Substance Flow Analysis for Dioxin 2002

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The Danish Environmental Protection Agency will, when opportunity offers, publish reports and contributions relating to environmental research and development projects financed via the Danish EPA.

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The reports are, however, published because the Danish EPA finds that the studies represent a valuable contribution to the debate on environmental policy in Denmark.
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CHEMICALS
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Manufacturing of pharmaceuticals
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MATERIALS MANUFACTURED BY HIGH-TEMPERATURE PROCESSES
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Tile and bricks based on clay
Cement
Lime
Other materials
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Metal casting
Hot-dip galvanising
Steel reclamation
Aluminium reclamation
FEEDSTUFF
Fish oil and meal
Meat and bone meal
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Feedstuff products
FOOD PRODUCTS

PENTACHLOROPHENOL
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 overall 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.

More specifically the objective of the study has been to collect the new Danish knowledge from 2000 – 2002 and incorporate the knowledge in the substance flow analysis for dioxin earlier made. The new Danish knowledge is primarily new analyses from The National Environmental Research Institute on air, water, deposition and residues as well as measurements from industry and waste combustion plants. This report is therefore an update of the substance flow analysis from 2000 /Hansen, 2000/ and the update is made as additions to the report from 2000. As a consequence the report also has the objective to narrow the intervals that have so far been reported from Denmark with respect to the significant amount of knowledge made internationally available during the recent years. The international knowledge is still essential to the substance flow analysis, because many sources still exist where Danish data are minimal or absent.

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.

With the described objective the report is a contribution to meet the obligations in article 5 of the Stockholm Convention on Persistent Organic Pollutants (POPs). The article describes the demands on a national action plan, which shall among other things include an evaluation of current and projected releases, including the development and maintenance of source inventories and release estimates /Stockholm Convention, 2001/.

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

Helle Petersen, Danish EPA (Chair)
Mikala Klint, Danish EPA
Erik Thomsen, Danish EPA
Ulrik Torp, Danish EPA
Svend Erik Jepsen, Danish EPA
Lea F rimann Hansen, Danish EPA
Jørgen Vikelsøe, Danish National Environmental Research Institute
Ole Schleicher, dk-TEKNIK ENERGY and ENVIRONMENT
Jacob Hartmann, Greenpeace
Arne Buchert, Danish Veterinary and Food Administration, Ministry of Food, Agriculture and Fisheries

The report has been prepared by:

Erik Hansen, COWI A/S
Charlotte Libak Hansen, COWI A/S
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. D annelsen af chlorerede dioxiner i Danmark i 2000 - 2002 er estimeret til 72 - 689 g I-TEQ/år, mens emissionen til miljøet er estimeret til (bedste estimat er angivet i parentes):

Luft: 11 - 163 (87) g I-TEQ/år
Vand: 0.4 - 1.4 (1) g I-TEQ/år
Jord: 0.7 - 42 (21) g I-TEQ/år
Depoter: 5 - 126 (66) 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 emissioner. Derudover er det atmosfæriske nedfald over det danske landareal estimeret til 13 - 130 g I-TEQ/år. Endelig skal fremhæves, at der sker en eksport af dioxin med restprodukter til deponering i udlandet på 55-413 g I-TEQ/år.


D annelse af dioxiner afhænger i betydelig grad af de lokale procesforhold herunder råmateriel og temperaturforløbet i røggassystemer. Emissionen af dioxiner er derudover afhængig af, om der findes rensning af røggassen og i så fald hvilken type rensning, der er installeret. At estimere dannelsen og emissioner handler derfor om at håndtere et virvar af usikkerheder. De store intervaller for dannelsen og emissioner der er givet ovenfor afspejler de usikkerhed, der er knyttet til estimatorne.

Baggrund og formål

Denne undersøgelse er igangsat af Miljøstyrelsen i september 2002 for ud fra den nyeste danske viden at opnå en bedre forståelse af transporten og omsætningen af dioxiner i det danske samfund.

organisere den eksisterende viden om dioxiner i Danmark og som led i denne proces at indsnævre intervallerne, der indtil nu er rapporteret fra Danmark. På en række punkter er det danske datagrundlag dog stadig beskedent.

Med ovenstående formål er rapporten et bidrag til at opfylde betingelserne i artikel 5 i Stockholm konventionen om Persistent Organiske Forureningskilder (POPs).


Undersøgelsen

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

Vigtigste konklusioner


Figur 1
Balance for chlorerede dioxiner for Danmark 2000 - 2002 (alle tal i g-I-TEQ/år)

Det danske samfund

Dannelse 72 - 689
Affaldsbehandling 61 - 468
Energidannelse 1 - 91
Industri 6 - 19
Andre aktiviteter 3 - 114
Destruktion 13 - 1435

Importert med varer 3.4 - 106
Udvinding fra naturen 5 - 1010
Eksport af varer 0.8 - 8
Eksport af restprodukter 55 - 413

Brande og bål 1 - 58
Perkolat <0.05

Lossepladser, anlægsarbejder etc.

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 (med et PCP-indhold på mindre end 5 ppm), men også ler, papir og pap samt foderstoffer. De udvundne råmaterialer omfatter 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.

<table>
<thead>
<tr>
<th>Aktivitet</th>
<th>Emissioner/tab (g l-TEQ/år)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>til luft</td>
</tr>
<tr>
<td><strong>Industriel fremstilling</strong></td>
<td></td>
</tr>
<tr>
<td>Kemikalier 1)</td>
<td>0.001 - 0.007?</td>
</tr>
<tr>
<td>Cement og kalk</td>
<td>0.2 - 14</td>
</tr>
<tr>
<td>Andre materialer fremstillet ved høj temperatur 2)</td>
<td>0.02 - 0.3</td>
</tr>
<tr>
<td>Stål- og aluminiumsmelting</td>
<td>0.1 - 3.2</td>
</tr>
<tr>
<td>Anden metalforarbejdning 3)</td>
<td>0.02 - 0.5</td>
</tr>
<tr>
<td>Andre industrielle processer 4)</td>
<td>0.04 - 0.17</td>
</tr>
<tr>
<td><strong>Energiproduktion</strong></td>
<td></td>
</tr>
<tr>
<td>Forbrænding af kul</td>
<td>0.1 - 3.2?</td>
</tr>
<tr>
<td>Andre fossile brændsler</td>
<td>0.4 - 1.3</td>
</tr>
<tr>
<td>Forbrænding af biomasse, private brændeovne</td>
<td>0.4 - 22</td>
</tr>
<tr>
<td>Forbrænding af biomasse, andre mindre anlæg</td>
<td>0.3 - 15</td>
</tr>
<tr>
<td>Forbrænding af biomasse, andre større anlæg</td>
<td>0.03 - 4.4</td>
</tr>
<tr>
<td><strong>Brug af produkter</strong></td>
<td></td>
</tr>
<tr>
<td>PCP-behandlet træ</td>
<td>0.5 - 26?</td>
</tr>
<tr>
<td>Andre PCP-behandlede materialer</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Blegemidler og blegeprocesser</td>
<td>&lt;0.5 5)</td>
</tr>
<tr>
<td>Foderstoffer</td>
<td>?</td>
</tr>
<tr>
<td><strong>Diverse aktiviteter</strong></td>
<td></td>
</tr>
<tr>
<td>Brande</td>
<td>0.5 - 20?</td>
</tr>
<tr>
<td>Bål m.m.</td>
<td>0.03 - 6.5</td>
</tr>
<tr>
<td>Trafik</td>
<td>1.3 - 17</td>
</tr>
<tr>
<td>Kremering</td>
<td>0.01 - 0.1</td>
</tr>
<tr>
<td>Andre aktiviteter 6)</td>
<td>0.1 - 0.2?</td>
</tr>
<tr>
<td><strong>Affaldsbehandling og bortskaffelse</strong></td>
<td></td>
</tr>
<tr>
<td>Genvinding af kabelskrot</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Kemikalieaffald 7)</td>
<td>0.004 - 0.03</td>
</tr>
<tr>
<td>Affaldsforbrænding 8)</td>
<td>6.4 - 29</td>
</tr>
<tr>
<td>Lossepladser/depoter 9)</td>
<td>0.25 - 10?</td>
</tr>
<tr>
<td>Spildevand og regnvand</td>
<td>0.4 - 14</td>
</tr>
<tr>
<td>Spildevandslam</td>
<td>0.002</td>
</tr>
<tr>
<td>Andre aktiviteter 10)</td>
<td>&lt;0.003 - 0.6</td>
</tr>
<tr>
<td>Emission af bromerede dioxiner (ikke inkluderet i total) 11)</td>
<td>0.01 - 0.17</td>
</tr>
<tr>
<td><strong>Total (afrundet)</strong></td>
<td>11 - 163</td>
</tr>
</tbody>
</table>
Tal kan ikke estimeres p.g.a. mangel på data - bør ikke overses.

Tal eller data bedømt som højst usikre.

1. Dækker fremstilling af pesticider og medicinalvarer.
2. Dækker fremstilling af isoleringsmateriale, tegl og mursten, glas og andre lignende produkter.
3. Dækker støbning og varmegalvanisering.
4. Dækker production af foderstoffer inklusiv fiskeolie og mel, kød- og benmel og grænsten, samt derudover asfaltfremstilling/genanvendelse og andre processer som det ikke har været muligt at kvantificere.
5. Dækker emissioner til spildevand. Emissioner fra rensningsanlæg er specificeret i kategorien "Spildevand og regnvand".
6. Dækker et antal aktiviteter som fyrværkeri, havegrills, madlavning og diverse andre mindre aktiviteter der kun delvist kan kvantificeres.
7. Tallet vil kun være gyldigt for perioden 2000-2002. Når grænseværdien på 0,1 ng I-TEQ/Nm³ er opfyldt på alle ovne vil den maksimale emission totalt set være 0,09 g I-TEQ/år.
8. Når grænseværdien på 0,1 ng I-TEQ/Nm³ er opfyldt for alle affaldsforbrændingsanlæg vil den totale emission svare til cirka 2 g I-TEQ/år.
10. Dækker shredder-affald, klinisk risikoaffald, spildolie samt biologisk affaldsbehandling.

Tabel 1 indeholder estimerer på samtlige identificerede kilder til dioxin emission i Danmark. Nogle af estimererne er dog behæftet med en væsentlig usikkerhed på grund af manglende præcise data, hvilket resulterer i at maksimumsværdien i de pågældende intervaller er høj. I tabel 2 er de usikre kilder ikke medtaget og tabellen viser derfor emissionsniveauet for de velbestemte kilder.
### Tabel 2

**Estimerede emissioner til miljøet og depoter i Danmark 2000 - 2002, kun velbestemte kilder.**

<table>
<thead>
<tr>
<th>Aktivitet</th>
<th>Emissioner/tab (g I-TEQ/år)</th>
<th>til luft</th>
<th>til luft</th>
<th>til luft</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td><strong>Industriel fremstilling</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kemikaler 1)</td>
<td>0.001 - 0.007?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cement og kalk</td>
<td>0.2 - 14</td>
<td>?</td>
<td>?</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Andre materialer fremstillet ved høj temperatur 2)</td>
<td>0.02 - 0.3</td>
<td>?</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>Steel and aluminium reclamation</td>
<td>0.1 - 2.4</td>
<td>1 - 3</td>
<td>5.0 - 10.5</td>
<td></td>
</tr>
<tr>
<td>Anden metalforarbejdning 3)</td>
<td>0.02 - 0.5</td>
<td>?</td>
<td>&lt;0.002?</td>
<td></td>
</tr>
<tr>
<td>Andre industrielle processer 4)</td>
<td>0.04 - 0.1?</td>
<td>&lt;0.01</td>
<td>0.004 - 0.35</td>
<td></td>
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<tr>
<td><strong>Energiproduktion</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Forbrænding af kul</td>
<td>0.1 - 3.2?</td>
<td>0.2 - 40?</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Andre fossile brændsler</td>
<td>0.4 - 13</td>
<td>0?</td>
<td></td>
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</tr>
<tr>
<td>Forbrænding af biomasse, andre større anlæg</td>
<td>0.03 - 4.4</td>
<td>&lt;0.001 - 0.03</td>
<td></td>
<td></td>
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<tr>
<td><strong>Brug af produkter</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Andre PCP-behandlede materialer</td>
<td>&lt;0.05</td>
<td>0.2 5)</td>
<td>0.8?</td>
<td></td>
</tr>
<tr>
<td>Bleached processes and bleaching agents</td>
<td>&lt;0.5 5)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Feedstuff products</td>
<td>?</td>
<td>&lt;10 ?</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td><strong>Diverse aktiviteter</strong></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>Trafik</td>
<td>1.3 - 1.7</td>
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<tr>
<td>Kremering</td>
<td>0.006-0.1</td>
<td>?</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Andre aktiviteter 6)</td>
<td>0.1 - 0.2?</td>
<td>?</td>
<td>?</td>
<td>?</td>
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<tr>
<td><strong>Affaldsbehandling og bortskaffelse</strong></td>
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</tr>
<tr>
<td>Genvinding af kabelskrot</td>
<td>&lt;0.001</td>
<td>?</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Farligt affald 7)</td>
<td>0.004 - 0.03</td>
<td>&lt;0.001</td>
<td>0.9?</td>
<td></td>
</tr>
<tr>
<td>Affaldsforbrænding 8)</td>
<td>6.4 - 29</td>
<td>2 - 5</td>
<td>50 - 402</td>
<td></td>
</tr>
<tr>
<td>Spildevand og regnvand</td>
<td>0.4 - 14</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spildevandsslam</td>
<td>0.002</td>
<td>0.7 - 13</td>
<td>0.2 - 0.3</td>
<td>0.1 - 0.2</td>
</tr>
<tr>
<td>Andre aktiviteter 9)</td>
<td>&lt;0.003 - 0.6</td>
<td>0.01 - 0.07</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td><strong>Total (afrundet)</strong></td>
<td>9 - 45</td>
<td>0.4 - 14</td>
<td>0.7 - 12</td>
<td>3 - 49</td>
</tr>
</tbody>
</table>

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8. Når grænseværdien på 0,1 ng l-TEQ/Nm³ er opfyldt for alle affaldsforbrændingsanlæg vil den totale emission svare til cirka 2 g l-TEQ/år.


D et er valgt at bruge tabel 1 til vurdering af emissionsniveauet i Danmark. Dette er gjort for at tage hensyn til bidragene for de kilder der endnu er usikre.

Størsteparten af den mængde chlorerede dioxiner, der dannes i Danmark emitteres til miljøet eller depoter i Danmark. I mangel af indenlandske behandlingsmetoder er Danmark dog begyndt at eksportere den overvejende del af flyveaske og regrensningssaffald fra de danske affaldsforbrændingsanlæg til deponering i udlandet. Affaldet er klassificeret som farligt. D en løbende produktion af affaldt eksporterer og derudover er der indgået kontrakter om opgravning og eksport af allerede deponeret regrensningssaffald. D et forklarer, hvorfor Danmark eksporterer den relativt høje andel (55-413 g l-T E Q/år ud af en samlet årlig dioxindannelse på 72 - 689 g l-T EQ/år) til udlandet.

En væsentlig destruktion af chlorerede dioxiner påregnes også at finde sted i Danmark. D en destruktion er anslået til 13 – 1435 g l-T EQ/år og omfatter dioxiner i ler o.lign, der bruges til fremstilling af tegl, mursten og andre produkter i Danmark, idet disse produkter brænderes ved en temperatur, der må antages at nedbryde dioxiner. D er 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, slammforbrænding og cementfremstilling må antages i væsentligt omfang at nedbryde dioxiner. Hertil kommer en ukendt dioxinmængde i specielle dioxinfiltre, som brænderes i ovne ved de anlæg, hvor de har været benyttet.

En række af de anlæg, hvor der sker en destruktion af dioxiner er samtidig blandt de vigtigste kilder til dannelse og emission af dioxiner. D ette gælder også 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.


D en samlede emission til luft i Danmark er estimeret til 11 - 163 g l-T EQ/år. D enne emission blev i massestrømsanalyse fra 2000 /Hansen, 2000/ estimeret til 19 - 170 g l-T EQ/år. D e dominerende kilder omfatter:
• Affaldsforbrænding

• Afbrænding af biomasse i mindre enheder uden røggasrensning som brændeovne og gårdfyr - for brændeovne gælder, at rent træ 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 engangspapper 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 fordampes. 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 fordampes.

• 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. Hertil kommer en lang række andre kilder, fx. Kommunekemi, som tidligere var en signifikant kilde, men som nu har installeret dioxinrensning på alle ovne.


D et atmosfæriske nedfald over det danske landareal er estimeret til 13 - 130 g I-T EQ/år på bagside af nye målinger fra 2002 lavet af D anmarks M iljøundersøgelser.

Den samlede emission til vand i 2000 - 2002 er på cirka samme niveau som i 1998 - 1999 svarende til 0,4 - 1,4 g I-T EQ/år. D en dominerende kilde synes at være atmosfærisk nedfald, men congener profiler ligner på visse punkteroså congener profiler for dioxinindholdet i tekstiler. D en foreliggende viden er for spinkel til at drage sikre konklusioner.

D et beregnede totale bidrag fra dioxin kilder til spildevand svarer til cirka 0,4 - 4,8 g I-T EQ/år, hvoraf atmosfærisk deposition i kloakerede områder udgør 0,4 - 4 g I-T EQ/år. Intervalllet for dioxin kilder til spildevandet kan sammenlignes med det beregnede indhold i udledt spildevand og regnvand, svarende til 0,4 - 1,4 g I-T EQ/år samt det beregnede totale indhold i spildevandsslam 1,2 - 2,3 g I-T EQ/år. D enne sammenligning indikerer at
bidraget til rensningsanlæg i Danmark som minimum er 1,6 - 3,7 g I-TEQ/år og det indikerer samtidig at det estimerede depositionsniveau er realistisk set i forhold her til.

Den samlede emission til jord er i forhold til 1998-1999 reduceret til 0,7 - 42 g I-T EQ, hvor den tidligere blev estimeret til 1,3 - 54 g I-T EQ. D enne reduktion skyldes et fald i estimet fra afbrænding af biomasse. D en dominerende kilder skønnes at være rester fra diverse bål (fx havebål, sankthansbål) som efterlades og med tiden blandes med jorden samt udsprædning af husdyrgødning.

Det samlede tab til lossepladser og andre depoter er estimeret til 5 - 126 g I-T EQ/år, hvilket i SFA 2000 /Hansen, 2000/ blev estimeret til 38 - 420 g I-T EQ/år. D ette fald skyldes at røgbesningsprodukterne fra affaldsforbrænding nu eksporteres til deponi i udlandet og derfor ikke er med i ogpæringen. Mængden af dioxin der eksporteres er derfor steget til 55 - 413 g I-T EQ/år. M ængden til deponi i D anmark stammer primært fra aske fra biomassefyr, kulkraftværker og brande samt filterstøv fra røgbesnings hos diverse virksomheder. D en foreliggende viden om skæbnen for dioxiner i lossepladser er meget beskeden.


D er eksisterer et lager af chlorerede dioxiner i træ tidligere behandlet med pentachlorphenol. D en nuværende størrelse af dette lager er groft skønnet til 100 - 5.000 g I-T EQ. L ageret 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.

E n anden gruppe dioxiner er de bromerede dioxiner. D er er i 2002 blevet foretaget målinger af koncentrationen af bromerede dioxiner i røggassen fra affaldsforbrændingsanlægget V estforbrænding samt fra K ommunekemi. A nvedes resultaterne af disse få målinger som udtryk for emissionen af bromerede dioxiner fra afbrændingsforbrænding og behandling af kemikaliefald, opnås en årlig uddeling på cirka <0,01-0,1 g I-T EQ/år. D ette tal er dog meget usikker på grund af de ganske få målinger, der endnu er foretaget, og på grund af at der endnu ikke findes en officiel metode til beregning af I-T EQ for bromerede dioxiner. D eroverover inkluderer estimatet ikke alle målte congenergrupper, da det kun har været muligt at beregn I-T EQ-værdier for de målte specifikke congener. D e målte ikke specifikke congenergrupper er derfor ikke inkluderet i intervallet <0,01 - 0,1 g I-T EQ/år. Intervallet er derfor med sikkerhed underestimeret, men et estimat af det reelle emissionsniveau vurderes at blive højst usikker. D fra analyserne af chromatogrammerne for
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 2000 - 2002 has been estimated at 72 – 689 g l-T EQ/year, whereas the emissions to the environment have been estimated at (best estimate in parenthesis):

- Air: 11 – 163 (87) g l-T EQ/year
- Water: 0.4 - 1.4 (1) g l-T EQ/year
- Soil: 0.7 – 42 (21) g l-T EQ/year
- Depots: 5 - 126 (66) g l-T EQ/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. Moreover the atmospheric deposition on the Danish land area is estimated at 13 - 130 g l-T EQ/year. This estimate is made on the basis of measurements conducted by The National Environmental Research Institute in 2002. Finally may be emphasized that an export of dioxin with residual products for landfilling abroad of 55-413 g l-T EQ/year is taking place.

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. The emission of dioxins furthermore depends on whether a flue gas cleaning system exists - and if so, the kind of system is used. 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 September 2002 in order to improve the existing understanding of the circulation of dioxins in the Danish society on the basis of the newest Danish knowledge.

The objective of the study has been to collect and integrate the latest Danish knowledge concerning formation of dioxins primarily through new measurements from 2000 - 2002 from The National Environmental Research Institute, municipal waste incineration plants and industrial sources. This
The report is therefore an update of the substance flow analysis from 2000 /Hansen, 2000/, and the update is made on the basis of the report from 2000. As a consequence of this the report also has the objective to narrow the intervals that have so far been reported from Denmark. On a number of sources Danish data are however still limited. With the described objective the report is a contribution to meeting the obligations in article 5 of the Stockholm Convention on persistent Organic Pollutants.

Previous studies on emissions of dioxins in Denmark have been published in 1995, 1997 and 2000.

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, among these especially the counties and the National Environmental Research Institute, as well as from private organisations and companies. In the analysis, all the information has been held together to describe the flow of dioxins through the Danish society.

