustion systems concentrations of 0.23 – 1.12 ng I-TEQ/kg in bottom ash and 117 – 272 ng I-TEQ/kg in filter ash has been reported / Oehme & Müller 1995/. The same study reported concentrations of 22 ng TEQ/kg bottom ash and 722-7620 ng TEQ/kg in filter ash after burning a mixture of PCP-treated and untreated wood.

In a Swiss study /Wunderli et al 1996/ of natural wood incineration in installations of from 20 kW to 1.8 MW fly ash collected in cyclones and bottom ash contained only low levels of dioxins (0.6 - 8.5 ng I-TEQ/kg) and lower than bio compost. Fly ashes from waste wood incineration had much higher dioxin content of 700-21,000 ng I-TEQ/kg. If the combustion process has been efficient, bottom ashes were as low in dioxin concentration as ashes from clean wood incineration. Otherwise the concentration could be as high as for fly ashes.

At a German test facility for industrial wood combustion burning *contaminated* wood the dioxin content in filter dust and bottom ash ranged from 30 to 23,300µg I-TEQ/ton dust and 30-3,300 µg I-TEQ/ton ash, respectively /Landesumweltamt Nordrhein-Westfalen 1997/.

In a UK study of a boiler burning treated wood (however, not PCP-treated) was reported grate ash concentrations of 584-1090 ng TEQ/kg and grit ash levels of 891-1070 ng TEQ/kg /Dykes et al. 1997/.

For a stoker burning wood slightly contaminated by PUR, soot collected from the inside of the stack was reported to contain 0.2 µg I-TEQ/kg /Bremmer et al. 1994/.

Based on these data, that does not allow for distinguishing between straw and wood burning the choice has been made to adopt a concentration range of 1 - 1000 ng I-TEQ/kg as representative to ash produced at Danish plants. Based on the data in table 4.3 the total quantity of ash from Danish biomass combustion plants can be added up to around 36,000 tonnes/year corresponding to a dioxin quantity of 0.04 – 36 g I-TEQ/year. The dominant part of this dioxin should be expected to be directed to landfills. However, part of the production from farm boilers may likely be spread on soil. As ash from farm boilers counts for around 36% of the total ash production, the dioxin quantity to be spread on soil could be up to 0.01 – 13 I-TEQ/year.

3.4 Summary

The assessments and estimates related to formation and turnover of dioxins by energy production activities in Denmark by the end of the nineties and presented in section 3.1 to 3.3 are summarised in table 3.4.

Table 3.4
Summary of formation and turnover of dioxins by energy production activities in Denmark

Activity/product	**Consumption by products**	**Formation**	**Emissions/losses (g I-TEQ/year)**				
			to air	**to water**	**to soil**	**to waste**	**Other routes**
	g I-TEQ/year	g I-TEQ/year					
Coal power plants 1)		0.7 – 42.3?	0.4 – 2.3			0.23 – 31?	0.07 – 9?
Other fossil fuels		0.14 - 0.46	0.14 - 0.46			0?	
Biomass							
- wood stoves 2)		0.75 – 24.2?	0,43 – 22		0.32 – 2.2?	0.32 – 2.2?	
- other plants 3)		0.34 – 55?	0.3 – 19		0.01 – 13?	0.04 – 36?	
Total (rounded)		**2 - 122**	**1.3 – 44**		**0.3 - 15**	**0.6 – 69**	**0.07 – 9**

? Figure cannot be estimated due to lack of data. The flow in question should be overlooked.
x? Figure or some of the subfigures referred to is deemed highly uncertain.
1) The quantity disposed of by other routes covers export of fly ash for cement manufacturing abroad (0.03 – 4 g I-TEQ/year) and use of fly ash for cement manufacturing i Denmark (0.04 – 5 g I-TEQ/year).
2) The quantity disposed of to soil and waste adds up to a total of 0.32-2.2 g I-TEQ/year. The precise distribution between soil and waste is not known.
3) The quantity disposed of to soil and waste adds up to a total of 0.04-36 g I-TEQ/year. The precise distribution between soil and waste is not known, but the quantity disposed of to soil will be less than 0.01 – 13 g I-TEQ/year.

4 Formation and turnover by miscellaneous human and natural activities

4.1 Fires

4.1.1 Accidental fires in buildings, installations and transport equipment

It is generally accepted /Cleverly et al 1999, Landesumweltamt Nordrhein-Westfalen 1997/, that accidental fires may be a significant source of dioxin formation. In buildings as well as transport equipment a mixture of materials including chlorine sources (like PVC), organic matters and copper are present, meaning that conditions are appropriate to "*de novo* synthesis" of dioxins. Many buildings may, furthermore, contain wood preserved by PCP-preservatives that were widely used in Denmark for industrial wood preservation as well as surface preservation/priming of wood before painting up to the late seventies (reference is made to section 2.6.1). Attention should also be paid to the use of brominated flame retardants in plastics, because such plastics in themselves may contain brominated dioxins, and more brominated dioxins may be formed by burning of the flame retarded plastics.

Activity in Denmark
The amount of material burned by accidental fires in Denmark can only be estimated with significant uncertainty. Based on information from /Beredskabsstyrelsen 1999 and Beredskabsstyrelsen 2000/ it may be roughly assumed

- that approx. 2000 large fires take place yearly. A large fire is in this context defined as a fire involving the use of 2 or more fire hoses for fire-fighting and will typically involve a complete house, one or more apartments, or at least part of an industrial complex
- that approx. 6000 medium fires take place yearly. A medium fire is in this context defined as a fire involving the use of 1 fire hose only for fire-fighting and will typically involve a part of a single room in an apartment or house
- that approx. 7000 small fires take place yearly. A small is in this context defined as the fires statistically defined as "extinguished before arrival" , "extinguished by small tools" or "chimney fires" .

Is it furthermore assumed

- that a large fire as a rough average in each case will lead to combustion of 5-10 tonnes of materials equalling the weight of combustible construction materials and furniture and other combustible materials in a typical Danish residential house
- that a medium fire as a rough average in each case will lead to combustion of around 100 kg of materials equalling the weight of some household equipment or pieces of furniture
- that a small fire as a rough average in each case will lead to combustion of around 1-10 kg of materials equalling the content of a paperbasket, a small garden fire or a chimney fire.

Based on these assumptions the total amount of materials combusted by accidental fires annually in Denmark may be roughly estimated at 10-20,000 tonnes.

In this estimate medium and small fires carry no weight that could lead to an underestimate of the importance of especially fires in vehicles, as significant dioxin formation from vehicle fires have been registered. Therefore vehicle fires are estimated separately as follows.

Insurance reports from all Danish insurance companies from 1999 and 2000 on cars and other vehicles characterised as totally damaged by fire (meaning that repair was deemed not feasible) indicate a total number of damaged vehicles of 1535 per year /Forsikrings-oplysningen 2000/. Not all vehicles will actually be completely burned out, for which reason it is deemed fair to compare the 1535 incidents with around 1000 completely burned-out cars.

To these types of fire accidents may be added fires in trains, ships, aeroplanes and equipment containing PCBs. No efforts have been done to quantify these fires and the amount of materials combusted. In general the total volume will be small compared to building fires with the exception of fires in larger passenger liners (e.g. the Scandinavian Star accident) that fortunately is a quite unusual accident. Electrical equipment containing PCBs, e.g. transformers and capacitors, is nowadays banned, although some equipment may still be in operation.

Formation of dioxins

Measurement of dioxin formation related to accidental fires has been carried out in Denmark in 1997 and in May 2000. In 1997 a factory with a stock of approx. 50 tonnes of PVC burned down in Århus. Soil measurements (depth 4 -5 cm) showed dioxin concentrations of 0.2 ng I-TEQ/kg and 0.05 ng I-TEQ/kg for contaminated and reference samples respectively /Vikelsøe 2000/. The accident in May 2000 involved a company north of Copenhagen manufacturing office utilities e.g. based on PVC. The amount of materials consumed by the fire has been estimated at a total of 600 tonnes including 2 tonnes of PVC. During most of the fire the smoke went straight up for several hundred metres. The smoke has been characterised as very heavy and black. Measurements of 6 soot samples were undertaken. One sample from a window at the place of the accident showed a dioxin content of 9 ng I-TEQ/m^2, whereas 4 other samples taken at distances of 90-450m from the company showed dioxin contents varying from 6 to 1 ng I-TEQ/m^2. The background level was also determined to 1 ng I-TEQ/m^2 /Danish EPA 2000a/. The data available are however to a few to allow for a reliable quantification of the dioxin formation and emissions occurred.

Formation of dioxins by accidental fires is generally difficult to quantify and only limited data are available. Generally estimates are based on the content of dioxins in soot samples collected from surfaces on the place of fire and in the vicinity. Based on this approach an estimate for Germany of 81 g I-TEQ/year (estimated margin of uncertainty: 2.5 - 2,500 g I-TEQ/year) has been developed. This estimate covers accidental fires in buildings as well as vehicles. Transferring the German estimate to Danish conditions by the use of per capita calculations, the European Dioxin Inventory states a dioxin emission to air for Denmark of 5.3 g I-TEQ/year /Landesumweltamt Nordrhein-Westfalen 1997/. For the dioxin content of fire residues an estimate for Germany of 139 g I-TEQ/year (estimated margin of uncertainty: 4.3 - 4,300 g I-TEQ/year) has also been developed /Landesumweltamt Nordrhein-Westfalen 1997/. If similar per capita calculations are applied to this figure, the dioxin content of fire residues in Denmark may be estimated at 9.1 g I-TEQ/year.

It should be noted that estimates for emission to air based on soot samples in the vicinity may likely underestimate the total emission to air, as some dioxin may likely be attached to very small particles and transported far.

Another approach could be to utilise the experience from recent investigations of uncontrolled domestic waste burning (reference is made to section 5.3.1), in which domestic waste known to contain 0.2 %, 1% and 7.5 % PVC generated 80 ng I-TEQ/kg respectively 200 ng I-TEQ/kg and 4900 ng I-TEQ/kg waste.

The average content of PVC in houses in Denmark could well be in the range of 0.2-1%, but will be below 7.5%. A figure of 50-1000 ng I-TEQ/kg material and 10,-20,000 tonnes of material would equal a total emission of 0.5-20 g I-TEQ per year.

Vehicles tunnel experiments in Germany (/Wichmann et al 1995/ quoted in /Jensen 1997/) has shown a generation of dioxin of 0.044 and 0.052 mg I-TEQ for two different cars. Assuming these figures to be valid for all 1000 Danish incidents of vehicle fires, the total generation of dioxins by vehicle fires in Denmark may be estimated at approx. 0.05 g I-TEQ/year.

Considering the uncertainties involved in these estimates, and paying respect to the fact that independent assessments methods give results of similar order of magnitude, it is hereby proposed to accept the following estimates for dioxin generation in relation to accidental fires in Denmark:

Emission to air:	0.5 - 20 g I-TEQ/year
Collected with residues:	1 - 30 g I-TEQ/year

The estimate for collection with residues is based on the German estimate that the amount of dioxin in fire residues is approximately 70% higher than the amount estimated as emission to air, but the emission to air is likely underestimated.

Dioxin collected with residues will partly be removed as waste that should be assumed dominantly to be directed to landfills, although it cannot be ruled out that some materials like metals and bricks are directed to recycling and left-overs of combustibles may be directed to incineration plants. Some of the dioxin should, however, be assumed to be transported in the smoke by wind and fall-out on land or waters, and others by extinguishing water to the ground and the sewage system.

4.1.2 Other fires

Other fires cover bonfires, camp fires and forest fires. The dominating bonfire event in Denmark is the celebration of midsummer (Skt. Hans) at the 23 June. Camp fires include private fires in gardens and in particular burning of garden waste as well as camp fires in summer camps etc.

