

Survey of Dioxin Emission from PCP-treated Wood

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Environmental Project **Nr. 940** 2004
Miljøprojekt

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Preface

PCP-treated wood has in the Substance Flow Analyses for Dioxin from 2000 and 2003 been identified as a possible source of dioxin emission in Denmark. This identification has however only been based on international studies of comparable substances and the physical and chemical properties of dioxin, as so far no international studies have been made of the dioxin emission to air from PCP-treated wood.

The objective of this project is to examine whether dioxin emission from PCP-treated wood should be regarded as a substantial source of the total Danish dioxin emission and if possible to obtain a more precise interval of the Danish dioxin emission from PCP-treated wood.

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 among other things shall include an evaluation of current and projected releases, including the development and maintenance of source inventories and release estimates /Stockholm Convention, 2001/.

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Sammenfatning og konklusioner

Baggrund og formål

I forbindelse med de hidtil udførte massestrømsanalyser for dioxin fra henholdsvis 2000 og 2003 er pentachlorphenol-behandlet træ (PCP-behandlet træ) fremhævet som en mulig væsentlig kilde til emissionen af dioxin i Danmark. Emissionen af dioxin til luften fra PCP-behandlet træ er her estimeret til 0,5 - 26 g I-TEQ/år.

Der er ikke tidligere foretaget detaljerede undersøgelser af størrelsen af dioxinmissionen fra pentachlorphenol-behandlet træ. Derfor bygger estimatet i de to massestrømsanalyser for dioxin på litteratur studier af de fysiske-kemiske egenskaber for dioxin og lignende stoffer. Størrelsen af intervallet afspejler skønnets usikkerhed, og det er således størrelsen af intervallet, der i forlængelse af Miljøstyrelsens Dioxinmåleprogram, ønskes belyst gennem en vurdering af mulige kilder, samt målinger for de væsentligste kilder.

Formålet med projektet er således at få en indikation af om PCP-behandlet træ fremover skal anses som en væsentlig kilde til den danske dioxinmission og om muligt at revurdere intervallet for emission fra PCP-behandlet træ. Derudover er undersøgelsen en del af Danmarks bidrag til at møde forpligtelserne i artikel 5 i Stockholm Konventionen om Persistent Organic Pollutants (POPs).

Undersøgelsen

Projektet er udført i et samarbejde mellem COWI A/S og Danmarks Miljøundersøgelser (DMU), hvor DMU har udført PCP- og dioxin-analyser, og COWI har foretaget markedsanalyse, prøveudvælgelse samt vurdering af de fremkomne analyseresultater.

Det har inden for projektets rammer været muligt at analysere 10 prøver fra engangspaller samt fem prøver fra PCP-behandlet træværk. På grund af det begrænsede antal analyser kan undersøgelsen kun give en indikation af det generelle niveau for dioxinindhold i engangspalletræ og PCP-behandlet træ. Fordampningen fra træet er vurderet ud fra dioxinindholdet i træet, men da fordampningen ikke kan måles, er også dette estimat behæftet med usikkerhed. Estimer for dioxinkoncentration og -emission er derfor opgivet som 90 % konfidensintervaller.

Projektresultater

De følgende kilder til emission af dioxin til luft fra PCP-behandlet træ er blevet overvejet:

- Import af træ, der er behandlet med PCP
- Tilbageværende træ, der i perioden 1950 til cirka 1977 er blevet behandlet med PCP-træbeskyttelse i Danmark

Det har siden 1996 været forbudt at sælge produkter indeholdende 0,1 % PCP eller højere koncentrationer i EU. Ligeledes er salg, import og eksport af varer med et PCP-indhold på 5 ppm eller højere forbudt. Dette gælder dog ikke for lande med ocean-kyst, og det sidst registrerede forbrug af PCP og Na-PCP viser, at det derfor nu kun er Frankrig, Spanien, England og Portugal, der anvender stofferne, svarende til et forbrug på 339 tons Na-PCP og PCP (1999).

Na-PCP anvendes til imprægnering mod blåsplint i landene Frankrig, Spanien og Portugal, blandt andet til engangspaller. Med hensyn til importeret træ er den største import-kilde i Danmark derfor på nuværende tidspunkt import af engangspaller fra Spanien, Frankrig og Portugal. Behandlingen mod blåsplint er også blevet anvendt på nogle typer tropisk træ produceret uden for EU men er nu også ved at være forbudt i de lande, der eksporterer store mængder tropisk træ.

Den anden fomedentligt væsentlige kilde til dioxinmission fra PCP-behandlet træ er træ, der tilbage i perioden cirka 1950 - 1977 er blevet behandlet med træbeskyttelse indeholdende pentachlorphenol. Det er erfaringen, at stort set alle typer træbeskyttelse anvendt i denne periode indeholdt pentachlorphenol.

Engangspaller

På baggrund af markedsanalysen er der udtaget 10 prøver fra engangspaller, som er importeret til Danmark med varer fra henholdsvis Spanien, Portugal og Frankrig. Til trods for at det ikke har været muligt detaljeret at spore oprindelseslandet for selve engangspallerne men kun for varerne på pallerne, viser analyserne af PCP-indholdet i de ti prøver, at der findes PCP i seks af de ti prøver. Dette viser, at brugen af PCP stadig er udbredt i såvel Spanien, Portugal og Frankrig. Tabel 1 viser resultaterne af PCP-screeningen.

Tabel 1
Målte PCP-koncentrationer i engangspalletræ.

Prøve nr.	Varetype	Land	Målt PCP-koncentration [µg/kg]
1	Vin	Spanien	nd ¹
2	Portvin	Portugal	231
3	Champagne	Frankrig	nd
4	Vin	Spanien	nd
5	Langostillos klør i lage	Spanien	nd
6	Grønne oliven a la Provence	Frankrig	21
7	Grønne oliven	Spanien	33
8	Oliven	Spanien	75
9	Vin	Frankrig	166
10	Portvin	Portugal	26
Blind			7

* Resultaterne er fratrukket værdien for blindprøven.

1 nd = not detected (ikke fundet).

Palletræsprøven med det største PCP-indhold (nr. 2) er efterfølgende blevet analyseret for dioxin, og prøven indeholdt 4,6 ng I-TEQ/kg træ, hvilket er en lav koncentration sammenlignet med det PCP-behandlede træværk.

På trods af at den nuværende import af dioxin og PCP med importeret PCP behandlet træ således sandsynligvis er beskeden er emissionen af dioxin til luften stadig væsentlig, da den primært er bestemt af den mængde dioxin der stadig er tilstede i PCP-behandlet træ importeret i løbet af 1980'erne og 1990'erne. Emissionen er blevet revideret til 0.03 – 5 g I-TEQ/år, hvilket kun er svagt mindre end det emissions estimat på 0.03 – 6 g I-TEQ/år, der tidligere er antaget.

Det pågældende træ er anvendt til konstruktions formål og vil med tiden langsomt blive bortskaffet hvilket ligeledes langsomt vil mindske emissionen af dioxin til luften fra denne kilde. Det understreges, at de beregninger, der er præsenteret ovenfor, er meget usikre og alene har til formål at angive den relevante størrelsesorden for de pågældende dioxin emissioner.

PCP-behandlet træværk

Prøveudvælgelsen til undersøgelsen af PCP-behandlet træværk er foretaget på baggrund af en kortlægning af historikken for en række huse med træ fra perioden. Det er blandt andet blevet kortlagt, hvilken type træbeskyttelse, der er anvendt, samt hvor mange gange det er anvendt. Ud fra historikken blev der udtaget fem træværksprøver, som er blevet analyseret for dioxinindhold.

Tabel 2
Målte koncentrationer og forventede intervaller for koncentrationen i 2003.

Prøve nr.	Bygget år:	Antal påføringer 1960 - 1977	Forventet koncentration, 2003 (middelværdi) ¹ ng I-TEQ/kg træ	Målt koncentration, 2003 ng I-TEQ/kg træ]
1	1960	1 grunding og 3 overflade behandlinger	121,7 - 5324,8 (2973)	1097
2	1972	1 grunding	80,0 - 3498,4 (1789)	84
3	1968	1 grunding og 2 overfladebehandlinger	110,0 - 4810,9 (2460)	279
4	1970	1 grunding og 1 overfladebehandling	95,0 - 4156,2 (2126)	398
5	1972	1 grunding og 2 overfladebehandlinger	112,2- 4908,4 (2510)	212
Statistical analysis of measured concentrations				ng I-TEQ/kg træ]
90 % konfidensinterval for målte koncentrationer, minimum				34
90 % konfidensinterval for målte koncentrationer, maksimum				793

- Den forventede koncentration er beregnet baseret på viden om antal grundinger og overfladebehandlinger, indholdet af PCP i grundingsmidler (typisk 5 %) og overfladebehandlingsmidler (typisk 1 %) samt mængden af træ behandlet ved hver påføring. Der er antaget en årlig fordampning på 0,5 % af det aktuelle indhold af dioxin.
- De målte koncentrationer er antaget at være normal fordelte. De angivne minimums og maksimums koncentrations repræsenterer det interval indenfor hvilket 90 % af alle koncentrationer må forventes at blive registreret.

Der blev fundet dioxin i alle fem prøver, og tabel 2 viser koncentrationerne, som stemmer forholdsvis godt overens med de intervaller, der er beregnet for indholdet af dioxin i de fem prøver ud fra en antagelse om en årlig fordampningsrate på cirka 0,5 % af det aktuelle indhold af dioxin. Det totale indhold af dioxin i PCP-behandlet konstruktions træ, som stadig var i brug i Danmark er estimeret til 42 - 974 g I-TEQ for 2003. Den årlige emission fra denne træmængde er baseret på en antaget årlig fordampning på 0,5 % af indholdet af dioxin, estimeret til 0,2 - 4,9 g I-TEQ for 2003.

Hovedkonklusioner

- Indholdet af dioxin i den enkelte palletræsprøve, der blev analyseret for dioxin, var lavt. Koncentrationen af PCP i de importerede palletræsprøver var også lav sammenlignet med de koncentrationer der kunne findes i importeret træ i begyndelsen og midten af 1980'erne. Denne viden peger på at den nuværende import af engangspaller sandsynligvis ikke er en væsentlig kilde til emission af dioxin i Danmark.
- På trods af at den nuværende import af dioxin og PCP med importeret PCP behandlet træ således sandsynligvis er beskeden er emissionen af dioxin til luften stadig væsentlig, da den primært er bestemt af den mængde dioxin der stadig er tilsted i PCP-behandlet træ importeret i løbet af 1980'erne og 1990'erne. Emissionen er blevet revideret til 0.03 - 5 g I-TEQ/år, hvilket kun er svagt mindre end det emissions estimat på 0.03 - 6 g I-TEQ/år, der tidligere er antaget.
- Den tilbageværende mængde dioxin i dansk PCP-behandlet træværk, er estimeret til 42 - 974 g I-TEQ i 2003.
- De målinger af dioxin, der er foretaget på konstruktions træ har ikke bekræftet eller afkræftet antagelsen om en årlig dioxin fordampning på ca. 0,5 % af dioxin indholdet i det PCP-behandlede træ. Denne fordampningsrate passer rimeligt godt med de øvrige data for de enkelte prøver af konstrukstræ, såsom de målte koncentrationer, antallet og tidspunktet for grundning og overfladebehandling etc. Da de målte koncentrationer er i den lave ende af intervallet for de forventede koncentrationer vurderes det som usandsynligt at fordampningsraten skulle være lavere end antaget. En højere fordampningsrate kan på den anden side nemt forklares ved at antage en højere start koncentration af dioxin i det behandlede konstruktions træ.
- I det en fordampningsrate på 0,5 % af det aktuelle dioxin indhold i det PCP-behandlede træ accepteres som et bedste estimat kan den årlige dioxin emission fra PCP-behandlet konstruktions træ i Danmark i 2003 estimeres til 0,2-4,9 g I-TEQ.
- Den samlede emission fra PCP-behandlet træ kan dermed på baggrund af projektet opgøres til 0,23 - 9.9 g I-TEQ/år, hvilket er lavere end det tidligere anvendte estimat på 0,5 - 26 g I-TEQ/år [Hansen og Hansen, 2003]. På trods af at intervallet for emissionen er blevet indskrænket må PCP-behandlet træ stadig anses som en nævneværdig kilde til den samlede danske dioxin emission.