During 2000 – 2002 several dioxin analyses have been undertaken at Danish industries and plants, and many measurements have been made on soil, bioash, compost and air. These measurements especially cover emissions to air. The update of the substance flow analysis from 2000 /Hansen, 2000/ has meant that Danish emission factors can be used to a greater extent to estimate the dioxin emission. Nevertheless it is still necessary to use international emission factors either as a supplement to the Danish measurements or as best estimate, as there are still processes with too few Danish measurements, non-reliable measurements or no Danish measurements at all. In adopting such international 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 total Danish formation of chlorinated dioxins in 2000 - 2002 is estimated at 72 – 689 g I-TEQ/year. The dominant source is municipal waste incineration. Other significant sources also include private wood stoves and other smaller plants for biomass combustion as well as PCP-treated wood and fires, both accidental fires and others. The interval for formation contains estimates for all identified dioxin sources in Denmark. Some of the estimates are however subject to substantial uncertainty due to lack of precise data, which has resulted in high maximum values for the concerned sources. If the uncertain sources are not included the total emission to air, water, soil and
depots would correspond to 13 - 107 g I-TEQ/year. It is however in this report chosen to use the values for all known Danish sources and the mentioned results are therefore based on the total emission to air, water, soil and depots which is 17 - 332 g I-TEQ/year.

Most chlorinated dioxins formed by processes in Denmark are emitted to the environment. In absence of domestic treatment opportunities Denmark has started to export the majority of fly ash and flue gas treatment products from the Danish waste incineration plants for deposit abroad. The waste is classified as hazardous. The continuous production of the waste is exported and contracts have moreover been made concerning digging-up and export of already deposited flue gas treatment products. This explains why Denmark exports a relatively high share (55-413 g I-TEQ/year of the total annual formation of 72 - 689 g I-TEQ/year) to other countries.

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 2000 - 2002 is estimated at 11-163 g I-TEQ/year. This emission was in the substance flow analysis from 2000 (Hansen, 2000) 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 and fires. 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 hazardous waste was a significant source as well, but the kiln with high dioxin emission is closed down for reconstruction until 2003, and dioxin abatement will be installed. The other kilns have already dioxin abatement installed and this has resulted in a lower annual emission in 2000 – 2002 than in 1998 – 1999. The contribution from this source is likely to be further reduced due to redesign of the kilns.

The atmospheric deposition on the Danish land area is estimated at 13 - 130 g I-TEQ/year. This estimate is made on the basis of measurements conducted by the National Environmental Research Institute in 2002.

The total Danish emission to water in 2000 - 2002 is estimated at 0.4 – 1.4 g I-TEQ/year, approximately the same level as in 1998 - 1999, where the interval was 0.3 - 1.4 g I-TEQ/year. The dominant source seems to be atmospheric deposition, but congener profiles for sewage sludge partly also correspond to textiles. The knowledge is limited, and any definite conclusions on this issue should be taken as premature.

The calculated total contribution of 0.4 - 4.8 g I-TEQ/year should be taken as comparable to the estimated total content in discharged waste and storm water of 0.4 - 1.4 g I-TEQ/year and the calculated total content in sewage...
sludge of 1.2 - 2.3 g I-TEQ/year indicating that the contribution to waste water treatment plants in Denmark is at least 1.6 - 3.7 g I-TEQ/year. These observations indicate that the deposition level stated in chapter 6 is a realistic estimate.

The total direct emission of chlorinated dioxins to the soil environment is estimated at 0.7 - 42 g I-TEQ/year, which is lower than the estimate in SFA 2000 /Hansen, 2000/ which was 1.3 - 54 g I-TEQ/year. The dominant sources are 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.

Especially for combustion of biomass on industrial plants there has been a substantial reduction of the interval for emission of dioxin to soil and depots. This reduction means that the total emission equals approximately 0.3-20 g I-TEQ/year. The total emission from industrial plants was in SFA 2000 /Hansen, 2000/ estimated at 0.34 - 55 g I-TEQ/year. The narrowing of the interval is caused by new Danish measurements on industrial plants (district heating, large stoker boilers and CHP plants), which show lower emissions than earlier estimated. The Danish Environmental Protection Agency has in 2001 started a campaign about dioxin and private wood stoves, but the effect of the campaign is difficult to evaluate as it depends on to what extent the citizens in fact change their habits regarding firing and only use clean wood for combustion. At the same time there is still only few measurements regarding this subject.

The total quantity of chlorinated dioxins directed to landfills and other types of depots in Denmark is estimated at 5 - 126 g I-TEQ/year, which was in 2000 estimated at 38 - 420 g I-TEQ/year. The reduction is caused by the flue gas treatment residues which are now exported for landfilling. The major sources of the quantity of dioxins directed to Danish landfills, are primarily residues from coal combustion; but neither biomass combustion nor fires should be overlooked. The quantity of dioxin being exported can in the period 2000 - 2002 be estimated at 55 - 413 g I-TEQ/year.

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 dioxin measurements from 2001 apparently succeeded in reducing emissions considerably (The plant has been closed down for a period in 2002, but was reopened at the end of 2002. The electrostatic furnaces, where the reported measurements have been conducted, are however not expected to be opened again). The same development is seen at the Danish aluminium reclamation plant, where a heavy excess of the limit value was found in 2000. This plant is now keeping to the limit value after installation of dioxin cleaning. The Danish waste incineration plants are at the moment focussing on the dioxin emission, as the plants have to comply the limit value of 0.1 ng I-TEQ/Nm$^3$ before 2005. This means that some plants have installed dioxin abatement in the period 2000 - 2002, and more plants have plans of installing it in the coming years. For other industrial plants and activities the focus on dioxin emissions in Denmark is still limited, however growing.

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 from special dioxin abatement 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 2002 the size of this stock was roughly estimated at 100 - 5,000 g I-TEQ, the same as in 1999, as no new measurements have been found. 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. New Danish measurements of brominated dioxins in flue gas from the waste incineration plant Vestforbrænding and from Kommunekemi have been made in 2002. If the results of these measurements are used to estimate the total annual emission of brominated dioxins from waste incineration plants and treatment of hazardous waste, the annual emission will be approximately <0.01 - 0.1 g I-TEQ/year. This range is however very uncertain due to the few measurements and to the fact that no official method for calculating I-TEQ for brominated dioxins exists. Furthermore the estimate does not include all measured congener groups, as it has only been possible to calculate I-TEQ-values for the specific congeners. The non specific congener groups are therefore not included in the interval of 0.01 - 0.1 g I-TEQ/year. This emission value represents with certainty an under estimate of the real emission, but any estimate of the real emission value must be regarded as highly uncertain. Based on an analysis of the chromatographies for the congeners it is estimated that the real estimate can be up to approximately a factor 5 higher, but most likely not a factor 100 /Vikelsøe, 2003a/. Because of the uncertainty the value for emission of brominated dioxins is not included in the overall dioxin emission for Denmark.

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.

![Chemical structure of 2,3,7,8-TCDD and 2,3,7,8-TCDF](image)

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 into:

- 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 250°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 contain 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 assigns 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/IPC S 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**

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<td>0.1</td>
<td>0.01</td>
<td>0.1</td>
</tr>
<tr>
<td>1,2,3,6,7,8-HxCDF</td>
<td>0.1</td>
<td>0.1</td>
<td>0.01</td>
<td>0.1</td>
</tr>
<tr>
<td>2,3,4,6,7,8-HxCDF</td>
<td>0.1</td>
<td>0.1</td>
<td>0.01</td>
<td>0.1</td>
</tr>
<tr>
<td>1,2,3,7,8,9-HxCDF</td>
<td>0.1</td>
<td>0.1</td>
<td>0.01</td>
<td>0.1</td>
</tr>
<tr>
<td>Other HxCDFs</td>
<td>0</td>
<td>0</td>
<td>0.0001</td>
<td>0</td>
</tr>
<tr>
<td>1,2,3,4,6,7,8-HpCDF</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>1,2,3,4,7,8,9-HpCDF</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Other HpCDFs</td>
<td>0</td>
<td>0</td>
<td>0.00001</td>
<td>0</td>
</tr>
<tr>
<td>OCDF</td>
<td>0.0001</td>
<td>0.001</td>
<td>0</td>
<td>0.001</td>
</tr>
</tbody>
</table>

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-T CDD 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 remain stable at temperatures below 750°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 might be degraded to the more toxic hepta-, hexa-, penta- or tetrachlorinated dioxins.

1.5 Sampling methods for measurements of dioxin emission

1.6 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
The paradigm distinguishes between intended uses and non-intended uses. 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:

\[ \text{Import} + \text{formation} + \text{extraction} = \text{export} + \text{destruction} + \text{emissions} + \text{stock building} \]

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 intentionally 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-intentionally 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.

Dealing with uncertainty

In the update of the substance flow analysis the number of Danish measurements has grown and it has been considered practical to develop some general guidelines for assessment of data uncertainty. The aim of the guidelines is to obtain consistency in the treatment of data.

The guidelines appear in table 1.1. The measurements are evaluated in each case, which means that deviations from the guidelines might occur.
Table 1.1: Guidelines for estimating uncertainty of measurements.

<table>
<thead>
<tr>
<th>Number of productions/plants in Denmark</th>
<th>Number of measurements at Danish plants</th>
<th>How is uncertainty estimated?</th>
</tr>
</thead>
<tbody>
<tr>
<td>One</td>
<td>1-2</td>
<td>± factor 3 will be used as standard, but it can be estimated differently in the respective situations. This uncertainty interval reflects both the uncertainty connected with sampling and analyzing as well as the variation in emission level from time to time and from one source to another. ¹</td>
</tr>
<tr>
<td>More than one</td>
<td>1-2</td>
<td>The same as with one measurement ², but the emission level will be compared with emission interval from the SFA 2000 /Hansen, 2000/, and adjustments can be made.</td>
</tr>
<tr>
<td>One</td>
<td>More than two</td>
<td>Statistics. Mean value and 90 % confidence interval.</td>
</tr>
<tr>
<td>More than one</td>
<td>More than two</td>
<td>Statistics. Mean value and 90 % confidence interval. The calculated values will be compared to the emission level from the SFA 2000 /Hansen, 2000/ and be adjusted.</td>
</tr>
<tr>
<td>One or more</td>
<td>0</td>
<td>Emission level from SFA 2000 /Hansen, 2000/ is used.</td>
</tr>
</tbody>
</table>

¹ ± factor 3 means that the low interval limit is 3 times smaller than the measurement, and that the upper interval limit is 3 times larger than the measurement.

² It should be noted that the uncertainty interval of ± factor 3 is a preliminary estimate of the range in which the emission is expected to be present. This assumption is made on a minimal data basis, as few data series can be used to define such an estimate. The interval limits shall as a consequence of this not be seen as definitive.

With only one Danish plant and one or two measurements from this plant the emission level is not satisfactorily covered, but it is assumed that the measurements can be used to indicate the emission level when an uncertainty interval of ± factor 3 is used. The uncertainty interval of ± factor 3 is a preliminary estimate of the range in which the emission is expected to be available. This estimate is primarily based on Danish experiences with waste incineration plants. It is considered that the interval limits can be regarded as a 90 % confidence interval around the true value.

If there exists more than one Danish plant and only one or two measurements are present, the emission level derived from the Danish data is considered to be too uncertain. The emission level will then be compared with the emission level stated in SFA 2000 /Hansen, 2000/.

With more than two measurements from the same plant the mean value, minimum and maximum is calculated on the basis of a 90 % confidence level. With more than two measurements and more than one plant the same statistics will be made. The calculated values will be compared to the emission level from SFA 2000 /Hansen, 2000/, as the uncertainty is larger in this situation because the measurements have not necessarily been made on all Danish plants.

Brominated dioxins

Measurements on brominated dioxins and in particular congener-specific measurements are relatively few, but in autumn 2002 the National Environmental Research Institute in Denmark has carried out such
measurements on flue gas from Vestforbrænding, a major Danish waste incineration plant and from Kommunekemi, the central treatment plant for hazardous waste. These measurements are in this report used to estimate the total annual emission of brominated dioxins from waste incineration and from treatment of hazardous waste. Furthermore an attempt has been made to estimate the consumption of brominated dioxins present in electronic 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 800-1000°C 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.

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 1000°C or above like brickworks and cement manufacturing plants will be completely destructed. 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.

Finally it is emphasized that dioxin after destruction is often generated again later on in the chimney and the flue gas cleaning process either by "De Novo synthesis", formation from precursors or in some cases by chemical reactions below 300°C.

1.7 Guidance for reading the report

The updating of the substance flow analysis for dioxin has been made through supplements and changes to the report from 2000 /Hansen, 2000/. This method is chosen because the original substance flow analysis from 2000 is still relatively new.
Table 1.2 summarises the sections in the report where new data have resulted in changes, meaning that the data presented in this report are different from the data in SFA 2000 /Hansen, 2000/. The amount of Danish investigations is divided into three categories: None, some and good.

Table 12  
Changes in the updating of the Substance flow analysis for dioxin.

<table>
<thead>
<tr>
<th>Activity/process</th>
<th>Danish investigations SFA 2000 /Hansen, 2000/</th>
<th>Danish investigations 2002</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 Chemicals</td>
<td>Some-none</td>
<td>Some-none</td>
</tr>
<tr>
<td>2.2.4 Cement</td>
<td>Some</td>
<td>Some</td>
</tr>
<tr>
<td>2.2.5 Lime</td>
<td>None</td>
<td>Some-none</td>
</tr>
<tr>
<td>2.2.6 Other high-temperature materials</td>
<td>None</td>
<td>Some</td>
</tr>
<tr>
<td>2.3.3 Steel reclamation</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>2.3.4 Aluminium reclamation</td>
<td>None</td>
<td>Good</td>
</tr>
<tr>
<td>2.3.5 Other metal manufacturing</td>
<td>None</td>
<td>Some</td>
</tr>
<tr>
<td>2.4 Feedstuff</td>
<td>Some</td>
<td>Some</td>
</tr>
<tr>
<td>2.5 Foodproducts</td>
<td>None</td>
<td>Some-None</td>
</tr>
<tr>
<td>2.6 Pentachlorphenol</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>2.7 Use of chlorine for bleaching and disinfecting</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>2.8 Other industrial processes</td>
<td>None</td>
<td>Some-None</td>
</tr>
<tr>
<td>3.1 Coal power plants</td>
<td>Some</td>
<td>Some</td>
</tr>
<tr>
<td>3.2 Other fossil fuels</td>
<td>None</td>
<td>Some-None</td>
</tr>
<tr>
<td>3.3 Biomass</td>
<td>Some</td>
<td>Some</td>
</tr>
<tr>
<td>4.1 Fires</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>4.2 Traffic</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>4.3 Crematories</td>
<td>Some</td>
<td>Good</td>
</tr>
<tr>
<td>4.4 Other miscellaneous activities</td>
<td>Some</td>
<td>Some</td>
</tr>
<tr>
<td>5.1.1 Reclamation of cable scrap</td>
<td>None</td>
<td>Some-None</td>
</tr>
<tr>
<td>5.1.2 Shredder plants</td>
<td>Some-None</td>
<td>Some</td>
</tr>
<tr>
<td>5.2 Hazardous waste</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>5.3 Municipal solid waste</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>5.4 Healthcare risk waste</td>
<td>Some</td>
<td>Good</td>
</tr>
<tr>
<td>5.5 Municipal landfills</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>5.6 Biological waste treatment</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>5.7.1 Wastewater treatment</td>
<td>Some</td>
<td>Some</td>
</tr>
<tr>
<td>5.7.2 Treatment and disposal of sewage sludge</td>
<td>Good - some</td>
<td>Good</td>
</tr>
</tbody>
</table>

1 These columns give a brief assessment of the existing Danish investigations with the purpose of indicating the subjects of which 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 Danish figures are available - typically combined with literature values if available.
- None: No Danish experience at all - estimates rely completely on literature values.

1 New measurement.
2 New measurements.
3 One new measurement.
4 New measurements.
5 New measurements for insulation materials.
6 Other metal manufacturing covers metal casting and hot-dip galvanising.
7 New measurements from aluminium foundries.
8 New measurements.
9 One new measurement.
10 New measurements.
11 One new measurement.
12 New measurements.
13 New measurements.
14 New measurements.
15 One new measurement.
16 New measurements.
17 New measurements.
18 National Environmental Research Institute is conducting measurements in 2002-2003, but the results were not available, when this report was made.
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/Nm³ corresponding to a total emission of 0.4-0.5 g total dioxin per year. No recordings of collected filter dust have been made, as the quantity is assumed marginal.

The dioxin concentration in the air flow after the burning process has been measured again in June 2001. The measurement showed a concentration of 0.006 ng I-TEQ/Nm³. The airflow is estimated at 400 million Nm³/year, and the emission per year is therefore approximately 0.8-7.1 mg I-TEQ/year. No knowledge from similar processes abroad is available.

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-T EQ/Nm³, corresponding to an emission of < 90 µg N-T EQ 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 Nm³/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 m³/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 tons/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 2001 /Bekämpelsesmiddelstatistik 2001/:
Table 2.1
Danish consumption of pesticides confirmed or suspected to contain dioxins, 2001

<table>
<thead>
<tr>
<th>Common name</th>
<th>Consumption in Denmark 2001 kg active substance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bromoxynil</td>
<td>44,909</td>
</tr>
<tr>
<td>Chlorfenvinphos 1)</td>
<td>-</td>
</tr>
<tr>
<td>Chlorothalonil</td>
<td>-</td>
</tr>
<tr>
<td>2,4-D</td>
<td>-</td>
</tr>
<tr>
<td>Dicamba</td>
<td>3690</td>
</tr>
<tr>
<td>Dichlorprop</td>
<td>-</td>
</tr>
<tr>
<td>Dichlor-P</td>
<td>-</td>
</tr>
<tr>
<td>Diflubenzuron</td>
<td>-</td>
</tr>
<tr>
<td>Diuron</td>
<td>-</td>
</tr>
<tr>
<td>Imazalil</td>
<td>5350</td>
</tr>
<tr>
<td>Linuron</td>
<td>8982</td>
</tr>
<tr>
<td>MCPA</td>
<td>238,208</td>
</tr>
<tr>
<td>Mechlorprop</td>
<td>-</td>
</tr>
<tr>
<td>Mechlorprop-p</td>
<td>-</td>
</tr>
<tr>
<td>Paclobutrazol</td>
<td>-</td>
</tr>
<tr>
<td>Tetradifon</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td>301,139</td>
</tr>
</tbody>
</table>

1) "-" means that the substance is no longer registered in the Danish Pesticide statistics from 2002 /Bekæmpelsesmiddelstatistik, 2002/. The given substances were used in 1998 when SFA 2000/Hansen, 2000/ was carried out, so the substances have been substituted.

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 was in 1998 roughly calculated to be 56 mg I-TEQ/year. As the annual amount of pesticides has been reduced from 1998 to 2001, it is still reasonable to expect that the consumption of dioxin with pesticides is still less than 1 g I-TEQ/year, taking all uncertainties related to lack of complete and updated information into account. 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 retardants and are furthermore created by manufacturing and other processing (including recycling) of plastic products based on flame retarded 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 TBD; 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 is 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 <1 - 37 mg I-TEQ/tonnes and for circuit boards in the range of <1 - 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 PBBs, 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-T EQ/kg at 88% dry matter /Plantedirektoratet 2000/. A single sample, however, was measured to 16738 pg I-T EQ/kg at 88% dry matter /Plantedirektoratet 2000/. For moler originating from Denmark was on 5 samples measured an average of 139 pgI-T EQ/kg with a variation of 90-173 pg I-T EQ/kg at 88% dry matter /Plantedirektoratet 2000/. It should be noted that EU has established an emission limit value 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 2001a and 2001b/, Danish production, import and export of the relevant commodity items in 2001 is summarised as stated in table 2.2 below.

**Table 2.2**

<table>
<thead>
<tr>
<th>Item</th>
<th>Production (tonnes)</th>
<th>Import (tonnes)</th>
<th>Export (tonnes)</th>
<th>Supply (tonnes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolin</td>
<td>0</td>
<td>16900</td>
<td>80</td>
<td>16800</td>
</tr>
<tr>
<td>Kaolin-clay</td>
<td>0</td>
<td>2400</td>
<td>1000</td>
<td>1400</td>
</tr>
<tr>
<td>Bentonite</td>
<td>12200</td>
<td>40300</td>
<td>10900</td>
<td>41600</td>
</tr>
<tr>
<td>Clay-others</td>
<td>17 (2)</td>
<td>11300</td>
<td>805</td>
<td>10500</td>
</tr>
<tr>
<td>Moler (1998)</td>
<td>50000 (2)</td>
<td>7900</td>
<td>48400 (2)</td>
<td>9500</td>
</tr>
</tbody>
</table>

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).
3. The figures for moler are from SFA 2000 /Hansen, 2000/.
Dioxin balance
Assuming dioxin concentrations as follows

Kaolin: A s "clay-others"
Kaolin-clay: 0.1 - 1100 ng I-TEQ/kg dry matter
Bentonite: A s "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>
<thead>
<tr>
<th>Item</th>
<th>Production (mg I-TEQ)</th>
<th>Import (mg I-TEQ)</th>
<th>Export (mg I-TEQ)</th>
<th>Supply (mg I-TEQ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolin</td>
<td>0</td>
<td>2600 (68 - 18600)</td>
<td>12 (0.3 - 88)</td>
<td>2600 (67 - 18500)</td>
</tr>
<tr>
<td>Kaolin-clay</td>
<td>0</td>
<td>0.2 - 2600</td>
<td>0.1 - 1100</td>
<td>0.1 - 1500</td>
</tr>
<tr>
<td>Bentonite</td>
<td>1900 (49 - 13400)</td>
<td>6200 (161 - 44300)</td>
<td>1700 (44 - 12000)</td>
<td>6400 (166 - 45800)</td>
</tr>
<tr>
<td>Clay - others</td>
<td>3 (0.07 - 19) (^1)</td>
<td>1700 (45 - 12400)</td>
<td>120 (3 - 890)</td>
<td>1600 (42 - 13600)</td>
</tr>
<tr>
<td>Moler (^2)</td>
<td>5 - 10</td>
<td>0.8 - 1.6</td>
<td>4.8 - 9.7</td>
<td>1 - 19</td>
</tr>
<tr>
<td>Total</td>
<td>1900 (49 - 13400)</td>
<td>10500 (274 - 77900)</td>
<td>1800 (50 - 14100)</td>
<td>10600 (275 - 77400)</td>
</tr>
</tbody>
</table>

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.
2. Based on figures from SFA 2000 /Hansen, 2000/.

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-T EQ/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% O₂ (because of massive surplus of air) and is cleaned by passing an electrostatic precipitator. 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-T EQ per year and most likely within the range of 0.0006 - 0.24 g I-T EQ/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 and 18% 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 (Murvaerkcentralen 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-T EQ/ton of material and a variation of 0.001 – 0.23 μg I-T EQ/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 are 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. Meat and bone meal is now also being used as alternative fuel for the kiln. Waste containing more than 0.1% chlorine is not accepted. The air emission from this kiln is cleaned in an electrostatic precipitator 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 precipitator at around 250°C. The air emission from the 4 kilns used for white cement is cleaned first in an electrostatic precipitator at around 300°C and afterwards by a scrubber.