At best practice these fires consist of pure wood. But other kinds of waste as plastics or preserved or painted wood may occasionally be included. Camp fires may also be based on driftwood that contains chloride from the sea.

The significance of bonfires (and fireworks - see section 4.4) may be illustrated by British observations that the concentration of dioxins in ambient air increased fourfold during the dominant bonfire event in the UK (/Dyke and Coleman 1995/ quoted in /Dyke et al 1997/).

Landfill or depot fires are a special type of fire that is discussed in section 5.5 and not here.

Activity
No statistics on the number of these fires and the amount of material combusted are available. The following considerations should be regarded as a rough estimate only.

The midsummer bonfire takes place all over Denmark. All cities and villages will have at least one fire and depending on their size often several. In Denmark there are 1421 cities with more than 200 inhabitants /Danmarks Statistik 2000/. Thus, it is reasonable to assume that the number of midsummer bonfires in Denmark come up to somewhat between 5,000 and 20,000 fires. The materials used for these fires will typically be twigs and branches from bushes and trees. Assuming the typical fire to have a size of around 100 m^3, of which approx. 5% is wood with a density of 0.8, the total amount of wood combusted may be estimated at 20,000 - 80,000 tonnes/year.

Private fires and in particular burning of garden waste are banned in some districts, but allowed in others. There are 1.4 million houses in Denmark with some kind of garden /Danmarks Statistik 1999/. Assuming that 10% of these burn 10-50 kg of twigs and branches 2-6 times a year, the amount of material combusted may be roughly estimated at 3,000 - 40,000 tonnes/year.

Camp fires are frequent during the summertime in Denmark. The amount of wood consumed, however, are likely less than for burning of garden waste. As a very rough estimate the amount of wood consumed is here assessed to 2,000 – 10,000 tonnes.

Forest fires are seldom in Denmark and should not be expected to cover more than very few hectares per year. Compared to other fires forest fires should be regarded as insignificant for Denmark.

Straw burning on the fields has been banned in Denmark since 1990. However, exemption has been granted to burning of grass seeds, and farmers may occasionally still burn piles of old straws harvested the previous year and left behind on the fields during winter. Neither reliable information about the extent of field burning nor dioxin measurements is available.

Dioxin formation and disposal
No measurements of dioxin formation related to such fires has been carried out in Denmark.

For natural fires the European dioxin inventory (section on UK) proposes emission factors (the very large intervals are due to different assessment methods /Landesumweltamt Nordrhein-Westfalen 1997/):

Mean values:	14.5 – 571.5 µ I-TEQ/ton of wood
Min./Max:	1 - 1,125 µ I-TEQ/ton of wood

Attention should also be paid to the experience on wood burning in open fire places and the default emission factors of the European dioxin inventory for domestic wood combustion (reference is made to section 3.3.1):

Clean wood:	1 µ I-TEQ/ton
Slightly contaminated (without PCP):	50 µ I-TEQ/ton
Strongly contaminated (with PCP):	500 µ I-TEQ/ton

Considering that the dominant part of the material burned are clean wood, but that other materials may occasionally be involved as well, it is deemed fair to expect the overall picture to be somewhat between a clean wood situation and a slightly contaminated wood situation. An activity of approx. 25,000 – 130,000 tonnes/year burned and an air emission factor of 1-50 µ I-TEQ/t equal a total emission of 0.03 – 6.5 g I-TEQ/year.

Residues
/Dyke et al 1997/ assessed dioxin content in residues from bonfire events by referring to measurements of dioxin in ash from a wood stove and soot from a stove burning wood, coal and waste on 75 µ I-TEQ/ton and 42048 µ I-TEQ/ton respectively. Assuming an amount of ash of approx. 1% of the amount of wood, 25,000 – 130,000 tonnes of wood will result in 250 – 1300 tonnes of ash. Assuming a dioxin content of 75 – 42000 µ I-TEQ/t ash, bonfires and the like will result in 0.02 – 55 g I-TEQ/year with ash and other residues that are dominantly is spread on the ground and partly disposed of as waste. It is noted that the high end of this interval may most likely be overestimated. Disposal as waste will primarily be the case for residues from bonfire events. As a rough estimate 50% of the residues is assumed to be spread on the ground and the rest to be disposed of as waste.

4.2 Traffic

Dioxin emission from vehicles is mainly related to chlorine or bromine additives used in leaded gasoline. The use of leaded additives for gasoline in Denmark has now ceased completely. The previous estimate made in /Jensen 97/ of a dioxin emission from vehicles in Denmark of less than 0.2 g I-TEQ/year will still be valid.

This estimate does not include emissions from trains and ships.

The consumption of fuel for such purposes in 1998 was as follows /Energistyrelsen 2000/:

Ships – fuel oil: Approx. 300.000 tonnes
Ships – gas oil: Approx. 100.000 tonnes
Trains – gas oil: Approx. 250.000 tonnes

The consumption figures for ships cover inland traffic only.

Based on results from the Dutch national dioxin measurement programme /Bremmer 1994/ estimates the following emissions factor:

Ships – heavy fuel oil: 4 ng I-TEQ/kg fuel
Ships – gas oil: 1 ng I-TEQ/kg fuel

No data of trains are available. The emission factor for trains is here assumed to be somewhat between the factors known for ships-gasoil (see above) and diesel vehicles (0 .03 ng I-TEQ/kg fuel /Bremmer 1994/.

Based on these assumptions the total emission from ships and trains in Denmark can be roughly estimated at 1.3 –1.5 g I-TEQ/year, and the total emission from traffic to 1.3 –1.7 g I-TEQ/year.

4.3 Crematories

32 crematories are currently operating in Denmark. All crematories treat flue gasses by afterburning (850°C for one second), without further filtering. The temperature of the off-gases before the chimney will be in the range of 150-400°C /Danish Crematories 2000/.

Plant activity
Approx. 40,000 bodies are cremated yearly. The average mass per creamation (body plus coffin) is 110 kg equalling a total mass of approx. 4,400 t/year /Danish Crematories 2000/.

Dioxin emission
Measurement of dioxin emission from one crematory in Denmark was carried out in 2000 /dk-TEKNIK 2000/. The oven operated was installed in 1996 and is heated by natural gas. 4 measurements each lasting 6 hours corresponding to the cremation of 4 bodies (1.5 hour/body) were undertaken. The flue gas temperature was approx. 345°C. The air emission reported ranged between 183 and 336 ng I-TEQ/cremation with an average of 283 ng I-TEQ/cremation. The crematory is taken as representative of Danish crematories as per today. Based on these figures the emission to air in Denmark from crematories can be estimated at approx. 0.01 g I-TEQ/year.

It is noted that the European Dioxin inventory assumes a default emission factor for emission to air of 8 µg I-TEQ/cremation and minimum/maximum values of 3 - 40 µg I-TEQ/cremation /Landesumweltamt Nordrhein-Westfalen 1997/.

It is also noted that the air emission of dioxins from cremation in Denmark in a previous report /Jensen, 1997/ has been estimated as 0.16 g I-TEQ/year, mainly based on Dutch investigations (reference is made to /Bremmer et al. 1994/). These investigations also form part of the fundament for the emission factors assumed by the European Dioxin inventory.

No knowledge exists regarding the content of dioxin in ashes from crematories. The dominant route of disposal for ash will be burying in the ground on cemeteries.

4.4 Other activities

A number of other activities that may be suspected to develop dioxins exist in Denmark. The available knowledge related to these activities is presented in the following. Generally the potential for dioxin formation may be assumed to be small, but no precise knowledge is available.

Fireworks
Fireworks should be suspected to develop dioxins, but no measurements seem to be available. The significance of fireworks (and bonfires - see section 4.1.2) may be illustrated by British observations that the concentration of dioxins in ambient air increased fourfold during the dominant bonfire event in the UK (/Dyke and Coleman 1995/ quoted in /Dyke et al 1997/).

Roof cardboard
In Denmark roof cardboard impregnated by bitumen is a common roof covering material, in particular on rather flat roofs. Construction and maintenance of such roofs is normally done by melting layers of roof cardboard together by heating with a gas flame. Formation of dioxins may likely take place by such operations, but no measurements are available.

Other burning/heating operations
Burning/heating operations are used for several activities and might in several cases be the cause of dioxin formation. Examples on such operations include:

- Removal of seed as an alternative to pesticide use.
- Heating of pipes and plates of copper for sanitation or construction purposes.
- Blacksmith activities and similar artisan's work.

Charcoals and charcoal briquettes used in garden grills and cooking in general
Danish investigations on garden grills have confirmed dioxin formation by food preparation on garden grills /dk-TEKNIK 2000/. 4 measurements each involving 2 kg of charcoal (briquettes) used for preparation of approx. 2 kg of meat were carried out. In each test sampling lasted for 2 hours including lighting of charcoal and preparation of meat. In 2 tests oil, salt and pepper was added to the meat in a quantity typical for meat grilling (approx. 15 g of salt per test). In each test 3 paraffin blocks of 18 g/block were used for the lighting process. The dioxin emission observed corresponded to emission factors ranging from 6 to15 ng I-TEQ/kg charcoals. The Danish import of charcoal for grilling and other purposes comes up to approx. 15,000 tonnes/year / Danmarks Statistik 1999a/. Assuming this quantity is used solely for garden grills, the total dioxin emission by garden grilling in Denmark can be estimated at 0.09 - 0.22 g I-TEQ/year. No measurements of the content of dioxins in ash or the grilled meat are available.

It is noted that dioxin formation may well be possible for other cooking operations, e.g. frying.

Smoking
Dioxin formation by cigarette smoking has been confirmed, and smoking is regarded as a source for direct human impact /Jensen 1997/. In an overall context it is likely marginal.

4.5 Summary

The assessments and estimates related to formation and turnover of dioxins by miscellaneous human and natural activities in Denmark by the end of the nineties and presented in section 4.1 to 4.4 are summarised in table 4.1

Table 4.1
Summary of formation and turnover of dioxins by miscellaneous human and natural activities in Denmark

Activity/product	**Consumption by products**	**Formation**	**Emissions/losses (g I-TEQ/year)**				
			to air	**to water**	**to soil**	**to waste**	**Other routes**
	g I-TEQ/year	g I-TEQ/year					
Fires							
- accidental fires		1.5 – 50?	0.5 – 20?	?	?	1 - 30	?
- other fires		0.05 – 61.5?	0,03 – 6.5?		0.01 - 27.5?	0.01 - 27.5?	
Traffic		1.3 –1.7	1.3 –1.7				
Crematories		0.01	0.01		?		
Other activities		0.09-0.22?	0.09-0.22?	?	?	?	?
Total		3 – 113?	2 – 28?	?	0.01 - 28?	1 - 58?	?

? Figure cannot be estimated due to lack of data. The flow in question should be overlooked.
x? Figure or some of the subfigures referred to is deemed highly uncertain.

5 Formation and turnover by waste treatment and disposal activities

5.1 Metal scrap

5.1.1 Reclamation of cable scrap

Reclamation of cable scrap in Denmark today concerns reclamation of electrical cables with lead sheath used for power supply or communication purposes buried in the ground or at the sea bottom. The cables typically consist of solid copper conductors separated by oil-saturated paper surrounded by a solid and impermeable lead sheath wrapped in tar-impregnated textile and finally covered by a thin flexible ring of steel. One reclamation plant for such cables exists in Denmark.

By the reclamation process the lead sheath is melted away at 500-600°C. The air stream that has a high content of soot, is afterwards treated in an afterburner at 875°C with a minimum of 6% O_2 for 2 seconds. Via a heat exchanger the air stream is finally led through a bag filter with an inside layer of lime. The temperature around the bag filter is approx. 100°C.