Summary and conclusions

Pentachlorophenol-treated wood has in the two Substance Flow Analyses from 2000 and 2003 been identified as a possibly substantial source of the Danish dioxin emission [Hansen, 2000] and [Hansen and Hansen, 2003]. The emission of dioxin to air from this source was estimated to 0.5 - 26 g I-TEQ/year.

This interval is however uncertain, as no detailed investigations on the subject have been available so far. The estimate was therefore based on literature studies of the physical and chemical properties of dioxins and similar substances. The size of the interval reflects the uncertainty of the estimate which has been examined in this project through an assessment of potential sources and measurements of the most substantial sources.

The objective of the project has therefore been to get a confirmation of whether PCP-treated wood should be regarded as a substantial source of dioxin in Denmark that may contribute to dioxin emissions in Denmark e.g. by evaporation of dioxin from the wood, and if possible to reduce the estimated intervals of dioxin emission from PCP-treated wood. The survey is furthermore a part of Denmark's contribution to fulfil the obligations in article 5 in the Stockholm Convention on Persistent Organic Pollutants (POPs).

The survey

The project has been carried out by COWI A/S in cooperation with the National Environmental Research Institute (NERI). NERI has undertaken the chemical analyses for PCP and dioxin, while COWI A/S has been responsible for the market analysis, selection of samples and evaluation of the analysis results.

Within this project it has been possible to analyse 10 samples of disposable pallet wood and five samples of PCP-treated construction wood.

Because of the limited number of analyses the survey can only give an indication of the general level of dioxin content in disposable pallet board wood and PCP-treated construction wood. The evaporation from the wood is assessed on the basis of the dioxin concentration in the wood, but as the evaporation is difficult to measure, the estimate of evaporation is subject to some uncertainty. The estimates of dioxin concentration and evaporation are therefore given as 90 % confidence intervals, assuming a normal distribution.

Project results

The following sources of dioxin emission to air from PCP-treated wood have been considered:

- Import of wood treated with PCP used for anti-sap-stain control.
- The construction wood treated with PCP preservation in Denmark in the period 1950 to 1977 and still in use.

Since 1996 it has been prohibited to sell products containing 0.1 % PCP or higher concentrations. Sale, import and export of goods with a PCP content of 5 ppm or higher are also prohibited. 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, and a statement of sales from 1999 shows that only France, Spain, England and Portugal still use the substances Na-PCP and PCP.

Na-PCP is used for anti-sap-stain control in France, Spain and Portugal on disposable pallet boards and other types of wood. Disposable pallet boards from the three countries are regarded to be the primary source of import of PCP-treated wood to Denmark. The use of PCP anti-sap-stain control has also been common to some types of tropical wood produced outside the EU, but new legislation is also being implemented in these countries.

The other substantial source of dioxin emission from PCP-treated wood is wood that in the period 1950 - 1977 was treated with wood preservation containing PCP. Experience shows that almost all types of wood preservation used in this period contained pentachlorophenol.

Disposable pallet boards

The 10 samples have been selected from disposable pallet boards imported to Denmark with goods from Spain, Portugal and France.

In spite of the fact that it has not been possible to state the country of origin of the pallet boards, but only of the goods on the pallet boards, the analyses of PCP content show that PCP is found in 6 out of 10 samples. This result indicates that the use of PCP is still common in Spain, France and Portugal. Table 1 shows the results of the PCP-screening:

Table 1
Measured PCP concentrations in wood from disposable pallet boards.

Sample nr.	Type of goods	Country	Measured PCP concentration [$\mu\text{g}/\text{kg}$]
1	Wine	Spain	nd ¹
2	Port wine	Portugal	231
3	Champagne	France	nd
4	Wine	Spain	nd
5	Langostillos claw in pickle	Spain	nd
6	Green olives a la Provence	France	21
7	Green olives	Spain	33
8	Olives	Spain	75
9	Wine	France	166
10	Port Wine	Portugal	26
Blind			7

The sample with the highest PCP concentration (no. 2) has subsequently been analysed for dioxin, and the analysis showed a dioxin concentration of 4.6 ng I-TEQ/kg wood which is a low concentration compared to PCP-treated construction wood.

Although the present import of dioxin and PCP with PCP preserved wood thus probably is small the emission of dioxin to air must be expected basically to be determined by the quantity of dioxin still present in PCP-preserved wood imported during the 1980'ties and the 1990'ties. The emission has consequently been recalculated to 0.03 – 5 g I-TEQ/year, which is only slightly less than the emission figure of 0.03 – 6 g I-TEQ/year previously assumed.

The wood in question is used for construction purposes and will by time slowly will be disposed of resulting in that the emission of dioxin also slowly by time should be expected to be reduced. It is emphasised that the above calculations must be taken as extremely uncertain and should be regarded as an indication only of the relevant order of magnitude for the dioxin flows in question.

Construction wood

The selection of samples for the analyses on PCP-preserved construction wood was made on the basis of a mapping of the historical facts for a number of houses from the period. The year of construction, type of wood protection and the number of applications have among other things been examined. The samples for dioxin analyses were afterwards selected based on the available information.

Table 2
Measured concentrations and expected intervals of the concentration in 2003.

Sample no.	Year of construction	No. of applications 1960 - 1977	Expected concentration, 2003 (mean value) ¹ ng I-TEQ/kg wood	Measured concentration, 2003 ng I-TEQ/kg wood]
1	1960	1 priming and 3 preservations	121.7 - 5324.8 (2973)	1097
2	1972	1 priming	80.0 - 3498.4 (1789)	84
3	1968	1 priming and 2 preservations	110.0 - 4810.9 (2460)	279
4	1970	1 priming and 1 preservation	95.0 - 4156.2 (2126)	398
5	1972	1 priming and 2 preservations	112.2- 4908.4 (2510)	212
Statistical analysis of measured concentrations				ng I-TEQ/kg wood]
90 % confidence interval for measured concentrations, minimum ²				34
90 % confidence interval for measured concentrations, maximum ²				793

1 The expected concentration is calculated based on knowledge on number of primings and preservations, the content of PCP in primers (typical 5%) and preservatives (typical 1 %) and the amount of wood treated by each application. Furthermore an annual evaporation of 0.5 % of the actual dioxin content in the wood has been assumed.

2 The measured concentrations have been assuming to follow a normal distribution. The indicated minimum and maximum concentrations represent the interval within which 90 % of all concentrations are likely to be registered.

Dioxin was detected in all five analysed samples, and table 2 shows the registered concentrations which corresponds rather well to the estimated

intervals expressing the expected concentrations of dioxin in 2003 in the five samples. The intervals are based on the assumption of an annual evaporation rate of 0.5 % of the actual content of dioxin.

The total amount of dioxin in PCP-treated construction wood still in use in Denmark by 2003 is estimated at 42 - 974 g I-TEQ for 2003. The annual emission from the amount of wood is based on an assumed annual evaporation rate of 0.5 % of the actual content of dioxin, estimated at 0.2 - 4.9 g I-TEQ/year for 2003.

Main conclusions

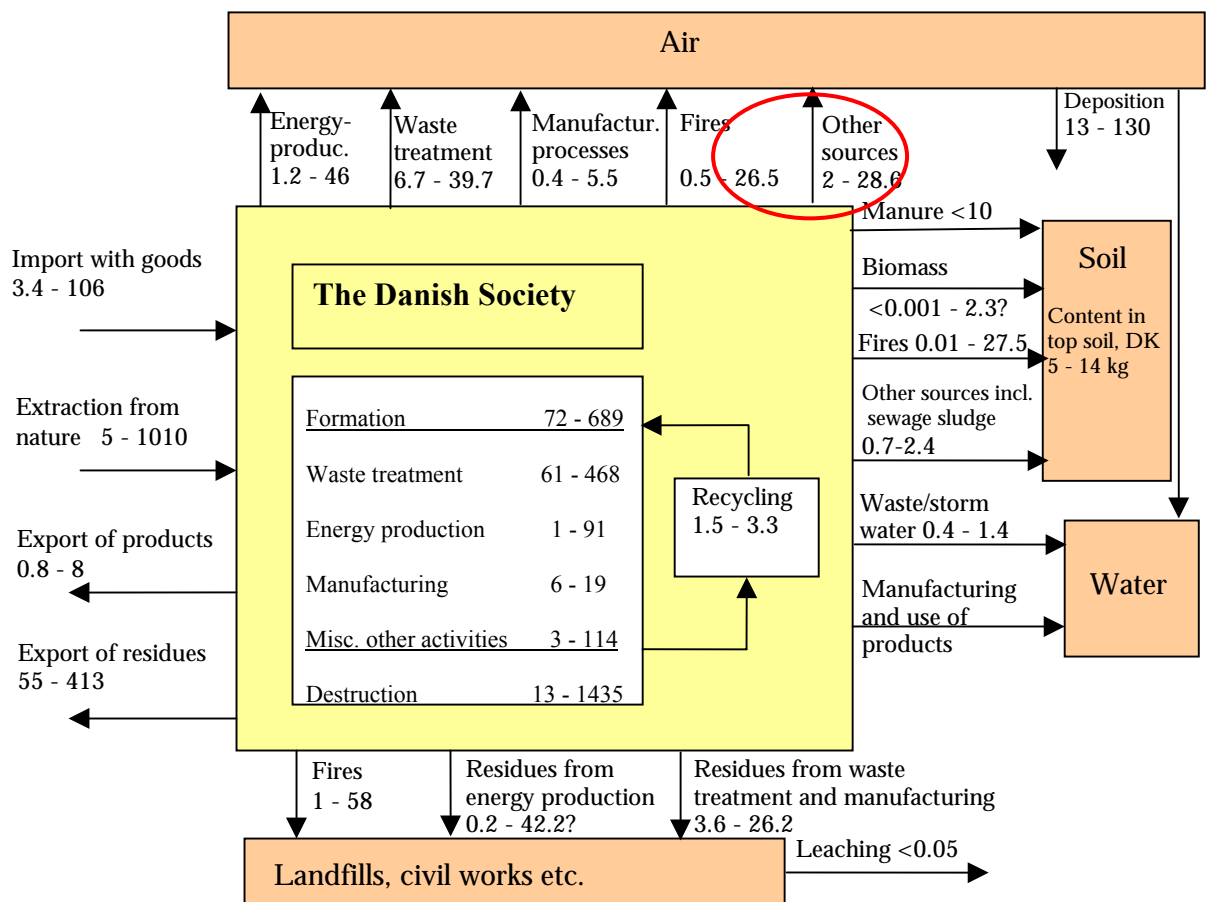
- The content of dioxin in the single sample from disposable pallet board analysed for dioxin was low. The concentration of PCP in the imported pallet boards was also low compared to the concentrations that could be found in imported wood in the beginning and middle of the 1980'ties. This knowledge indicates that the present import of disposable pallet boards is probably not a serious source of dioxin emission in Denmark.
- Although the present import of dioxin and PCP with PCP preserved wood probably is small the emission of dioxin to air from imported PCP preserved wood must be expected basically to be determined by the quantity of dioxin still present in PCP-preserved wood imported during the 1980'ties and the 1990'ties. The emission has consequently been recalculated to 0.03 - 5 g I-TEQ/year, which is only slightly less than the emission figure of 0.03 - 6 g I-TEQ/year previously assumed.
- The remaining amount of dioxin in Danish PCP-treated construction wood is estimated at 42 - 974 g I-TEQ.
- The dioxin analyses made on the construction wood samples have neither confirmed nor rejected the assumption of an annual evaporation rate of approximately 0.5 % of the actual content of dioxin in the PCP-treated wood. This evaporation rate fits reasonable well with the other data available on the samples inclusive of the measured concentrations, the number and timing of applications of primer and preservatives etc. As the measured concentrations are in the low end of the interval of the expected concentrations it is deemed unlikely that the evaporation rate should be lower than assumed, while a higher evaporation rate may be easily explained by assuming a higher initial concentration of dioxin in the wood.
- Accepting an evaporation rate of 0.5 % of the actual content of dioxin in the PCP-treated wood as the best estimate the annual dioxin emission from PCP-treated construction wood in Denmark in 2003 is estimated to 0.2-4.9 g I-TEQ.
- The total emission from PCP-treated wood can on the basis of the experiences from the project be summed up to 0.23 - 9.9 g I-TEQ/year, which is lower than the earlier used estimate of 0.5 - 26 g I-TEQ/year [Hansen and Hansen, 2003]. In spite of that the interval has been reduced PCP-preserved wood must still be regarded as a noteworthy source to the total Danish dioxin emission.