Plant activity:
Based on information from the company a total of approx. 2.6 million tonnes of cement were manufactured in 2001.

In the largest kiln approx. 1.7 million tonnes cement with an airflow of 3150-3500 million N m³/year was manufactured. In the other kilns approx. 0.9 million ton cement with an airflow of around 3200 million N m³/year was manufactured, and a discharge of cleaned scrubber water of approx. 400,000 m³ water/year.

Filter dust from electrostatic precipitators 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/N m³ 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. In 2001 a new measurement has been carried out at the same kiln. The sample was made while using meat and bone meal as a part of the fuel. The measurement resulted in an emission of 0.035 ng I-TEQ/N m³ or 0.0001 mg I-TEQ/ton manufactured. The annual emission calculated on the basis of this measurement is approximately 167 mg I-TEQ/year, and this indicate that the dioxin emission increases, when meat and bone meal is used as an alternative fuel in the cement production. This
conclusion is however not definitive, as only one measurement has been taken - there may be other influencing conditions.

In 1995 a measurement was made on one of the smaller kilns. The measurement showed a dioxin emission of 0.15 ng N-T EQ/N m³, which means an annual emission of 162 mg N-T EQ/year. The emission factor is approximately 0.0005 mg N-T EQ/ton. There have not been made any measurements on the relevant kiln since 1995.

No measurements have been undertaken for the other kilns and scrubber water.

The best possible estimate is assumed to be based on the company’s own measurements, although only one measurement has been made on one of the small kilns back in 1995. Using the value from this measurement at the 0.9 million tonnes manufactured on the smaller kilns and the emission factor 0.00001 mg I-T EQ/ton for the 1.7 million tonnes manufactured at the large kiln, the total annual emission is estimated to be in the range of 156 - 1401 mg I-T EQ/year. This interval is calculated assuming an uncertainty of ± factor 3. (Reference is made to section 1.5) Best estimate is 467 mg I-T EQ/year.

In SFA 2000 /Hansen, 2000/ the dioxin emission from production of cement was estimated to be approximately 0.045 - 0.92 g I-T EQ/year.

### 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 precipitator and out the chimney at about 280°C. The oxygen concentration through these last processes is 8-9%. Dust collected in the electrostatic precipitator 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 2001 approx. 90,000 tonnes of burned lime was produced /Danmarks Statistik 2001b/.

**Dioxin formation and disposal**

One measurement of dioxin emission to air from the burning process has been carried out in spring 2001. The measurement was made with combustion of 100 % coal, and the sampling lasted 7.5 hours. The result of the measurement showed a concentration of 0.01 ng I-T EQ/N m³. This concentration corresponds to an emission factor of approximately 0.02 µg I-T EQ/ton.
Based on this emission factor the current Danish emission is estimated to be approximately 0.6 - 5.4 mg l-T EQ/year, assuming an uncertainty of ± factor 3 of the measurement. (reference is made to section 1.5)

In SFA 2000 /Hansen, 2000/ the dioxin emission from production of lime was estimated to be approximately 0.001 - 2.6 g l-T EQ/year.

European measurements indicate emission factors in the range of 0.01-29µg l-T EQ/ton /Landesumweltamt Nordrhein-Westfalen 1997/.

Simultaneously with the measurement of the air emission the dioxin concentration in the filter dust was also measured. This measurement showed a concentration < 0.006 l-T EQ/m³, which gives an emission factor less than approximately 0.0009 mg l-T EQ/ton filter dust. The total amount of filter dust is estimated to be approximately 6 tons per year, which results in emission of approximately 0.002 - 0.02 mg l-T EQ/year, assuming ± factor 3 as the uncertainty of the measurement.

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

Three Danish production sites for insulation materials have made measurements of the dioxin emissions from the production.
One of the plants has measured the dioxin emission in 2000. The measurement was taken in the central smoke stack. The measurement resulted in an emission of 0.012 ng I-TEQ/Nm$^3$ or approximately 25 mg I-TEQ/year. This corresponds to an emission factor of approximately 0.0007 mg I-TEQ per ton insulation material produced.

The second plant has measured dioxin concentration in air emission, fly ash and ash from cyclone cleaning in 2001. The dioxin concentration in the air from the smoke stack was 0.3 ng I-TEQ/Nm$^3$, whereas the content in the fly ash was 9 ng I-TEQ/kg dry substance. The dioxin concentration in the ash from cyclone cleaning was 109 ng I-TEQ/kg dry substance. The amount of cyclone ash and fly ash is not known, so it has not been possible to estimate an annual emission.

At the third plant the dioxin emission to air has been measured in 2001 resulting in an emission of 0.2 ng I-TEQ/Nm$^3$. Based on information from the inspection authorities this measurement corresponds to an emission factor of approximately 0.0002 mg I-TEQ/ton produced.

It has not been possible to estimate the emission factors for some of the measurements because of lacking information. The two emission factors on 0.0002 mg I-TEQ/ton produced and 0.0007 mg I-TEQ/ton produced are therefore used to calculate the annual dioxin emission from production of insulation materials.

Using the highest and lowest emission factors and assuming an uncertainty of ± factor 3 (reference is made to section 1.5), the annual dioxin emission can be estimated to be 12 - 305 mg I-TEQ/year.

The European Dioxin Inventory (section on Germany) and UNEP give air emission factors for glass production 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. The dioxin emission to air from production of glass and china and ceramics, is on the basis of these assumptions estimated to be approximately 0.003 - 0.02 g I-TEQ/year.

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

Total emission to air: 0.02 - 0.32 g I-TEQ/year

Residues for disposal: Assessment not possible.

In SFA 2000 /Hansen, 2000/ the dioxin emission from production of insulation materials, glass, china and ceramics was estimated to be approximately 0.004 - 0.024 g I-TEQ/year.

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 tonnes/year. Aprox. ¾ of this quantity is exported, whereas the rest is directed to Kommunekemi as hazardous 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 $\mu$g 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 0.032 $\mu$g I-T EQ/ton of material /UNEP 1999/. Based on local conditions, the Danish measurement is considered a better estimate than the UNEP value.

In the past two years dioxin measurements have been carried out in two Danish aluminium foundries. For one of the productions the measurements showed an emission of 0.002 ng/Nm$^3$, which corresponds to an emission of approximately 0.04 mg I-T EQ/year. The measurement was made in 2001 and gave an emission factor at 0.04 ng I-T EQ/ton aluminium manufactured.

In the second aluminium foundry a dioxin emission of 0.03 ng I-T EQ/Nm$^3$ was measured in 2001. The measurement applies to an annual emission of approximately 0.05 mg/Nm$^3$ and an emission factor of 0.01 ng I-T EQ/ton aluminium manufactured.

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 $\mu$g I-T EQ/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 $\mu$g I-T EQ/ton of material /Landesumweltamt Nordrhein-Westfalen 1997/.

Based on the Danish measurements it is chosen to lower the interval for the emission of dioxin to air by metal casting in Denmark to <1 mg I-T EQ/year - 10 mg I-T EQ/year. The estimated upper interval limit has been reduced compared to the 60 mg I-T EQ/year used in SFA 2000 /Hansen, 2002/ because of the low emission level shown by the Danish measurements. 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.

In SFA 2000 /Hansen, 2000/ the dioxin emission from metal casting was estimated to be approximately 0.032 - 0.06 g I-T EQ/year.

### 2.3.2 Hot-dip galvanising

About 15 companies in Denmark carry out hot-dip galvanising. First the iron is cleaned of organic pollution by the use of tensides, HCl and occasionally also sand blasting. Then the iron is treated with NH$_3$Cl 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 N m\(^3\)/tonnes product.

Generation of filter dust from air cleaning varies, as some plants have no cleaning facilities at all (emission of 50 mg dust/N m\(^3\)), whereas larger plants generally are equipped with bag filters allowing an air emission of less than 0.5 mg dust/N m\(^3\). It is known that one major company produces 8-10 tonnes of filter dust 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

Until 2002 one company in Denmark has carried out reclamation of iron and steel scrap. This production has however been closed down since early summer 2002, but has re-opened on a smaller scale in November 2002. In the future, production will focus on purchased slabs and billets. There are at the time being no plans to re-open the steelmaking plant.

It is chosen still to include steel reclamation in the report, as the production has been ongoing in most of the period from 2000 - 2002. The estimated emission is therefore a picture of the dioxin emission before the production ceased. It is not known how the emission will be for the re-opened production. The production quantity has not been updated since SFA 2000. The reason is that it has not been possible to get new information, as the factory is closed.

The production process as it has been in the main period from 2000-2002 can be described as the following:

The scrap is melted in an electric arc furnace at around 1,600\(^\circ\)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\(^\circ\)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 tons/year
Raw steel production: 800,000 tons/year
Filter dust exported (own estimate): 10,000 tons/year
Production waste to Kommunekemi: 1,118 tons/year
Reused production waste, excl. filter dust: approx. 90,000 tons/year
Production waste deposited in the plant area: approx. 29,000 tons/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
During the past two years the factory has made an effort to minimize and control the emission of dioxin and other hazardous substances from production. In January 2001 two measurements were taken from the smoke stack. The measurements showed a dioxin emission of 0.16 ng I-TEQ/Nm$^3$ and 0.042 ng I-TEQ/Nm$^3$, which correspond to approx. 1000 and 300 ng I-TEQ/ton manufactured steel respectively. This emission level is lower than the earlier made measurements, and if the two new measurements are considered representative of the total emission from the production, the total dioxin emission will be approximately 0.1 - 2.4 g I-TEQ/year, assuming a production of 800,000 tons/year and ± factor 3 of the two measurements.

In SFA 2000 /Hansen, 2000/ the dioxin emission from the steel reclamation production was estimated to be approximately 1.1 - 2.3 g N-TEQ/year. The amount of filter dust, which is exported, was in SFA 2000 /Hansen, 2000/ expected to be 5.0 - 10.5 g I-TEQ/year. These values are maintained in this report.

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 660°C dioxin formation should be assumed likely.

Plant activity
Based on information from the company, the activity of the plant in the period 2000-2001 can be summarised as follows:

- Total production: approx. 30,000 tons/year
- Air flow from melting process: approx. 63,000 N m³/h
- Salt slag to landfill: 7,600 tons/year (1998)
- Filterdust to landfill: 360 tons/year (1998)

No discharge of industrial wastewater took place.

Dioxin formation and disposal
In November 2000 a high dioxin concentration was registered in the air outlet from the production. The dioxin emission was measured to be 183 ng I-T EQ/N m³. This value considerably exceeded the limit value then in force, which was 1 ng I-T EQ/N m³/Vejle Amt, 2000/. After this measurement two additional measurements were made, which showed 113 and 14 ng I-T EQ/N m³. To lower the dioxin emission the company promptly established dioxin abatement. Three measurements have been carried out after dioxin abatement has been installed. These measurements have resulted in an average emission of 0.88 ng I-T EQ/N m³ and are ranging from <0.001 ng I-T EQ/N m³ to 2.4 ng I-T EQ/N m³ when a 90% confidence level is used. The latest measurement complies with the new Danish limit value of 0.1 ng I-T EQ/N m³.

The measurements November 2000 till December 2001 correspond to emission factors within the range of approximately 0.0001 mg I-T EQ/ton product manufactured to 1.8 mg I-T EQ/ton product manufactured.
The emission at 183 ng I-TEQ/N m$^3$ would result in an emission of approximately 60 g I-TEQ/year, if the emission was representative of a whole year. Best estimate of the actual annual emission after dioxin abatement is 290 mg I-TEQ/year, corresponding to the range <0.001 - 792 mg I-TEQ/year when a 90 % confidence level is used. It is likely that the annual emission will be in the lower end of the interval, because the measured emission has consistently decreased considerably from measurement to measurement. It is noted that the limit value of 0.1 ng I-TEQ/N m$^3$ corresponds to an annual emission of 30 mg I-TEQ/year. However, in this assessment the range <0.001 - 792 mg I-TEQ/year will be used.

A measurement of the dioxin concentration in the filter dust has also been made showing a dioxin concentration of 5120 ng/kg filter dust. Using the amount of filter dust from 1998 the annual amount of dioxin in filter dust can be estimated to be approximately 1 - 3 g I-TEQ/year.

In SFA 2000 /Hansen, 2000/ the dioxin emission from aluminium reclamation was estimated to be approximately 0.43 - 4.8 g I-TEQ/year, of which 0.17 - 3.3 g I-TEQ/year was dioxin emission to air.

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 Nm³/year
- Air flow through boiler: Approx. 500 million Nm³/year
- Discharge of scrubber water: Approx. 18 million m³/year

Dioxin formation and disposal

The dioxin emission to air from one of the Danish plants has been measured in 2001. Three measurements were made on process air after passing through a thermal combustion facility (the boiler principle). The measurements showed dioxin emissions ranging from 0.0008 to 0.003 ng I-TEQ/Nm³, equalling an annual emission of less than 15 mg I-TEQ/year. No Danish measurements from ceramic filter units are available.

The dioxin emission to air from production of fish and oil meal was in SFA 2000 /Hansen, 2000/ with high uncertainty estimated to be around zero.

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 release 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 230°C, 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 850°C.

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 408,000 tonnes per year. 307,000 tons are exported and 130,000 tonnes is imported to the country. This means that around 75% of the Danish production is assumed exported. /Danmarks Statistik, 2002a/ and
The airflow exposed to burning before emission from the relevant plant is expected to be 620 million N m$^3$/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-T EQ/kg for the fat fraction. Meat meal manufactured without spray drying had a dioxin content of 36 - 260 pg I-T EQ/kg dry matter, whereas the dioxin content in a product from the spray drier was only 19 pg I-T EQ/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, but it is estimated that the emission per N m$^3$ will be nearly the same as for burning off-gases from production of fish oil and meal. On the basis of this assessment and taking the uncertainty in consideration, the annual emission is considered to be less than 10 mg I-T EQ/year.

The content of dioxin in manufactured products can, based on the figures stated above, be estimated at 0.008 – 0.63 g I-T EQ/year, of which approximately 0.006 – 0.5 g I-T EQ/year is 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-T EQ/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-T EQ/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). Thus 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. The existing knowledge regarding deposition of dioxin in Denmark is presented in section 6.

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.

<table>
<thead>
<tr>
<th>Category</th>
<th>Consumption 1997/98 1000 t</th>
<th>Assumed dioxin content pg I-TEQ/kg</th>
<th>Consumption of dioxin g/year</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Comments pg/kg fish, mainly based on herrings</td>
<td>Min.</td>
</tr>
<tr>
<td>Fish meal, fish silage and wastel</td>
<td>1048</td>
<td>1.000 - 8.000 pg/kg fish</td>
<td>1.0</td>
</tr>
<tr>
<td>Grass, silage, hay, root crops</td>
<td>26519</td>
<td>10 - 60 pg/kg product based on vegetables</td>
<td>0.27</td>
</tr>
<tr>
<td>Cereal products</td>
<td>6246</td>
<td>20 pg/kg product</td>
<td>0.12</td>
</tr>
<tr>
<td>Oil cakes and oil meal</td>
<td>2229</td>
<td>10 - 170 pg/kg product based on vegetables and vegetable fat</td>
<td>0.02</td>
</tr>
<tr>
<td>Straw</td>
<td>1797</td>
<td>10 - 60 Assumed similar to grass, silage, hay etc.</td>
<td>0.02</td>
</tr>
<tr>
<td>Other vegetable feeding stuff</td>
<td>733</td>
<td>10 - 170 Assumed similar to oil cakes and meal</td>
<td>0.007</td>
</tr>
<tr>
<td>Meat and bone meal</td>
<td>231</td>
<td>19 - 1540 pg/kg product</td>
<td>0.004</td>
</tr>
<tr>
<td>Grass pills and grass meal etc.</td>
<td>131</td>
<td>100 - 400 pg/kg product</td>
<td>0.01</td>
</tr>
<tr>
<td>Milk products</td>
<td>9</td>
<td>490 pg/kg fat</td>
<td>0.004</td>
</tr>
<tr>
<td>Sum</td>
<td></td>
<td></td>
<td>1.5</td>
</tr>
</tbody>
</table>

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, draf, yeast, molasses, tapioka and citrus meal etc.
4. Consumption for 2001. The production used in Denmark is 101,000 tons and 130,000 tons are imported to the country.
5. 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.

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 for regarding spray drying as a dioxin generating process.

A measurement from a Danish fish processing factory shows a dioxin emission of 0.001 ng I-T EQ/Nm³ in the air flow or approximately 0.1 - 1 mg I-T EQ/year from the plant in question. This corresponds to an emission factor of approximately 16 ng I-T EQ/ton fish processed. The air flow comes from the process, where the skin is removed from the fish and from cooking. The dioxin content in the air flow must relate to the natural dioxin in the fish, as no combustion is taking place during these processes. If the dioxin emission
is compared to the dioxin content in one ton fish, the dioxin emission per ton fish processed is approximately 0.2 % of the dioxin content in one ton fish.

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.

<table>
<thead>
<tr>
<th>Product group</th>
<th>Consumption 1997/98 1000 t (^3)</th>
<th>Fat % (^2)</th>
<th>Assumed dioxin content pg I-TEQ/kg (^3)</th>
<th>Consumption of dioxins g/year</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>comments</td>
<td>min</td>
<td>max</td>
</tr>
<tr>
<td>whole milk, junket, yoghurt</td>
<td>546.6</td>
<td>3</td>
<td>490 pg/kg fat</td>
<td>0.008</td>
</tr>
<tr>
<td>skimmed and buttermilk</td>
<td>113.6</td>
<td>0.3</td>
<td>490 pg/kg fat</td>
<td>0.0002</td>
</tr>
<tr>
<td>Cream</td>
<td>50.4</td>
<td>20</td>
<td>490 pg/kg fat</td>
<td>0.005</td>
</tr>
<tr>
<td>Butter</td>
<td>9.8</td>
<td>85</td>
<td>490 pg/kg fat</td>
<td>0.004</td>
</tr>
<tr>
<td>Cheese</td>
<td>86.8</td>
<td>25</td>
<td>490 pg/kg fat</td>
<td>0.11</td>
</tr>
<tr>
<td>Milk products (sum)</td>
<td>807.2</td>
<td></td>
<td></td>
<td>0.028</td>
</tr>
<tr>
<td>Margarine</td>
<td>51.1</td>
<td>85</td>
<td>260 - 1510 pg/kg fat</td>
<td>0.011 / 0.066 / 0.039</td>
</tr>
<tr>
<td>Cereals</td>
<td>506.9</td>
<td></td>
<td>20</td>
<td>pg/kg</td>
</tr>
<tr>
<td>Fruit and vegetables</td>
<td>590</td>
<td></td>
<td>10 - 60 pg/kg</td>
<td>0.008 / 0.048 / 0.028</td>
</tr>
<tr>
<td>Fish</td>
<td>20</td>
<td></td>
<td>100 - 8000 pg/kg</td>
<td>0.002 / 0.160 / 0.081</td>
</tr>
<tr>
<td>Eggs</td>
<td>85.9</td>
<td>10</td>
<td>460 - 2670 pg/kg fat</td>
<td>0.004 / 0.023 / 0.013</td>
</tr>
<tr>
<td>Meat</td>
<td>568</td>
<td>10</td>
<td>200 - 2000 pg/kg fat</td>
<td>0.011 / 0.113 / 0.062</td>
</tr>
<tr>
<td>Sum</td>
<td>2660</td>
<td></td>
<td></td>
<td>0.06 / 0.44 / 0.26</td>
</tr>
</tbody>
</table>

1. Consumption figures for the listed product groups have been taken from /Danmarks Statistik 1999c/. However, consumption of fruit and vegetables is estimated as 0.403 kg 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 derivatives.

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/. As an exception, countries with ocean coast (France, Ireland, Portugal, Spain and the United Kingdom) can choose to use products with more than 0.1% PCP until the end of year 2008. This exception can only be used in industrial plants for treatment of wood (for outdoor) and waterproofing of fibres and heavy textiles. The total content of HCDD in PCP must however not exceed 2 ppm in preparations used for this purpose./European Commission, 1999/

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 the 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 tons PCP/year.
- Around 1960 with 100 tons PCP/year
- Maximum in 1972 with 250 - 300 tons PCP/year
- Decreasing to 0 tons 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 tons 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 tons. 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 tons 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 equaling 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 tons 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 tons /COWI consult 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; COWI consult 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 tons 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 tons PCP in 1983 should equal a dioxin import of 0.6 - 105 g I-TEQ/year. Similarly should an import of 1 - 10 tons 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 is 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 tons 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 tons 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:

\[10\% \times \frac{(0.5+0.05)/2 - (105+21)/2}{g \text{ I-TEQ/year}} = 0.03 - 6 \text{ g I-TEQ/year}\]

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

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

#### 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 emission limit value 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 tons 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. A gain 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 (COWI consult 1985). Today in Europe PCP is used 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 tons /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/. His 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 /Lasmeier & 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 representative 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 tons. 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 include 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 Cl₂/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 distilled 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 tons/year
- Chlorinated compounds:            3000 – 5000 tons/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 Cl₂/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-T EQ/kg and 12.6 ng BGA-T EQ/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 tons/year, whereas import of other cork items apart from natural cork and waste comes up to around 800 tons/year /Danmarks Statistik 1999/.

Assuming that BGA-T EQ 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 was found whereas in cardboard materials and wrapping paper a content of 4.5 - 11.5 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

<table>
<thead>
<tr>
<th>Item</th>
<th>Production (tons/year)</th>
<th>Import</th>
<th>Export</th>
<th>Supply</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paper</td>
<td>110.000</td>
<td>450.000</td>
<td>60.000</td>
<td>500.000</td>
</tr>
<tr>
<td>Cardboard and wrapping materials</td>
<td>280.000</td>
<td>380.000</td>
<td>150.000</td>
<td>510.000</td>
</tr>
<tr>
<td>Total</td>
<td>390.000</td>
<td>830.000</td>
<td>210.000</td>
<td>1010.000</td>
</tr>
</tbody>
</table>

Dioxin balance (g I-TEQ/year)

<table>
<thead>
<tr>
<th>Item</th>
<th>Production</th>
<th>Import</th>
<th>Export</th>
<th>Supply</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paper</td>
<td>0.11 - 0.33</td>
<td>0.45 - 1.35</td>
<td>0.06 - 0.18</td>
<td>0.5 - 1.5</td>
</tr>
<tr>
<td>Cardboard and wrapping materials</td>
<td>1.4 - 2.8</td>
<td>1.9 - 3.8</td>
<td>0.75 - 1.5</td>
<td>2.5 - 5.1</td>
</tr>
<tr>
<td>Total</td>
<td>1.5 - 3.1</td>
<td>2.2 - 4.2</td>
<td>0.8 - 1.7</td>
<td>3.0 - 6.6</td>
</tr>
</tbody>
</table>

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 concentration figures of 5 - 10 ng I-TEQ/kg have been assumed.