The reclamation plant is also receiving and separating old transformers. The oil is tapped of and burned as fuel. However, this only applies for oil with less than 50 ppm of PCB. In those cases - happens very seldom - in which the oil contains 50 ppm of PCB or more, the transformers are directed to the central Danish facility for chemical waste (Kommunekemi - reference is made to section 5.2).

Danish cable scrap not treated at this plant is believed to be exported for reclamation in India or the Far East. Illegal cable burning, if any, is believed to be insignificant. However, a separate plant exists for reclamation of modern PEX-coated cables that is separated by purely mechanical processes. Other cables may be treated as mixed metallic waste for shredding (section 5.1.2) or as municipal solid waste directed to incineration (section 5.3.1).

Plant activity
Based on information from the company, the activity of the plant can be summarised as follows:

Total cable waste:	approx. 2,500 tonnes/year
Total transformer waste	approx. 1,400 tonnes/year
Filter dust	approx. 1 kg/year
Air emission	approx. 3.4 million Nm^3/year

Filter dust is sent to the central Danish facility for chemical waste (Kommunekemi).

Dioxin formation and disposal
No measurements of dioxin emission have been undertaken at the plant or of the filter dust. In the Netherlands air emission factors of 3.7- 2280 μ I-TEQ/ton scrap has been determined, based on which the investigation assumed an emission factor of 40μ I-TEQ/ton scrap /Bremmer et al 1994/. The maximum figure of 2280 is, however, based on one observation only, whereas the other observations give 21 as the highest figure. The US Dioxin inventory contains one partly congener specific analysis showing that an air emission factor for scrap electrical wire recovery of between 2 and 50 μ I-TEQ/ton scrap /US Dioxin Inventory 1998/. No literature data is available addressing filter dust from cable reclamation.

Assuming an air emission factor of 2-2000 µ I-TEQ/ton scrap, the total emission to air can be calculated as 0.005 - 5 g I-TEQ/year. Disposal of dioxin with filter dust should most likely be considered insignificant.

5.1.2 Shredder plants

5 shredder plants for treatment of cars, white goods and mixed metallic scrap exist in Denmark. In a shredder plant the waste is torn to pieces by large rotating steel hammers. The temperature of the hammers and other parts of the shredder may rise to 600-800°C due to friction, and part of the organic materials present (e.g. as paint and plastics) may actually be burnt away. Air emission from shredders is typically cleaned by scrubbers.

Activity
Approx. 700.000 tonnes yearly of metal scrap was treated by the Danish shredders in the middle of the nineties (H. Dalgaard, Danish EPA quoted by /Jensen 1997/). The figure is believed still to be valid.

Dioxin formation and disposal
One measurement of dioxin emission from a Danish shredder was made in 1999. The emission factor obtained was 0,0104 µg I-TEQ/ton scrap /Fyns Amt 2000/. Apart from this no measurements of dioxin related to shredder plants have been carried out in Denmark. The European Dioxin Inventory (section on Germany) states values for dioxin emission to air of 0.06 - 0.67 µ I-TEQ/ton scrap /Landesumweltamt Nordrhein-Westfalen 1997/. Adopting the Danish measurement as valid to all Danish plants; the total emission from shredder plants in Denmark can be estimated at approx. 7 mg I-TEQ/year.

No data on the content of dioxin in scrubber sludge and other shredder residues are available. These residues are normally directed to landfills.

5.2 Chemical waste

5.2.1 Chemical waste incineration

Kommunekemi that is the central facility for treatment of chemical waste in Denmark, has 3 kilns, of which 2 kilns (F3 and F4) are now equipped with dioxin filters. Hazardous waste is for the time being treated only in these two kilns. The third kiln (F1) has been used for oil and tar polluted soils but F1was closed for rebuilding in July 2000. In connection with the rebuilding F1 will also be equipped with a special dioxin filter. Before the air stream enters the dioxin filters, it is cleaned by a bag filter (one kiln) or an elector filter (the other kilns). The temperature in the bag filter and the electro-filter is around 195°C, whereas the temperature over the dioxin filters is around 145°C. The experience of Kommunekemi confirms the general experience that the temperature through the flue gas system is of the outmost significance to dioxin formation and should be below 200°C.

Besides Kommunekemi, another minor Danish plant has permission for incineration of special types of chemical waste. This plant also treats clinical hospital waste. Totally the plant treats 4,700 tonnes waste/year of which 1,600 t is chemical waste, and the rest is clinical hospital waste /Danish EPA 1999c/. This plant is covered by section 5.4 on incineration of clinical hospital waste.

Plant activity
The activity of Kommunekemi can be briefly summarised as follows:

Oil and chemical waste burned	approx. 90,000 tonnes/year
Oil and tar polluted soils burned	approx. 20,000 tonnes/year
Air emission cleaned by dioxin filter	approx. 600 million Nm^3/year
Air emission without special dioxin filtering	approx. 100 million Nm^3/year

Fly ash deposited	approx. 6,000 tonnes/year
Slag deposited	approx. 11,000 tonnes/year
Gypsum	approx. 1,150 tonnes/year
Filter cakes and other materials	approx. 12,000 tonnes/year

Dusts from the dioxin filters are incinerated in the kilns, and the content of dioxins is assumed to be destroyed. The fly ash collected by the bag filter and the electrostatic filter is landfilled on Kommunekemi's own depot.

Kommunekemi has no knowledge of and is not analysing dioxin concentrations in waste received for treatment and disposal.

Formation and disposal of dioxin

Kommunekemi has carried out several measurements of dioxin emission by air and water and some measurements have shown very high concentrations of dioxin. In order to fulfil the present limit value of 0.1 ng I-TEQ/Nm^3 Kommunekemi has redesigned kilns and flue gas cleaning systems. Also dioxin filters have been installed.

In 1999 Kommunekemi used the eldest kiln F1 for incineration of different waste fractions such as polluted soil, car-fluff and liquid chemical waste. The total operation time in 1999 was 3,109 hours /Danish EPA 2000b/.

From 1999 until today the following emission results for dioxin (I-TEQ) have been obtained /Danish EPA 2000b/:

1999 June	Car-fluff	2.7	ng/Nm^3
1999 August	Liquid waste	36	ng/Nm^3
1999 September	Liquid waste/polluted soil	200	ng/Nm^3
1999 October	Liquid waste	3.5	ng/Nm^3
2000 January	Polluted soil	0.6	ng/Nm^3
2000 March	Polluted soil	0.5	ng/Nm^3
2000 April	Polluted soil	0.4	ng/Nm^3
2000 May	Polluted soil	0.2	ng/Nm^3
2000 May	Polluted soil	0.2	ng/Nm^3
2000 June	Polluted soil	0.2	ng/Nm^3

According to /Danish EPA 2000b/ Kommunekemi has estimated the total emission from F1 during 1999 to 2 – 2.5 g I-TEQ.

For 0.2 ng/Nm^3 as found in 2000 the yearly emission based on 200 million Normal m^3 per year can be calculated to 0.04 g I-TEQ /year /Danish EPA 2000b/.

For the two other incinerators F3 and F4 equipped with dioxin filters the following emission measurement results for dioxin (I-TEQ) have been obtained /Danish EPA 2000b/:

F 3

1999 April	Normal Operation	0.7	ng/Nm^3 *
1999 December	Normal Operation	0.04	ng/Nm^3
2000 March	Normal Operation	0.01	ng/Nm^3
2000 May	Polluted Earth	0.008	ng/Nm^3

*)Without dioxin filter

F4

1999 April	Corrosion Problems	1.2	ng/Normal m^3
1999 April	Corrosion Problems	0.4	ng/Normal m^3
1999 June	Corrosion Problems	0.35	ng/Normal m^3
1999 August	Corrosion Problems	0.06	ng/Normal m^3
1999 December	Normal Operation	0.05	ng/Normal m^3
2000 May	Normal Operation	0.003	ng/Normal m^3

According to /Danish EPAb/ the total emission for F3 and F4 in 1999 can be calculated as follows:

F3: Average emission 0.37 ng/Nm^3, 300 million Nm^3/year. Total emission 0.11 g I-TEQ /year.
F4: Average emission 0.412 ng/Nm^3, 300 million Nm^3/Year. Total emission 0.12 g I-TEQ /year.

According to the /Danish EPA 2000b/ the total emission from the ovens F1+F2+F3 can be calculated to 2.23 - 2.73 g I-TEQ /year.

It is the opinion of the authors of this report that the precision expressed by these estimates and calculations is questionable.

F 1 is closed down for reconstruction the next two years. When it goes in operation again it is equipped with a dioxin filter.

With dioxin filters on all three kilns, an emission limit of 0.1 ng/Normal m^3 limit and 300 million Nm^3 stack gas from each kiln, the maximum emission from all three kilns together will be 0.09 g I-TEQ /year /Danish EPA 2000b/.

Regarding emission with wastewater, Kommunekemi has estimated a total emission of 0.001 mg I-TEQ/year for 1998 /Kommunekemi 1999/.

Regarding dioxin in fly ash and slag from the incineration processes, measurements from March 2000 have given concentrations of 69 ng I-TEQ/kg and 39 ng I-TEQ/kg respectively /Kommunekemi 2000/ equalling a total dioxin quantity of:

Fly ash	approx. 0.4 g I-TEQ/year
Slag	approx. 0.5 g I-TEQ/year

The figures, at least the figure for fly ash, are likely to underestimate the amount of dioxin collected during 1999, at least the amount collected from kiln F1. However, measurements for fly ash and slag corresponding to measurements of air emissions are not available. Measurements of dioxin content of gypsum, filter cakes and other materials deposited, if any, are not available either.

The fly ash and slag are deposited on Kommunekemi's own landfill at Klintholm.

5.2.2 Incineration of waste oil

Apart from the waste oil received and incinerated at the central Danish facility for chemical waste (reference is made to section 5.2.1), waste oil is also incinerated by district heating plants. Before incineration at district heating plants the oil is typically re-refined in order to reduce the content of heavy metals and other contaminants. The focus on waste oil e.g. comes from the possibility that waste oil may contain traces of PCB originating from transformers and condensers. The knowledge available (reference is made to /Danish EPA1995/) is that PCBs are only registered in unrefined waste oil and in concentrations below 1 mg/kg.

In 1997 around 22,600 tonnes waste oil was incinerated at district heating plants /Danish EPA 1999d /. Measurements of the air emission of dioxins caused by incineration of waste oil at district heating plants have been carried out in Denmark on one plant during spring/summer 2000.

The plant in question is equipped with an alkaline scrubber for cleaning of off-gases. The fuel incinerated was unrefined waste oil. 4 measurements were conducted each lasting for 4 hours. Air emission factors ranging between 295 and 1,476 ng I-TEQ/m^3 waste oil were reported /dk-TEKNIK 2000/. Assuming a density of 0.9 ton/m^3 these emission factors correspond to a total dioxin emission to air in Denmark from waste oil incineration of 0.006 - 0.03 g I-TEQ/year. As the plant is using unrefined waste oil and is equipped with a scrubber, it is likely representative to other waste oil based district heating plants in Denmark.

Adopting an air emission factor of 2 µg I-TEQ/ton waste oil as in /Jensen 1997/, who was quoting /Bremmer et al 1994/ leads to an estimated emission of 0.045 g I-TEQ/year.

No knowledge is available concerning residues from waste oil incineration at district heating plants. Such residues will be directed to landfills.

5.3 Municipal solid waste

5.3.1 Incineration

Solid waste incineration is generally accepted as an important source of dioxin formation and emission. A detailed discussion of the many investigations related to solid waste incineration is outside the agenda for this report – reference is made e.g. to /Jensen 1995, Jensen 1997 and Dam-Johansen 1996 /. As a very brief summary it can be concluded that dioxins will be present in waste materials directed to incineration. Dioxins may furthermore be formed by the incineration process and afterwards during treatment and cooling of flue gasses either from precursors or by "*de novo* synthesis".