1 Introduction

In the Substance Flow Analyses for dioxin from 2000 and 2003, evaporation of dioxin from pentachlorophenol treated wood is mentioned as a possible source of a perhaps significant dioxin emission to air in the order of 0.5 - 26 g I-TEQ/year [Hansen, 2000] and [Hansen and Hansen, 2003].

The size of the interval reflects the large uncertainty connected with the estimate due to the lacking knowledge regarding the fate of the dioxins in pentachlorophenol-treated wood. Figure 1 shows the total mass balance of chlorinated dioxins in Denmark, as it was summed up in [Hansen and Hansen, 2003]. The emission from PCP-treated wood is included in the figure of "Other sources" and it shows that dioxin from PCP-treated wood can be both a rather important and a modest source of the total dioxin emission to air, depending on the end of the interval in which the true size of the emission can be found.

Figure 1
Balance of chlorinated dioxins in Denmark 2000 - 2002 (all figures in g I-TEQ/year).
[Hansen and Hansen, 2003]



This project has the objective of giving an indication at the screening level, of whether dioxin emission from PCP-treated wood shall be considered as a substantial source of the total dioxin emission to air. Because of the limited amount of samples of PCP-treated wood the project is not a full investigation of the problem, but it can give a more precise knowledge regarding the dioxin content in PCP-preserved wood in Denmark and its emission to the environment.

2 Dioxin and pentachlorophenol treated wood

Technical pentachlorophenol has been shown to contain a large number of impurities, depending on the manufacturing method. Pentachlorophenol and its derivatives are therefore generally accepted as precursors of polychlorodibenzodioxins (PCDDs) and polychlorodibenzofurans (PCDFs) and will naturally contain traces of dioxin (used as abbreviation for PCDDs and PCDFs) developed during the formation process of pentachlorophenol. Other impurities can be polychlorodiphenyl ethers, polychlorophenoxyphenols, chlorinated cyclohexenones and polychlorinated biphenyls (PCBs) [Hansen, 2000]. Technical PCP is typically about 86 % pure [Borysiewicz and Kolsut, 2002]. By now most of the PCP in the PCP-preserved wood still in use in Denmark is expected to have evaporated [Borsholt, 2003], but no precise knowledge exists as to what extent the dioxin has also evaporated. If a parallel is drawn to evaporation of PCB from joint foam for construction purposes, a dioxin evaporation of 10 % of the original content can be expected over a 20-year period. Based on this thesis the annual emission to air from PCP-treated wood was estimated to 0.5 - 20 g I-TEQ/year [Hansen and Hansen, 2003]. The evaporation rate assumed corresponds reasonable well to Dutch assumptions of a half-life of dioxin in wood of 150 years [Bremmer et al 1994].

Pentachlorophenol and its derivatives have been used as wood preservatives in Denmark in a period from approximately 1950 to 1977, where restrictions on the content of dioxin in PCP were introduced [Bylaw, 582-1977]. These restrictions actually functioned as a ban, eliminating by and large all intended use and consumption of PCP in Denmark. Chlorophenols are extremely toxic to the aquatic environment, where chlorophenols can accumulate in sediments. Furthermore infiltration in soil might be a threat to the groundwater resource. Finally PCP and other chlorophenols are a source of formation and dispersal of dioxins and dibenzofurans. Small amounts of dioxins and furans are formed as impurities during production of PCP, and PCP can furthermore be converted into dioxins during combustion processes, primarily waste incineration processes [COWIConsult, 1985]. The health effects by PCP were another reason for the restrictions. The use of PCP in wood preservatives has among other things resulted in cancer deaths in the lumber industry [Alexander, 1996].

The restriction from 1977 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 outdoors) and waterproofing of fibres and heavy textiles. The total content of HCDD (HexaChloroDibenzoDioxin) in PCP must, however, not exceed 2 ppm [European Commission, 1999].

The use of PCP as wood preservatives has decreased dramatically in Europe since 1980, but it is still used in some scale in Southern Europe for among other things disposable pallets that can be imported to Denmark with goods.

3 Market analysis

The concern regarding use of PCP as wood preservative has focused on:

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

The essential experience regarding these two subjects has been examined through studies of existing Danish and international literature.

3.1 Use of PCP as wood preservative in Denmark

Up to 1977 PCP was widely used in Denmark for industrial wood preservation of windows and doors as well as for surface preservation and 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 consumption reached 100 tons PCP/year
- Maximum in 1972 with 250 - 300 tons PCP/year
- Decreased to 0 ton 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. 3,900 tons PCP. According to [Borsholt, 2003] PCP-based wood protection was dominating the market in the late 1960'es and the early 1970'es because of its very effective preservation of the wood. Almost all types of wood preservation used in this period contained PCP, irrespective of brand, coloured or non-coloured, industrial or private use. PCP was not used in indoor paints, as the PCP resulted in an obnoxious smell. Due to the health and environmental effects of the substance, the use of PCP decreased dramatically from the middle of the 1970'es [Borsholt, 2003].

There is no precise knowledge as to what extent PCP-preserved wood is still in use in Denmark. 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 in Denmark by year 2003 should equal an initial PCP quantity of approx. 430 tons.

An initial PCP quantity of 430 tons will assuming an average concentration for PCP of 3 % in wood preservatives and a density of the preservation liquids of 0,85 kg/l correspond to 16860000 liter of preservation liquids. Assuming, furthermore, a consumption of wood preservatives of 7m²/l, and an average thickness and density of the wood treated of approximately 2 cm and 520 kg/m³ respectively, the PCP quantity of 430 tons will correspond to around 1.230.000 tons of wood treated.

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. Assuming that the dioxin content in the PCP used for wood preservation was in the range of 0.16 – 7 mg I-TEQ/kg PCP, 430 tons of PCP, furthermore, correspond to an amount of dioxin of 70 – 3000 g I-TEQ [Hansen and Hansen, 2003].

3.2 Import and consumption of PCP in Europe

Production of PCP and Na-PCP ceased in EU in 1992, and since then PCP and Na-PCP have been imported to the European market, primarily from USA and perhaps also from South East Asia. The European consumption of Na-PCP was in 1996 378 tonnes and of PCP 30 tonnes. The distribution of the 378 tons of Na-PCP was as follows:

Table 2.1: Consumption of Na-PCP in 1996, EU. [Borysiewicz and Kolsut, 2002]

Country	Amount of Na-PCP [tonnes]
Spain	144
France	126
Portugal	108
Total	378

Na-PCP is used for treatment of wood as a sap-stain control agent for freshly cut timber (preservation to avoid discolouring fungi). For industrial anti-sap-stain control a concentration of 2-5 % Na-PCP dissolved in water is used [Bywater, 2000 or Lassen, 2000]. Na-PCP is applied to the freshly sawn timber during the drying process. The preservation lasts 6 - 11 months [Kirk Othmer, 1993]. The consumption for this purpose covers almost 90 % of the total consumption of PCP, Na-PCP and PCP laurate. In Portugal three products are treated with Na-PCP: Pallet boards, construction timber and fencing panels [Borysiewicz and Kolsut, 2002].

Out of the 30 tonnes PCP imported in 1996 28 tonnes were synthesized to 46 tonnes PCP laurate in the UK. PCP laurate is used for preservation of textiles exposed to fungi and bacteria (tent textiles and military equipment). 15 tonnes of PCP laurate were used in the UK and France and the rest was exported to countries outside the EU. This means that no more than 2 tonnes of PCP can have been used for wood preservation in 1996 [Borysiewicz and Kolsut, 2002]. The import of PCP and Na-PCP to the EU has also been stated for 1999, and the development in import for 1996 and 1999 can be seen in table 2.2:

Table 2.2: Imports of PCP and Na-PCP to the European Union in 1996 and 1999. [Borysiewicz and Kolsut, 2002]

Substance	1996 [tonnes per year]	1999 [tonnes per year]	Import countries
PCP	30	15	UK
Na-PCP	378	324	Spain, France and Portugal

Production of PCP laurate in the EU ceased in 1999 according to the Commission Directive 1999/51/EC which prohibits the use of PCP and its compounds as a synthesizing agent in industrial processes from the 1 September 2000 [European Commission, 1999]. This means that the import of PCP probably is close to zero. It is however possible that a small amount is still imported for other uses, such as wood treatment [Borysiewicz and Kolsut, 2002]. Na-PCP is therefore the most used substance.

3.3 Import of PCP-treated wood to Denmark

The amount of PCP-treated wood that is imported to Denmark is unknown, but it must be assumed that a part of the PCP-treated wood from Southern Europe will be imported to Denmark, e.g. via disposable pallet boards arriving with different types of goods. The consumers cannot see if the disposable pallet boards are treated with PCP, and this means that the pallet boards easily can be disposed of in a wrong way, e.g. by using the wood as fuel in for example private wood-burning stoves.