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 67°C. 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 200°C, 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 2001 came up to approx. 2,700,000 tons /Danmarks Statistik 2002b/, of which approx. 870,000 tons are reused or recycled materials (the estimated number for 2000) /Dall et al., 2002/.

Measurements from 1999 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 product /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 41 mg I-TEQ/year.

In SFA 2000 /Hansen, 2000/ the dioxin formation from production of other industrial materials was with some uncertainty estimated to be less than 0.04 g I-T EQ/year.

Coal tar production
According to /Danmarks Statistik 2002b/ the production of coal tar in Denmark is approximately 79,000 tons per year.

In connection with the production of coal tar an incinerator is used for quenching the noncondensible gasses from the coal tar distillation plant. This
process was assumed to be a potential source for dioxin and a measurement was therefore made in 1999. The measurement of dioxin to air gave an emission factor of 0.21 ng I-TEQ/tonnes products /Fyns Amt 2000/.

No international measurements have been found for production of coal tar, but on the basis of the Danish measurement the annual emission from production of coal tar is estimated to be within the range of 0.008 mg I-TEQ/year to 0.03 mg 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 NOx 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

<table>
<thead>
<tr>
<th>Activity/product</th>
<th>Consump. on by products</th>
<th>Formation</th>
<th>Emissions/losses (g I-TEQ/year)</th>
<th>to air</th>
<th>to water</th>
<th>to soil</th>
<th>to waste</th>
<th>Export</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g I-TEQ/year</td>
<td>g I-TEQ/year</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemicals</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pesticides 1)</td>
<td>&lt;1?</td>
<td>?</td>
<td>0.001 - 0.007</td>
<td>&lt;1?</td>
<td>?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pharmaceuticals</td>
<td>?</td>
<td>?</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bleaching agents</td>
<td>&lt;0.001</td>
<td>?</td>
<td></td>
<td>&lt;0.001</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brominated flame retardants 2)</td>
<td>2 – 60</td>
<td>?</td>
<td></td>
<td>?</td>
<td>?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other chemical products</td>
<td>?</td>
<td>?</td>
<td></td>
<td>?</td>
<td>?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>High-temperature materials</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raw materials 3)</td>
<td>4 – 1050</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.004 - 5</td>
</tr>
<tr>
<td>Clay-based insulation materials</td>
<td></td>
<td></td>
<td>0.001 - 0.2</td>
<td>0.001 - 0.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tiles and bricks</td>
<td></td>
<td></td>
<td>0.001 - 0.2</td>
<td>0.001 - 0.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cement</td>
<td></td>
<td></td>
<td>0.2 - 14</td>
<td>0.2 - 14</td>
<td>?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lime 4)</td>
<td></td>
<td></td>
<td>0.001 - 0.005</td>
<td>0.001 - 0.005</td>
<td>&lt;0,0001</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other Materials</td>
<td></td>
<td></td>
<td>0.02 - 0.3</td>
<td>0.02 - 0.3</td>
<td>?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metal manufacturing</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metal casting</td>
<td></td>
<td></td>
<td>&lt;0.001 - 0.01</td>
<td>&lt;0.001 - 0.01</td>
<td>?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hot-dip galvanising</td>
<td></td>
<td></td>
<td>0.02 - 0.4</td>
<td>0.02 - 0.4</td>
<td>&lt;0.002</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steel reclamation 5)</td>
<td>5.1 - 12.9</td>
<td>0.1 - 2.4</td>
<td>0?</td>
<td>&lt;0.005</td>
<td>5.0 – 10.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminium reclama.</td>
<td>1 - 38</td>
<td>&lt;0.001 - 0.8</td>
<td>0</td>
<td>1.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feedstuff</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fish oil/meal</td>
<td></td>
<td></td>
<td>&lt;0.03?</td>
<td>0.02?</td>
<td>&lt;0.01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Meat/bone meal 6)</td>
<td>0.003 - 0.2</td>
<td>?</td>
<td>&lt;0.01</td>
<td>0.004 - 0.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Green feed drying 7)</td>
<td>0.05</td>
<td>0.004 - 0.04?</td>
<td>0.004 - 0.04</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feedstuff prod. 8)</td>
<td>1.511</td>
<td>?</td>
<td>&lt;10?</td>
<td>?</td>
<td>?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Food products</td>
<td>0.06 - 0.4</td>
<td>?</td>
<td></td>
<td>?</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pentachlorophenol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- wood</td>
<td>0.11 - 42?</td>
<td>0.5 - 26?</td>
<td>5 - 240?</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- leather</td>
<td>0.5</td>
<td>&lt;0.05</td>
<td>0.57</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- textiles</td>
<td>0.5</td>
<td>0.2</td>
<td>0.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorine bleaching</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- bleaching in DK</td>
<td></td>
<td></td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- cork</td>
<td></td>
<td></td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- paper/cardboard 9)</td>
<td>3.0 - 6.6</td>
<td>?</td>
<td>15 - 33</td>
<td>15 - 33</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other industrial processes</td>
<td></td>
<td></td>
<td>&lt;0.04?</td>
<td>&lt;0.04?</td>
<td>?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total (rounded)</td>
<td>12 - 1200?</td>
<td>6.3 - 19.2?</td>
<td>0.8 - 29.2?</td>
<td>0.2 - 0.7</td>
<td>&lt;11?</td>
<td>8.3 - 249?</td>
<td>6.5 - 14?</td>
<td></td>
</tr>
</tbody>
</table>
Figure cannot be estimated due to lack of data. The flow in question should be overlooked.

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 “export” covers dioxin in filter dust sold as material for flue gas cleaning operations.
5. The quantity stated under “export” covers dioxin in filter dust exported for zinc recovery. An estimated < 0.016 g l-TEQ will be reused in asphalt and cement manufacturing.
6. The quantity stated under “export” 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 “export” 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.

Since the substance flow analysis from 2000 the information from the source /dk-T E N I K 2000/ has been completed and published under the name of: “Measurements of dioxin emissions from selected secondary sources” /Schleicher et al. 2001/. The remaining information from this investigation is included in this update of the substance flow analysis, and the data that was already included have been revised because of minor differences between the temporary data used and the data published in the report /Schleicher et al. 2001/. In this report is therefore referred to /Schleicher et al. 2001/.

3.1 Coal power plants

Consumption of coal and coke in Denmark in 2001 accounted for approx. 175,000 TJ or approx. 6.9 million tonnes /Energistyrelsen 2002/, of which approx. 95% was used for production of electricity and heat by central power plants. The remainder was primarily used for energy supply for manufacturing purposes.

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-T EQ/year corresponding to an emission factor of 0.2 μg I-T EQ/ton, whereas an estimated 40 g I-T EQ 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-T EQ.

From an investigation in 1999 at a Danish coal powder power plant an emission to air of 4.7 pg I-T EQ/m³ (n,t at 5.8% oxygen) was reported /Fyns Amt 2000/. This emission corresponds to an emission factor of 33 ng I-T EQ/ton coal. The plant in question (Section 7 at Fynsværket) 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/.
At the same power plant, but in another section, dioxin measurement was made in July 2001. This section is firing with a mixture of coal, fuel oil, natural gas, meat and bone meal and straw. The sample from July was only made on coal and meat and bone meal. The result of the measurement shows an emission of 0.0006 ng I-TEQ/Nm$^3$. The yearly emission and the emission factor have not been calculated because of the different fuel types used.

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-T EQ/TJ. Assuming a conversion factor of 25 GJ/tonne of coal this equals a range of 0.027 - 0.18 µg I-T EQ/t. For residential heating the Inventory (section on Germany) states air emission factors of (Landesumweltamt Nordrhein-Westfalen 1997):

<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>Emission Factor (µg I-T EQ/ton)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>0.83 (0.36 - 1.92)</td>
</tr>
<tr>
<td>Lignite briquettes</td>
<td>0.62 (0.13 - 2.92)</td>
</tr>
<tr>
<td>Coke</td>
<td>0.61 (0.55 - 0.68)</td>
</tr>
</tbody>
</table>

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/:

<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>Emission Factor (µg I-T EQ/TON)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal power plant</td>
<td>0.35 µg I-T EQ/ton</td>
</tr>
<tr>
<td>Industrial plant</td>
<td>1.6 µg I-T EQ/ton</td>
</tr>
</tbody>
</table>

However the given international figures are substantially higher than the Danish measurement from Section 7 at Fynsværket. It is therefore chosen to consider the Danish measurement as valid for the Danish combustion of coal in power plants. To comply with the uncertainty from this estimate, the emission level will be used with an uncertainty of ± factor 10.

Based on this assumption, it seems reasonable to accept that

- approx. 6.5 million tonnes were combusted at an emission rate of approximately 3.3 - 330 ng I-T EQ/ton = 0.02 - 2.2 g I-T EQ/year
- approx. 0.4 million tonnes were combusted at an emission rate of 0.13 - 2.92 µg I-T EQ/ton = 0.05 - 1.0 g I-T EQ/year

These assumptions result in a total emission to air of 0.07 - 3.2 g I-T EQ/year which is a bit higher than the previous estimate of 0.4 - 2.3 g I-T EQ/year /Hansen, 2000/.

The amount of residues from coal combustion generated in Denmark in 2000 was approx. 1.2 million tons which are 100% recycled for cement, concrete, filling and other purposes. /Danish EPA, 2001/.

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-T EQ/kg for grate ash and 0.23 - 0.87 ng I-T EQ/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 0.2 - 1.1 g I-T EQ/year. It is noted that this estimate is considerably below the previous estimate for Denmark (40 g I-T EQ – see the beginning of this section) which is due to different data sources. Recognizing that neither of the data sources likely are representative of the coal types and operating conditions found at coal power plants in Denmark today, the choice is made here to accept a range of 0.2 - 40 g I-T EQ/year as the best estimate of the dioxin amount collected with residues from coal combustion in Denmark.

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 2002/):

Natural gas: 191,800 T J ~ 4,800 million Nm\(^3\)

Oil products for other purposes than transport: 170,000 T J ~ 3.95 million tonnes

Around 80% of the consumption of natural gas was used for industrial processes, power generation and other large-scale uses, whereas the remaining 20% mainly was used for residential heating [Energistyrelsen 2002/].

The Danish consumption of orimulsion is approximately 33,400 T J or 1,094,000 tons [Energistyrelsen, 2002/ (included in the 3.95 million tonnes)

Dioxin formation and disposal

In connection with the data collection for the update of the substance flow an analysis for dioxin a measurement from combustion of orimulsion from 1997 has shown up.

The measurement shows a dioxin emission of 0.0124 ng I-T EQ/Nm\(^3\), which correspond to an annual emission from combustion of orimulsion at approximately 38 - 343 mg I-T EQ/year, assuming an uncertainty of ± factor 3 (reference is made to section 1.5). The emission factor is approximately 0.0001 mg I-T EQ/ton orimulsion used.

No other 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-T EQ/T J. Assuming a conversion factor of 40 GJ/1000 Nm\(^3\) this equals a range of 0.0008 - 0.0012 ng I-T EQ/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-T EQ/m\(^3\)
Heating oil: 0.04 (0.02 - 0.09) ng I-T EQ/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: 0.24 - 0.48 g I-TEQ/year
Total, natural gas and oil: 0.38 - 0.91 g I-TEQ/year

Adding the emission for orimulsion the total emission from other fossil fuels is equal to 0.4 - 1.3 g I-TEQ/year.

The total emission for other fossil fuels is a little higher than the estimate from SFA 2000 /Hansen, 2000/, where the total emission was 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 decentral, combined heat and power plants (CHP).

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

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

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.

<table>
<thead>
<tr>
<th>Number of plants</th>
<th>Firewood</th>
<th>Forest wood chips</th>
<th>Wood pellets</th>
<th>Wood waste</th>
<th>Straw</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood stoves</td>
<td>370,000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Farm boilers</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>9000</td>
</tr>
<tr>
<td>District heating</td>
<td>50</td>
<td>40</td>
<td></td>
<td></td>
<td>50</td>
</tr>
<tr>
<td>Smaller stoker boilers</td>
<td>50</td>
<td>200</td>
<td>200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Industrial CHP plants</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>De-central CHP plants</td>
<td>5</td>
<td>1</td>
<td>1</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Central CHP plants</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
<td>1</td>
</tr>
</tbody>
</table>

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

3.3.1 Private 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 of good quality of hardwood from forestry. The rest included wood from private gardens, replacement of old hedges, industrial surplus wood etc. Paper, cardboard, milk cartons, 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, which can act as catalysts of the dioxin formation. 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.

The Danish Environmental Protection Agency has in 2001 introduced a campaign on private wood stoves and dioxin. The effect of this campaign can however not be evaluated as measurements on flue gas from private wood stoves are not present on a larger scale.

Plant activity
Number of stoves in 1998 370,000
Total consumption of wood 1998 429,800 tonnes dry weight
Energy production 8,339 T J
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-T EEq/year with an uncertainty range of 10 - 50 g N-TEQ/year based on an annual wood consumption of 222,000 tons. 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-T EQ/Nm$^3$. The emission factor was 1.9 µg N-T EQ/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-T EQ/year ± 60%. In 1995 the Danish consumption of firewood had increased to 578,231 tons and the dioxin emission correspondingly to 1.1 g N-T EQ/year.

In a new Danish investigation clean birch and dried clean excess wood from manufacturing was fired in a new stove /Schleicher et al. 2001/. 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-T EQ/tonnes wood for birch and 1.9 µg I-T EQ/tonnes wood for excess wood. Night firing gave emissions factors of 0.61 µg I-T EQ/tonnes wood for birch and 0.64 µg I-T EQ/tonnes wood for excess wood. The results for ordinary firing and night firing are mean values of two samples made at the same time. There is no official explanation why ordinary firing with clean birch results in a higher dioxin emission than the ordinary firing with excess wood.

In 1993 the Swedish Environmental Protection Agency reported an emission factor for stoves of 0.13 - 0.3µg N-T EEq/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-T EQ/tonnes dry clean wood and 13 - 29 µg I-T EQ/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-T EQ/tonnes clean wood and 3.230 µg I-T EQ/tonnes household waste /Schawitz 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-T EQ/tonnes wood and ranged 0.53 - 0.94 µg I-T EQ/tonnes wood. Burning of wood at open fireplaces resulted in a lower typical value of 0.46 µg I-T EQ/tonnes wood and a range of 0.07 - 1.25 µg I-T EQ/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: \(1 \mu g \text{ I-TEQ/ton}\)
- Slightly contaminated (without PCP): \(50 \mu g \text{ I-TEQ/ton}\)
- Strongly contaminated (with PCP): \(500 \mu g \text{ I-TEQ/ton}\)

This assessment is here accepted as a reasonable illustration of the variations caused by different types of combustible materials used in wood stoves. The Danish results from day and night firing correspond quite well to the value for clean wood. 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 \(\mu g \text{ I-TEQ/ton}\) equals a total air emission of 0.43 – 22 g I-T EQ/year.

The National Environmental Research Institute has in November 2002 conducted a dioxin measurement of air in a housing area with several private wood stoves. The measurement showed a dioxin content of 70 femtogram I-TEQ/m\(^3\) (femtogram = \(10^{-15}\)g), which is almost three times as much as the measured level in rural area /Vikelsøe, 2003/.

Residues

The National Environmental Research Institute has in 2002 made a measurement of the dioxin content in ash from a wood stove. This measurement shows a dioxin content of 0.03 ng I-T EQ/kg dry matter /The Environmental Research Institute, 2002. Dumler-Gradl et al. 1993 & 1995 quoted by Dyke et al. 1997/ gives figures of 75 – 500 ng I-T EQ/kg ash and 500 – 9000 ng I-T EQ/kg soot for a wood based household heating system. They also give soot values of 4 – 42000 ng I-T EQ/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 \(\mu g \text{ I-T EQ/kg soot}\) /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 tons and a dioxin content of 0.03 – 500 ng I-T EQ/kg ash, the amount of dioxin to be disposed of with ash is estimated at 0.0001 – 2.2 g I-T EQ/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 in this context has not been estimated, but most of the soot will be directed to incineration, as it is normally disposed of with the household waste /Schleicher, 2003a/.
3.3.2 Other biomass combustion 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-T EQ/GJ. That will correspond to about 3 ng I-TEQ/GJ. The translation factor from Eadon-T EQ 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

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

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/Nm³). From the grated bale boiler the air emission concentration was calculated to 16 ng N-TEQ/m³ (n, t) at 10% O₂. The airflow was about 600 m³/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/tons straw. As an average for all 3 plants investigated, the emission factor can be calculated to 77 µg N-TEQ/tons 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/tons straw /Schleicher et al. 2001/.

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/m³). 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 °C/176°C
- Air flows: 3,500/4,500 m³/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 1.7 µg N-T EQ/ton and min./max. factors of 0 and 5 µg N-T EQ/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 24, 21 and 24 ng I-TEQ/ton straw /Schleicher et al. 2001/. The investigation was originally based on 4 samplings, but one of the samplings was discarded, so only results from 3 samplings, each lasting for 6 hours, are recorded. The temperature of the flue gas over the filter ranged from 110 to 120ºC.

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 /Schleicher et al. 2001/. 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 18, 19 and 46 ng I-TEQ/ton chips respectively, whereas the factors for crushed chipboards were determined as 19, 23 and 35 ng I-TEQ/ton chipboard /Schleicher et al. 2001/.

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-T EQ/ton pellets /Schleicher et al. 2001/.

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 accounted 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-T EQ/Nm$^3$/ELSAM projekt 2000b/. Assuming 10 N m$^3$/kg of straw or chips, emission factors of 4 – 53 ng I-T EQ/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-T EQ/ton wood with a best estimate of 5 µg I-T EQ/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-T EQ/TJ for clean wood and 0.75 – 6,200 µg I-T EQ/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 \( \mu g \) I-TEQ/ton wood for clean wood and 0.015 – 125 \( \mu g \) I-TEQ/ton contaminated wood.

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

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

In December 2000 measurements were carried out on a Danish 51 MW combined heat and power station, which fires with industrial wood waste. The flue gas is purified through an electrostatic precipitator. The two measurements resulted in a mean dioxin emission of 0.016 ng I-TEQ/Nm\(^3\). The average emission factor of two simultaneous measurements was 95 ng I-TEQ/ton wood./Schleicher et al., 2001/

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

<table>
<thead>
<tr>
<th>Burning Type</th>
<th>Emission Factor (( \mu g ) I-TEQ/ton)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Straw burning – no flue gas cleaning</td>
<td>1 - 50</td>
</tr>
<tr>
<td>Straw burning – flue gas cleaning</td>
<td>0.004 - 2</td>
</tr>
<tr>
<td>Wood burning – no flue gas cleaning</td>
<td>0.2 – 10</td>
</tr>
<tr>
<td>Wood burning – flue gas cleaning</td>
<td>0.01 – 5</td>
</tr>
</tbody>
</table>

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. These 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 and bag filters and to a lesser extent electrostatic precipitators, whereas real dioxin abatement is 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 100\(^\circ\)C and will certainly not exceed 200\(^\circ\)C. 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 /Schleicher et al. 2001/. 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 (smaller plants):

\[ 311,000 \text{ tonnes} \sim 0.3 - 15 \text{ g I-TEQ/year} \]

Straw burning – flue gas cleaning (larger plants):

\[ 425,000 \text{ tonnes} \sim 0.002 - 0.9 \text{ g I-TEQ/year} \]

Wood burning – no flue gas cleaning (larger plants):

\[ 88,900 \text{ tonnes} \sim 0.02 - 0.9 \text{ g I-TEQ/year} \]

Wood burning – flue gas cleaning (larger plants):

\[ 524,400 \text{ tonnes} \sim 0.005 - 2.6 \text{ g I-TEQ/year} \]

The total emission of dioxins to air from biomass combustion plants in Denmark can thus be estimated at 0.3 - 19.4 g I-TEQ/year, corresponding to 0.3 -15 g I-TEQ/year for smaller plants and 0.03 - 4.4 g I-TEQ/year for larger plants.

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

Seven measurements of dioxin content in ash from four straw furnaces have been made by the National Environmental Research Institute in 2002. The highest measurement shows a dioxin content of 12.4 ng I-TEQ/kg dry matter and the lowest result is 0.2 ng I-TEQ/kg dry matter. Assuming that the data are normally distributed the mean value equals 3.7 ng I-TEQ/kg dry matter and the true average can be expected to be found in the range 0.38 - 7 ng I-TEQ/kg dry matter, using a 90 % confidence level.

Furthermore two measurements have been made on ash from two district heating stations firing with straw showing a dioxin content of 0.1 and 0.7 ng I-TEQ/kg dry matter respectively. Two measurements of the dioxin content in ash from two woodchip-fired district heating stations have also been carried out. The dioxin content in the ash from the two stations was measured to be 0.03 ng I-TEQ/kg and 1.4 ng I-TEQ/kg dry substance respectively. The 90 %
The confidence level of these four measurements corresponds to <0.01-1.3 ng I-TEQ/year.

The new Danish measurements indicate that the dioxin concentration in residues from smaller plants, as farm boilers and smaller stoker boilers, is higher than the dioxin concentration in residues from larger plants.

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-T EQ/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-T EQ/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-T EQ/kg in bottom ash and 117 - 272 in filter ash has been reported /Oehme & Müller 1995/. The same study reported concentrations of 22 ng T EQ/kg bottom ash and 722 - 7620 ng T EQ/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-T EQ/kg) and lower than bio compost. Fly ashes from waste wood incineration had much higher dioxin content of 700 - 21,000 ng I-T EQ/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 23,300 µg I-T EQ/ton dust and 30 - 3,300 µg I-T EQ/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 T EQ/kg and grit ash levels of 891-1070 ng T EQ/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-T EQ/kg /Bremmer et al. 1994/.

The new Danish measurements will be used to estimate the annual content of dioxin in residues from biomass combustion. Because of the fact that measurements from smaller plants have shown higher dioxin levels than measurements from larger plants, it is chosen to divide the estimate for dioxin in residues into two categories:

- Smaller plants: Farm boilers and small stoker boilers: 13,700 tons residues per year.
Larger plants: District heating plants, Industrial CHP plants and decentral and central CHP plants: 22,300 tons per year.

Using the Danish concentration range obtained from the new measurements on biomass residues from smaller plants (0.38 - 7 ng I-TEQ/kg dry matter), the annual content of dioxin in residues from these plants can be estimated at approximately 0.005 - 0.1 g I-TEQ/year.