As the temperatures in modern Danish incineration plants are typically around 1000°C, which should be appropriate for degradation of dioxins present in the waste, it is assumed fair to believe that most dioxins in the incoming waste (see table 5.1) are destroyed by the process (reference is made to section 1.5).

However, as indicated by tables 5.2 and 5.3 a very significant emission of dioxins also takes place. As the amount of dioxins emitted from waste incineration by flue gas and incineration residues is significantly higher than the amount destroyed the figures presented documents that municipal waste incineration also in Denmark should be regarded as a very important source of dioxin formation and emission.

Table 5.1
Sources of dioxins in combustible waste assumed to be directed to municipal waste incineration in Denmark

Source	Estimated quantity g I-TEQ/year	Reference to section
Chlorinated dioxins:		
Clay for decoration and educational purposes	0.004 – 5	2.2.1
PCP treated wood 1)	5 - 240?	2.6.1
PCP treated leather 1)	0.5?	2.6.2
PCP treated textiles 1)	0.3	2.6.3
Cork – bleached	<0.01	2.7.2
Paper and cardboard	1,5-3.3	2.7.2
Residues from wood stoves	0.32 – 2.2?	3.3.1
Residues from accidental fires 2)	1 – 30	4.1.1
Residues from other fires 2)	0.01 - 27.5?	4.1.2
Lime filter dust as filter material	<0.08	2.2.5
Other sources	?	4.4
Total	9 – 310	
Brominated dioxins:		
Brominated flame retardants (in plastics)	<(2 – 60)	2.1.3

1) The figures indicate the quantity of dioxins assumed to be present in wood, leather and textiles directed to waste incineration. The phrase "PCP treated" should be regarded as a description indicating the reason for the presence of dioxins. Some of the materials will besides dioxins also contain PCP.
2) Only a part of these residues will be directed to incineration

It should be noted that investigations on dioxin emission from incineration plants have focused on chlorinated dioxins only, and no precise knowledge on brominated dioxins or "mixed" dioxins containing bromine as well as chlorine exists. The following discussion is therefore addressing chlorinated dioxins only.

Uncontrolled burning of waste in backyards etc. is not widespread in Denmark, but cannot be excluded, particularly in rural areas. No statistics covering this practice are available, and the amount of waste disposed of this way can only be estimated with a high degree of uncertainty.

Plant activity

In Denmark 31 municipal waste incineration plants (MWI) are currently operating. As per spring 2000 only 7 plants has established special dioxin filters for treatment of the flue gas besides the normal flue gas cleaning equipment. Dioxin filtration is done with charcoal/coal dust, and the filter material with its content of dioxin is disposed of by being fed into the oven.

The total amount of waste incinerated in Denmark comes up to approx. 2.6 million tonnes per year (1998 - figure /Teknologisk Institut 2000/). In table 5.2 is indicated the knowledge available as per spring 2000 regarding installation of special dioxin filters and for plants without such filter the type of flue gas cleaning process otherwise employed.

Dioxin formation and disposal

The available knowledge regarding dioxin emissions from Danish waste incineration plants is also indicated in table 5.2. As shown the total emission may as best estimate be stated as approx. 21 g I-TEQ/year, with a likely min./max. range of 11 – 42 g I-TEQ/year. To the best of knowledge none of the measurements undertaken is based on a sampling time exceeding 6 hours. A Belgian study indicates that continuos 14 days sampling – thus capturing deviating operating conditions – detects dioxin emissions 3 - 50 larger than detected by 6 hour sampling /De Fré & Wevers 1998/. Details in this study may be discussed, and it is not known whether the observations may be valid also to Danish conditions. The study, anyway, is raising the question of the importance of deviating process conditions and their significance to the total dioxin emission. No other studies addressing this question exist. The available Danish measurements (data is collected early 2000) is summarised in table 5.2. Considering the uncertainty related to e.g. the importance of deviating operation conditions, the choice is made to rely more on the assumed interval of uncertainty than on the calculated best estimate.

Table 5.2
Dioxin emissions to air from municipal waste incineration in Denmark.

Flue gas cleaning process 1)		Dioxin concentration ng I-TEQ/Nm3 2)				Waste incinerated 1000 tonnes	Dioxin emission g I-TEQ/year 3)	
		Mean	Min.	Max.	Samples		Best estimate	Assumed interval of uncertainty
No dioxin filter	Wet	1.49	0.1	5.6	7	1,240	17.3	9 - 35
	Semidry	1.40	1.3	1.5	2	348	2.9	1.5 - 6
	Dry	0.26	0.04	0.75	5	252	0.3	0.15 - 0.6
Dioxin filter		0.068	0.005	0.254	5	839	0.5	0.25 - 1
Sum						2,679	21.1	11 - 42

1) The figures presented are based on data from the following Danish waste incineration plants:

No dioxin filter, wet::
Skive-Egnens Renovationsselskab, Forbrændingsanlæg AVV, Århus Nord, Haderslev, Hadsund, Hammel, Thisted, Reno-Syd, Vestforbrænding, Knudmoseværket, Kolding, Måbjergværket,, Nordforbrænding, Næstved, SWS, Sønderborg and Års.

No dioxin filter, semidry: Reno-Nord, Nyborg, KARA and Slagelse.

No dioxin filter, dry: REFA, BOFA, Grenaa, Horsens, Skagen, VEGA, Vejen and Vestfyn.

Dioxin filter: REFA, Fynsværket, Vestforbrænding, Nordforbrænding, KARA, Svendborg, Amagerforbrænding

2) Samples represent plants, as each plant is represented by one figure. Average is used for plants with more than one measurement. Some plants have two or more incinerators with different flue gas cleaning equipment.

3) Assumed 6.6 Nm^3/kg. The best estimate is calculated based on the actual measurements (average figures) for the individual plants to the extent measurements are available. For plants for which measurements have not been available the calculation is based on the mean dioxin concentration for other plants with the same flue gas cleaning process. The assumed interval of uncertainty is assessed by statistically analysing the available data set from individual plants. On 2 data set covering 4 measurements or more from the same plant a 90% confidence interval corresponded to 37-131% of the mean value of the measurements for the plant. For other data sets of only 2 measurements per set a 90% confidence interval corresponded to 30-580% of the mean value of the measurements from the plant. Based on these data, the choice has been made to assume an interval of uncertainty as -50% to +100% of the calculated best estimate. The argument for assuming a larger interval of uncertainty upwards than downwards is, that as the number of measurements are still limited, the data available could be biased by not adequately including events of deviating process conditions that most likely would correspond to higher levels of emission.

For plants without dioxin filter it seems that the type of flue gas cleaning process employed to some extent determines the dioxin emission, and that dry processes are better than wet and semidry processes. However, the data available are limited and do not allow for solid conclusions.

With respect to uncontrolled burning of waste recent American investigations have revealed that such burning of domestic waste containing 0.0%, 0.2 %, 1% and 7.5 % PVC generated 14 ng I-TEQ/kg respectively 80, 200 and 4900 ng I-TEQ/kg waste /Gullett et al 1999/. The tests with 0.2 % PVC were considered baseruns illustrating the normal content of PVC in domestic waste.

As already stated the amount of waste burned uncontrolled in Denmark is not known, but should be considered small. Assuming a figure of 2,700 tonnes of waste, corresponding to 0.1 % of the total waste quantity, and an emission factor of 80 ng I-TEQ/kg waste, the total emission may be estimated at 0.2 g I-TEQ/year. It is noted that a figure of 2,700 tonnes of waste burned uncontrolled most likely should be regarded as an overestimate rather than the opposite. Thus, uncontrolled burning cannot be expected to significantly contribute to the total dioxin emission from waste incineration in Denmark.

Residues

The available knowledge regarding dioxin content in residues from Danish waste incineration plants is indicated in table 5.3. As shown the total quantity may be estimated at 63 – 495 g I-TEQ/year. Of this quantity around 97% is collected with flue gas cleaning residues.

Table 5.3
Dioxin in residual products from waste incineration.

	Waste quantity 1)	**Dioxin concentration** ng I-TEQ/kg dry matter 2)				**Dioxin 90% confidence interval**
	t/year	**90% confidence interval around the mean** 3)	Min. 4)	Max. 4)	Number of samples	g I-TEQ/year
Clinker	468,500	8.8 ± 3.7	5.1	17.8	6	2 - 5
Flue gas treatment residues	82,500	4,162 ± 3,236	135	35,566	21	61 – 490
Sum (rounded)						63 - 495

1) / Danish EPA 2000d/ - 1998 figures. The figures should be expected to include a content of water of around 20% /COWI 2000/.

2) Data on dioxin concentration in clinker originate from 5 different plants and are provided by /Ansaldo Vølund 1997/, whereas data on flue gas treatment residues are provided by /Dansk RestproduktHåndtering 2000/. Flue gas treatment residues cover flyash, filter dust and filter cakes.

3) The "true" average is with a 90% certainty within the interval.

4) Min. and max. are the lowest and highest measurements respectively.

Three of the measurements of dioxin of "flue gas treatment residues" were on filter cakes. These measurements constitute both the two highest and the lowest figure, i.e. 35,566 and 22,176 ng I-TEQ/kg and 135 ng I-TEQ/kg respectively. The other 18 measurements show much lower difference. The highest and lowest figures are 380 and 6,476 ng I-TEQ/kg respectively with a 90% confidence interval around the mean of 1,037 – 2,243 ng I-TEQ/kg /Dansk RestproduktHåndtering 2000/.

Whereas clinker will partly be landfilled and partly be utilised for civil works (in this context also regarded as landfilling), flue gas cleaning residues will be directed to landfilling only. However, around 38,000 tonnes of flue gas cleaning residues (1998-figure /Teknologisk Institut 2000/) assumed to correspond to 28 – 220 g I-TEQ/year are exported for landfilling abroad.

5.4 Healthcare risk waste

The dominant part of healthcare risk waste generated in Denmark is incinerated together with municipal solid waste in 7 of the ordinary municipal waste incineration plants, and all small incineration plants previously operating at hospitals have been closed. Danish investigations have concluded, that incineration of healthcare risk waste together with ordinary solid waste do not seem to influence the dioxin emission to air from ordinary waste incineration plants /Vikelsøe 2000; Vestforbrænding 2000/. The emission from healthcare risk waste in that context is thus assumed to be included in the figures stated for waste incineration (reference is made to section 5.3.1).

However, one small plant incinerating partly chemical waste and partly healthcare risk waste is in operation. This plant treats approx. 4,000 tonnes waste per year. The plant is equipped with bag filter, but has no special dioxin filter. 2 measurements from 1999 gave results of 1.4 and 5.8 ng N-TEQ/Nm^3 respectively. Assuming 6 Nm^3/kg waste and that an N-TEQ may be considered equal to I-TEQ, the yearly emission to air can be calculated as 34 – 140 mg I-TEQ/year. No measurements exist of filter dust and clinkers. The amount of dioxin collected with these residues is assessed as insignificant compared with residues from municipal waste incineration.

5.5 Municipal landfills

The total quantity of waste to be directed to landfills comes up to approx. 1.87 million tonnes/year (1998 – figure /Teknologisk Institut 2000/). From 1 January 1997 it has not been permitted to landfill waste which is suitable for incineration.

Included in this quantity will be around 37 - 415 g I-TEQ/year of dioxins as detailed in table 5.4.

The fate of dioxins in landfills is not well known, and no Danish investigations on this issue have been undertaken. Based on the physical-chemical characteristics of dioxins it should be expected that transport of dioxins out of landsfills is a very slow process. Evaporation as well as leaching would have to be considered. Concerning leaching attention should be paid to the risk that dioxins may be transported by leachate adsorbed to organic matter.