Pallet board is regarded to be the most likely source of import of PCP-treated wood, but import of other PCP-treated wood products from countries outside the EU is also possible. The following studies report of PCP contents in other types of wood from countries outside the EU, but it is not known if wood with such conditions have been imported to Denmark.

In a Swiss investigation from 1996 PCP and TeCP was measured in 47 samples of different kinds of wood. 9.3 % of the total amount of samples contained more than 5 mg/kg of PCP + TeCP together. PCP and TeCP were found in different kinds of wood from Finland, Canada and Africa. 30 % of the samples with tropical wood from Africa contained more than 5 mg/kg of PCP+TeCP [OFEFP, 1998].

Until a few years ago PCP was also used in Malaysia for anti-sap-stain control/preservation of the exotic wood species called hevea or rubber wood. The PCP is typically applied when the timber is freshly sawn and still wet. This means that the absorbency of the wood is rather low and that some of the PCP will be removed again during the processing. The use of PCP is now illegal in Malaysia, but it is questionable if the ban has been fully implemented at present [Witterseh, 2003] and [Henriksen, 2003]. Countries like Indonesia, Phillippines and Cambodia which also produce large amounts of hevea might also be using PCP preservation of wood and are perhaps still using it [Henriksen, 2003].

The Danish Technological Institute (Teknologisk Institut) has in a project for The Danish Environmental Protection Agency in the autumn of 2003 analysed for chemical substances in different types of tropical wood. The PCP content in hevea has been examined, but the tests showed no signs of PCP-content in the samples [Witterseh, 2003].

The implementation of the FSC marking and the focus on the environmental effects of tropical wood must also influence the amount of PCP-preserved tropical wood imported to Denmark, and it is generally believed that the amount of PCP-treated tropical wood imported to Denmark is very low. It may however be possible that small amounts of PCP-treated tropical wood is imported to Denmark due to the large quantities that is imported in the present years from Asia and Africa.

4 Selection of sampling material

4.1 Construction wood from the period 1960 - 1972

There have been selected samples of construction wood from five different houses. All houses are built in the period 1960 - 1972 and they still contain -at least partly - the original woodwork. Table 4.1 shows information about the selected samples of construction wood.

A precondition for the selection of the samples has been that the history of the houses and the treatment of the woodwork were well known.

Table 4.1: Data of selected samples of construction wood.

Sample number	Origin of wood	Year of construction	Type of wood preservative(s)	Number of preservations during 1960 - 1974 (1980)	Weight /thickness of the selected sample 1)
1	From shutter	1960	Primer and wood preservation of the "Gori" brand, coloured (brown)	Assumed priming and 2 times preservation in the period of 1960 - 1968 and 1 preservation around 1970. 2)	4 g/2cm
2	From overhang	1972	Primer of the "Gori" brand, non-coloured	Priming in 1972. Next treatment in 1976/77, which likely was not a PCP - treatment.	2 g/2 cm
3	From overhang	1968	Primer and wood preservation of the "Pinotex" brand, coloured (brown)	Assumed priming and preservation in 1968. Extra preservation in the beginning of the 1970'ties. Perhaps also late in the 1970'ties. 3)	2 g/2 cm
4	From overhang	1970	Primer and wood preservation (coloured) of either the "Pinotex" or the "Solignum" brand	Priming and preservation in 1970. Painted again around 1976 with emulsion paint	10 g/2 cm
5	From overhang	1972	Primer and wood preservation of the "Pinotex" brand, coloured (brown)	Assumed priming and preservation in 1972. Extra preservation around 1975. Later painted with emulsion paint.	4 g/2 cm

- 1) Figures are approximate.
- 2) The present owner took over the house in 1968. The woodwork was well maintained. After around 1970 no more PCP preservations were carried out.
- 3) The present owner took over the house with well maintained woodwork in 1970.
- 4) The present owner took over the house with well maintained woodwork in 1974.

4.2 Imported wood from disposable pallet boards

4.2.1 Selection of sampling material

Anti-sap-stain control with PCP leaves no visible signs on the pallet boards, and it is therefore not possible to visibly check if the disposable pallet boards have been PCP-treated. The selection of sampling material has instead focused on where the pallet boards came from or more precisely where the goods transported on the pallets came from. It was therefore chosen to select samples from goods that were imported directly from Spain, Portugal and France - countries that are reported to still import PCP for the use of for example anti-sap-stain control.

The samples have been taken from COOP Denmark's central storehouse for dry goods, which distribute dry goods to all COOP supermarkets in Denmark. The pallets, chosen for sampling, have according to COOP's entry dock been imported directly to COOP Denmark's central storehouse for dry goods from producers in Spain, France and Portugal [Larsen, 2003].

Two other major supermarket chains have been contacted, but it is not possible for these chains to locate disposable pallet boards that origin Spain, Portugal and France. It is quite normal that goods are re-placed on other pallet boards once or several times during the transport from Southern Europe to Denmark, and it can therefore be difficult to trace which goods that are received on disposable pallet boards from the three countries.

4.2.2 The selected samples

Table 4.2 shows the 10 selected samples and information about the type of goods they have been used for and the country from which the goods have been imported.

Table 4.2: Selected pallet board samples.

Sample number	Date of selection	Type of goods	Country
1	14.10. 2003	Wine	Spain
2	14.10.2003	Port wine	Portugal
3	14.10. 2003	Champagne	France
4	14.10.2003	Wine	Spain
5	10.11.2003	Langostillos claw in pickle	Spain
6	10.11.2003	Green olives a la Provence	France
7	10.11.2003	Green olives	Spain
8	30.11.2003	Olives	Spain
9	30.11.2003	Wine	France
10	30.11.2003	Port Wine	Portugal

Table 4.2 shows that the samples cover all three European countries still expected to be using Na-PCP. Because of the limited number of samples it is not possible to make a reliable evaluation of the extent of the use of PCP in

disposable pallet boards from each of the three countries. It can, however, give an indication of whether PCP can be found in imported disposable pallet boards.

The sampling material was as a first step analysed for PCP in the wood. Based on the results of the PCP-screening the dioxin analysis was made on the sample with the highest measured concentration of PCP. The method for analyzing is further described in Appendix A. Each sample had a weight of approximately 10 grams.

5 Results

5.1 PCP screening of pallet board samples

Table 5.1 shows the analysed concentrations of pentachlorophenol in the pallet board samples. All samples have only been single-determined. The results show that 6 out of 10 samples contained pentachlorophenol. Sample number 2 from Portugal had the highest concentration of pentachlorophenol, and the dioxin concentration in this sample was therefore afterwards measured (see result in next section).

Table 5.1 shows that out of the 6 samples with a detected pentachlorophenol concentration, two of the samples came from Spain; two came from France and two from Portugal. This means that both analysed samples from Portugal and 2 out of the three samples from France were positive.

It should be noted that the concentration of PCP registered in the samples represents an average of the concentration over the entire thickness of the individual samples.

Table 5.1
Results of screening of pentachlorophenol in pallet board samples.

Sample number	Type of goods	Country	Analysed amount [g]	Concentration of pentachlorophenol [$\mu\text{g}/\text{kg}$]
1	Wine	Spain	0.102	nd ¹
2	Port wine	Portugal	0.103	231
3	Champagne	France	0.102	nd
4	Wine	Spain	0.100	nd
5	Langostillos claw in pickle	Spain	0.100	nd
6	Green olives a la Provence	France	0.101	21
7	Green olives	Spain	0.100	33
8	Olives	Spain	0.101	75
9	Wine	France	0.100	166
10	Port Wine	Portugal	0.101	26
Blind			0.100	7

* The results have been deducted the value of the blind sample.

¹ Not detected.

5.2 Dioxin analysis of pallet board sample

Pallet board sample number 2 was analysed for dioxin, but as table 5.2 shows the dioxin concentration in the pallet board sample is low. It is noted that only

one analysis has been made, and the result may thus be regarded as an indication of the dioxin level in these items rather than solid documentation. As for PCP the concentration of dioxin registered in the sample represents an average of the concentration over the entire thickness of the sample.

Table 5.2
Results of dioxin analysis of pallet board sample no. 2

Sample number	2
Analysed amount [g]	0.103
Dioxin concentration	ng/kg
2378-TCDD	nd
12378-PeCDD	nd
123478-HxCDD	nd
123678-HxCDD	nd
123789-HxCDD	nd
1234678-HpCDD	nd
OCDD	nd
2378-TCDF	9.7
12378-PeCDF	4.9
23478-PeCDF	nd
123478-HxCDF	6.8
123678-HxCDF	4.9
123789-HxCDF	nd
234678-HxCDF	nd
1234678-HpCDF	nd
1234789-HpCDF	nd
OCDF	nd
WHO-TEQ	4.6
I-TEQ	4.6

nd = Not detected

5.3 Construction-wood samples

The five samples of construction wood have been analysed for dioxin by single determination. The pentachlorophenol concentration in the samples has not been analysed.

Table 5.3 shows the concentration of the different isomers measured and the total concentration of the dioxin isomers given in ng I-TEQ/kg and in ng WHO-TEQ/kg.

The concentration of dioxin registered in the samples represents an average of the concentration over the entire thickness of the individual samples.

Table 5.3
Results of dioxin analyses of the five samples of construction wood.

Sample number	1	2	3	4	5	Blind
Analysed amount [g]	1.03	1.00	1.00	1.01	1.00	1
Dioxin concentration	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg
2378-TCDD	8.6	nd	nd	<i>0.3</i>	0.9	0.1
12378-PeCDD	20.3	2.3	1.3	5.9	9.2	
123478-HxCDD	nd	nd	nd	nd	23	
123678-HxCDD	1527	88	201	470	159	
123789-HxCDD	189	8	13	133	48	0.1
1234678-HpCDD	47547	2958	9704	10223	8180	1.4
OCDD	189140	10243	89588	55519	55982	11.2
2378-TCDF	9.8	nd	<i>0.1</i>	1.9	11.6	
12378-PeCDF	6.4	1.1	0.6	4.0	6.5	
23478-PeCDF	26.0	2.4	3.0	17.7	33.6	
123478-HxCDF	217.1	18.1	181.0	75.6	33.0	
123678-HxCDF	139.2	18.5	24.3	59.0	44.5	
123789-HxCDF	31.7	2.0	9.6	18.8	12.6	
234678-HxCDF	151.4	16.6	27.9	84.3	58.0	
1234678-HpCDF	18503	1672	3995	12845	1472	0.4
1234789-HpCDF	1251	122	654	158	120	
OCDF	77128	9730	33396	20211	8648	1.3
WHO-TEQ	950	68	200	333	158	0.1
I-TEQ	1097	84	279	398	212	0.1

* The values have been deducted the values of the blind sample.

** The values written in italics are detected with high uncertainty.

nd = Not detected

6 Interpretation of results

6.1 Interpretation of results - construction wood

The results presented in section 5.3 clearly documents that dioxin is still present in construction wood treated with PCP-preservatives before 1977. However, the results do not in itself address the issues of evaporation of dioxin from PCP-preserved wood and likely evaporation rates.