For larger plants the interval of <0.001 - 1.3 ng I-TEQ/kg dry matter results in an annual dioxin content of <0.001 - 0.03 g I-TEQ/year.

The total of the two intervals for annual dioxin content is considerably lower than the estimate used in SFA 2000 /Hansen, 2000/, where the dioxin quantity was added up to 0.04 - 36 g I-TEQ/year based on international values.

As ash from farm boilers often is spread on soil the dioxin content to soil could be up to 0.005 - 0.09 g I-TEQ/year, as ash from farm boilers correspond to 12,800 tons of the 13,700 tons of ash from smaller plants.

### 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 is presented in section 3.1 to 3.3 are summarised in table 3.4.

<table>
<thead>
<tr>
<th>Activity/product</th>
<th>Consumption by products</th>
<th>Formation to air</th>
<th>Formation to water</th>
<th>Formation to soil</th>
<th>Formation to waste</th>
<th>Export</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal power plants</td>
<td>0.3 - 43?</td>
<td>0.1 - 3.2</td>
<td></td>
<td></td>
<td></td>
<td>0.2 - 40?</td>
</tr>
<tr>
<td>Other fossil fuels</td>
<td>0.4 - 1.3</td>
<td>0.4 - 1.3</td>
<td></td>
<td></td>
<td></td>
<td>0?</td>
</tr>
<tr>
<td>Biomass</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Private wood stoves (1)</td>
<td>0.4 - 24.2?</td>
<td>0.4 - 22</td>
<td></td>
<td></td>
<td></td>
<td>0.0001 - 2.2?</td>
</tr>
<tr>
<td>- Other smaller plants (2)</td>
<td>0.3 - 15.2</td>
<td>0.3 - 15</td>
<td></td>
<td>0.0003 - 0.09</td>
<td></td>
<td>&lt;0.001 - 0.01</td>
</tr>
<tr>
<td>- Other larger plants</td>
<td>0.03 - 4.4</td>
<td>0.03 - 4.4</td>
<td></td>
<td></td>
<td></td>
<td>&lt;0.001 - 0.03</td>
</tr>
<tr>
<td>Total (rounded)</td>
<td>1.4 - 90</td>
<td>1.1 - 48</td>
<td></td>
<td>0.0004 - 2.3</td>
<td></td>
<td>0.2 - 42.2</td>
</tr>
</tbody>
</table>

? 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 to soil and waste adds up to a total of 0.0001 - 2.2 g I-TEQ/year. The precise distribution between soil and waste is not known.
2. The precise distribution between soil and waste is not known, but the quantity disposed of to soil will be less than 0.0003 - 0.9 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 firefighting 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 firefighting 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 luckily 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/m², whereas 4 other samples taken at distances of 90 - 450m from the company showed dioxin contents varying from 6 to 1 ng I-T EQ/m². The background level was also determined to 1 ng I-T EQ/m² /Danish EPA 2000a/. The data available are however too 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-
T E Q/year (estimated margin of uncertainty: 2.5 - 2,500 g I-T E Q/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-T E Q/year /Landesumweltamt Nordrhein-Westfalen 1997/. For the dioxin content of fire residues an estimate for Germany of 139 g I-T E Q/year (estimated margin of uncertainty: 4.3 - 4,300 g I-T E Q/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-T E Q/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-T E Q/kg respectively 200 ng I-T E Q/kg and 4900 ng I-T E Q/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-T E Q/kg material and 10,-20,000 tons of material would equal a total emission of 0.5 - 20 g I-T E Q per year.

For 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-T E Q 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-T E Q/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-T E Q/year
Collected with residues: 1 - 30 g I-T E Q/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 leftovers 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 tons/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 tons.

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. Reliable information about neither the extent of field burning nor dioxin measurements is available.
Dioxin formation and disposal
No measurements of dioxin formation related to such fires have 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: \(14.5 - 571.5 \mu \text{I-TEQ/ton of wood}\)

Min./Max: \(1 - 1,125 \mu \text{g I-TEQ/ton of wood}\)

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: \(1 \mu \text{I-TEQ/ton}\)

Slightly contaminated (without PCP): \(50 \mu \text{I-TEQ/ton}\)

Strongly contaminated (with PCP): \(500 \mu \text{I-TEQ/ton}\)

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 \(1 - 50 \mu \text{I-TEQ/t}\) equal a total emission of \(0.03 - 6.5 \text{g I-TEQ/year}\).

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 \(75 \mu \text{I-TEQ/ton}\) and \(42048 \mu \text{I-TEQ/ton}\) respectively. Assuming an amount of ash of approx. 1% of the amount of wood, \(25,000 - 130,000\) tons of wood will result in \(250 - 1300\) tons of ash. Assuming a dioxin content of \(75 - 42000 \mu \text{I-TEQ/t ash}\), bonfires and the like will result in \(0.02 - 55 \text{g I-TEQ/year}\) with ash and other residues that are dominantly 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 \(0.2 \text{g I-TEQ/year}\) 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 /Eneristyrelsen 2000/:

- Ships – fuel oil: Approx. 300,000 tons
- Ships – gas oil: Approx. 100,000 tons
- Trains – gas oil: Approx. 250,000 tons

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 gases 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 cremation (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 two crematories in Denmark were carried out in 2000 /Schleicher et al. 2001/.

The first crematory has a quite new oven which was installed in 1996 and is heated by natural gas. Each cremation in this oven lasts 6 hours corresponding to the cremation of 4 bodies (1.5 hour/body). There was totally made 4 measurements, where each sampling consisted of two simultaneous measurements carried out with 24 hours time difference. The flue gas temperature was approx. 345°C. The mean values of the two set of samplings was respectively 265 ng I-TEQ/cremation and 215 ng I-TEQ/cremation.

For the second crematory there are two oven lines, which both represent the old type of crematorium furnaces which have been extended with for example afterburning chambers. The type of oven is estimated to represent approximately 1/3 of the 50 crematorium furnaces in Denmark. There has been made one 5-6 hours measurement for each of the oven lines (cremation
of 3 bodies). The results of the two measurements were 930 ng I-TEQ/cremation for oven number 1 and 310 ng I-TEQ/cremation for the second oven. In February 2001 an additional measurement for each of the ovens was made. The results showed approximately 900 ng I-TEQ/cremation for oven number 1 and approximately 110 ng I-TEQ/cremation for the second oven.

The two ovens are not identical, so the difference in emission level can be caused by differences in the construction of the ovens. The differences can also be caused by disparity in weight and content of the bodies.

The two types of crematories is taken as representative of Danish crematories as per today. Furthermore two measurements have been made on a third crematory in 2002. The measurements, each lasting one cremation on the same oven, showed a dioxin emission of approximately 850 ng I-TEQ/cremation and approximately 400 ng I-TEQ/cremation. The measurements show high variation in emission concentration, although the samples are from the same oven, but they are at the same level as the other Danish measurements. Based on these figures the emission to air in Denmark from crematories can be estimated to range between 6 mg I-TEQ/year and 70 mg I-TEQ/year (90 % confidence level) with a best estimate of 38 mg I-TEQ/year.

This estimate is a little higher than the estimate from SFA 2000 /Hansen, 2000/ where the total emission to air was estimated at 10 mg I-TEQ/year.

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

It is also noted that the air emission of dioxins from cremations 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 foundation 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 /Schleicher et al. 2001/. 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 to 15 ng I-TEQ/kg charcoals. The Danish import of charcoal for grilling and other purposes comes up to approx. 15,000 tons/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 0.0001 - 0.0002 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

<table>
<thead>
<tr>
<th>Activity/product</th>
<th>Consumption by products</th>
<th>Formation g I-TEQ/year</th>
<th>Emissions/losses (g I-TEQ/year)</th>
<th>Export</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>to air</td>
<td>to water</td>
</tr>
<tr>
<td>Fires</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- accidental fires</td>
<td>1.5 – 50?</td>
<td>0.5 – 20?</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>- other fires</td>
<td>0.05 - 61.5?</td>
<td>0.03 - 6.5?</td>
<td>0.01 - 27.5?</td>
<td>0.01 - 27.5?</td>
</tr>
<tr>
<td>Traffic</td>
<td>1.3 - 17</td>
<td>1.3 - 17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crematories</td>
<td>0.01-0.1</td>
<td>0.01-0.1</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>Other activities</td>
<td>0.1-0.2?</td>
<td>0.1-0.2?</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>Total</td>
<td>3 - 114?</td>
<td>2 - 29?</td>
<td>?</td>
<td>0.01 - 28?</td>
</tr>
</tbody>
</table>

? 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 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 has existed in Denmark until 2002. The company have from 2002 chosen to shut down the reclamation of cable scrap and will in the future only deal with transformer waste. The annual emission in next section will therefore only be valid for 2000-2001.

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% O₂ 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, which will be the main future activity. 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 hazardous 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 in the periode 2000 - 2001 can be summarised as follows:

- Total cable waste: approx. 2000 tonnes/year
- Total transformer waste: approx. 1800 tonnes/year
- Filter dust: approx. 1 kg/year
- Air emission: approx. 3.4 million N m³/year
Filter dust is sent to the central Danish facility for hazardous waste (Kommunekemi).

Dioxin formation and disposal
The dioxin emission to air has been measured once during reclamation of a mixture of scrap and transformer waste. This measurement was undertaken in December 2000 and showed a dioxin emission of 0.08 ng I-TEQ/Nm$^3$. Taking the result of this measurement as the level of dioxin emission from cable reclamation the total annual emission is estimated to be within the range of 0.03 - 0.2 mg I-TEQ/year. This interval includes an uncertainty of ± factor 3 (reference is made to section 1.5).

In SFA 2000/Hansen, 2000/ the total emission to air was estimated to be 0.005 - 5 g I-TEQ/year based on international experience.

5.1.2 Shredder plants

6 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 of the Danish shredder plants has made measurements of the dioxin emission from the production air flow in 2000 and 2001. The results of the two measurements show a total dioxin emission within the range of 1 - 15.4 mg I-TEQ/year.

A measurement of dioxin air emission from a second Danish shredder was made in 1999. The annual emission based on this measurement is approximately 0.5 - 4.3 mg I-TEQ/year, assuming an uncertainty of ± factor 3 /Fyns Amt 2000/.

The measurements from the Danish shredder plants correspond to air emission factors in the range of 0.01 - 0.09 µg I-TEQ/ton scrap manufactured. The European Dioxin Inventory (section on Germany) states values for dioxin emission to air of 0.06 - 0.67 µg I-TEQ/ton scrap /Landesumweltamt Nordrhein-Westfalen 1997/.

Adopting the three Danish measurement as valid to all Danish plants the total emission from shredder plants in Denmark the emission level can be estimated at approximately <1 - 79 mg I-TEQ/year, when a 90 % confidence level is used.

No data on the content of dioxin in scrubber sludge and other shredder residues are available. These residues are normally directed to Kommunekemi.
In SFA 2000 /Hansen, 2000/ the total dioxin emission from shredder plants was estimated at 7 mg I-TEQ/year.

5.2 Hazardous waste

5.2.1 Hazardous waste incineration

Kommunekemi that is the central facility for treatment of hazardous waste in Denmark, has 3 kilns, of which 2 kilns (F3 and F4) are now equipped with dioxin abatement. Hazardous waste is for the time being treated only in these two kilns. The third kiln, F1, has been closed down due to reconstruction in the period 2000 - 2002. In connection with the rebuilding this kiln has also been equipped with dioxin abatement.

Before the air stream enters the dioxin abatement, it is cleaned by a bag filter (one kiln) or an electrostatic precipitator (the other kilns), and a wet flue gas facility. The temperature in the bag filter and the electrostatic precipitator is around 195°C, whereas the temperature over the dioxin abatement 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 hazardous waste. This plant also treats clinical hospital waste. Totally the plant treats 4,700 tonnes waste/year of which 1,600 t is hazardous 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.

Furthermore a Danish company uses turpentine waste as fuel for a combustion plant, which generates heat for the production.

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

- Oil and hazardous waste burned: approx. 90,000 tonnes/year
- Oil and tar polluted soils burned: approx. 20,000 tonnes/year
- Air emission cleaned by dioxin abatement: approx. 600 million Nm³/year
- Air emission without dioxin abatement: approx. 100 million Nm³/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 abatement is 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 earlier measurements have shown very high concentrations of dioxin. In order to fulfil the present limit value of 0.1 ng I-TEQ/N m$^3$, Kommunekemi has redesigned rotary kilns and flue gas cleaning systems, which means that F3 and F4 have complied with the limit value since July 2000. Dioxin abatement has also been installed in order to comply with the legal conditions for burning of waste.

Until June 2000 Kommunekemi had permission to carry out thermal treatment of polluted soil on F1. In 1999 Kommunekemi also used F1 for experiments on incineration of shredder waste (ASR, Automotive Shredder Residues). For a short period Kommunekemi had also permission to use it for treatment of liquid hazardous waste, because F3 and F4 were under reconstruction. The use of F1 for other purposes than thermal treatment of soil gave high emissions and was therefore stopped. /Kjærgaard, 2003/

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) from F1 have been obtained /Danish EPA 2000b/:

<table>
<thead>
<tr>
<th>Year</th>
<th>Type</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1999</td>
<td>ASR</td>
<td>2.7</td>
</tr>
<tr>
<td>1999</td>
<td>Liquid waste</td>
<td>36</td>
</tr>
<tr>
<td>1999</td>
<td>Liquid waste/polluted soil</td>
<td>200</td>
</tr>
<tr>
<td>1999</td>
<td>Liquid waste</td>
<td>3.5</td>
</tr>
<tr>
<td>2000</td>
<td>Polluted soil</td>
<td>0.6</td>
</tr>
<tr>
<td>2000</td>
<td>Polluted soil</td>
<td>0.5</td>
</tr>
<tr>
<td>2000</td>
<td>Polluted soil</td>
<td>0.4</td>
</tr>
<tr>
<td>2000</td>
<td>Polluted soil</td>
<td>0.2</td>
</tr>
<tr>
<td>2000</td>
<td>Polluted soil</td>
<td>0.2</td>
</tr>
</tbody>
</table>

The kiln F1 has been closed down due to reconstruction in the period from July 2000 - 2002, but has re-opened in December 2002. F1 has been closed down because the kiln no longer will be used for treatment of polluted soil. It will instead be used for treatment of hazardous waste like F3 and F4. The adjustment means that F1 has to comply with the demands for combustion of waste and the kiln will therefore be equipped with dioxin abatement, when it goes into operation again. /Kjærgaard, 2003/.

According to /Danish EPA 2000b/ Kommunekemi has estimated the total emission from F1 during 1999 to 2 – 2.5 g I-TEQ. This estimate will probably not correspond to the dioxin emission, when kiln F1 is put into service again. The annual emission for kiln F1 is therefore not calculated.

For the two other incinerators F3 and F4 equipped with dioxin abatement the following emission measurement results for dioxin (I-TEQ) have been obtained:
F 3

1999 April  Normal Operation   0.7 ng/Nm
1999 December Normal Operation   0.04 ng/Nm
2000 March Normal Operation   0.01 ng/Nm
2000 May Normal Operation   0.007 ng/Nm
2000 August Normal Operation   0.012 ng/Nm
2000 October Normal Operation   0.034 ng/Nm
2001 May Normal Operation   0.02 ng/Nm
2001 October Normal Operation   0.007 ng/Nm
2002 April Normal Operation   0.006 ng/Nm
2002 October Normal Operation   0.006 ng/Nm

*) Without dioxin abatement

F 4

1999 April  Corrosion Problems  1.2 ng/Nm
1999 April  Corrosion Problems  0.4 ng/Nm
1999 June  Corrosion Problems  0.35 ng/Nm
1999 August Corrosion Problems  0.06 ng/Nm
1999 December Normal Operation  0.05 ng/Nm
2000 May Normal Operation  0.003 ng/Nm
2000 November Normal Operation  0.100 ng/Nm
2001 May Normal Operation  0.100 ng/Nm
2001 August Normal Operation  0.006 ng/Nm
2001 October Normal Operation  0.009 ng/Nm
2002 May Normal Operation  0.01 ng/Nm
2002 October Normal Operation  0.01 ng/Nm

The total dioxin emission for kiln F3 and F4 during the period 2000 - 2002 can be calculated as follows:

F3: Average emission for 2000 - 2002 0.013 ng/Nm^3 and 300 million Nm^3/year. Best estimate for total emission is 3.8 mg I-TEQ/year, ranging from 2.1 - 5.5 mg I-TEQ/year using a 90% confidence level.

F4: Average emission 0.04 ng/Nm^3 and 300 million Nm^3/year. Best estimate for total emission is 12 mg I-TEQ/year, ranging from 2.3 - 21.8 mg I-TEQ/year.

In addition to F3 and F4 a CIS plant is used. This plant is a container-based rotary kiln combustion system, which has a capacity of approximately 300 kg/hour and an operation temperature at 1100°C - 1200°C. Contrary to F3 and F4 this kiln is a removable pilot plant. It also has a very low capacity compared to these two kilns.

Three measurements of dioxin emission to air have so far been made on the CIS plant during combustion of a combination of fluid and solid waste with low chlorine load:

2000 May 0.04 ng I-TEQ/Nm^3
2001 January 0.001 ng I-TEQ/Nm^3
2002 October 0.01 ng I-TEQ/Nm^3
The measurements correspond to an emission of approximately <0.01 - 0.7 mg I-TEQ/year, when a 90% confidence level is used.

Assessed on the basis of the measurements during 2000 - 2002 from F3, F4 and the CIS plant, the best estimate for the total dioxin emission from Kommunekemi is approximately 16 mg I-TEQ/year with an uncertainty interval ranging from 4.4 - 28 mg I-TEQ/year. The estimate does not include a future emission from the F1 kiln, as F 1 will be equipped with dioxin abatement, when it goes in operation again.

In SFA 2000 /Hansen, 2000/ the total emission to air was calculated at 2.2 - 2.7 g I-TEQ/year, of which F1 had an emission of approximately 2-2.5 g I-TEQ/year. This emission from F1 must be expected to decrease significantly.

Regarding emission with wastewater from flue gas cleaning, Kommunekemi has estimated a total emission of 0.003 mg I-TEQ/year for 2001 /Kommunekemi 2002/.

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. 0.4 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 are not available either.

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

The dioxin emission in the flue gas from a Danish plant that combusts turpentine waste was measured in 2001. The result shows a dioxin emission at 0.052 ng I-TEQ/N m³, which means an emission of approximately 0.2 - 1.6 mg I-TEQ/year. This interval is assuming an uncertainty of ± factor 3. The emission factor of the combustion plant is approximately 0.0018 mg I-TEQ/ton turpentine incinerated.

Emission of brominated dioxins
In autumn 2002 the National Environmental Research Institute has conducted four measurements of the air emission of brominated dioxins on kiln 3 and kiln 4 respectively /the National Environmental Research Institute, 2002/.

No official method is at the time being available for converting the measured values into I-TEQ, but as earlier mentioned WHO suggests that the current toxicity equivalency factors for chlorinated dioxins are also applied to brominated dioxins on an interim basis /IPCS 1998/. This is done for the new measurements to get an estimate of the annual dioxin emission of brominated dioxins from treatment of hazardous waste. The measurements do not represent a complete investigation as it only has been possible to include
congeners on the tetra and penta level. Hexa-, hepta- and octa-congeners are thus not included in the results presented. Furthermore many of the congeners cannot be identified specifically from the measurements, and this means that it is not possible to use I-TEF for these measured concentrations of brominated dioxins and thereby calculate a total emission in g I-TEQ/year. The measurements have however identified some specific congeners, where I-TEF will be used to estimate a total I-TEQ concentration for the specific congeners, compare table 5.1:

<table>
<thead>
<tr>
<th>Measured specific congeners</th>
<th>I-TEF</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Br-2378-Cl4-DD</td>
<td>0.5</td>
</tr>
<tr>
<td>23-Br2-78-Cl2-DD</td>
<td>1</td>
</tr>
<tr>
<td>2378-TeBDD</td>
<td>1</td>
</tr>
<tr>
<td>12378-PeBDD</td>
<td>0.5</td>
</tr>
<tr>
<td>3-Br-278-Cl3-DF</td>
<td>0.1</td>
</tr>
<tr>
<td>1-Br-2378-Cl4-DF</td>
<td>0.05</td>
</tr>
<tr>
<td>2378-TBDF</td>
<td>0.1</td>
</tr>
<tr>
<td>12378-PeBDF</td>
<td>0.05</td>
</tr>
<tr>
<td>23478-PeBDF</td>
<td>0.5</td>
</tr>
</tbody>
</table>

On the basis of the measured values for the specific congeners and the I-TEF values from table 5.1, the annual emission of brominated dioxins can be estimated to be approximately <0.009 - 0.06 g I-TEQ/year with a best estimate of approximately <0.04 g I-TEQ/year (90 % confidence level). This emission value represents with certainty an under estimate of the real emission, but any estimate of the real emission value must be regarded as highly uncertain. Based on an anlysis of the chromatographies for the congeners it is estimated that the real estimate can be up to approximately a factor 5 higher, but most likely not a factor 100 /Vikelsøe, 2003a/.

5.2.2 Incineration of waste oil

Apart from the waste oil received and incinerated at the central Danish facility for hazardous 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 EPA, 1995/) is that PCBs are only registered in unrefined waste oil and in concentrations below 1 mg/kg.

In year 2000 around 20,000 tons waste oil was incinerated at local district heating plants /Danish EPA, 2001/. Measurements of the air emission of dioxins caused by incineration of waste oil at district heating plants have been carried out in three plants during spring/summer 2000 and at one plant in 1999.

One of the plants in question is equipped with an alkaline scrubber for cleaning of off-gases. The fuel incinerated was unrefined waste oil.
measurements were conducted each lasting for 4 hours. Air emission factors are ranging between 300 and 1,640 ng I-TEQ/ton waste oil /Schleicher et al. 2001/.

The second district heating plant, which is firing with re-refined waste oil, shows an emission factor of approximately 30 ng I-TEQ/ton waste oil. At the third plant, also firing with re-refined waste, a similar result has shown, as the one sample taken under normal operation shows an emission factor of 36 ng I-T EQ/ton waste oil. At the same plant a sample was taken under abnormal combustion conditions, and it shows an emission of 970 ng I-T EQ/ton waste oil. /Schleicher et al. 2001/.

In 1999 a measurement was made at a fourth Danish district heating plant, which is also using re-refined waste oil. This measurement also showed an emission factor of approximately 30 ng I-TEQ/ton waste oil.