Investigations on the content of dioxins in leachate have been carried out in Japan. Dioxin concentrations of <0.001-50 pg I-TEQ/l raw leachate have been reported /Yoshikawa et al 1999; Nishikawa et al 1999/. Assuming a leachate generation from Danish landfills of around 5 million m^3/year, the dioxin emission may be estimated at < 0,05 g I-TEQ/year. This emission will primarily be directed to municipal wastewater treatment plants.

Tabel 5.4
Sources and quantities of dioxins assumed to be directed to landfills in Denmark

Source	Quantity g I-TEQ/year	Reference to section
Hot-dip galvanising	<0.002	2.3.2
Steel reclamation	<0.005	2.3.3
Aluminium reclamation	0.26 - 1.5	2.3.4
Other industrial sources	?	2.1, 2.2, 2.3.1, 2.4, 2,8
Coal combustion	0.27 - 31?	3.1
Biomass combustion	0.03 - 33?	3.3.2
Residues from accidental fires 1)	1 – 30?	4.1.1
Residues from landfill fires 2)	0.4-17?	5.5 (this section)
Residues from other fires 1)	0.01 – 27,5?	4.1.2
Residues from shredder plants	?	5.1.2
Residues from incineration plants 3)	35 – 275	5.3.1
Sewage sludge	0.42 – 0.46	5.7.2
Other sources	?	
Total (rounded)	**37 – 415**	

1) Only a part of these residues will be directed to landfills
2) Covers residues from fires in temporary depots for combustible waste
3) Of this quantity a little amount of dioxin will in reality be included in clinkers used for road construction and other types of civil works.

Formation of dioxins may take place by landfill fires. However, the frequency and extent of such events in Denmark is small, as it is standard procedure in Danish landfills to cover the waste with soil. Thus landfill fires can hardly be expected to be a source of any significance in Denmark, and in particular not after the landfilling of combustible waste has been banned.

For combustible waste temporarily stored on landfills or other depots awaiting adequate incineration capacity to be established the situation is different. This procedure became necessary as a consequence of the Danish ban on landfilling of waste suitable for incineration. One major accident has occurred.

In July 2000 a temporary depot of 25,000 tonnes of waste was accidentally set on fire. The fired continued most of a week until more than 75% of the waste had burned out. A significant part of the waste consisted of wood and plastics. The wind direction changed several times during the fire. Measurements of a few soot samples taken from the most exposed areas in a neighbouring city were undertaken. 4 samples taken in distances of 380-3500m from the depot showed dioxin contents varying from 1-2 to 21 ng I-TEQ/m^3. The data available are however to a few to allow for a reliable quantification of the dioxin formation and emissions occurred.

Available information indicates that a number of similar fires takes place every year in Denmark. No exact recordings of the number of fires and the amount of waste burned are made. Assuming that on average 5000 –10,000 tonnes per year of waste are consumed by such fires, and assuming the dioxin formation to be somewhat between 50 and 1000 ng I-TEQ/kg waste (regarding for fires in general - reference is made to section 5.3.1 and 4.1.1 – although typical PVC-products are not included in the waste, the waste should be assumed still to contain small amounts of PVC), the air emission of dioxins may be roughly estimated at 0.25 - 10 g I-TEQ/year. Assuming as for accidental fires that the amount collected and landfilled with residues from the fires comes up to 170% of the amount emitted to air, an amount of 0.4 – 17 g I-TEQ should be expected to be directed to landfills.

It is emphasised that these calculations should be taken as rough estimates likely to indicate the relevant order of magnitude of the flows in question. It is noted that the amount of waste assumed to be consumed by fires in the calculations above may well be underestimated /Hansen 2000/.

5.6 Biological waste treatment

In Denmark in 1998 around 550,000 tonnes of organic garden waste (branches, leaves and grass) together with around 200,000 tonnes of food waste and other organic materials were recycled /Teknologisk Institut 2000/ mainly by composting and bio-fermentation processes.

Organic garden waste and food waste will contain dioxins due to e.g. atmospheric deposition. No dioxin measurements of raw materials nor products and residues from biological waste treatment have been undertaken in Denmark. Thus, the amount of dioxins present in the materials directed to biological waste treatment may only be estimated as follows:

It is assumed that the content of dioxins in organic garden waste is in the range of 10 – 60 ng I-TEQ/ton materials corresponding to the estimates made for grass, silage, hay and root crops (reference is made to table 3.4 in section 3.4.4). Concerning food waste an estimate of 23 – 165 ng I-TEQ/ton can be developed based on table 3.6 assuming that the content of dioxin in food waste corresponds to the content of food products. Based on these assumptions the quantity of dioxins directed to biological waste treatment in Denmark can be calculated as 0.01 – 0.07 g I-TEQ/year.

The fate of dioxins by biological waste treatment is not well investigated. Based on a general understanding of the characteristics and behaviour of dioxins (reference is made to section 2.2 and 2.4) and design of Danish plants for biological waste treatment, little or no formation and degradation is assumed to take place. Consequently, the input of dioxins to such processes will also be present in the products produced that dominantly consist of compost and other residues used as soil improvement material and fertiliser in farming, private and public gardens and parks.

5.7 Wastewater and sewage sludge

5.7.1 Wastewater treatment

The total amount of wastewater discharged from Danish wastewater treatment plants sums up to approx. 770 million m^3 as an average for the years 1989 - 1996, whereas storm water systems discharges an extra 200 million m^3 in a normal year /Danish EPA 1997/.
Only few measurements of dioxins in wastewater are available from Denmark. 3 samples from a single plant showed dioxin levels of 0.4-1.4 ng I-TEQ/m^3 in the outlet from the plant /Vikelsøe 2000/, whereas no measurements are available for inlets. Assuming this level to be valid to all Danish wastewater, the amount of dioxins discharged from Danish wastewater treatment plants can be estimated at 0.3 – 1.1 g I-TEQ/year. No measurements of dioxin in water from storm water drainage systems are available from Denmark. Assuming the same content of dioxins as in wastewater would correspond to a total quantity of 0.08 – 0.3 g I-TEQ/year, assumed to be emitted directly to the water environment. As the number of measurements are very few, the estimate should be considered very uncertain.

Based on the knowledge presented in this report the sources of dioxin in wastewater and storm water may be outlined as indicated in table 5.5. The calculated contribution of 1- 8.7 g I-TEQ/year should be taken as comparable to the estimated total content in discharged waste and storm water of 0.3-1.4 g I-TEQ/year (see above) and the calculated total content in sewage sludge of 2.1 g I-TEQ/year (reference is made to section 5.7.2) paying respect to the uncertainties related to these estimates and calculations. However, it is not possible based on these data to discuss the fate of dioxins in wastewater treatment plants. /Vikelsøe 2000/ points out that observed congener profiles for dioxins in sewage sludge is correlated far better to congener profiles for textiles than to profiles for air deposition. Any definite conclusions on sources for dioxins in wastewater and sewage sludge should thus be considered premature. For a more detailed review of existing international experience related to the fate of dioxins by wastewater treatment and sludge treatment and disposal reference is made to /Jensen 1997/ and /Jones & Sewart 1997/.

It should be noted, that sewage systems as well as storm water systems contain a number of sinks for dioxins e.g. sediment traps as well as the sewage hide inside the sewage pipes. In sediment from sediment traps on storm water systems in the Copenhagen area has e.g. been registered 1.2-1.9 ng N-TEQ/kg dry matter (2 samples, 1996 - /Kjølholt et al 1997/). Thus, it seems quite reasonable that the contribution from sources exceeds the amount registered by analysis of wastewater samples and sewage sludge. The content of sediment traps, when cleaned, should be expected to be directed to landfills. It is however, not possible to estimate the amount of dioxins directed this way.

Table 5.5
Sources and quantities of dioxins assumed to be directed to wastewater and storm water drainage in Denmark

Source	Quantity g I-TEQ/year	Reference to section
Chlorine bleaching	<0.5	2.7.1
PCP preserved textiles	0.2	2.6.3
Atmospheric deposition 1)	0.8 – 8	
Leachate from landfills	<0.05	5.5
Other sources	?	
Total (rounded)	1-8.7?	

1) Estimate is based on a total Danish area served by sewage systems of 2,230 million m^2 and a deposition of 1-10 pg I-TEQ/m^2 per day (assumed background value - see section 2.4.4). The estimate does not take into account the likely higher deposition in city areas. On the other hand is part of the served areas without tight surface (garden areas etc.), meaning that deposition in these situations are directed to soil and not to sewage systems.

5.7.2 Treatment and disposal of sewage sludge

In 1997 the total production of sewage sludge from municipal wastewater treatment plants was 1,160,768 t wet weight corresponding to 151,159 tonnes of dry matter /Danish EPA 1999a/. The sludge is applied to farmland as well as to special sludge incineration plants and landfills as detailed in table 5.6 below.

The content of dioxins in Danish sewage has been thoroughly investigated during the recent years. 38 samples of sewage sludge covering city areas as well as rural districts have been analysed during the years 1996 - 98. The average content of dioxins was determined as 13.8 ng I-TEQ/kg with min./max. values of 1.9/80.0 ng I-TEQ/kg /Vikelsøe 2000/. Based on the value of 13.8 ng I-TEQ/kg, the total quantity of dioxins collected in sewage sludge i Denmark can be calculated to 2.1 g I-TEQ/year. The distribution of this dioxin on the relevant disposal routes is also indicated in table 5.6.

Table 5.6
Disposal of sewage sludge and dioxins contained in sewage sludge in Denmark 1997.

Disposal	Sewage sludge		Dioxin g I-TEQ/year
	Tonnes dry matter	%	
Farmland etc.	91,845	60.8	1.27
Landfill 1)	26,475	17.5	0.37
Incineration	32,840	21.7	0.45
Total	151,160	100	2.1

1) Distribution figures originates from /Danish EPA 1999a/.
2) Around 9% of the quantity are actually directed to long-term stocks for mineralisation. It is assumed that the sludge after being mineralised later on will be landfilled.

Incineration of sewage sludge takes place at 5 plants in Denmark (reference is made to table 5.7). Of these Lynetten and Spildevandscenter Avedøre are the two major plants. The emission from Lynetten and Avedøre will be reduced in the coming years because of new installations at the two plants. Avedøre will e.g. be equipped with dioxin filter /Stads- og havneingeniøren 1999/. As the temperature in the incineration chamber exceeds 1000ºC, it seems justified to assume that all or at least most of the dioxins present in sludge will be destroyed by the process.

Table 5.7
Dioxin emission to air in Denmark from burning of sludge.

	Sludge tonnes dry matter	Emission factor µg/ton dry weight	Emission g I-TEQ/year
Lynetten 1)	19,000	0.07	0.0013
Avedøre 2)	6,264	10.9	0.068
Others 3)	7,576	0.07-10.9	0.0005 – 0.083
Total	32,840		0.07 – 0.15

1) Based on an air flow of 180 million Nm^3/year and dioxin content of 0.007 ng I-TEQ/Nm^3 (as found by measurement per November 1999 /Lynetten 2000/
2) Yearly emission is estimated at 68 mg I-TEQ based on measurements from 1996 /Spildevandscenter Avedøre 1999/.
3) Other minor sludge incineration plants include Køge, Bjerringbro and Brønderslev. However, for around 5000 tonnes dw the plants used for incineration are not indicated by /Danish EPA 1999a/. They could be municipal waste incineration plants. The estimated emission is based on the emissions factors from Lynetten and Avedøre.