In order to address these issues it is necessary to compare the results with the present knowledge regarding dioxin in construction wood preserved with PCP in Denmark during 1950 - 1977. The fundamental knowledge and assumptions can be summarised as follows:

- The content of dioxin in technical PCP during the 1970'es and the beginning of the 1980'es was in the range of 0.16 - 7 mg I-TEQ/kg PCP (reference is made to section 3.1). It is assumed, that these figures are representative also for technical PCP used during the 1950'ties and the 1960'ties.
- The evaporation rate for dioxin in wood is estimated to around 0.5 % of the actual content per year in accordance with the knowledge on evaporation rates presented in section 2. It should be noted that in the original study (reference is made to [Hansen, 2000]), the evaporate rate was calculated as 0.5 % of the original content per year meaning that the evaporation per unit of wood was taken to be constant over the years no matter the amount of dioxin left in the wood. To assume that the evaporation rate is related to the actual content of dioxin instead of the original content seems more logic besides that it represents a better approximation to the knowledge on evaporation rates presented in section 2.
- The PCP-content in the wood preservatives varied between 1 % (preservation) and 5 % (primer) [COWIconsult, 1985].

Assuming a mean-consumption of the wood preservatives of 7 m²/litre, a density of 0.85 kg/l, a thickness of the samples of approx. 2 cm and a mean density for wood of 520 kg/m³, the total dioxin content applied to the wood can be calculated as follows:

Preservation:

$(0.85\text{kg preservative/l preservative}) (0.01\text{kg PCP/kg preservative}) (0.16 - 7 \text{ mg I-TEQ/kg PCP}) / (7\text{m}^2 * 0.02\text{m} * 520 \text{ kg wood/m}^3) = 18.7 - 817.3 \text{ ng I-TEQ/kg wood}$

Priming:

$(0.85\text{kg preservative/l preservative}) (0.05\text{kg PCP/kg preservative}) (0.16 - 7 \text{ mg I-TEQ/kg PCP}) / (7\text{m}^2 * 0.02\text{m} * 520 \text{ kg wood/m}^3) = 93.4 - 4086.5 \text{ ng I-TEQ/kg wood.}$

Table 6.1: Estimate of expected dioxin concentration in the selected construction wood samples assuming 0.5 % evaporation per year of actual content.

Year	Sample 1, min. [ng I-TEQ/kg]	Sample 1, max. [ng I-TEQ/kg]	Sample 2, min. [ng I-TEQ/kg]	Sample 2, max. [ng I-TEQ/kg]	Sample 3, min. [ng I-TEQ/kg]	Sample 3, max. [ng I-TEQ/kg]	Sample 4, min. [ng I-TEQ/kg]	Sample 4, max. [ng I-TEQ/kg]	Sample 5, min. [ng I-TEQ/kg]	Sample 5, max. [ng I-TEQ/kg]
No. of applications	4 (1960, 1960, 1965, 1971)	4(1960, 1960, 1965, 1971)	1 (1972)	1 (1972)	3 (1968, 1968, 1971)	3 (1968, 1968, 1971)	2 (1970, 1970)	2 (1970, 1970)	3 (1972, 1972, 1975)	3 (1972, 1972, 1975)
1960	112.1	4903.8								
1961	111.5	4879.3								
1962	111.0	4854.9								
1963	110.4	4830.7								
1964	109.9	4806.5								
1965	128.0	5599.8								
1966	127.4	5571.8								
1967	126.7	5543.9								
1968	126.1	5516.2			112.1	4903.8				
1969	125.5	5488.6			111.5	4879.3				
1970	124.8	5461.2			111.0	4854.9	112.1	4903.8		
1971	142.9	6251.2			129.1	5648.0	111.5	4879.3		
1972	142.2	6219.9	93.4	4086.5	128,5	5619.7	111.0	4854.9	112.1	4903.8
1973	141.5	6188.8	92.9	4066.1	127,8	5591.6	110.4	4830.7	111.5	4879.3
1974	140.8	6157.9	92.5	4045.8	127,2	5563.7	109.9	4806.5	111.0	4854.9
1975	140.0	6127.1	92.0	4025.5	126,5	5535.8	109.3	4782.5	129.1	5648.0
1976	139.3	6096.5	91.6	4005.4	125,9	5508.2	108.8	4758.6	128.5	5619.7
1977	138.7	6066.0	91.1	3985.4	125,3	5480.6	108.2	4734.8	127.8	5591.6
1978	138.0	6035.6	90.6	3965.5	124,6	5453.2	107.7	4711.1	127.2	5563.7
1979	137.3	6005.5	90.2	3945.6	124,0	5426.0	107.1	4687.5	126.5	5535.8
1980	136.6	5975.4	89.7	3925.9	123,4	5398.8	106.6	4664.1	125.9	5508.2
1981	135.9	5945.6	89.3	3906.3	122,8	5371.8	106.1	4640.8	125.3	5480.6
1982	135.2	5915.8	88.8	3886.7	122,2	5345.0	105.5	4617.6	124.6	5453.2

Year	Sample 1, min. [ng I-TEQ/kg]	Sample 1, max. [ng I-TEQ/kg]	Sample 2, min. [ng I-TEQ/kg]	Sample 2, max. [ng I-TEQ/kg]	Sample 3, min. [ng I-TEQ/kg]	Sample 3, max. [ng I-TEQ/kg]	Sample 4, min. [ng I-TEQ/kg]	Sample 4, max. [ng I-TEQ/kg]	Sample 5, min. [ng I-TEQ/kg]	Sample 5, max. [ng I-TEQ/kg]
1983	134.5	5886.3	88.4	3867.3	121.6	5318.3	105.0	4594.5	124.0	5426.0
1984	133.9	5856.8	88.0	3848.0	121.0	5291.7	104.5	4571.5	123.4	5398.8
1985	133.2	5827.5	87.5	3828.7	120.3	5265.2	104.0	4548.7	122.8	5371.8
1986	132.5	5798.4	87.1	3809.6	119.7	5238.9	103.4	4525.9	122.2	5345.0
1987	131.9	5769.4	86.6	3790.5	119.1	5212.7	102.9	4503.3	121.6	5318.3
1988	131.2	5740.6	86.2	3771.6	118.6	5186.6	102.4	4480.8	121.0	5291.7
1989	130.6	5711.9	85.8	3752.7	118.0	5160.7	101.9	4458.4	120.3	5265.2
1990	129.9	5683.3	85.3	3734.0	117.4	5134.9	101.4	4436.1	119.7	5238.9
1991	129.3	5654.9	84.9	3715.3	116.8	5109.2	100.9	4413.9	119.1	5212.7
1992	128.6	5626.6	84.5	3696.7	116.2	5083.7	100.4	4391.8	118.6	5186.6
1993	128.0	5598.5	84.1	3678.2	115.6	5058.2	99.9	4369.9	118.0	5160.7
1994	127.3	5570.5	83.7	3659.9	115.0	5033.0	99.4	4348.0	117.4	5134.9
1995	126.7	5542.6	83.2	3641.6	114.5	5007.8	98.9	4326.3	116.8	5109.2
1996	126.1	5514.9	82.8	3623.3	113.9	4982.7	98.4	4304.6	116.2	5083.7
1997	125.4	5487.3	82.4	3605.2	113.3	4957.8	97.9	4283.1	115.6	5058.2
1998	124.8	5459.9	82.0	3587.2	112.8	4933.0	97.4	4261.7	115.0	5033.0
1999	124.2	5432.6	81.6	3569.3	112.2	4908.4	96.9	4240.4	114.5	5007.8
2000	123.6	5405.4	81.2	3551.4	111.6	4883.8	96.4	4219.2	113.9	4982.7
2001	122.9	5378.4	80.8	3533.7	111.1	4859.4	96.0	4198.1	113.3	4957.8
2002	122.3	5351.5	80.4	3516.0	110.5	4835.1	95.5	4177.1	112.8	4933.0
2003	121.7	5324.8	80.0	3498.4	110.0	4810.9	95.0	4156.2	112.2	4908.4
2004	121.1	5298.1	79.6	3480.9	109.4	4786.9	94.5	4135.4	111.6	4883.8

Based on these assumptions the concentration of dioxin to be expected in the samples has been calculated in table 6.1. For each sample a calculation based on the low limit of dioxin content in PCP as well as a calculation based on the high limit has been presented. The calculations further take into consideration the number of applications of wood preservatives (for each sample and the year of the individual applications).

In table 6.2 is the expected dioxin concentration (2003-figures) for the five samples as calculated in table 5.1 compared with the measured 2003 concentrations as stated in table 4.3.

Table 6.2: Expected dioxin concentration in wood in 2003 compared to measured values.

Sample no.	Expected concentration, 2003 (mean value) [ng I-TEQ/kg wood]	Measured concentrations, 2003 [ng I-TEQ/kg wood]
1	121.7 - 5324.8 (2973)	1097
2	80.0 - 3498.4 (1789)	84
3	110.0 - 4810.9 (2460)	279
4	95.0 - 4156.2 (2126)	398
5	112.2- 4908.4 (2510)	212
Statistical analysis of measured concentrations		[ng I-TEQ/kg wood]
Min. (90 % confidence level) ¹	-	34
Max. (90 % confidence level) ¹	-	793

1. The measured concentrations have been assuming to follow a normal distribution. The indicated minimum and maximum concentrations represent the interval within which 90 % of all concentrations are likely to be registered.

All measurements are within the interval that could be expected. However, it is obvious that generally the measurements belong to the low end of the interval and generally far below the average of the expected values.

The fact that the measurements generally are low could be explained by assuming:

- Either that the dioxin content in PCP generally was in the low end of the range 0.16 - 7 mg I-TEQ/kg PCP identified in [Hansen, 2000]. This hypothesis fits reasonable well with the fact that the sample with the highest content is sample no. 1 from a house constructed and initially treated in 1960 at a time when the dioxin issue were hardly calling for any attention. The other four samples and in particular sample 2 and 5 are from houses constructed and initially treated at a time when dioxin was beginning to become an issue - studies on toxicology etc. of dioxin was published in 1971 [MST 1977] indicating that dioxin was an issue at that time - and manufacturers of PCP and wood preservatives were aware of the need to minimize the content of dioxin in PCP and wood preservatives.
- Or that the rate of evaporation of dioxin from wood is underestimated.

It must, however, be recognised that the measurements also may be

influenced by the following factors:

- The exact quantity of primer or preservative used in each case. The calculation of expected concentration is based on an assumed consumption of 1 litre of primer/preservative per 7 m² of wood surface. In reality this consumption rate may have been higher as well as lower.
- The actual content of dioxin in the primer/preservative. The primers/preservatives used represent different brands and the dioxin content may well have differed between the brands.

Based on the discussion above it is obvious that the outcome of the measurements is influenced by a number of factors. Thus the results do neither confirm nor reject the assumed evaporation rate of 0.5 %/year of the actual content of dioxin in the wood. However, the fact that the results are in the low end of the interval that could be expected and for one of the measurements almost equal to the lower limit makes it unlikely that the evaporation rate should be lower than assumed. A higher evaporation rate may on the other hand be easily explained by assuming a higher initial concentration of dioxin in the wood.

The emission rate of 0.5 % will therefore be used as a best estimate together with the measured values to assess the annual evaporation from PCP-treated construction wood.