In addition to the measurements from district heating plants measurements have been carried out in 2002 at two waste-oil fuelled boilers generating heat for productions. The emission factor is approximately 2.5 µg I-T EQ/ton waste oil for the one boiler and 600 ng I-T EQ/ton waste oil for the other. An earlier measurement from 2001 showed an emission factor of approximately 8 µg I-T EQ/ton waste oil, but this measurement was made while using a too high concentration of salt in the scrubber-cleaning water. This concentration was normalized in the measurements from 2002.

Using the emission factors from the Danish plants, the best estimate of the total dioxin emission to air is 65.4 mg I-TEQ/year, with the uncertainty interval ranging from <1 - 167.3 mg I-T EQ/year, using 90% confidence level. The total emission is most likely not as high as the high interval limit, because most of the waste oil used is incinerated in district heating plants and re-refined before incineration. Re-refined waste oil can according to Schleicher (2003c) be compared to normal oil.

In SFA 2000 /Hansen, 2000/ the annual emission is estimated at 45 mg I-T EQ/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 N ovo 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 5.2) 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 5.2
Sources of dioxins in combustible waste assumed to be directed to municipal waste incineration in Denmark

<table>
<thead>
<tr>
<th>Source</th>
<th>Estimated quantity g l-TEQ/year</th>
<th>Reference to section</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorinated dioxins:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clay for decoration and educational purposes</td>
<td>0.004 - 5</td>
<td>2.2.1</td>
</tr>
<tr>
<td>PCP treated wood 1)</td>
<td>5 - 240?</td>
<td>2.6.1</td>
</tr>
<tr>
<td>PCP treated leather 1)</td>
<td>0.5?</td>
<td>2.6.2</td>
</tr>
<tr>
<td>PCP treated textiles 1)</td>
<td>0.3</td>
<td>2.6.3</td>
</tr>
<tr>
<td>Cork - bleached</td>
<td>&lt;0.01</td>
<td>2.7.2</td>
</tr>
<tr>
<td>Paper and cardboard</td>
<td>1.5 - 3.3</td>
<td>2.7.2</td>
</tr>
<tr>
<td>Residues from wood stoves</td>
<td>0.32 - 2.2?</td>
<td>3.3.1</td>
</tr>
<tr>
<td>Residues from accidental fires 2)</td>
<td>1 - 30</td>
<td>4.1.1</td>
</tr>
<tr>
<td>Residues from other fires 2)</td>
<td>0.01 - 27.5?</td>
<td>4.1.2</td>
</tr>
<tr>
<td>Lime filter dust as filter material</td>
<td>&lt;0.08</td>
<td>2.2.5</td>
</tr>
<tr>
<td>Other sources</td>
<td><em><strong>?</strong></em></td>
<td>4.4</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>9 - 31D</td>
<td>2.13</td>
</tr>
<tr>
<td>Brominated dioxins:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brominated flame retardants (in plastics)</td>
<td>&lt;2 - 60)</td>
<td></td>
</tr>
</tbody>
</table>

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. By the end of year 2002 2/3 of the Danish waste was incinerated at waste incineration plants which are capable of complying with the new limit value for dioxin of 0.1 ng l-T EQ/N m³ /Danish EPA 2002/. Most of the remaining waste incineration plants are planning to install dioxin abatement before the end of year 2004. Two of the 31 incineration plants are however first planning to finish the installation of filters in 2005 and three of the 31 incineration plants have no intention of installing dioxin abatement, because they already have measured low emissions that comply with the limit value 0.1 ng I-T EQ/N m³ /Danish EPA 2003/. 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 municipal solid waste incinerated in Denmark comes up to approx. 2.9 million tonnes per year (2000-figure /Danish EPA 2001/). In table 5.3 is indicated the knowledge available as per spring 2000 regarding installation of special dioxin abatement and for plants without such abatement 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 5.3. To the best of knowledge none of the measurements undertaken is based on a sampling time exceeding 6 hours. Continuous long term measurements, lasting 2 - 6 weeks, is a new way of measuring the emission, but so far Belgium is the only country that has implemented long term measurements on municipal waste incineration plants. Long term measurements were implemented in Belgium after a number of long term measurements detected emissions limits being exceeded massively, namely exceedings and/or deviating process conditions that the random 6 hour sampling did not detect. The annual expenses to long term measurements constitute more than 2 - 3 time as much as the annual expenses to conventional biannual 6 hour sampling. /Schleicher, 2003b/. 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. Only little factual knowledge is available on this issue, but the significance to the total emission should not be overlooked.

The available Danish measurements from the period 2000 - 2002 is summarised in table 5.3. 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 5.3
Dioxin emissions to air from municipal waste incineration in Denmark 2000 - 2002.

<table>
<thead>
<tr>
<th>Flue gas cleaning process 1)</th>
<th>Dioxin concentration (ng I-TEQ/Nm³ 2)</th>
<th>Waste incinerated 1000 tonnes³)</th>
<th>Dioxin emission g I-TEQ/year ⁴)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Min.</td>
<td>Max.</td>
</tr>
<tr>
<td>No dioxin abatement Wet</td>
<td>2.3</td>
<td>0.9</td>
<td>4.0</td>
</tr>
<tr>
<td>Semidry</td>
<td>0.2</td>
<td>0.1</td>
<td>0.3</td>
</tr>
<tr>
<td>Dry</td>
<td>0.4</td>
<td>0.2</td>
<td>0.6</td>
</tr>
<tr>
<td>Dioxin abatement</td>
<td>0.04</td>
<td>0.02</td>
<td>0.1</td>
</tr>
<tr>
<td>Sum</td>
<td>2911</td>
<td>15.7</td>
<td>6.4</td>
</tr>
</tbody>
</table>

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

No dioxin abatement, wet:

No dioxin abatement, semi-dry: I/S KARA (line 3), I/S KAVO, Affaldscenter Århus, I/S Reno-Nord.

No dioxin abatement, dry: VEGA, REFA, BOFA, Vestfyn.

Dioxin abatement: REFA, Fynsværket, Vestforbrænding, Nordforbrænding, KARA (line 4 and 5), Svendborg, Mønderupforbrænding, Vejen Kraftvarmeværk, Horsens Kraftvarmeværk, Grenå Kraftvarmeværk.

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. The amount of waste incinerated is in general reported from the municipal waste incineration plants. If no information has been available, the amount has been estimated from the amount used in the substance flow analysis from 2000.

4. Assumed 6.5 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 ± factor 3 of the calculated best estimate, when only two measurements are available.

The total annual emission of dioxin from Danish municipal waste incineration plants can, on the basis of the 92 measurements used in the investigation, be estimated at approximately 15.7 g I-TEQ/year. The assumed interval of uncertainty for this value is 6.4 - 28.9 g I-TEQ/year. The annual value was estimated to be 21.1 g I-TEQ/year in SFA 2000 /Hansen, 2000/, within a range of 11 - 42 g I-TEQ/year (also 90% confidence).

The investigation from 2002 supports the theory that the type of flue gas cleaning system to some extent determines the dioxin emission level. In the report from 2000 it was found that dry processes are better than wet and semidry - the same picture can by and large be seen in the investigation from 2002.

During the period from 1999 to 2001 the amount of waste that is dioxin-cleaned has grown from 839,000 tons to 1,423,000 tons. This is the primary reason for the reduction of the annual emission, since the amount of waste has moved from wet flue gas cleaning to dioxin cleaning. It should be noted that the dioxin abatement systems are still in commissioning phase on some of the plants. The full effect of the installed dioxin abatement has perhaps not shown yet, as most of the abatement equipment has a running-in period before it is getting the total efficiency.

With respect to uncontrolled burning of waste recent American investigations have revealed that burning of domestic waste containing 0.0%, 0.2 %, 1% and 7.5 % PVC generated 14 ng I-T EQ/kg respectively 80, 200 and 4900 ng I-T EQ/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.

Emission of brominated dioxins
The National Environmental Research institute has in autumn 2002 conducted an investigation of the content of brominated dioxins in the flue gas from the municipal waste incineration plant Vestforbrænding /the National Environmental Research Institute, 2002/. These measurements have been made according to the same method as the measurements that have been carried out at Kommunekemi, compare section 5.4, and the same problem with estimating I-TEQ emission is therefore present. As for Kommunekemi the measurements from Vestforbrænding A/S only include tetra- and penta congeners.

Only five measurements from the same plant are available, but it is chosen to use these measurements as an indication of the level of the annual emission of brominated dioxins. This estimate is indeed very uncertain, because the 31 Danish plants have different processes, waste and flue gas cleaning systems (Vestforbrænding has installed dioxin abatement). Furthermore the calculation only includes the specific measured congeners with an I-TEF value (compare section 5.2.1).

Using the measured values for the specific congeners and the I-TEF-values in table 5.1, the annual emission from Danish waste incineration plants can be estimated to be approximately <0.001 - 0.03 g I-TEQ/year. This emission value represents with certainty an under estimate of the real emission, but any estimate of the real emission value must be regarded as highly uncertain. Based on an analysis of the chromatographies for the congeners it is estimated that the real estimate can be up to approximately a factor 5 higher, but most likely not a factor 100 /Vikelsøe, 2003a/.

Residues
The available knowledge regarding dioxin content in residues from Danish waste incineration plants is indicated in table 5.4 from SFA 2000 /Hansen, 2000/. More measurements have been carried out in 2000 after finishing SFA 2000, but these measurements are covered by the 90% confidence interval stated in table 5.4. The waste quantities have been updated, which means that the annual emission has changed. As shown the total quantity may be estimated at 52 - 407 g I-TEQ/year. Of this quantity around 98% is collected with flue gas cleaning residues.
Table 5.4

<table>
<thead>
<tr>
<th>Waste quantity 1)</th>
<th>Dioxin concentration 2)</th>
<th>90% confidence interval around the mean 3)</th>
<th>Min. 4)</th>
<th>Max. 4)</th>
<th>Number of samples</th>
<th>Dioxin 90% confidence interval 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>t/year</td>
<td>ng I-TEQ/kg dry matter</td>
<td>g I-TEQ/year</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clinker</td>
<td>494,000</td>
<td>8.8 ± 3.7</td>
<td>5.1</td>
<td>17.8</td>
<td>6</td>
<td>2 - 5</td>
</tr>
<tr>
<td></td>
<td>68,000</td>
<td>4.162 ± 3.236</td>
<td>135</td>
<td>35.566</td>
<td>21</td>
<td>50 - 402</td>
</tr>
<tr>
<td>Sum (rounded)</td>
<td>562,000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>52 - 407</td>
</tr>
</tbody>
</table>

1) / Danish EPA, 2001/ - 2000 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 Valund 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-T EQ/kg respectively. The other 18 measurements show much lower difference. The highest and lowest figures are 380 and 6.476 ng I-T EQ/kg respectively with a 90% confidence interval around the mean of 1.037 – 2.243 ng I-TEQ/kg /Dansk RestproduktHåndtering 2000/.

Clinker will primarily be utilised for civil works (in this context also regarded as landfilling) or secondly landfilled, whereas flue gas treatment residues will be directed to landfilling only. In 2000 85,700 tonnes of flue gas treatment residues were exported for landfilling. This number is higher than the actual amount of created flue gas treatment residues, probably due to export of stored up flue gas cleaning products. It is therefore assumed that the major part of the dioxin in the flue gas treatment residues is exported.

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 hazardous waste and partly healthcare risk waste is in operation. This plant treats approx. 4,000 tons waste per year. The plant is equipped with bag filter, but has no special dioxin abatement. 2 measurements from 1999 gave results of 1.4 and 5.8 ng N-
respectively. Since then 10 measurements have been carried out, where the highest value is 31.4 ng I-TEQ/N m$^3$ and the lowest value is 0.1 ng I-TEQ/N m$^3$. Assuming that the measurements are normal distributed the average emission equals 3.9 ng I-TEQ/N m$^3$. The measurement are within the range of <1 - 9.5 ng I-TEQ/N m$^3$ using a 90 % confidence level. This interval results in annual emissions that range from approximately <1 - 350 mg I-TEQ/year, using the annual air flow of approximately 37400000 N m$^3$/year.

In SFA 2000 /Hansen, 2000/ the annual emission was estimated at 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 suitable for incineration.

Included in this quantity will be around 37 - 415 g I-T EQ/year of dioxins as detailed in table 5.5.

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 landfills 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-T EQ/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-T EQ/year. This emission will primarily be directed to municipal wastewater treatment plants.

Dioxin concentrations in leachate have been investigated from four Danish landfills during 2002. These investigations have shown that leachate from normal Danish landfills does not contain traceable amounts of dioxin. Leachate from special deposits containing for example sludge, ash or other types of special waste will be investigated, but only one result is so far available. One measurement has been taken from a deposit for hazardous waste. The result showed a dioxin content of 0.02 pg I-T EQ/l when the dioxin content in the blind test is deducted. /Vikelsøe, 2002/ and /the National Environmental Research Institute, 2002/. The dioxin content in leachate from Danish municipal landfills is so far maintained at the level of <0.05 g I-T EQ/year.
### Table 5.5
Sources and quantities of dioxins assumed to be directed to landfills in Denmark

<table>
<thead>
<tr>
<th>Source</th>
<th>Quantity g I-TEQ/year</th>
<th>Reference to section</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot-dip galvanising</td>
<td>&lt;0.002</td>
<td>2.3.2</td>
</tr>
<tr>
<td>Steel reclamation</td>
<td>&lt;0.005</td>
<td>2.3.3</td>
</tr>
<tr>
<td>Aluminium reclamation</td>
<td>1 - 3</td>
<td>2.3.4</td>
</tr>
<tr>
<td>Other industrial sources</td>
<td>?</td>
<td>2.1, 2.2, 2.3.1, 2.4, 2.8</td>
</tr>
<tr>
<td>Coal combustion</td>
<td>0.27 - 317</td>
<td>3.1</td>
</tr>
<tr>
<td>Biomass combustion</td>
<td>0.03 - 32?</td>
<td>3.3.2</td>
</tr>
<tr>
<td>Residues from accidental fires 1)</td>
<td>1 - 30?</td>
<td>4.1.1</td>
</tr>
<tr>
<td>Residues from landfill fires 2)</td>
<td>0.4 - 177</td>
<td>5.5 (this section)</td>
</tr>
<tr>
<td>Residues from other fires 1)</td>
<td>0.01 - 27.5?</td>
<td>4.1.2</td>
</tr>
<tr>
<td>Residues from shredder plants</td>
<td>?</td>
<td>5.1.2</td>
</tr>
<tr>
<td>Residues from incineration plants 3)</td>
<td>35 - 275</td>
<td>5.3.1</td>
</tr>
<tr>
<td>Sewage sludge</td>
<td>0.42 - 0.46</td>
<td>5.7.2</td>
</tr>
<tr>
<td>Other sources</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>Total (rounded)</td>
<td>37 - 415</td>
<td></td>
</tr>
</tbody>
</table>

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 at 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 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 tons of waste was accidentally set on fire. The fire 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 (as 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 2000a/.

5.6 Biological waste treatment

In 2001 450,000 tons organic garden waste was brought to composting plants /Danish EPA, 2002/. Furthermore 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.

12 measurements on organic garden waste have been carried out in 2001. The measurements come from 9 different locations. These measurements show an average dioxin content of 4.5 ng I-TEQ/kg dry matter with a minimum value of 0.5 ng I-TEQ/kg dry matter and a maximum of 15.9 ng I-TEQ/kg dry matter.

The amount of dioxin collected with organic garden waste equals 1.7 g I-TEQ/year, when the average value is used, and using a 90% confidence level the uncertainty range corresponds to 0.8 - 2.6 g I-TEQ/year.

Concerning food waste an estimate of 23 – 165 ng I-TEQ/ton waste 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 to 0.8 – 2.6 g I-TEQ/year, as the dioxin content in food waste is marginal compared to the content in the organic garden waste.

The new information on organic garden waste has developed a higher estimate than the one made in SFA 2000 /Hansen, 2000/, where the dioxin amount directed to biological waste treatment was estimated at 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 approximately 770 million m³ as an average for the years 2000 and 2001. The storm water systems furthermore discharges an extra 190 million m³ in a normal year and from separate industrial sources the
average discharge has been approximately 70 million m³ during 2000 and 2001 (Danish EPA, 2002a) and (Danish EPA, 2001a).

In the SFA 2000 (Hansen, 2000) 3 samples from 1995 from a single Danish treatment plant were reported which showed dioxin levels of 0.4-1.4 ng I-TEQ/m³ in the outlet from the plant (Vikelsøe 2000). More measurements from outlets of waste water treatment plants have been made available from the period 2000 - 2002 due to analytical work undertaken by the National Environmental Research Institute on behalf on clients. However, the origin of the samples is in most cases poorly described making data interpretation difficult. In total 26 measurements are available, of which 3 originates from a semilarge treatment plant (the one described above), 3 measurements originates from an industrial textile processing plant and 3 from other industrial plants. The origin of the remaining 19 measurements is not stated and they must be assumed to represent a mix of municipal and industrial waste water treatment plants.

Considering all measurements available from Denmark, they can be described as ranging within 0 - 3 ng I-TEQ/m³, and an average value of 0.5 ng I-TEQ/m³ with a 90% confidence level that ranges from 0.23 - 0.75 ng I-TEQ/m³ (Vikelsøe, 2002). No measurements of dioxin in water from storm water drainage systems have so far been carried out in Denmark.

Based on the data available the emission of dioxin with waste water and storm water to Danish water recipients may roughly be estimated as follows:

- Municipal waste water: 770 million m³ with 0.4-1.4 ng I-T EQ/m³ corresponds to 0.31-1.08 g I-T EQ yearly.
- Industrial waste water: 70 million m³ with 0.23-0.75 ng I-T EQ/m³ corresponds to 0.02-0.05 g I-T EQ yearly.
- Storm water - direct discharges: 190 million m³ with 0.4-1.4 ng I-T EQ/m³ corresponds to 0.08-0.27 g I-T EQ yearly.

Total emission: 0.4-1.4 g I-T EQ yearly.

This emission should be considered equal to the previous estimate for year 2000 of 0.3 - 1.4 g I-T EQ/year (Hansen, 2000).

It is noted that the dioxin concentrations assumed for storm water should be regarded as a best estimate only, as the concentration of dioxin in storm water could well be higher than in municipal waste water, as storm water will be a carrier of dioxin originating from atmospheric deposition which seemingly is the dominating source of dioxin to the waste water and storm water system.

The sources of dioxin in wastewater and storm water may be outlined as indicated in table 5.6.
Table 5.6 
Sources and quantities of dioxins assumed to be directed to wastewater and storm water drainage in Denmark

<table>
<thead>
<tr>
<th>Source</th>
<th>Quantity g l-TEQ/year</th>
<th>Reference to section</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine bleaching</td>
<td>&lt;0.5</td>
<td>2.7.1</td>
</tr>
<tr>
<td>PCP preserved textiles</td>
<td>0.2</td>
<td>2.6.3</td>
</tr>
<tr>
<td>Atmospheric deposition 1)</td>
<td>0.4 - 4?</td>
<td>6</td>
</tr>
<tr>
<td>Leachate from landfills</td>
<td>&lt;0.05</td>
<td>5.5</td>
</tr>
<tr>
<td>Other sources</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>Total (rounded)</td>
<td>0.4 - 4.8?</td>
<td></td>
</tr>
</tbody>
</table>

1 The estimate is based on a total Danish area served by sewage systems of 2,230 km² and a deposition rate of 0.3 - 3.6 ng l-TEQ/m²/year. A collection rate of 50% is assumed. The collection rate reflects the amount storm water directed to waste water treatment plants. The remainder will be directed directly to water recipients. 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.

The calculated total contribution of 0.4 - 4.8 g l-T EQ/year should be taken as comparable to the estimated total content in discharged waste and storm water of 0.4 - 1.4 g l-T EQ/year (see above) and the calculated total content in sewage sludge of 1.2 - 2.3 g l-T EQ/year (reference is made to section 5.7.2) indicating that the contribution to waste water treatment plants in Denmark is at least 1.6 - 3.7 g l-T EQ/year. These observations indicate that the deposition level stated in chapter 6 is a realistic estimate.

It is, however, not possible based on the existing data to discuss the fate of dioxins in wastewater treatment plants. Nlkelse, 2002/ points out that observed congener profiles for dioxins in sewage sludge only partly are correlated to profiles for air deposition. Some correlation to congener profiles for textiles may also be argued. Any definite conclusions on sources for dioxins in wastewater and sewage sludge should so far 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-T EQ/kg dry matter (2 samples, 1996 - /Kjølholmer 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.

5.7.2 Treatment and disposal of sewage sludge

In 1999 the total production of sewage sludge from municipal wastewater treatment plants was 1,442,930 t wet weight corresponding to 155,622 tonnes of dry matter /Danish EPA 2001b/. The sludge is applied to farmland as well as to special sludge incineration plants and landfills as detailed in table 5.7 below.
The content of dioxins in Danish sewage has been thoroughly investigated during the recent years. 95 samples of sewage sludge covering city areas as well as rural districts have been analysed during the years 1995 - 2002. The average content of dioxins has been determined as 11.4 ng I-TEQ/kg dry matter with min./max. values of 0.7/201.3 ng I-TEQ/kg dry matter/Vikelsøe 2002/. The measurements correspond to an average annual quantity of dioxin collected with sewage sludge of approximately 1.8 g I-TEQ/year. The estimated uncertainty is 1.2 - 2.3 g I-TEQ/year, when a 90% confidence level is used.

The distribution of this dioxin on the relevant disposal routes is also indicated in table 5.6.

Table 5.7 Disposal of sewage sludge and dioxins contained in sewage sludge in Denmark 2000-2002.

<table>
<thead>
<tr>
<th>Disposal</th>
<th>Sewage sludge</th>
<th>Dioxin g I-TEQ/year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Farmland etc.</td>
<td>87852</td>
<td>56.5</td>
</tr>
<tr>
<td>Landfill 1)</td>
<td>21007</td>
<td>13.5</td>
</tr>
<tr>
<td>Incineration</td>
<td>32853</td>
<td>21.1</td>
</tr>
<tr>
<td>Other</td>
<td>13909</td>
<td>8.9</td>
</tr>
<tr>
<td>Total</td>
<td>155,621</td>
<td>100</td>
</tr>
</tbody>
</table>

1) Distribution figures originate from /Danish EPA 2001b/.

In SFA 2000 /Hansen, 2000/ the total amount of dioxin in sewage sludge was estimated at 2.1 g I-TEQ/year. The reduction is caused by slightly decreasing concentrations of dioxins in sewage sludge, as the total amount of dry matter has increased by approximately 3% compared to the figures from 1997, used in SFA 2000 /Hansen, 2000/.

Incineration of sewage sludge takes place at 5 plants in Denmark (reference is made to table 5.8). 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 has been equipped with dioxin abatement. 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 5.8 Dioxin emission to air in Denmark from incineration of sludge.