The resulting ash from burning of sludge constitutes between 25-45% of the dry matter, and 8,000-15,000 tonnes of ash yearly are currently being directed to landfills. As part of the flue gas cleaning system – at least at the major plants – also a scrubber system is employed. The scrubber water is normally directed to the wastewater treatment plant and mixed with the raw wastewater. No recent measurements of the dioxin content in ash and scrubber water from sludge incineration from Denmark are available. The only available measurements date back to 1989, at which time measurements at Lynetten showed a dioxin content of bottom ash of 6.3 ng N-TEQ/kg and of scrubber water of 0.28 ng N-TEQ/l /Jensen 1997/.

Assuming the data for bottom ash still to be valid and relevant to all sludge incineration plants in Denmark, and furthermore assuming N-TEQ to equal I-TEQ, the quantity of dioxins collected by bottom ash and directed to landfills can be calculated as 0.05 – 0.09 g I-TEQ/year. Concerning scrubber water it may, based on data from Lynetten /Lynetten 2000/ and assuming that all air emissions from sludge incineration in Denmark is treated by scrubber, be estimated that the total amount of scrubber water comes up to approx. 1.8 million m^3/year. A content of 0.28 ng I-TEQ/l will correspond to a total quantity of 0.5 g I-TEQ/year. The dioxin formation by sludge incineration plants can thus be summed up to (0.07-0.15 + 0.05-0.09 + 0.5 = 0.62-0.74) g I-TEQ/year. The amount of dioxins collected by the scrubber water and redirected to wastewater treatment will to some extent be included in the figure for discharges from wastewater treatment plants (unknown – reference to section 5.7.1).

5.8 Summary

The assessments and estimates related to formation and turnover of dioxins by waste treatment and disposal activities in Denmark by the end of the nineties and presented in section 5.1 to 5.8 are summarised in table 5.8.

Table 5.8

Summary of formation and turnover of dioxins by waste treatment and disposal activities in Denmark

Activity/product	**Formation**	**Emissions/losses (g I-TEQ/year)**				
	g I-TEQ/year	**to air**	**to water**	**to soil**	**to depots**	**Other routes**
Cable scrap	0.005 – 5?	0.005 - 5			?	
Shredder plants	0.007?	0.007			?	
Chemical waste incineration 1)	3.1-3.6?	2.2-2.7	0.000001		0.9?	
Incineration of waste oil	0.045?	0.045			?	
Municipal waste incineration 2)	74 – 537?	11 – 42			35 - 275	28 – 220
Healthcare risk waste	0.03 - 0.14?	0.03 – 0.14			?	
Landfills 3)	0.65-27?	0.25-10?	<0.05?		0.4 - 17?	
Biological waste treatment				0.01 – 0.07		
Waste and storm water treatment/discharges	?		0.3-1.4?			
Sewage sludge disposal	0.62-0.74	0.07-0.15		1.27	0.42 – 0.46	
Total (rounded)	**78 – 570**	**14 - 60**	**0.3-1.4?**	**1.3**	**37 – 290?**	**28 - 220**

? Figure cannot be estimated due to lack of data. The flow in question should be overlooked.

x? Figure or some of the subfigures referred to is deemed highly uncertain.

1) The figure stated for emission to air is valid to 1999 only. When the threshold of 0.1 ng I-TEQ/Nm^3 is fulfilled for all ovens the total emission will be less than 0.07 g I-TEQ/year.

2) The quantity stated under "formation" is the sum of the quantities estimated to be emitted to air or directed to depots and other routes (covers export to depots abroad). It may be so, that part of the dioxin contained in the in-coming waste is not destroyed and is therefore included in the figures.

3) Formation and transport of dioxins in landfills are in general believed to be non-significant, although the factual knowledge is very limited. However, fires in temporary depots of combustible waste occasionally take place. The figures of formation, emission to air and to depots are related to such fires. Emission to water represents leachate directed to wastewater treatment.

6 Total picture for Denmark

6.1 Formation and consumption

The dioxin brought into circulation in the Danish society and emitted to the environment in Denmark partly originates from processes taking place in Denmark and partly from raw materials extracted and manufactured in Denmark or imported to Denmark.

Table 6.1 summarises the available estimates regarding formation of chlorinated dioxins in Denmark and the extent to which these estimates are based on Danish investigations or literature values.

The calculation of formation of dioxins by each activity or process takes into account the amount emitted to air and water as well as the amount collected and disposed of with waste products. Formation does in principle also include the amount created in the products manufactured, but no information has been available to allow estimates of these quantities that to the best of knowledge regarding chlorinated dioxins are also insignificant in Denmark, but could well be important to brominated dioxins in plastics containing brominated flame retardants.

The total formation of chlorinated dioxins in Denmark in 1998-99 is estimated at 90-830 g I-TEQ/year. The most important activity is waste treatment and disposal activities of which municipal waste incineration is the dominant source for dioxin generation. Several other activities are, however, also adding significantly to the total formation. These activities include steel reclamation, coal and biomass combustion and fires, both accidental fires and other fires like the dominant Danish bonfire event – Sct. Hans Evening (Midsummer Day).

The formation of dioxins is widespread in the society, as it e.g. is connected to all types of combustion processes. It is noted that for several activities the formation cannot be quantified due to lack of data. It is, however, believed that the results presented in this report cover all major activities relevant in this context.

The large intervals given for most activities in table 6.1 reflect the uncertainty of the estimates. These uncertainties are partly related to the absence of reliable Danish data making it necessary in many cases to rely on international literature data. As dioxin formation is extremely process specific, this calls for a very critical attitude to all available data and in particular to whether the data available are representative to the process in question. However, the uncertainties also reflect the fact that for several important activities, e.g. fires, the knowledge available is actually inadequate, and the estimates presented may in reality only be justified by the need for obtaining an impression of the significance of such activities. It would be fair to conclude that dealing with dioxins is a matter of dealing with a host of uncertainties.

To make the picture complete, it is also necessary to consider the amount of dioxins brought into circulation by raw materials extracted and manufactured in Denmark or imported to Denmark. In table 6.2 the available estimates on this topic are summarised.

As stated in table 6.2 around 10 –1110 g I-TEQ/year should be expected to be in circulation of chlorinated dioxins alone. To this figure may be added brominated dioxins that are primarily brought into circulation by the use of brominated flame retardants in plastics.

The dominant part of this quantity will most likely be destroyed by heating or incineration processes, thus never being emitted to the environment. This is the case for dioxins in clay that are dominantly used for tiles, bricks and insulation materials manufactured of high-temperature processes. This is also the case for the dominant part of brominated dioxins, as they should be expected as plastics to be directed to municipal waste incineration.

Table 6.1
Formation of chlorinated dioxins by activities/processes in Denmark 1998-1999

Activity/process	**Danish investigations 1)**	**Formation**	
		g I-TEQ/year	**% 2)**
Manufacturing activities			
- Chemicals 3)	Some-none	?	?
- Cement	Some	0.045 – 0.92?	0.1
- Lime	None	0.0009 – 2.7	0.03
- Other high-temperature materials 4)	None	0.006 – 0.46	<0.1
- Steel reclamation	Good	6.1 – 12.8	2
- Aluminium reclamation	None	0.43 – 4.8	0.6
- Other metal manufacturing 5)	None	0.06 – 0.5	<0.1
- Feedstuff 6)	Some	0.004 – 0.05?	<0.1
- Other manufacturing processes 7)	None	<0.54?	<0.1?
Manufacturing activities - subtotal		***6.5 – 23***	***3***
Energy production activities			
- Coal combustion	Some	0.7 – 42?	5
- Combustion of other fossil fuels	None	0.1 – 0.5	<0.1
- Biomass combustion	Some	1.1 – 79	9
Energy production activities – subtotal		***2 – 122***	***13***
Miscellaneous human and natural activities			
- Fires	None	1.6 – 112	11
- Traffic	None	1.3 – 1.7	0.2
- Crematories	Some	0.01?	<0.1
- Other miscellaneous activities 8)	Some	0.09 - 0.22?	<0.1?
Miscellaneous human and natural activities – subtotal		***3 – 114?***	***13***
Waste treatment and disposal activities			
- Cable scrap reclamation	None	0.005 – 5?	0.5?
- Chemical waste incineration 9)	Good	3.1 – 3.6?	0.7?
- Municipal waste incineration	Good	74 – 537	66
- Landfills 10)	None	0.65 – 27?	3?
- Wastewater treatment	Some	?	?
- Sewage sludge incineration	Good – some	0.62-0.74	0.1
- Other waste treatment activities 11)	Some	0.04 – 0.15	<0.1
Waste treatment and disposal activities – subtotal		***78 – 570?***	***70***
Total (rounded)		90 – 830?	100

? Figure cannot be estimated due to lack of data. The flow in question should be overlooked.
x? Figure or some of the subfigures referred to is deemed highly uncertain.
1) This column gives a brief assessment of the existing Danish investigations with the purpose of indicating on which subjects improved efforts may be relevant and to what extent others may benefit from Danish experience. The assessment is mainly related to air emission measurements, as measurements of solid waste or water discharges are scarce. The assessment uses the following terminology:
  - Good: Reliable Danish investigations – estimates based solely on these investigations.
  - Some: Some Danish figures are available - typically combined with literature values if available.
  - None: No Danish experience al all – estimates rely completely on literature values.
2) Calculated based on the average value from each activity/process. Should be taken as an uncertain rough impression of the significance of each source.
3) Covers manufacturing of pesticides and pharmaceuticals.
4) Covers manufacturing of insulation materials, tiles and bricks, glass and similar products.
5) Covers metal casting and hot-dip galvanising
6) Covers feedstuff production including fish oil/meal, meat and bone meal and green feed drying.

7) Covers asphalt preparation/recycling and several other processes only partly possible to quantify.
8) Covers a number of activities as fireworks, garden grills, cooking, and miscellaneous small-scale heating/burning operations, which can only partly be quantified
9) The figure stated is valid to 1999 only and should be expected to decrease significantly from year 2000.
10) Formation and transport of dioxins in landfills are in general believed to be non-significant, although the factual knowledge is very limited. However, fires in temporary depots of combustible waste occasionally take place. The figure for formation is related to such fires.
11) Covers shredder plants, healthcare risk waste and biological waste treatment.

Table 6.2
Presence of dioxins in products brought into circulation in the Danish society 1998-1999

Activity/process	**Consumption by products**
	g I-TEQ/year
Clay-like raw materials	4 – 1050
Pesticides	<1?
Feedstuff products	1,5 – 11
Food products	0.06 – 0.44
PCP treated wood	0.11 – 42?
PCP treated leather	0.5
PCP treated textiles	0.5
Bleaching/disinfection agents	<0.001
Bleached cork	<0.01
Bleached paper/cardboard	3.0 – 6.6
Other chemical products	?
Total – Chlorinated dioxins	10 – 1110?
Brominated flame retardants	2 – 60?
Total – brominated dioxins	2 – 60?
Total (rounded)	12 – 1200?

? Figure cannot be estimated due to lack of data. The flow in question should be overlooked.
x? Figure or some of the subfigures referred to are deemed highly uncertain.

However, this fate is certainly not the case for all types of products. Dioxins in feedstuff will partly be re-circulated to farmland by manure, dioxins in paper and cardboard will likely continue to be re-circulated for paper/cardboard manufacturing and preserved wood and leather may to some extent remain in the society, and slowly release dioxins to air by evaporation.

The assessment of the consumption of dioxins by products should for many reasons be regarded as premature. An important reason is that so far insignificant efforts internationally have been devoted to products, and measurements are generally few and old and in no way systematic. The recognition of the presence of dioxins in natural clay is mainly due to a larger investigation reported recently. The question naturally arises whether dioxins might not be present in other sedimentary materials like e.g. lime or chalk. Despite these uncertainties, it is deemed relevant to bring forward these estimates in order to illustrate the magnitude of the dioxin flows in question.