6.2 Revised estimate of emission of dioxin for construction wood

The measured concentrations have been analysed statistically, and the minimum and maximum concentration levels corresponding to a 90 % confidence interval have been identified in table 6.2. Based on these concentration levels and the estimated amount of PCP-treated wood left in Denmark by 2003 the amount of dioxin in the wood and the annual evaporation can be estimated. The calculation is presented in table 6.3.

Table 6.3: Amount of dioxin in construction wood, 2003 and evaporation in 2002.

Amount of PCP-treated wood still in use in Denmark by 2003 ¹	1.230.000 tons
Assumed minimum concentration of dioxin in the wood ²	34 ng I-TEQ/kg
Assumed maximum concentration of dioxin in the wood ²	793 ng I-TEQ/kg
Amount of dioxin in the remaining amount of construction wood, 2003, minimum	42 g I-TEQ
Amount of dioxin in the remaining amount of construction wood, 2003, maximum	974 g I-TEQ
Annual evaporation in 2003 in Denmark, minimum ³	0.2 g I-TEQ ⁴
Annual evaporation in 2003 in Denmark, maximum ³	4.9 g I-TEQ

1. Reference is made to section 2.

2. Reference is made to table 6.2.

3. Calculated on the basis of an annual evaporation rate of 0.5 % of the actual dioxin content in the wood.

As stated in table 6.3 the evaporation of dioxin from PCP-treated wood still in use in Denmark in 2003 can be estimated to be in the range of 0.2 - 4.9 g I-TEQ/year. This figure can be compared with the estimate presented for year 2000 of 0.5 - 20 g I-TEQ/year [Hansen, 2000] and repeated for 2002 [Hansen and Hansen, 2003].

The revised estimate presented for 2003 must be regarded as a considerable improvement compared to the previous estimates, as the estimate is now based on actual measurements documenting that significant quantities of dioxin can be found in PCP. Among the assumptions still causing uncertainty may be mentioned the following:

- The exact rate of evaporation of dioxin from PCP-treated wood. The estimate is based on an assumed rate of 0.5 % of actual content per year. As discussed in section 6.1 this assumption could be in the low end, but is so far accepted as the best estimate based on the present knowledge.
- The life of PCP-preserved construction wood. In the calculations in this report is assumed a maximum life of 40 years. As documented by sample no. 1 from 1960 the actual life of PCP-preserved wood may in some cases exceed this maximum.

The reduced estimate for 2003 compared to the estimate from 2000 is apart from being based on actual measurements also explained by the following:

- The amount of PCP-treated wood still in use in Denmark was in 2000 assumed to correspond to an initial PCP quantity of approx. 680 tons, while the estimate for 2003 is assumed to correspond to an initial PCP-quantity of 430 tons. This change which is due to natural replacement of construction wood is in itself causing a 37 % lowering of the estimate for dioxin evaporation from PCP-treated construction wood in Denmark.
- The assumed rate of evaporation has been changed from 0.5 % of the original content to 0.5 % of the actual content. This change in itself will lower the estimate for dioxin evaporation by around 10-15 %.

It is possible that some dioxin having migrated to the surface of the wood may be washed off together with the precipitation to different recipients. Evaporation to air is however expected to be the predominant type of emission.

It is noted that the estimate of the amount of PCP-treated wood still in use in Denmark is based on an assumption of that the wood treated in all cases have a thickness of approximately 2 cm. The calculation of the amount of PCP-treated wood still in use thus corresponds to the characteristics of the samples of construction wood analysed in study (reference is made to section 4.1) meaning that the estimate of amount of dioxin still present in construction wood should be regarded as reliable.

However, the estimated amount of amount of PCP-treated wood still in use in Denmark may not be reliable, as the actual dimensions of the construction wood treated with PCP may differ from the dimensions of the samples, especially with respect to the thickness of the wood.

6.3 Interpretation of results - disposable pallet board

It is quite surprising that it has been possible to find traces of PCP in 6 out of 10 randomly chosen samples, chosen only on the basis of the country of origin of the imported goods. Although 10 samples are a relatively small number of samples the analyses indicate that the use of PCP anti-sap-stain control is still common in Portugal, France and Spain.

The registered PCP concentration levels are however of a limited scale compared to the previously used estimates of imported PCP-preserved wood. In the publication [COWIconsult, 1985] is given an estimate of the PCP concentration range of 50 - 100 g PCP/m³ wood for imported anti-sap-stain preserved wood (corresponding to approximately 0.1 - 0.2 g PCP/kg wood, when a mean density of wood of 520 kg/m³ is used). The PCP screening of the samples have shown PCP concentrations in the range of 20-164 µg PCP/kg wood (90 % confidence level and assuming that data follows a normal distribution). The measured values are therefore considerably lower than the estimated value of 0.1 - 0.2 g PCP/kg wood.

There might be several different explanations of the difference between the estimate and the measured values:

- The anti-sap-stain control is carried out when the timber is freshly sawn, and before the wood is being worked up to pallet boards or other products. As the predominant part of the PCP is applied to the upper 1.5 mm surface wood [COWIconsult, 1985], the wood products will have a much lower concentration if it does not contain the surface wood. Therefore the analysed samples do therefore not necessarily include the lowest and the highest values of the preserved wood.
- PCP anti-sap-stain control can at present perhaps be made with lower PCP concentrations than earlier.
- It is possible that some of the PCP has evaporated from the samples of pallet-board wood, before the samples were taken as the exact age of the pallet wood is not known and the sap-stain protection is not assumed to be effective for more than 6 - 11 months [Kirk-Othmer 1993].

It is difficult to say which of these explanations that are credible, and most likely a combination of them explains the lower values. On the basis of the results it was decided to carry out a single dioxin analysis of the sample with the highest concentration of PCP in order to examine the concentration of dioxin in the sample.

As table 4.2 shows, the sample with the highest PCP concentration only contained approx. 4.6 ng I-TEQ/kg wood. The estimate of 0.1 - 0.2 g PCP/kg imported preserved wood stated above combined with the assumed content of dioxin in PCP of 0.11-4.2 mg I-TEQ/kg PCP [Edujlee 1999 quoted by Hansen and Hansen 2003] corresponds to a concentration of 11- 840 ng I-TEQ/kg wood.

Assuming that the registered value of 4.6 ng I-TEQ/kg wood is representative of all PCP-preserved wood imported in 2003 the quantity of dioxin imported may now be estimated as

$$(1-10 \text{ tons PCP/year}) * (4.6 \text{ ng I-TEQ/kg wood}) / (0.1-0.2 \text{ g PCP/kg wood}) = 0.046 - 0.230 \text{ g I-TEQ/year}$$

In this expression is assumed an import of PCP to Denmark of the same size (1-10 tons PCP/year) as assumed in the Substance Flow Analysis from 2003. This import of PCP has been translated to wood by assuming the same

concentration of PCP in the wood that was assumed by [Hansen and Hansen 2003].

It may be noted that the import calculated in Substance Flow Analysis from 2003 for year 2000 came to 0.11 - 42 g I-TEQ/year [Hansen and Hansen 2003].

The resulting emission of dioxin to air caused by evaporation of dioxin from anti-sap-stained preserved wood imported from the beginning of the 1980'ties and until 2003 was in the Substance Flow Analysis from 2003 [Hansen and Hansen 2003] estimated as

$$10\%^1((0.6+0.05)/2 - (105+21)/2 \text{ g I-TEQ/year}) = 0.03 - 6 \text{ g I-TEQ/year}$$

As an elaboration of this expression it may be noted that the import of dioxin with PCP-preserved wood at the beginning of the 1980'ties had been estimated as 0.6 -105 g I-TEQ/year of which all was used for construction purposes while around 50% of the import in year 2000 of 0.11 - 42 g I-TEQ/year was assumed to be with disposable pallet anticipated to be directed by and large directly to incineration. Futhermore, the expression assumes a liniar development of the amount of dioxin introduced in the Danish society besides that the expression does not consider the evaporation of dioxin to the air that already has taken place. The us the expression in reality estimates the evaporation based on the average consumption over the period of around 1980 to around 2000 assuming an average emission of 0.5% of the consumption per year..

The emission of dioxin to air from anti-sap-stained preserved wood assuming a present import of only 0.046 - 0.230 g I-TEQ/year of which 50% is directed to incineration can correspondingly be recalculated as

$$10\%((0.6+0.023)/2 - (105+0.115)/2 \text{ g I-TEQ/year}) = 0.03 - 5 \text{ g I-TEQ/year}$$

As the measured dioxin concentration should be taken as an example mainly, as only one measurement on a disposable pallet has been carried out, it may indicate that the present import of dioxin with imported PCP-preserved wood is lesser than previously assumed.

However, as illustrated by the calculatios above the immediate consequence regarding emission of dioxin to air is small, as the emission must be expected basically to be determined by the quantity of dioxin still present in PCP-preserved wood imported during the 1980'ties and the 1990'ties.

As the wood in question also is used for construction purposes and by time slowly will be disposed of also the emission of dioxin slowly by time should be expected to be reduced. However, it will be difficult to estimate the development as the precise uses of the wood are not well known and may cover a multitude of applications.

As already emphasised by [Hansen and Hansen 2003] the above calculations must be taken as extremely uncertain and should be regarded as an indication only of the relevant order of magnitude for the dioxin flows in question.

1 10% should actual be read as 20 times 0.5% meaning an evaporation of 0,5% of the content per year accumulated over 20 years.

7 Conclusion

Pentachlorophenol-preserved wood has been discussed as a source of dioxin emission to the Danish society. The Substance Flow Analyses made on dioxin in Denmark have until now estimated the emission to air at 0.5 - 26 g I-TEQ/year [Hansen and Hansen, 2003]. The emission from PCP-preserved wood can therefore be both a quite substantial and a less significant source of the total Danish dioxin emission. Especially the question regarding evaporation from the PCP-preserved wood is unclear, as only the dioxin concentration in newly PCP-treated wood has been examined in a few international studies.

It is expected that there are two sources of dioxin from PCP-preserved wood: Construction wood that has been treated with PCP preservation in the period of 1950 to approximately 1977 and different types of wood preserved with PCP and imported to Denmark. The present import of PCP-preserved wood is expected primarily to be disposable pallet boards from Southern Europe which have been anti-sap-stain controlled with PCP. These two sources of dioxin have therefore been examined in the present study.

Because of the number of available analyses the project have only been able to give an indication of the size of the two sources, but succeeds in documenting that especially construction wood should be regarded as a noteworthy source of dioxin emission.

Imported PCP preserved wood

The samples of disposable pallet boards were selected only on the basis of the country of origin the goods were imported from, as it would be very difficult to trace the history of the pallet boards. It was not known whether the pallet boards actually contained PCP. It was therefore quite surprising that PCP could be traced in 6 out of the 10 selected pallet board samples. The use of PCP for anti-sap-stain control is therefore still regarded to be quite common both in Spain, Portugal and France - as PCP was found in samples from all three countries. The concentrations of PCP in the pallet board samples were however considerably lower than previously estimated concentrations, as the measured values were in the range of 20 - 164 µg/kg wood (90 % confidence level), and the previously used concentrations for industrial, preserved wood were in the range of approximately 0.1 - 0.2 g/kg wood. Only one dioxin analysis was made on pallet board. The sample with the highest PCP concentration was selected for the analysis. The measurement showed a dioxin content of 4.6 ng I-TEQ/kg wood, which is low compared to the construction wood.