<table>
<thead>
<tr>
<th></th>
<th>Sludge tonnes dry matter</th>
<th>Emission factor µg/ton dry weight</th>
<th>Emission mg I-TEQ/year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lynetten 1)</td>
<td>19,000</td>
<td>0.07</td>
<td>1.3</td>
</tr>
<tr>
<td>Avedøre 2)</td>
<td>6,279</td>
<td>0.025</td>
<td>0.2</td>
</tr>
<tr>
<td>Others 3)</td>
<td>7,564</td>
<td>0.037</td>
<td>0.3</td>
</tr>
<tr>
<td>Total 4)</td>
<td>32,843</td>
<td></td>
<td>1.8</td>
</tr>
</tbody>
</table>

1) Based on an air flow of 180 million Nm³/year and dioxin content of 0.007 ng I-TEQ/Nm³ (as found by measurement per November 1999 /Lynetten 2000/.
Based on an air flow of 53 million N m\(^3\)/year and dioxin content of 0.003 ng I-TEQ/N m\(^3\) (average of 2 measurements from 2001 of 0.004 and 0.002 ng I-TEQ/N m\(^3\)). 6279 tons was manufactured in 2001.

3. Other minor sludge incineration plants include e.g. Køge, Bjerringbro, Lundtofte and Brønderslev. The plant in Brønderslev has carried out a measurement of dioxin emission to air in 2002. This measurement shows a dioxin emission of 0.007 ng I-TEQ/N m\(^3\) while the air flow was approx. 5 million N m\(^3\). /Nordjyllands Amt 2002/ The plant in Lundtofte has also made a measurement in 2001 with 0.005 ng I-TEQ/N m\(^3\). This measurement is used as an indication of the level at the minor incineration plants. The emission factor used for the minor plants is an average of the emission factors from Brønderslev, Lundtofte, Lynetten and Avedøre, as it seems there is no considerable difference between the emissions from large and minor plants.

4. The total amount of sludge, dry matter, from /Hansen et al. 2000/ has been maintained, as no new information is available.

The new measurements at sludge incineration plants result in a reduction of the estimated level of the dioxin emission from sludge incineration, compared to SFA 2000 /Hansen, 2000/.

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. A 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-T EQ/kg and of scrubber water of 0.28 ng N-T EQ/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-T EQ to equal I-T EQ, the quantity of dioxins collected by bottom ash and directed to landfills can be calculated as 0.05 – 0.09 g I-T EQ/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-T EQ/l will correspond to a total quantity of 0.5 g I-T EQ/year. The dioxin formation by sludge incineration plants can thus be summed up to (0.0018 + 0.05 - 0.09 + 0.5 = 0.55 - 0.59) g I-T EQ/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 (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 5.9.
Table 5.9
Summary of formation and turnover of dioxins by waste treatment and disposal activities in Denmark

<table>
<thead>
<tr>
<th>Activity/product</th>
<th>Formation g l-TEQ/year</th>
<th>Emissions/losses (g l-TEQ/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>to air</td>
</tr>
<tr>
<td></td>
<td></td>
<td>g l-TEQ/year</td>
</tr>
<tr>
<td>Cable scrap</td>
<td>0.000004 - 0.001</td>
<td>0.00004 - 0.001</td>
</tr>
<tr>
<td>Shredder plants</td>
<td>&lt;0.001 - 0.1</td>
<td>&lt;0.001 - 0.1</td>
</tr>
<tr>
<td>Hazardous waste incineration</td>
<td>0.9?</td>
<td>0.004 - 0.03</td>
</tr>
<tr>
<td>Incineration of waste oil</td>
<td>&lt;0.001 - 0.2</td>
<td>&lt;0.001 - 0.2</td>
</tr>
<tr>
<td>Municipal waste incinerization 1)</td>
<td>58.4 - 436?</td>
<td>6.4 - 29</td>
</tr>
<tr>
<td>Healthcare risk waste</td>
<td>&lt;0.001 - 0.4</td>
<td>&lt;0.001 - 0.4</td>
</tr>
<tr>
<td>Landfills 2)</td>
<td>0.7 - 27?</td>
<td>0.25 - 10?</td>
</tr>
<tr>
<td>Biological waste treatment</td>
<td></td>
<td>0.01 - 0.1</td>
</tr>
<tr>
<td>Waste and storm water treatment/discharges</td>
<td>0.4 - 14</td>
<td>0.4 - 14</td>
</tr>
<tr>
<td>Sewage sludge disposal 3)</td>
<td>1.0 - 19</td>
<td>0.002</td>
</tr>
<tr>
<td>Total (rounded)</td>
<td>61 - 468</td>
<td>6.7 - 39.7</td>
</tr>
</tbody>
</table>

? 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 stated under “formation” is the sum of the quantities estimated to be emitted to air or directed to depots and exported 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.

2. 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.

3. The dioxin in sludge that is incinerated is not mentioned, as it is assumed that the dioxin in the sludge is likely completely destructed during the incineration process. The dioxin emission to air therefore is caused by the dioxin generated later on in the flue gas cleaning system and the chimney. The emission/losses to soil are the amount of dioxin in sludge directed to farmland, but there is a possibility that some of the dioxin is emitted to water. The emission to depots covers untreated sewage sludge and ash from sludge incineration.
6 Deposition

Air deposition measurements have been carried out in Denmark in 2002 and the results from all months of 2002 are included in this report. The deposition measurements include both bulk deposition measurements as well as measurements of dioxin in fir needle, where water is dripping through the needles.

The measurements have been conducted by the National Environmental Research Institute (NERI) at two locations, Fredensborg and Ulfborg. So far no measurements have been undertaken in urban area. The deposition measurements will continue in 2003.

The National Environmental Research Institute has on the basis of the available measurements on bulk deposition and dripping estimated an annual deposition of 0.9 - 3.6 ng I-TEQ/m²/year in a rural area (Fredensborg) and 0.3 - 1.2 ng I-TEQ/m²/year in a rural area on the west coast (Ulfborg). Considering the total Danish land area of approximately 44,000 km², this corresponds to 32 - 130 and 13 - 52 g I-TEQ/year, respectively /Vikelsøe, 2003/. The intervals include an uncertainty of ± factor 2, which NERI assumes is the size of the uncertainty connected with the measurements. If the two ranges 32 - 130 and 13 - 52 g I-TEQ/year both are considered representative for Denmark as a whole, the annual deposition in Denmark is approximately 13 - 130 g I-TEQ/year. The minimum and maximum value are equal to the lowest and highest value from the two estimates. The given interval does not include:

- The uncertainty due to the fact that the measurements originate from only two locations and in addition that the measurements encompasses only one single year. This uncertainty is at the time being very difficult to assess.

- Uncertainty coming from the fact that no measurements so far have been carried out in urban areas and in the vicinity of point sources.

Since all measurements so far have been carried out in rural areas the range of 13 - 130 g I-TEQ/year should be seen as an estimate of the background deposition, which does not necessarily include the anticipated higher deposition in urban areas and near point sources.

The County of Århus has together with dk-T E K N I K also conducted bulk deposition measurements in 2000. These measurements showed dioxin deposition in the range 1.2 - 2.5 pg I-TEQ/day/m², corresponding to a total annual deposition of 0.1 - 0.8 g I-TEQ/year if the range is used as representative for Denmark as a whole and if an uncertainty of ± factor 2 is added. The measurements are made using another sampling method than the measurements conducted by the National Environmental Research Institute in 2002. The National Environmental Research Institute has earlier made measurements employing the same sampling method as dk-T E K N I K and found that this method systematically creates too low results, most likely mainly because of UV-destruction of the dioxin during the sampling period /Vikelsøe, 2003/.
The range at 13 - 130 g I-TEQ made on the basis of the NERI measurements from 2002 agrees quite well with the interval earlier estimated in SFA 2000/ Hansen, 2000/ where the annual deposition range was 16 - 160 g I-TEQ/year. However it must be borne in mind that the NERI results are rural background values not including cities, which might considerably elevate the total levels /Vikelsøe, 2003/. The range of 13 - 130 g I-TEQ/year is however higher than the results from the European Monitoring and Evaluation Programme (EMEP) under the Geneva Convention on Long-Range Transport of Air Pollutants. Within the EMEP programme model computations of the emission, transport and deposition of e.g. dioxins and furans have been made for the European continent. The values for total deposition (dry particle and wet) for 1999 range from 0.06 - 0.3 ng I-TEQ/m²/year for Danish land area. These deposition rates equal a total deposition on Danish agricultural areas of between 2 - 10 g I-TEQ per year./Torp, 2002/

The National Environmental Research Institute has in addition to deposition also measured the dioxin content in air monthly during 2002 at the sampling position in Fredensborg. The average value of these measurements is 17 femtogram I-TEQ/m³ (femtogram = 10⁻¹⁵ g) for the whole period. A single measurement has been carried out in a village during the heating season with a value of 70 femtogram I-TEQ/m³, indicating that the dioxin content in urban air may be considerably higher than in rural areas (reference is made to section 3.3.1).
7 Total picture for Denmark

7.1 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.

Table 7.1 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 including waste products being exported. 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 2000 - 2002 is estimated at 72-689 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 private wood stoves and other smaller biomass combustion plants, as well as fires, both accidental fires and other fires like the dominant Danish bonfire event – sankthansaften (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 7.1 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 7.2 the available estimates on this topic are summarised.

As stated in table 7.2 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.
Table 7: Formation of chlorinated dioxins by activities/processes in Denmark 2000 - 2002

<table>
<thead>
<tr>
<th>Activity/process</th>
<th>Danish investigations</th>
<th>Formation</th>
<th>1</th>
<th>g I-TEQ/year</th>
<th>2</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Manufacturing activities</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Chemicals 3)</td>
<td>Some-none</td>
<td>?</td>
<td>?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Cement</td>
<td>Some</td>
<td>0.2 - 1.4?</td>
<td>0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Lime</td>
<td>Some-None</td>
<td>0.001 - 0.005</td>
<td>&lt;0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Other high-temperature materials 4)</td>
<td>Some</td>
<td>0.02 - 0.3</td>
<td>&lt;0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Steel reclamation</td>
<td>Good</td>
<td>5.1 - 12.9</td>
<td>1.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Aluminium reclamation</td>
<td>Good</td>
<td>1 - 3.8</td>
<td>0.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Other metal manufacturing 5)</td>
<td>Some</td>
<td>0.02 - 0.4</td>
<td>&lt;0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Feedstuff 6)</td>
<td>Some</td>
<td>0.004-0.07?</td>
<td>&lt;0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Use of chlorine for bleaching and disinfecting</td>
<td>None</td>
<td>&lt;0.5</td>
<td>&lt;0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Other industrial processes 7)</td>
<td>Some-none</td>
<td>&lt;0.04?</td>
<td>&lt;0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Manufacturing activities - subtotal</strong></td>
<td></td>
<td></td>
<td></td>
<td>6.3 - 19</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td><strong>Energy production activities</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Coal power plants</td>
<td>Some</td>
<td>0.3 - 43?</td>
<td>6.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Other fossil fuels</td>
<td>None</td>
<td>0.4 - 1.3</td>
<td>0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Biomass</td>
<td>Some</td>
<td>0.7 - 43.8</td>
<td>6.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Energy production activities - subtotal</strong></td>
<td></td>
<td></td>
<td></td>
<td>1.4 - 88</td>
<td>12.8</td>
<td></td>
</tr>
<tr>
<td><strong>Miscellaneous human and natural activities</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Fires</td>
<td>None</td>
<td>1.6 - 112</td>
<td>16.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Traffic</td>
<td>None</td>
<td>1.3 - 17</td>
<td>0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Crematories</td>
<td>Good</td>
<td>0.01 - 0.1</td>
<td>&lt;0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Other miscellaneous activities 8)</td>
<td>Some</td>
<td>0.09 - 0.22?</td>
<td>&lt;0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Miscellaneous human and natural activities - subtotal</strong></td>
<td></td>
<td></td>
<td></td>
<td>3 - 114</td>
<td>16.5</td>
<td></td>
</tr>
<tr>
<td><strong>Waste treatment and disposal activities</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Reclamation of cable scrap</td>
<td>Some-none</td>
<td>0.00004 - 0.001</td>
<td>&lt;0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Shredder plants</td>
<td>Some</td>
<td>&lt;0.001 - 0.1</td>
<td>&lt;0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Hazardous waste</td>
<td>Good</td>
<td>0.9?</td>
<td>0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Incineration of waste oil</td>
<td>&lt;0.001 - 0.2</td>
<td>&lt;0.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Municipal solid waste</td>
<td>Good</td>
<td>58.4 - 436</td>
<td>63.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Healthcare risk waste</td>
<td>Some</td>
<td>&lt;0.001 - 0.4</td>
<td>&lt;0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Municpals landfills 9)</td>
<td>None</td>
<td>0.7 - 27?</td>
<td>3.9?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Wastewater and storm water treatment/discharges</td>
<td>Good - some</td>
<td>0.4 - 1.4</td>
<td>0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Waste treatment and disposal activities - subtotal</strong></td>
<td></td>
<td></td>
<td></td>
<td>61 - 468</td>
<td>67.9</td>
<td></td>
</tr>
<tr>
<td><strong>Brominated dioxin from waste treatment (not included in total)</strong></td>
<td></td>
<td></td>
<td></td>
<td>&lt;0.01-0.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Total (rounded)</strong></td>
<td></td>
<td></td>
<td></td>
<td>72 - 689</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

* 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 at all – estimates rely completely on literature values.

2. Calculated based on the average value from each activity/process. Should be considered 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. 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.

Table 7.2
Presence of dioxins in products brought into circulation in the Danish society 2000 - 2002

<table>
<thead>
<tr>
<th>Activity/process</th>
<th>Consumption by products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay-like raw materials</td>
<td>4 – 1050</td>
</tr>
<tr>
<td>Pesticides</td>
<td>&lt;1?</td>
</tr>
<tr>
<td>Feedstuff products</td>
<td>1.5 – 11</td>
</tr>
<tr>
<td>Food products</td>
<td>0.06 – 0.44</td>
</tr>
<tr>
<td>PCP treated wood</td>
<td>0.11 – 42?</td>
</tr>
<tr>
<td>PCP treated leather</td>
<td>0.5</td>
</tr>
<tr>
<td>PCP treated textiles</td>
<td>0.5</td>
</tr>
<tr>
<td>Bleaching/disinfection agents</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Bleached cork</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Bleached paper/cardboard</td>
<td>3.0 – 6.6</td>
</tr>
<tr>
<td>Other chemical products</td>
<td>?</td>
</tr>
<tr>
<td>Total – Chlorinated dioxins</td>
<td>10 – 1110?</td>
</tr>
<tr>
<td>Brominated flame retardants</td>
<td>2 – 60?</td>
</tr>
<tr>
<td>Total – brominated dioxins</td>
<td>2 – 60?</td>
</tr>
<tr>
<td>Total (rounded)</td>
<td>12 – 1200?</td>
</tr>
</tbody>
</table>

? 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.

The dominant part of the quantity stated in table 7.2 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.

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. A new measurement of air emission from a Danish edible fish industry has shown a dioxin level of 0.001 ng I-TEQ/Nm$^3$. The source to the measured dioxin is difficult to explain as no combustion processes take place. The air emission can however indicate that some of the dioxin in the fish might be measured in the air emission.

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.

7.2 Emissions to the environment

Table 7.3 summarises the estimates made with respect to emissions to the environment and quantities directed to depots in Denmark.

7.2.1.1 Emissions to air

Concerning emission to air the total emission is estimated at 11 - 163 g I-TEQ/year or as a best estimate, assuming uncertainties compensate each other, at around 87 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

In SFA 2000 /Hansen, 2000/ steel and aluminium reclamation was also regarded dominant sources. Since then both the steel reclamation plant and the aluminium reclamation plant have done an effort to minimize the dioxin emission and the total air emission from these plants is today reduced to approximately 0.1 - 3.2 g I-TEQ/year. It is noted that at time of preparation of SFA 2000 no measurements were available for the aluminium plant. The first measurement for the plant from autumn 2000 showed an alarming emission of 183 ng I-TEQ/Nm$^3$ corresponding to 60 g I-TEQ/year. The estimate made in SFA 2000 (1.3 - 5.6 g I-TEQ/year) was thus too low, and the case shows that unexpected emissions might appear.

In 1999 incineration of hazardous waste was a significant source as well, but the contribution from this source has been heavily reduced since 2000 due to
redesign of ovens and installation of dioxin abatement. 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 abatement and the dioxin emission to air must thus be expected to decrease in the years to come. All municipal waste incineration plants must comply with the limit value of 0.1 ng I-TEQ/Nm$^3$ before 2005. By the end of year 2002 2/3 of the Danish waste was incinerated at waste incineration plants which are capable of complying with the new limit value for dioxin of 0.1 ng I-TEQ/Nm$^3$/Danish EPA 2002/. Most of the remaining waste incineration plants are planning to install dioxin abatement before the end of year 2004.

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.

The Danish Environmental Protection Agency has in 2001 introduced an information campaign on private wood stoves and dioxin. The effect of this campaign can however not be evaluated as measurements on flue gas from private wood stoves is not present on a larger scale. The focus on dioxins from combustion of biomass has also led to several new measurements on residues from larger biomass combustion plants have been made in 2002 by the National Environmental Research Institute, and these results decrease the interval for residues from 0.04 - 36 g I-TEQ/year to <0.001 - 0.04 g I-TEQ/year.

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 other types 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.
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 taking 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 7.3
Estimated emissions/losses to the environment and depots in Denmark 2000 - 2002

<table>
<thead>
<tr>
<th>Activity</th>
<th>Emissions/losses (g l-TEQ/year)</th>
<th>to air</th>
<th>to water</th>
<th>to soil</th>
<th>to depots</th>
<th>export</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Manufacturing processes</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemicals 1)</td>
<td>0.001 - 0.007?</td>
<td>&lt;0.001</td>
<td>&lt;1?</td>
<td></td>
<td></td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Cement and lime</td>
<td>0.2 - 14</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td></td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Other high temperature materials 2)</td>
<td>0.02 - 0.3</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steel and aluminium reclamation</td>
<td>0.1 - 3.2</td>
<td>1 - 3</td>
<td>50 - 10.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other metal manufac. 3)</td>
<td>0.02 - 0.5</td>
<td>?</td>
<td>&lt;0.002?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other manufacturing processes 4)</td>
<td>0.04 - 0.1?</td>
<td>&lt;0.01</td>
<td>0.004 - 0.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Energy generation</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coal combustion</td>
<td>0.1 - 3.2?</td>
<td></td>
<td>0.2 - 40?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other fossil fuels</td>
<td>0.4 - 1.3</td>
<td></td>
<td>0?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biomass combustion, private wood stoves</td>
<td>0.4 - 22</td>
<td>(&lt;0.001 - 2.2?)</td>
<td>0.001 - 2.2?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biomass combustion, other smaller plants 5)</td>
<td>0.3 - 15.0</td>
<td>0.0003 - 0.09</td>
<td>&lt;0.001 - 0.01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biomass combustion, larger plants 6)</td>
<td>0.03 - 4.4</td>
<td>&lt;0.001 - 0.03</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Use of products</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCP-treated wood</td>
<td>0.5 - 26?</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other PCP-treated materials</td>
<td>&lt;0.05</td>
<td>0.2?</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Bleached processes and bleaching agents</td>
<td>&lt;0.5?</td>
<td>&lt;0.01</td>
<td>&lt;0.001 - 0.01</td>
<td></td>
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<td></td>
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<tr>
<td>Feedstuff products</td>
<td>?</td>
<td>&lt;10?</td>
<td>?</td>
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<tr>
<td><strong>Miscellaneous other human and natural activities</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Fires – accidental</td>
<td>0.5 – 20?</td>
<td>?</td>
<td>1 - 30</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fires – others</td>
<td>0.03 - 6.5</td>
<td>0.01 – 27.5?</td>
<td>0.01 - 27.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Traffic</td>
<td>1.3 – 17</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cremation</td>
<td>0.01-0.1</td>
<td></td>
<td>?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other activities 8)</td>
<td>0.1 - 0.2?</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Waste treatment and disposal</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cable scrap reclamation</td>
<td>&lt;0.001</td>
<td>?</td>
<td>?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hazardous waste inc. 9)</td>
<td>0.004-0.03</td>
<td>&lt;0.001</td>
<td>0.9?</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Municipal waste inc. 10)</td>
<td>6.4 - 29</td>
<td>2 - 5</td>
<td>50 - 402</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Landfills 11)</td>
<td>0.25 - 10?</td>
<td>&lt;0.05?</td>
<td>0.4 - 17?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Waste and storm water</td>
<td>0.4 - 14</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sewage sludge disposal</td>
<td>0.002</td>
<td>0.7 - 13</td>
<td>0.2 - 0.3</td>
<td>0.1 - 0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other activities 12)</td>
<td>&lt;0.003 - 0.6</td>
<td>0.01 - 0.1</td>
<td>?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Emission of brominated dioxins (not included in total)13)</td>
<td>&lt;0.01-0.17</td>
<td>&lt;0.01-0.17</td>
<td>?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Total (rounded)</strong></td>
<td>11 - 163</td>
<td>0.4 - 14</td>
<td>0.7 - 42</td>
<td>5 - 126</td>
<td>55 - 413</td>
<td></td>
</tr>
</tbody>
</table>
1. Covers manufacturing of pesticides and pharmaceuticals
2. Covers manufacturing of insulation materials, tiles and bricks, glass and similar products.
3. Cover metal casting and hot-dip galvanising
4. 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.
5. Other smaller biomass combustion plants are smaller stoker boilers and farm boilers.
6. Other larger biomass combustion plants are District heating plants, Industrial CHP plants and de-central and central CHP plants
7. Covers emission to waste water. Emission from waste water treatment plants is specified in the category "waste and storm water".
8. Covers a number of activities like fireworks, garden grills, cooking and miscellaneous small-scale heating/burning operations that can only be partly quantified.
9. The figure stated is only valid to the period 2000-2002. When the emission limit value 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.
10. When the emission limit value of 0.1 ng I-TEQ/Nm$^3$ is fulfilled for all-waste incineration plants the total emission will be approximately 2 g I-TEQ/year.
11. Emission to air and depots relates to fires in temporary depots of combustible waste.
13. The emission of brominated dioxin derives from treatment of hazardous waste and municipal waste incineration. The interval is made on the basis of the estimated lowest and highest value, but does not include all measured congener groups.

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 hazardous 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. 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 awaiting adequate incineration capacity to be established. This source is in table 7.3 included under “landfills”. The
comments relevant to this source correspond by and large to the comments given above on accidental fires etc.