6.2 Emissions to the environment

Table 6.3 summarises the estimates made with respect to emissions to the environment and quantities directed to depots in Denmark.

Emissions to air
Concerning emission to air the total emission is estimated at 19 -170 g I-TEQ/year or as a best estimate, assuming uncertainties to compensate each other, to around 95 g I-TEQ/year. The dominant sources include:

- Municipal waste incineration
- Biomass combustion (in particular combustion in wood stoves and farm boilers)
- Evaporation from PCP-preserved wood
- Fires
- Steel and aluminium reclamation

In 1999 incineration of chemical waste was a significant source as well, but the contribution from this source is likely to be heavily reduced in 2000 due to redesign of ovens and installation of dioxin filters. Other sources for emission that could be significant include cable scrap reclamation, lime and cement manufacturing, traffic, and landfills that in this context cover fires in temporary depots for combustible waste.

Concerning municipal waste incineration more plants are in the process of installing special dioxin filters, and the dioxin emission to air should thus be expected to decrease in the near future. The choice has been made to report emission from waste incineration as an interval reflecting the assumed interval of uncertainty rather than as a calculated best estimate based on average figures, as the number of measurements available from Danish plants are still relatively few, and it is debatable to what extent the measurements available actually reflect the total emission. This discussion is elaborated at the end of this section and is in reality relevant to all sources of formation and emission of dioxins.

Biomass combustion in small units without flue gas cleaning like wood stoves, farm boilers and stoker boilers is deemed an important source although the estimates are subject to significant uncertainty. For wood stoves it is known that burning of pure wood only is hardly a serious problem. However, adding other materials like paper, milk cartons, plastics or treated wood into the stove should be believed to promote dioxin formation e.g. due to the use of copper pigments in such materials. Considering that around 370,000 wood stoves are being used in Denmark by households, one should be prepared to accept a high level of variation with respect to the materials burned. With respect to the use of treated wood attention should e.g. be paid to the fact that very few people – if any – are able, without measurements, to determine whether the disposable pallet cut to pieces to be used as firewood has actually been treated with PCP or not. One may also discuss how many Danes actually have knowledge enough to care.

Concerning farm boilers existing measurements have shown high variation of dioxin emission, and there is certainly a need for a better understanding of the factors causing this variation. As for wood stoves, one should be prepared to accept that also farm boilers are used for a number of other materials besides pure straw.

The contribution from other larger biomass combustion plants equipped with flue gas cleaning seems to be small compared to wood stoves, farm boilers and stoker boilers. In this context the larger plants should be expected to benefit from considerably better control of the materials burned and of operations in general. However, the number of measurements carried out so far is still small and may not necessarily be representative to the total number of plants in operation.

Concerning evaporation from PCP-preserved wood the dominant part of the emission is due to old construction wood (from before 1980) in houses etc. all over Denmark. This emission will continue, until the wood in question has been naturally replaced. This should be expected to take place within the next 20 years, in which period the emission will gradually decrease. However, emission from PCP-preserved materials will continue to take place, as long as PCP is produced and used in the world. Dioxins are a natural contaminant in PCP and the increasing globalisation ensures that chemical substances used for industrial production in other regions of the world to some extent also will end up in Denmark.

Table 6.3
Estimated emissions/losses to the environment and depots in Denmark 1998-99

Activity	Emissions/losses (g I-TEQ/year)			
	to air	to water	to soil	to depots
Manufacturing processes				
Chemicals 2)	?		<1?	
Cement and lime	0.045-3.5	?		
Other high temperature materials 3)	0.006-0.46		?	?
Steel and aluminium reclamation	1.3-5.6		<0.005	0.26-1.5
Other metal manufac. 4)	0.06-0.5		?	<0.002?
Other manufacturing processes 5)	0.004-0.08?	<0.01		
Energy generation				
Coal combustion	0.4 –2.3			0.23 – 31?
Other fossil fuels	0.14 – 0.46			0?
Biomass combustion	0.73 – 41		< 15.2	0.04 – 36?
Use of products				
PCP-treated wood	0.5 – 26?			
Other PCP-treated materials	< 0.05	0.2 10)		
Bleached processes and bleaching agents		<0.5 10)		
Feedstuff products		?	<10	?
Miscellaneous other human and natural activities				
Fires – accidental	0.5 – 20?		?	1-30
Fires – others	0.03 – 6.5		0.01 – 27.5?	0.01-27.5
Traffic	1.3 – 1.7			
Cremation	0.01		?	
Other activities 6)	0.09 - 0.22?	?	?	?
Waste treatment and disposal				
Cable scrap reclamation	0.005-5			?
Chemical waste inc. 7)	2.2-2.7	0.000001		0.9?
Municipal waste inc.	11 - 42			35-275
Landfills 8)	0.25-10?	<0.05?		0.4-17?
Waste and storm water		0.3 - 1.4?		
Sewage sludge disposal	0.07-0.15		1.3	0.42-0.46
Other activities 9)	0.08-0.2		0.01-0.07	?
Total (rounded)	**19 – 170**	**0.3 -1.4?**	**1.3 – 54**	**38-420**

? Figure cannot be estimated due to lack of data. The flow in question should be overlooked.
x? Figure or some of the subfigures included is deemed highly uncertain.
1) Includes quantities incorporated in residuals used for civil works like road construction etc.
2) Covers manufacturing of pesticides and pharmaceuticals
3) Covers manufacturing of insulation materials, tiles and bricks, glass and similar products.
4) Cover metal casting and hot-dip galvanising
5) Covers feedstuff production including fish oil/meal, meat and bone meal and green feed drying as well as asphalt preparation/recycling and several other processes not possible to quantify.
6) Covers a number of activities like fireworks, garden grills, cooking and miscellaneous small-scale heating/burning operations that can only be partly quantified.
7) The figure stated for emission to air is valid for 1999 only. When the threshold of 0.1 ng I-TEQ/Nm^3 is fulfilled for all kilns the total maximum emission will be 0.09 g I-TEQ/year.
8) Emission to air and depots relates to fires in temporary depots of combustible waste.
9) Cover shredder plants, healthcare risk waste, waste oil and biological waste treatment.
10) These figures represent contributions to wastewater directed to wastewater treatment. The emission from wastewater treatment plants is stated under wastewater treatment.

Accidental fires etc. are a source recognised, but not quantified in most dioxin inventories, as the factual knowledge available is small and all estimates thus are highly uncertain. The basic problem is that it is difficult to undertake realistic experiments or to undertake actual measurements of the emission to air. Still the significance of fires for dioxin formation and emission should not be underestimated. It should be noted, that fires cover accidental fires in building, vehicles etc. for which a mixture of many different materials containing all the elements needed for dioxin formation are present, as well as bonfires, garden fires etc. dominantly based on pure wood but occasionally involving other materials, too.

Steel and aluminium reclamation together with incineration of chemical waste and perhaps also cable scrap reclamation, cement and lime manufacturing are examples of single plant sources that should be considered significant at least in the perspective that one is dealing with the emission from a single plant. Whether or not chemical industries like manufacturing of pesticides and pharmaceuticals should be included in this focus, remains to be proven, as available measurements are both old and incomplete or non-existing. It should be noted that emissions from these companies can always be debated, based on the fact that spot measurements - even based on a standard procedure of 6-hours sampling - will normally not represent the total emission from such plants, and little experience exist to allow the importance of deviating process conditions to be assessed. This issue is further elaborated below. Concerning the estimated emission from steel reclamation in Denmark, the choice has been made to rely mainly on the company’s own measurements.

A special source developed in Denmark in the last years is fires in temporary depots of combustible waste awaiting adequate incineration capacity to be established. This source is in table 6.3 included under “landfills”. The comments relevant to this source correspond to a large extent to the comments given above on accidental fires etc.

The very large ranges given for most emissions reflect to the best judgement of the authors of this report the uncertainty actually related to the estimates presented. An issue, however, not necessarily fully covered by the ranges presented, is the consequences of deviating process conditions. As dioxin formation is extremely process dependent and the actual formation may differ considerably from “normal” process conditions to “deviating” process conditions, deviating process conditions may contribute significantly to the total dioxin formation and emission. E.g. even if deviating process conditions only rules 5% of the total operation time for a specific plant the dioxin formation during this time could perhaps be 10-100 times higher than under normal process conditions. It is the impression of the authors that most of the emission factors reported reflect normal process conditions and thus do not include the consequences of deviating process conditions. In this report the consequences of deviating process condition have been considered in relation to steel reclamation and to one municipal waste incineration plant. Only little factual knowledge is available on this issue, but the significance to the total emission should not be overlooked.

Emissions to water
The total emission to the water environment is estimated at 0.3 – 1.4 g I-TEQ/year based on very few samples. The estimate should accordingly be regarded as very uncertain. Based on the knowledge available the most important source for dioxins in Danish waste and storm water seems to be atmospheric deposition (reference is made to table 5.5), but congener

profiles of sludge correspond better to profiles of textiles. It must be concluded that knowledge is limited and any definite conclusions on this issue should be taken as premature.

Emissions to soil
The total direct emission of dioxins to the soil environment is estimated at 1.3-54 g I-TEQ/year. The dominant sources are:

- Ash from biomass combustion (wood stoves and farm boilers)
- Residues from miscellaneous fires
- Manure from domestic animals applied to farmland.

Other minor sources seem to be the use of pesticides and sewage sludge. It is, however, strongly emphasised that all estimates apart from sewage sludge are highly uncertain, as they are generally based on very few data of which most originates from foreign investigations. One must be prepared to accept that further and more detailed investigations could change the picture considerably. E.g. knowledge of the content of dioxins in pesticides should be regarded as almost non-existing and more detailed investigations could perhaps identify pesticides as a significant source.

The focus on ash from wood stoves relates to that ash may frequently be directed to garden composts or directly spread on the soil in gardens. Similar behaviour should be expected for farmers operating farm boilers.

Residues from fires deal with ash etc. from other fires than accidental fires – e.g. garden fires and bonfires - not removed from the place of the fire and in time mixed into the soil.

Manure from domestic animals is generally applied to farmland and will contain dioxins originating from the feedstuff. As detailed investigations of the turnover of dioxins in the Danish agricultural sector are not available, the estimated supply should be regarded as a rough first estimate indicating the relevant order of magnitude.

Losses to depots
The total quantity of dioxins directed to landfills and other types of depots in Denmark is estimated at 38 – 420 g I-TEQ/year. Again municipal waste incineration stands out as the dominant source. However, neither residues from coal combustion, biomass combustion nor fires should be overlooked. The significant quantities of dioxins ending on landfills naturally call for more knowledge of what is actually happening to dioxins on landfills.

Previous estimates
The figures presented in table 6.3 may be compared to previous estimates of dioxin emissions in Denmark presented in table 6.4. The main differences between the previous estimates and the present are due to the following:

- That the previous estimates have generally been expressed as “best estimates” giving relatively little consideration to the significant uncertainties connected to the estimates.
- That the present estimates have included a number of sources previously not quantified, e.g. fires and PCP-treated wood
- That the present estimates benefit from the significant knowledge developed internationally and in Denmark in the recent years and e.g. has included all measurements known to be available from Denmark.

Other differences may be due to different interpretation of the available data. It should e.g. be noted, how the estimates of biomass consumption and in particular wood stoves fluctuate.

The benefit of including uncertainties in the estimates and operating with intervals instead of “best estimates” becomes clear, when comparing to the atmospheric deposition. A significant difference between estimated total emissions to air and estimated total atmospheric deposition has for long been recognised internationally (reference is e.g. made to /Brzuzy & Hites 1996 and Landesumweltamt Nordrhein-Westfalen 1997/) and is also illustrated in the figures given in table 6.4. On the contrary the balance for Denmark presented in figure 6.1 indicates that Danish emissions are reasonably balanced with atmospheric deposition on the Danish land area. This could be taken as an indication of the fact that dioxin inventories are generally underestimating emissions and that giving proper attention to the significant uncertainties related to emission estimates may provide at least a part of the explanation of the difference generally noted between emissions and deposition.