Although the present import of dioxin and PCP with PCP preserved wood probably is small the emission of dioxin to air must be expected basically to be determined by the quantity of dioxin still present in PCP-preserved wood imported during the 1980'ties and the 1990'ties. The emission has consequently been recalculated to 0.03 - 5 g I-TEQ/year, which is only slightly less than the emission figure of 0.03 - 6 g I-TEQ/year previously assumed.

The wood in question is used for construction purposes and will by time slowly will be disposed of resulting in that the emission of dioxin also slowly by time should be expected to be reduced and eliminated.

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

Construction wood preserved with PCP in Denmark

The construction wood samples have been collected based on mini-interviews with house owners living in houses constructed in the period of 1960 - 1972. The chance of finding dioxin in these samples was therefore better, and dioxin was actually found in all five analysed samples. The measured concentrations range between 84-1079 ng I-TEQ/kg wood.

Assuming that the measured concentrations follows a normal distribution the 90 % confidence level (the concentrations representing the interval within which 90 % of all concentrations are likely to be registered) is defined as interval of 34 - 793 ng I-TEQ/kg wood. This corresponds to a total dioxin content of 42 - 974 g I-TEQ in the PCP-preserved construction wood that is left in Denmark by 2003.

Assuming an evaporation rate of 0.5 % of the actual dioxin content in the wood the dioxin emission from the PCP-treated construction wood in Denmark can be estimated to 0.2 - 4.9 g I-TEQ/year in 2003.

This estimate corresponds reasonable well to the estimate from [Hansen, 2003] on 0.5 - 20 g I-TEQ/year for the year 2000, considering inter alia that the quantity of PCP-treated wood still in use in Denmark is assumed to have been lowered by around 37 % between 2000 and 2003.

Based on the experiences from the present project the total estimate for dioxin emission from PCP-treated wood can be summed up to 0.23 - 9.9 g I-TEQ/year. This is lower than the earlier used estimate of 0.5 - 26 g I-TEQ/year [Hansen, 2000] and [Hansen and Hansen, 2003]. In spite that the interval for emission of PCP-preserved wood has been reduced, PCP-treated wood must still be regarded as a noteworthy contribution to the total dioxin emission in Denmark.

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Appendix A: Dioxin analysis - method

Dioxin analysis in general

Dioxin is not a single substance, but a family of approximately 200 isomers with different degrees of toxicity. An analysis for dioxins and furans is therefore not directly equal to a specific value of dioxin. The immediate result is a diagram showing an isomeric pattern. The isomeric pattern shows the mutual quantitative proportion between the present isomers. The isomeric pattern therefore functions as a finger print, as the presence and the amount of the different isomers can vary depending on the dioxin source. The total toxicity of the dioxin isomers can however be measured in the so-called tox equivalents, where the toxicity of the present types of isomers is compared to the most toxic isomer 2,3,7,8-TCDD. The conversion to tox equivalents is typically done by using International Tox Equivalent Factors (I-TEF), which means that the total toxicity is expressed in I-TEQ - International Tox Equivalents. The International Tox Equivalent Factors are shown in table 4.1, which also includes the Nordic and WHO Tox Equivalent Factors which were previously quite commonly used. The WHO-TEF system differs from I-TEF, because this system in contrast to previous systems gives separate toxicity equivalent factors for humans/mammals, fish and birds. However I-TEF is still the most used system.

In this project it has been chosen to use I-TEQ values as description of the total toxicity for dioxins. The results are also given in WHO-TEQ values, but only I-TEQ values are used in the text.

Analysis method for PCDD/F and PCP in wood

The method that has been used to analyse the wood samples from both construction wood and disposable pallet boards has earlier been used for dioxin analyses on sludge and textiles. These methods have earlier been described by the National Environmental Research Institute. The analyses and description of methods for this project have been carried out by Senior research associate Jørgen Vikelsøe and Laboratory technician Elsebeth Johansen from DMU (National Environmental Research Institute, Denmark), Department of Atmospheric Environment.

Table A.1
Important toxicity equivalency factor systems for dioxins

Congener	WHO 1998	Nordic 1988	International 1989
	WHO-TEF ¹⁾	Nordic-TEF ²⁾	I-TEF ²⁾
2,3,7,8-TCDD	1	1	1
Other TCDDs	0	0	0
1,2,3,7,8-PeCDD	1	0.5	0.5
Other PeCDDs	0	0	0
1,2,3,4,7,8-HxCDD	0.1	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1	0.1
Other HxCDDs	0	0	0
1,2,3,4,6,7,8-HpCDD	0.01	0.01	0.01
Other HpCDDs	0	0	0
OCDD	0.0001	0.001	0.001
2,3,7,8-TCDF	0.1	0.1	0.1
Other TCDFs	0	0	0
1,2,3,7,8-PeCDF	0.05	0.01	0.05
2,3,4,7,8-PeCDF	0.5	0.5	0.5
Other PeCDFs	0	0	0
1,2,3,4,7,8-HxCDF	0.1	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1	0.1
Other HxCDFs	0	0	0
1,2,3,4,6,7,8-HpCDF	0.01	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01	0.01
Other HpCDFs	0	0	0
OCDF	0.0001	0.001	0.001

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

2. From /Jensen 1997/.

Principle of the analysis method

The wood is divided into fine particles, and a mixture of ¹³C-marked PCDD/F standards (extraction spikes) is added. The sample is Soxhlet extracted in toluene; the extract is evaporated and parted in two part-extracts for PCP and PCDD/F respectively. For PCDD/F the decontamination is made by a four-step liquid-chromatographical method. For PCP the decontamination is made by an acid and alkaline shaking followed by methylation. Quantification by high-dissolving GC/MS using the isotope dilution method. Decontamination, detection and quantification for PCDD/F are based on an adaptation of European standard for analysis of dioxin in flue gas, DS/EN 1948 2-3.

Apparatus

Soxhlet extraction equipment 250 ml

Rotary vacuum evaporator

Nitrogen evaporator

Automatic pipettes: 20-100 μ l, 100 μ l, 500 μ l

Columns for liquid chromatography:

2.5x12 cm with reservoir 150 ml, Teflon tap, NS12 bottom cone ground joint

1x17 cm med Teflon tap, NS12 upper mantle ground joint

1x10 cm

Gas chromatography: Hewlett-Packard HP 5890 series II, connected to mass spectrometer

Pre-column: Chrompack Retention Gap, capillary quartz glass 2.5 m x 0.3 mm in diameter.

Column: J&W Scientific DB-5ms, capillary quartz glass 60 m x 0.25 mm in diameter, 25 μ m film thickness

Autosampler: LEAP Technologies CTC A200S

Mass spectrometer: Kratos Concept 1S, high-dissolving sector instrument

Chemicals

Toluene Rathburn, glass distilled

n-hexane Rathburn, glass distilled

Dichloromethane Rathburn, glass distilled

Methanol Merck, LiChrosolv

Na₂SO₄ Merck, anhydrous for analysis

Silica gel Merck, silica gel 60 0.063-0.20 mm

H₂SO₄ Merck for analysis

NaOH Merck for analysis

HCl Merck for analysis

Al₂O₃ ICN Biomedicals, Alumina A

n-dodecan BDH, Purity > 99% (GC area)

Active C Supelco, CarbopackC 80/100 mesh

Celite Fluka, Celite 545, 20-45 μ

PFK Fluka, Perfluorokerosine, high boiling, for mass spectroscopy

Internal and external standards

The applied marked and unmarked standards are all produced by CIL,

Andover, Massachusetts, USA. Original dissolution 1 or 2 μ g/ml in toluene, to be kept at 4°C.

Table A.2
Extraction spike dissolution

Substance	ng/ml	Marking
2378-TCDD		
12378-PeCDD		
123678-HxCDD	4	¹³ C ₁₂
1234678-HpCDD		
OCDD	8	¹³ C ₁₂
2378-TCDF		
12378-PeCDF		
23478-PeCDF		
123789-HxCDF		
123678-HxCDF		
234678-HxCDF	4	¹³ C ₁₂
1234678-HpCDF		
1234789-HxCDF		
OCDF	8	¹³ C ₁₂
Toluene	Dissolvent	

Table A.3
Injection spike dissolution

Substance	ng/ml	Marking
1234-TCDD		
123789-HxCDD	16	¹³ C ₁₂
n-dodecan	Dissolvent	

Table A.4
External standard dissolutions

Substance	Unmarked					¹³ C ₁₂
	ng/ml	ng/ml	ng/ml	ng/ml	ng/ml	ng/ml
1234-TCDD	-	-	-	-	-	4
2378-TCDD	0.4	1	4	10	40	4
12378-PeCDD	0.4	1	4	10	40	4
123478-HxCDD	0.4	1	4	10	40	-
123678-HxCDD	0.4	1	4	10	40	4
123789-HxCDD	0.4	1	4	10	40	4
1234678-HpCDD	0.8	2	8	20	80	8
OCDD	0.8	2	8	20	80	8
2378-TCDF	0.4	1	4	10	40	4
12378-PeCDF	0.4	1	4	10	40	4
23478-PeCDF	0.4	1	4	10	40	4
123478-HxCDF	0.4	1	4	10	40	-
123678-HxCDF	0.4	1	4	10	40	4
123789-HxCDF	0.4	1	4	10	40	4
234678-HxCDF	0.4	1	4	10	40	4
1234678-HpCDF	0.8	2	8	20	80	8
1234789-HpCDF	0.8	2	8	20	80	8
OCDF	0.8	2	8	20	80	8
n-dodecan	Dissolvent					

All dissolutions in the dilution row contain the same concentration of ¹³C₁₂ marked standards (spikes), stated in the last column.

Standard dissolutions level 1.4 and 10 ng/ml (2,3,7,8-TCDD) are used for quantification

Standard dissolution level 40 ng/ml is used for linearity sample

Standard dissolution level 0.4 ng/ml is used for check of sensibility

Pre-treatment of sample

The wood samples are bored up by means of a 10 mm spiral drill. The blocks are bored all through, the holes placed as close as technically possible. The drill is to be rinsed by means of n-hexane and acetone between each sample. The bore dust from each sample is mixed carefully, and approx. 1 g dry weight is weighed out. 100 µl extraction spike dissolution (Table 4.2, internal and external standards) is added.

Extraction

The spiked sample soxhlet is extracted for 20 hours in 700 ml toluene. The extract is added 0.5 ml n-dodecan as keeper and evaporated to approx. 0.5 ml under vacuum in rotary evaporator at 35°C, 25 torr. The samples to be separated (i.e. pallet wood that is to be analysed for both PCDD/F and PCP) are transferred to a 100 ml calibrated flask and redissolved in n-hexane. Thereafter part samples of 10 ml are taken with full pipette.