The sometimes very large ranges given for most emissions reflect to the best judgment 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 rule 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.

On the basis of the measurements on brominated dioxins in flue gas from Kommunekemi and Vestforbrænding the annual emission of brominated dioxins is estimated to be approximately <0.01 - 0.1 g I-TEQ/year. This estimate is very uncertain because of the few measurements and the variable processes used for waste incineration and cleaning of flue gasses. Furthermore there is no official method for calculating an I-TEQ-value, and the estimate does not include all measured congener groups, as it has only been possible to calculate I-TEQ-value for the specific congeners. The non specific congener groups are therefore not included in the interval of 0.01 - 0.1 g I-TEQ/year. This emission value represents with certainty an under estimate of the total emission, but any estimate of the reel emission value must be regarded as highly uncertain. Based on an analysis of the chromatographies for the congeners it is estimated that the reel estimate can be up to approximately a factor 5 higher, but most likely not a factor 100 /Vikelsøe, 2003a/. This value is not a part of the total emission to air and figure 7.1 because of the uncertainty of the estimate.

Emissions to water
The total emission to water environment is estimated at 0.4 - 1.4 g I-TEQ/year. This estimate should be regarded as uncertain, as only few measurements are available.

Based on the available knowledge 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 observed congener profiles for dioxins in sewage sludge only partly correlate to profiles for atmospheric deposition. Some correlation to congener profiles for textiles may also be argued. A definite conclusion on sources for dioxins in wastewater and sewage sludge should however so far be considered premature.

Emissions to soil
The total direct emission of dioxins to the soil environment is estimated at 0.7 - 42 g I-TEQ/year. The dominant sources are residues from miscellaneous fires and 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 5 - 126 g I-TEQ/year. Municipal waste incineration is no longer the dominant source because the flue gas treatment residues are exported. The major sources are dioxin residues in PCP-treated wood and residues from coal combustion however neither residues from steel and aluminium reclamation, 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 within landfills.

Export
The data in the category "export" cover products and residues which have been exported from Denmark. The total amount of exported dioxin in the Danish society equals approximately 55 - 413 g I-TEQ/year. This amount has grown because of the export of flue gas treatment residues from the Danish waste incineration plants.

Uncertain estimates
Some of the estimates in table 7.3 are made on a very weak basis of experience due to lack of precise data. Because of the uncertainty connected to these estimates, some of the intervals stated have a high maximum value that influences the interval of the total emission considerably. It is therefore chosen to show a second edition of table 7.3, where these high, uncertain estimates are excluded. By doing this it is tried to distinguish between sources for which relative precise information is available and sources which can only be quantified with high level of uncertainty. The following categories are left out of the second edition of table 7.3 (table 7.4):

- Biomass combustion - private wood stoves and other smaller plants
- PCP-treated wood
- Fires - accidental
- Fires - others
- Landfills
- (Brominated dioxins - were not included in the total in table 7.3)

**Table 7.4**

Estimated emissions/losses to the environment and depots in Denmark 2000 - 2002, well determined sources only.

<table>
<thead>
<tr>
<th>Activity</th>
<th>Emissions/losses (g I-TEQ/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>to air</td>
</tr>
<tr>
<td>Manufacturing processes</td>
<td></td>
</tr>
<tr>
<td>Chemicals 1)</td>
<td>0.001 - 0.007?</td>
</tr>
<tr>
<td>Cement and lime</td>
<td>0.2 - 1.4</td>
</tr>
<tr>
<td>Other high temperature materials 2)</td>
<td>0.02 - 0.3</td>
</tr>
<tr>
<td>Steel and aluminium reclamation</td>
<td>0.1 - 2.4</td>
</tr>
<tr>
<td>Other metal manufac. 3)</td>
<td>0.02 - 0.5</td>
</tr>
<tr>
<td>Other manufacturing processes 4)</td>
<td>0.04 - 0.1?</td>
</tr>
<tr>
<td>Energy generation</td>
<td></td>
</tr>
<tr>
<td>Coal combustion</td>
<td>0.1 - 3.2?</td>
</tr>
<tr>
<td>Other fossil fuels</td>
<td>0.4 - 1.3</td>
</tr>
<tr>
<td>Biomass combustion, other larger plants 5)</td>
<td>0.03 - 4.4</td>
</tr>
<tr>
<td>Use of products</td>
<td></td>
</tr>
<tr>
<td>Other PCP-treated materials</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Bleached processes and bleaching agents</td>
<td>&lt;0.5 - 6?</td>
</tr>
<tr>
<td>Feedstuff products</td>
<td>?</td>
</tr>
<tr>
<td>Miscellaneous other human and natural activities</td>
<td></td>
</tr>
<tr>
<td>Traffic</td>
<td>1.3 - 17</td>
</tr>
<tr>
<td>Cremation</td>
<td>0.006 - 0.1</td>
</tr>
<tr>
<td>Other activities 7</td>
<td>0.1 - 0.2?</td>
</tr>
<tr>
<td>Waste treatment and disposal</td>
<td></td>
</tr>
<tr>
<td>Cable scrap reclamation</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Hazardous waste inc. 8</td>
<td>0.004 - 0.03</td>
</tr>
<tr>
<td>Municipal waste inc. 9</td>
<td>6.4 - 29</td>
</tr>
<tr>
<td>Waste and storm water</td>
<td>0.4 - 14</td>
</tr>
<tr>
<td>Sewage sludge disposal</td>
<td>0.002</td>
</tr>
<tr>
<td>Other activities 10)</td>
<td>&lt;0.003 - 0.6</td>
</tr>
<tr>
<td><strong>Total (rounded)</strong></td>
<td>9 - 45</td>
</tr>
</tbody>
</table>

? 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. Covers manufacturing of pesticides and pharmaceuticals
2. Covers manufacturing of insulation materials, tiles and bricks, glass and similar products.
3. Cover metal casting and hot-dip galvanising

4. 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.

5. Other larger biomass combustion plants are District heating plants, Industrial CHP plants and de-central and central CHP plants

6. Covers emission to waste water. Emission from waste water treatment plants is specified in the category "Waste and Storm water".

7. Covers a number of activities like fireworks, garden grills, cooking and miscellaneous small-scale heating/burning operations that can only be partly quantified.

8. The figure stated is only valid to the period 2000-2002. When the emission limit value 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.

9. When the emission limit value of 0.1 ng I-TEQ/Nm$^3$ is fulfilled for all-waste incineration plants, the total emission will be approximately 2 g I-TEQ/year.


Comparing table 7.3 and 7.4 it is clear that it is the emission to air and depots that is considerably influenced by the uncertainty from the above-mentioned categories.

2000 - 2002 emission compared with 1998-1999 emission
Table 7.5 shows the estimated annual dioxin emission in the period 1998 - 1999. /Hansen, 2000/. Comparing the results from SFA 2000 with the results in table 7.3 it is clear that the data quality has been improved, especially for industry and waste treatment processes. However it is primarily dioxin emission to air that has been investigated during the past two years, and this means that the estimates of emissions to soil and water have not been improved.

Looking at the total dioxin emission to air there has been a reduction in the best estimate from 95 g I-TEQ/Nm$^3$ in 1998 - 1999 to 87 g I-TEQ/Nm$^3$ in the period 2000 - 2002. This reduction is caused by lower emission levels primarily for steel and aluminium reclamation, cable scrap reclamation, hazardous waste and municipal waste. Especially the dioxin emission from the municipal waste incineration companies has decreased. The main reason behind the decreased emission is improved dioxin cleaning caused by installation of dioxin abatement.

The categories Municipal waste, Steel- and aluminium reclamation, Fires, Evaporation from PCP-preserved wood and Biomass combustion were in 1999 considered to cause considerable dioxin emission. Out of these five categories new measurements have only been available for Municipal waste and Steel and aluminium reclamation. The new data from Steel and aluminium reclamation have resulted in the fact that this category no longer can be seen as a dominant source because of the reduction of the emission level.
Table 7.5: Estimated emissions/losses to the environment and depots in Denmark 1998-1999.

<table>
<thead>
<tr>
<th>Activity</th>
<th>Emissions/losses (g I-TEQ/year)</th>
<th>to air</th>
<th>to water</th>
<th>to soil</th>
<th>to depots</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Manufacturing processes</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemicals 1)</td>
<td></td>
<td>?</td>
<td>&lt;1?</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cement and lime</td>
<td>0.045 - 3.5</td>
<td>?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other high temperature materials 2)</td>
<td>0.006 - 0.46</td>
<td>?</td>
<td>?</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steel and aluminium reclamation</td>
<td>1.3 - 5.6</td>
<td>&lt;0.005</td>
<td>0.26 - 1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other metal manufac. 3)</td>
<td>0.06 - 0.5</td>
<td>?</td>
<td>&lt;0.002?</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other manufacturing processes 4)</td>
<td>0.004 - 0.08?</td>
<td>&lt;0.01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Energy generation</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coal combustion</td>
<td>0.4 – 2.3</td>
<td>0.23 – 31?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other fossil fuels</td>
<td>0.14 – 0.46</td>
<td>0?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biomass combustion</td>
<td>0.73 – 41</td>
<td>&lt; 15.2</td>
<td>0.04 – 36?</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Use of products</strong></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCP-treated wood</td>
<td>0.5 – 26?</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other PCP-treated materials</td>
<td>&lt;0.05</td>
<td>0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bleached processes and bleaching agents</td>
<td>&lt;0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feedstuff products</td>
<td>?</td>
<td>&lt;10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Miscellaneous other human and natural activities</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fires - accidental</td>
<td>0.5 - 20?</td>
<td>?</td>
<td>1-30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fires - others</td>
<td>0.03 - 6.5</td>
<td>0.01 - 27.5?</td>
<td>0.01 -27.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Traffic</td>
<td>1.3 – 1.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cremation</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other activities 5)</td>
<td>0.09 - 0.22?</td>
<td>?</td>
<td>?</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Waste treatment and disposal</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cable scrap reclamation</td>
<td>0.005 - 5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hazardous waste inc. 6)</td>
<td>2.2 - 2.7</td>
<td>0.000001</td>
<td>0.9?</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Municipal waste inc.</td>
<td>11 - 42</td>
<td>35 - 275</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Landfills 7)</td>
<td>0.25 - 10?</td>
<td>&lt;0.05?</td>
<td>0.4 - 17?</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Waste and storm water</td>
<td>0.3 - 147</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sewage sludge disposal</td>
<td>0.07 - 0.15</td>
<td>1.3</td>
<td>0.42 - 0.46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other activities 8)</td>
<td>0.08 - 0.2</td>
<td>0.01-0.07</td>
<td>?</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Total (rounded)</strong></td>
<td><strong>19 – 170</strong></td>
<td><strong>0.3 -1.4?</strong></td>
<td><strong>1.3 – 54</strong></td>
<td><strong>38-420</strong></td>
<td></td>
</tr>
</tbody>
</table>

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

x? Figure or some of the subfigures included is deemed highly uncertain.
2. Covers manufacturing of insulation materials, tiles and bricks, glass and similar products.
3. Covers metal casting and hot-dip galvanising.
4. 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.

5. Covers a number of activities like fireworks, garden grills, cooking and miscellaneous small-scale heating/burning operations that can only be partly quantified.

6. When the emission limit value 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.

7. Emission to air and depots relates to fires in temporary depots of combustible waste.


1998-1999 emission compared with 1995 emission

In SFA 2000 /Hansen, 2000/ a comparison between the results from 1998-1999 and 1995 emissions was made. This comparison is maintained in the update of the substance flow analysis for dioxins to show the development in emission sources and emission level.

The figures presented in table 7.5 may be compared to previous estimates of dioxin emissions in Denmark presented in table 7.6. 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 7.5. On the contrary the balance for Denmark presented in SFA 2000 /Hansen, 2000/ indicates that Danish emissions are reasonably balanced with atmospheric deposition on the Danish land area (Air emission equals 19 - 170 g I-TEQ/year and atmospheric deposition 16 - 160 g I-TEQ/year). 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 7.6
Estimated annual emissions of dioxins in Denmark in 1995 (1990 figures as N-TEQ in brackets - Jensen 1997).

<table>
<thead>
<tr>
<th>Activity/process</th>
<th>Emission to (all figures as g l TEQ/year)</th>
<th>Air</th>
<th>Water</th>
<th>Soil</th>
<th>Waste/ residue</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Manufacturing</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical industry</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Paper and pulp industry</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Asphalt-mixing industry</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steel reclamation</td>
<td>7.5 (12)</td>
<td></td>
<td></td>
<td>34</td>
<td>29</td>
<td>42</td>
</tr>
<tr>
<td>Cement industry</td>
<td>0.08-1.5</td>
<td>0.1</td>
<td></td>
<td>-</td>
<td>-</td>
<td>0.08 - 1.5</td>
</tr>
<tr>
<td><strong>Energy generation</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pit coal</td>
<td>2</td>
<td></td>
<td></td>
<td>-</td>
<td>40 (53)</td>
<td>42 (53)</td>
</tr>
<tr>
<td>Gas oil – heating of houses</td>
<td>0.02</td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>0.02</td>
</tr>
<tr>
<td>Wood stoves</td>
<td>1.1 (10-50)</td>
<td></td>
<td></td>
<td>-</td>
<td>1.1 (10-50)</td>
<td></td>
</tr>
<tr>
<td>Wood burning - other</td>
<td>0.25</td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>0.25</td>
</tr>
<tr>
<td>Straw burning</td>
<td>0.07-6.6 (0.05)</td>
<td></td>
<td></td>
<td>-</td>
<td>0.07-6.6 (0.05)</td>
<td></td>
</tr>
<tr>
<td><strong>Miscellaneous activities and use of products</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fires (building, landfill, vehicles)</td>
<td>?</td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>?</td>
</tr>
<tr>
<td>Traffic</td>
<td>0.2 (10)</td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>0.2 (10)</td>
</tr>
<tr>
<td>Cremation</td>
<td>0.16</td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>0.16</td>
</tr>
<tr>
<td>Textile products</td>
<td>-</td>
<td></td>
<td></td>
<td>0.08</td>
<td>-</td>
<td>0.08</td>
</tr>
<tr>
<td><strong>Waste treatment</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cable scrap reclamation</td>
<td>0.13</td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>0.13</td>
</tr>
<tr>
<td>Shredders</td>
<td>?</td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>?</td>
</tr>
<tr>
<td>Municipal waste incinerization</td>
<td>20 (34)</td>
<td></td>
<td></td>
<td>-</td>
<td>100 (250)</td>
<td>120 (284)</td>
</tr>
<tr>
<td>Inc. of hospital/health care risk waste</td>
<td>5 (14)</td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>5 (14)</td>
</tr>
<tr>
<td>Hazardous waste inc. (KK)</td>
<td>0.23 (17)</td>
<td></td>
<td></td>
<td>-</td>
<td>1.0</td>
<td>1.23 (17)</td>
</tr>
<tr>
<td>Inc. of waste oil (district heating)</td>
<td>0.038 (0.01)</td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>0.038 (0.01)</td>
</tr>
<tr>
<td>Sewage sludge</td>
<td>0.072 (1.5)</td>
<td>0.108</td>
<td>1.1</td>
<td>0.226</td>
<td>1.51 (1.5)</td>
<td></td>
</tr>
<tr>
<td>Compost</td>
<td>-</td>
<td></td>
<td></td>
<td>1.5</td>
<td>-</td>
<td>1.5</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>38-46</td>
<td>0.12</td>
<td>2.1 - 6.1</td>
<td>175</td>
<td>215-226</td>
<td></td>
</tr>
<tr>
<td><strong>Air deposition</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>120</td>
</tr>
</tbody>
</table>

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 abatement. For other plants and activities the focus on dioxin emissions in Denmark has so far been limited.
7.3 Substance flow balance for Denmark

The available knowledge and assessments on the flow of chlorinated dioxins in Denmark in 2000 - 2002 have been compiled and illustrated in Figure 7.1.

Figure 7.1
Balance for chlorinated dioxins Denmark 2000-2002 (all figures in g I-TEQ/year)

The Danish Society

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 abatement 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 on the basis of measurements from The National Environmental Research Institute estimated at 13 - 130 g I-T EQ/year assuming a total land area of 44,000 km² (reference is made to chapter 6). The given interval does not include:

- The uncertainty coming from the fact that the measurements originate from only two locations and in addition that the measurements encompasses only one single year. This uncertainty is at the time being very difficult to assess.

- Uncertainty coming from the fact that no measurements so far have been carried out in urban areas and in the vicinity of point sources.

The calculated total contribution from dioxin sources to waste water is approximately of 0.4 - 4.8 g I-T EQ/year of which atmospheric deposition from the Danish land area served by sewage systems, equals 0.4 - 4 g I-T EQ/year. The interval for dioxin sources should be taken as comparable to the estimated total content in discharged waste and storm water of 0.4 - 1.4 g I-T EQ/year and the calculated total content in sewage sludge of 1.2 - 2.3 g I-
These observations indicate that the contribution to waste water treatment plants in Denmark is at least 1.6 - 3.7 g I-TEQ/year and it also indicates that the stated deposition level is a realistic estimate.

It is emphasised that the estimate of atmospheric deposition on the Danish land area is based on measurements that are higher than international measurements and results from the European Monitoring and Evaluation Programme, EMEP.

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.

Content in soil
The National Environmental Research Institute, Denmark has in 2001 made an investigation of the dioxin content in soil in Denmark. Furthermore six measurements have been made in 1996. The concentration of dioxin has been measured at 33 different places all over the country, in different types of soil from both field, garden and park and near and far from expected sources to huge atmospherically emissions. The measurements were carried out in a depth of 0-10 cm, because a depth profile has shown that by far the most dioxin is situated in the top soil.

There is a general tendency to higher dioxin concentrations in urban areas than in rural areas. In the rural areas the dioxin concentration is approximately 0.5 - 0.66 ng I-TEQ/kg dry matter and in urban area the concentration is approximately 3.6 - 19 ng I-TEQ/kg dry matter. Both intervals are based on 90% confidence level. Soil samples taken near waste incineration plants, power plants and bigger industrial districts do not have higher dioxin content than samples from other areas in the same category. /The National Environmental Research Institute, 2002/

The density of top soil (the upper 10 cm) is assumed to be approximately 1.5 tonnes/m$^3$ (dry matter) and the total land area is 44,000 km$^2$. Approximately 8% of the Danish land area is urban areas and the remaining area is rural areas. /Ministry of Environment, 1999/ This means that the total dioxin content in soil from rural area is equal to 3 - 4 kg I-TEQ and in urban areas the content equals 2 - 10 kg I-TEQ.

The total content of dioxin in the Danish soil is therefore estimated to be in the range of 5 - 14 kg I-TEQ, assuming that dioxin is only present in the top soil (0 - 10 cm). This interval is based on a 90% confidence level. According to the results of the Danish measurements approximately 2/3 of this amount of dioxin will be found in urban areas.

Water
Two measurements on seawater have been conducted in 2002, but it has not been possible to identify dioxin in the samples /Vikelsøe, 2002/.
References

Andersen (2000). Personal communication by Finn Juel Andersen, the Danish Environmental Protection Agency, September 2000.


Beredskabsstyrelsen (2000). Personal information from Peter Hoffmann Bank, Birkerød.


Billettiki J. (2000). Personal communication from Janus Billettiki, the Danish Environmental Protection Agency, April 2000.


COWIconset (1983). PCB/PCT-pollution – A review on consumption, pollution and routes of transport for PCB and PCT in Denmark. Danish Environmental Protection Agency (in Danish).

COWIconset (1985). Consumption and pollution by chlorophenols – A qualitative assessment of consumption and pollution by chlorophenols in Denmark. Danish Environmental Protection Agency. Environmental project no. 69, Copenhagen. (In Danish)


Danish Crematories (2000). Personal communication by Ernst Jensen, technical consultant to Danish Crematories. April 2000.


Danish EPA (2000b). Personal communication by Erik Thomsen, Danish EPA, Copenhagen, September 2000.


Danish EPA (2002). Personal communication with Jørgen Nielsen, Danish EPA, Copenhagen, September 2002.


Danish EPA (2003). Personal communication with Erik Thomsen, Danish EPA, Copenhagen, March 2003.


Greenpeace (2000). Personal communication by Pat Costner and Jacob Hartmann, Greenpeace, Copenhagen, September 2000.


Jones KC, Sewart AP (1997). Dioxis and Furans in Sewage Sludges: A Review of their Occurrence and Sources in Sludge and of their Environmental Fate, Behavior, and Significance in Sludge-Amended


Nisbeth CT and Sarofim AF (1972). Rates and routes of transport of PCB’s in the environment. Environmental Health Perspectives, April 1972 pp 21-38.


Torp (2000). Personal communication with Ulrik Torp, Danish Environmental Protection Agency, Copenhagen, November 2000.

Torp (2002). Personal communication Ulrik Torp, Danish Environmental Protection Agency, Copenhagen, January 2003.


Wormgoor J.W. (1994): Sources of dioxin emissions into the air in Western Europe. TNO Institute of Environmental and Energy Technology, Apeldoorn, the Netherlands.


Annex A: List of Companies contacted

Ansaldo Vølund A/S, Brøndby
A/S Fynsværket, Odense
Asnæsværket, Kalundborg
BASF, Health & Nutrition A/S, Ballerup and Grenå
Boglas A/S, Brønderslev
Ceropa, Svendborg
Cheminova A/S, Harboøre
Dalum Papir, Odense
Dangrønt Products A/S, Ølgod
Dansk Leca A/S, Randers
Dansk Olie Genbrug, Kalundborg
Dansk Møler industri, Mors
Dansk Restprodukthåndtering A.m.b.a., Odense
Daka, Lösning
Dania Jernstøberi, Aars
Dyrup & Co., Kolding
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, Frederiksvberg
Gori, Kolding
Herning G alvaniserings A/S, Brande
Hals Metal smelteri, Hals
Herning Varmforzinkning A/S, Herning
H. J. Hansen, Odense
Holmegaard Glasværk, Næstved
H. Lundbeck A/S, Valby
I/S KARA, Roskilde
Isover, Vamdrup
Jysk Miljørens, Galten
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
Odense Krematorium, Odense
Optiroc Nr. Uttrup Teglværk, Nørresundby
Rockwool A/S, Hedehusene
Skamol, Nykøbing Mors
Scanglas, Korsør
Special Waste System, Nørre Alslev
Spildevandscenter Avedøre I/S
Statoil, Kalundborg
Stena Aluminium A/S, Kolding
Sun Chemical A/S, Køge
Svendborg Kraftvarmeværk, Svendborg
Uniscrap A/S, Kolding
Valdemar Birn Jernstøberi, Holstebro
Aalborg Portland, Aalborg