Table 6.4
Estimated annual emissions of dioxins in Denmark in 1995 (1990 figures as N-TEQ in brackets - /Jensen 1997/).

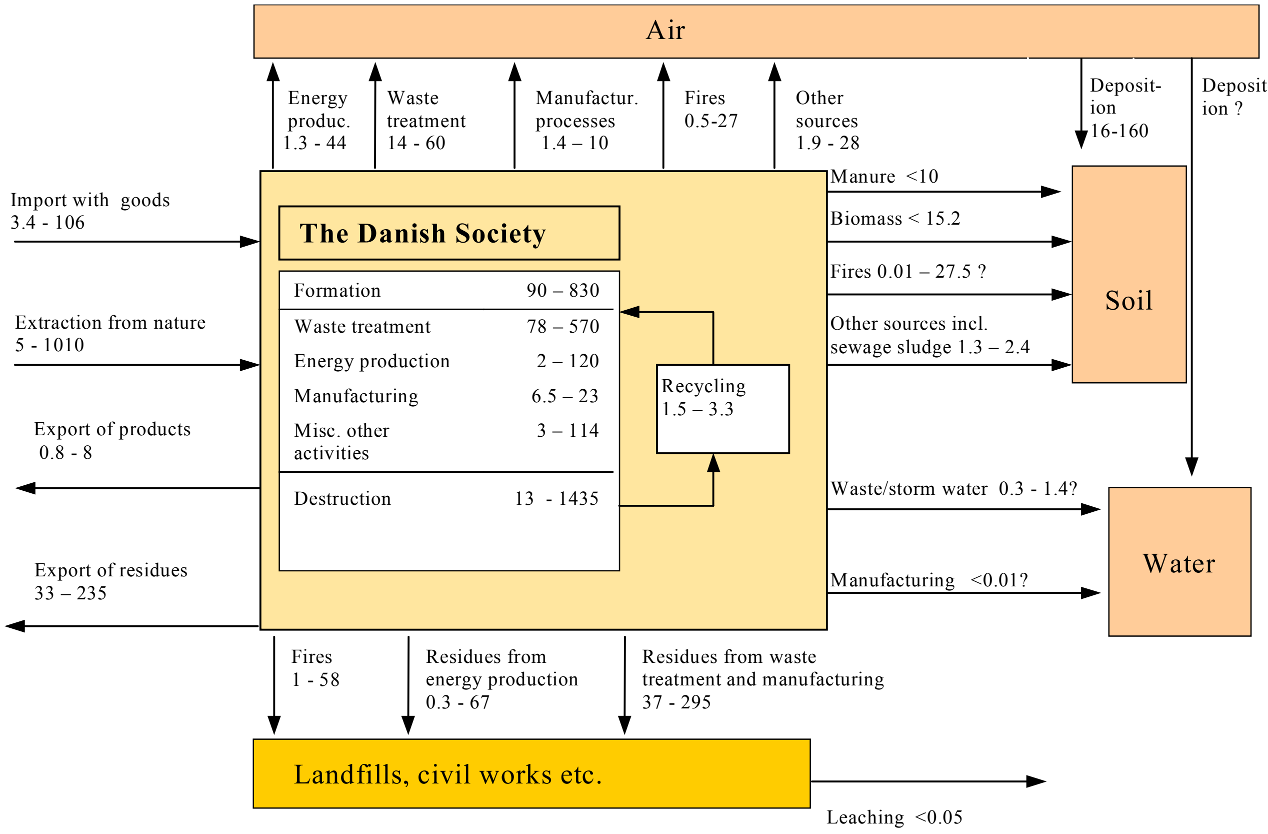
Activity/process	**Emission to (all figures as g I TEQ/year)**				
	Air	**Water**	**Soil**	**Waste/ residue**	**Total**
Manufacturing					
Chemical industry	-	-	-	-	-
Paper and pulp industry	-	-	-	-	-
Asphalt-mixing industry	0.1	-	-	-	-
Steel reclamation	7.5 (12)	-	-	34 (29)	42 (41)
Cement industry	0.08-1.5	-	-	-	0.08 – 1.5
Energy generation					
Pit coal	2	-	-	40 (53)	42 (53)
Gas oil – heating of houses	0.02	-	-	-	0.02
Wood stoves	1.1 (10-50)	-	-	-	1.1 (10-50)
Wood burning – other	0.25	-	-	-	0.25
Straw burning	0.07-6.6(0.05)	-	-	-	0.07-6.6(0.05)
Miscellaneous activities and use of products					
Fires (building, landfill, vehicles)	?	-	-	-	?
Traffic	0.2 (1.0)	-	-	-	0.2 (1.0)
Cremation	0.16	-	-	-	0.16
Textile products	-	0.08	-	-	0.08
Waste treatment					
Cable scrap reclamation	0.13	-	-	-	0.13
Shredders	?	-	-	?	?
Municipal waste incineration	20 (34)	-	-	100 (250)	120 (284)
Inc. of hospital/health care risk waste	5 (14)	-	-	-	5 (14)
Chemical waste inc. (KK)	0.23 (1.7)	-	-	1.0	1.23 (1.7)
Inc. of waste oil (district heating)	0.038 (0.01)	-	-	-	0.038 (0.01)
Sewage sludge	0.072 (1.5)	0.108	1.1	0.226	1.51 (1.5)
Compost	-	-	1-5	-	1-5
Total	**38-46**	**0.12**	**2.1 - 6.1**	**175**	**215-226**
Air deposition			120		

Apart from steel reclamation and waste incineration, no specific trend in dioxin emissions should be noted. The Danish steel reclamation plant has based on the company's own estimate for dioxin emission seemingly succeeded in reducing emissions considerable whereas Danish waste incineration plants are in the process of speeding up installations of special dioxin filters. For other plants and activities the focus on dioxin emissions in Denmark have so far been limited.

6.3 Substance flow balance for Denmark

The available knowledge and assessments on the flow of chlorinated dioxins in Denmark in 1998-99 have been compiled and illustrated in figure 6.1.

Figure 6.1
Balance for chlorinated dioxins Denmark 1998-99 (all figures in g I-TEQ/year)



Input to the Danish society
The Danish society receives dioxin by products imported to Denmark and by raw materials extracted from nature. The products in question are mainly materials like wood, leather and textiles preserved by pentachlorophenol, but also clay, paper/cardboard and feedstuff. The raw materials extracted are clay and clay-like materials that are mainly used for manufacturing purposes besides fish, grass and animals that mainly are turned into feedstuff and food products.

Export from the Danish Society
From Denmark is exported a number of items containing dioxins, mainly residues from waste and coal combustion, but also residues from manufacturing processes, like filter dust from steel reclamation. To this can be added small amounts of dioxin in exported feedstuff, clay and paper/cardboard etc.

Formation and destruction
Significant formation and destruction of dioxins is believed to take place in the Danish society. Formation is related to manufacturing, energy production and waste treatment and miscellaneous other processes as elaborated in the previous sections. Destruction is related to high-temperature manufacturing of products based on clay, besides that thermal waste treatment like incineration of municipal waste and sewage sludge is believed to destroy – more or less – the dioxins present in the waste materials treated. Attention should be paid to the possibility that recycling of materials like coal fly ash and paper sludge for cement

manufacturing also should imply destruction of the dioxins present in the recycled materials. To this may be added the unknown amount of dioxins in special dioxin filters assumed to be destructed by incineration in the plants own ovens/kilns. Whereas the destruction capacity of such thermal processes should be recognised, it should, however, not be forgotten that at the same time many of the processes – in particular municipal waste incineration – belong to the dominant sources for dioxin formation.

It should be noted that destruction for the time being might well be larger than formation, as the stock of dioxins in use in products in the Danish society should be expected to be decreasing (reference is made to the section on stock building below).

Recycling

Recycling of dioxins present in paper and cardboard will take place.

Emissions to the environment

From the Danish society emissions will take place both to air, soil and water as elaborated in the previous sections.

Stock building

A stock of dioxins in the Danish society exists in the form of dioxins in PCP-treated wood. The size of this stock per 1999 is roughly estimated at 100 – 5,000 g I-TEQ. The stock should be assumed slowly to decrease due to replacement of the wood in question as well as evaporation of dioxins from the wood corresponding to the fact that the use of PCP in Denmark is now banned.

Balance for air

Whereas Denmark emits dioxins to the air, Denmark also receives dioxin from the air by atmospheric deposition. The deposition on the Danish land area is estimated at 16-160 g I-TEQ/year assuming a total land area of 43,100 km^2 and a deposition of 1-10 pg I-TEQ/m^2 per day (reference is made to section 2.4.4). A deposition rate of 250 pg I-TEQ/ m^2 per year based on calculations on long-range transport of dioxins/furans (also reference to section 2.4.4) would correspond to a total deposition on the Danish land area of 11 g I-TEQ/year.

The Danish marine internal waters are assumed to cover 38,000 km^2 and will certainly also receive deposition that has however not been estimated due to lack of data. As an immediate conclusion it can be judged that a reasonable balance between the estimated emission and the calculated deposition seems to exist, assuming that the deposition on Danish internal waters is small compared to the deposition on the Danish land area. It is emphasised that the estimate of atmospheric deposition on the Danish land area is based on measurements from Germany (the Hamburg region), as no investigations so far have been undertaken in Denmark. The general experience with respect to airborne pollution considering the prevalent wind directions is that the emission generated in Denmark to some extent will be a source of deposition in Sweden. Denmark is on the other hand exposed to deposition caused by emissions in other parts of Europe like Germany, Belgium and the UK.

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Annex A
List of Companies contacted

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A/S Fynsværket, Odense
BASF, Health & Nutrition A/S, Ballerup and Grenå
Boglas A/S, Brønderslev
Cheminova A/S, Harboøre
Dalum Papir, Odense
Dangrønt Products A/S, Ølgod
Dansk Leca A/S, Randers
Dansk Olie Genbrug, Kalundborg
Dansk Moler industri, Mors
Dansk RestproduktHåndtering A.m.b.a., Odense
Daka, Løsning
Dania Jernstøberi, Aars
Det Danske Stålvalseværk A/S, Frederiksværk
Dumex-Alpharma A/S, København S
Esbjerg Fiskeindustri, Esbjerg
Faxe Kalk, Faxe Ladeplads
FeF Chemicals A/S, Køge
GEA Farmaceutisk Fabrik, Frederiksberg
Gori, Kolding
Gothard Aluminium AS, Kolding
Herning Galvanisering A/S, Brande
Herning Varmforzinkning A/S, Herning
H.J.Hansen, Odense
Holmegaard Glasværk, Næstved
H.Lundbeck A/S, Valby
I/S KARA, Roskilde
Kommunekemi, Nyborg
Lynettefællesskabet I/S
Løvens Kemiske Fabrik Produktionsselskab, Ballerup
Middelfart Galvanisering A/S, Middelfart
NKT-cables, Brøndby
NOPA-Nordisk Parfumerivarefabrik A/S
Novo Nordisk A/S, Bagsværd
Optiroc Nr. Uttrup Teglværk, Nørresundby
Skamol, Nykøbing Mors
Scanglas, Korsør
Special Waste System, Nørre Alslev
Spildevandscenter Avedøre I/S
Statoil, Kalundborg
Sun Chemical A/S, Køge
Svendborg Kraftvarmeværk, Svendborg
Valdemar Birn Jernstøberi, Holstebro
Aalborg Portland, Aalborg