Dioxin analysis

Decontamination by means of liquid chromatography

The evaporated extract or part-extract is placed on the upper one of two columns connected in series, containing (from the top)

Column 1: 2.5 x 12 cm m/ reservoir 250 ml

- 1 g anhydrous Na₂SO₄.
- 1 g silica gel (activated at 105°C),
- 4 g silica gel modified by 33% NaOH
- 1 g silica gel
- 4 g silica gel modified by 44% H₂SO₄
- 2 g silica gel

Column 2: 1 x 17 cm

- 1 g anhydrous Na₂SO₄.
- 6 g acid Al₂O₃ (activated at 250°C).

Elution with 90 ml n-hexane through both columns connected in series is made. The columns are separated, after which column 2 only is eluted with 20 ml n-hexane. Both eluates containing various impurities are to be discarded. The PCDD/F fraction, which is adsorbed on Al₂O₃ in column 2, is thereafter eluted with 20 ml dichloromethane/n-hexane 20/80. The eluate is placed on a column containing

Column 3: 1 x 10 cm

- 1g Carbo-pack C/Celite 40/60 (activated at 150°C).

The column is fastened with the clean end upwards. Before placement of the sample the column is to be rinsed by 8 ml toluene, 16 ml dichloromethane/methanol 75/20 and 8 ml n-hexane.

After placement of the sample the column is eluted by 8 ml n-hexane followed by 16 ml dichloromethane/methanol 75/20. The eluates are discarded. The column is placed with the clean end downwards and is finally eluted by 120 ml toluene.

The last eluate containing the decontaminated PCDD/F fraction is evaporated under vacuum in the rotary evaporator to some ml and thereafter under N₂ to almost dryness. The evaporation residue is redissolved in 25 µl internal standard mixture (Table 4.3) and 25 µl n-dodecan. After this the sample is ready for analysis by gas chromatography/mass spectrometry (GC/MS).

Gas chromatography

Injection	Automatic split/splitless, 2 μ l + 1 μ l n-dodecan, purge closed 40 sec.
Injector	290°C, gooseneck insert 4 mm
Pre-column	Chrompack Retention Gap, capillary quartz glass, 2.5 m x 0.3 mm in diameter
Column	J&W Scientific DB-5ms, capillary quartz glass, 60 m x 0.25 mm in diameter 0.25 μ m film thickness
Carrier gas	He, pressure 150 kPa
Temperature program	40 sec. at 200°C, 20°C/min. to 230°C, 3°C/min. to 290°C, 28 min. at 290°C
Transfer line	290°C

Mass spectrometry

Dissolving power	6000-10000
Ionization	Electron impact (EI)
Ionization energy	35-45 eV depending on tuning
Ionization current	5 μ A
Ion source temperature	290°C
Acceleration voltage	8 kV
Electron multiplier voltage	2.5-3 kV
Noise filter	300 Hz digital
Magnet stabilization	Current intensity
Solvent filament disconnect	10 min
Cooling water temperature	20-21°C
Calibration gas	PFK
Scan parameter	Cycle time 1 sec Lock mass sweep 500 ppm, dwell 100 msec ESA sweep 20 ppm Dwell per mass 90-100 msec Dwell for check mass 20 msec Skew (between masses) 10 msec Return time (between scan) 20 msec
Detection mode	Selected Ion Monitoring (SIM). 5 windows, each with its mass combination (Table 4.4), are used

2 masses for each substance, corresponding to the most intense lines in the molecular-ion group for both unmarked and marked substances, are monitored. Furthermore, in all windows a lock mass and a check mass, which are standing out in the spectrum of PFK, are used.

Table A.5
SIM masses for PCDD/F analysis

Substance	m/z 1	m/z 2	m/z 3 13C12-	m/z 4 13C12-	% I mz1/mz2
Group 1, tetra	10-18 min				
Lock/check	292.9824	304.9824			
TCDF	303.9016	305.8987	315.9419	317.9389	77.3/100
TCDD	319.8965	321.8936	331.9368	333.9339	77.2/100
Group 2, penta	18-24 min				
Lock/check	330.9792	342.9792			
PeCDF	339.8597	341.8567	351.9005	353.8976	154.3/100
PeCDD	355.8546	357.8517	367.8954	369.8925	154.3/100
Group 3, hexa	22-28 min				
Lock/check	392.9760	392.9760			
HxCDF	373.8207	375.8178	385.8610	387.8579	123.5/100
HxCDD	389.8156	391.8127	401.8559	403.8530	123.5/100
Group 4, hepta	28-34 min				
Lock/check	442.9729	442.9729			
HpCDF	407.7818	409.7788	419.8220	421.8189	102.9/100
HpCDD	423.7767	425.7737	435.8169	437.8140	102.9/100
Group 5, octa	34-45 min				
Lock/check	442.9729	442.9729			
OCDF	441.7428	443.7398	453.7860	455.7830	88.2/100
OCDD	457.7377	459.7348	469.7780	471.7750	88.2/100

Quantification, determination and identification of isomers

A chromatogram showing the signal of each mass (so-called mass traces) according to the SIM tables is recorded. For determination of a dioxin or furan isomer in the unknown sample, there must be a well-defined peak with signal/noise conditions on at least 3 on both the belonging mass traces. The retention times of the peaks must correspond to a 2,3,7,8-substituted dioxin isomer or furan isomer. This can be determined by comparing with the retention times of the corresponding isotope-marked standards, as there might be 1-2 sec. delay on the unmarked substances. The peaks fulfilling the above conditions are quantified on both mass traces. The relation between the areas of the peaks of the two mass traces must correspond to the natural chlorine isotope relation stated in table 4.5, with an error range of 25%. For the following calculations the sum of both areas is to be used.

Quantification, calculation of response factors from standard

For each peak of an unmarked isomer on the chromatograms of external standard a response factor is calculated according to the formula:

$$R_{is} = \frac{C_{rs}}{C_{is}} \cdot \frac{A_{is}}{A_{rs}}$$

in which

R_{is} = Response factor for the i 'th isomer

C_{is} = Concentration of the i 'th isomer in external standard (table c)

C_{rs} = Conc. of the belonging r 'th laboratory spike isomer in external standard (table 4.4)

A_{rs} = Area for the belonging r 'th spike isomer in external standard 1)*)

A_{is} = Area for the i 'th isomer *)

*) sum of peaks on both mass traces

1) in cases with an identical spike this spike is to be used in the calculation; otherwise the closest related spike is to be used for the calculation as follows:

13C12-1,2,3,6,7,8-HxCDF til 1,2,3,4,7,8-HxCDF

13C12-1,2,3,6,7,8-HxCDD til 1,2,3,4,7,8-HxCDD

In this way there are 17 response factors for each GC/MS analysis of the external standard, one for each congener.

In order to obtain further precision the average of the various standard levels of response factors is used - and normally 2-4 repetitions (average response factor method).

Quantification, calculation of concentration in sample

The concentration of the i 'th isomer in the unknown sample at the sample-taking, which is the final analysis result, is calculated according to the formula:

$$C_{ip} = \frac{A_{iu}}{A_{ru}} \cdot \frac{C_r \cdot V_s}{R_{is} \cdot M_p}$$

in which

C_{ip} = Concentration of the i 'th isomer in sample at the sample-taking corrected for loss

A_{iu} = Area of the i 'th isomer in unknown *)

A_{ru} = Area of belonging laboratory spike isomer in unknown 1)*)

C_r = Concentration of belonging spike in laboratory spike mixture (here 10 ng/ml) 1)

V_s = Volume of laboratory spike mixture added before extraction (here 0.1 ml)

R_{is} = Average response factor for the i 'th isomer calculated from external standard

M_p = Quantity of sample at the sample-taking

*) sum of peaks on both mass traces

1) see under calculation of standard

Calculation of toxic equivalents (TEQ)

Toxic equivalent (TEQ) is a measurement expressing the total toxicity of the sample, normally used for an environmental assessment. These TEQs express the toxicity of the individual isomers related to the toxicity of 2,3,7,8-TCDD, which is the most toxic one (the so-called Seweso dioxin) by means of toxic equivalent factors (TEF).

TEQ in the sample is calculated according to the formular:

$$E_{\text{tox}} = \sum C_{\text{ip}} \cdot T_i$$

in which

E_{tox} = Tox-equivalent concentration in the sample at sample-taking

C_{ip} = Concentration of i'th isomer in the sample at sample-taking

T_i = Tox-equivalent factor for the i'th isomer according to table 4.1.

Blank specimens

In each analysis series a blank laboratory specimen is included, produced as follows: The extraction and decontamination procedure is carried out simultaneously with the unknown samples as described above, an empty spiked soxhlet case being analysed.

Analysis sequence

Each analysis series is analysed in the following sequence: a) Diluted-solution series of external standard, b) a sample with solely n-dodecan for check of carry-over, c) blank specimen, d) the unknown samples, e) diluted-solution series of external standard. In connection with long analysis series one or more rows of external standard are included among the unknown samples. Standards in concentrations above the concentration area of the samples are not to be included. This rule was introduced to avoid spill-over effects from very strong standards on the unknown samples. The unknown samples are analysed in individual determinations.

Linearity

The linearity is checked at the deviation of response factors for each level of external standard. The deviation is calculated in the form of a standard deviation between the various levels. No significant deviations from the linearity for any congener in the concentration area (0.4 - 40 ng/ml) have been found.

Retrievals

The retrieval varies from 60 - 140%. It is calculated for each of the added extraction standards (extraction spikes) for each sample and appears from previously (in the paragraph of quantification of sample) mentioned Concentration Report and from the final result tables printed from the Quattro Pro spreadsheet (Appendix A). Retrievals below 50% or above 150% are not acceptable. However retrieval for 2,3,7,8-TCDF down to 20% might be found and must be accepted.

Detection limits

The detection limits range from around 0.6 ng/kg for 2,3,7,8-TCDD to 10 ng/kg for OCDD.

Detection limits are calculated on the basis of the signal/noise relation in the software of the mass spectrometer. The relevant detection limit is calculated as the sum of the blank-specimen value and the average of the detection limits of the analysis series at nominal sample quantity.

PCP-screening

Pre-treatment and shaking

The 10 ml part-extract taken out for PCP analysis is to be evaporated, added 25 ml CH₂Cl₂ and 50 ml H₂O, after which pH is adjusted to 10. The H₂O phase is to be shaken with 3 x 25 ml CH₂Cl₂, which is to be discarded. pH is adjusted to 2, after which the H₂O phase is shaken with 3 x 25 ml CH₂Cl₂. These CH₂Cl₂ phases are collected, dried by means of anhydrous Na₂SO₄ and filtered through glass wool. The sample is to be subjected to methylation with diazomethan and evaporated.

Injection spike

The sample is redissolved in injection spike, containing 10 ng/ml D6-33'44'-PCB dissolved in n-hexane.

External standard

An external standard containing 10 ng/ml PCP (like methyl ether) and 10ng/ml D6-33'44'-PCB dissolved in n-hexane.

Gas chromatography

As with the dioxin analysis.

Mass spectrometry

As with dioxin analysis - however the following SIM-descriptor is to be used.

Table A.6
SIM masses for PCP analysis

Substance	m/z 1	m/z 2
PCP-methyl ether	279.8597	281.8568
D ₆ -33'44'-PCB	295.9600	297.9571
PFK lock/check	292.9824	292.9824

1 scan per sec.

Quantification

Takes place under the same procedure as the one used for dioxin analysis.