

**Dioxin emissions to air from
MSW combustion – Data from
some IEA member countries**

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TECHNICAL REPORT

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Dioxin emissions to air from MSW combustion – Data from some IEA member countries

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RESULT (summary)

Through a questionnaire sent out to all members of the IEA Task 36, information has been gathered about the status on dioxin emissions to air for the member countries. The data that was collected had a varying degree of detailed information. Countries like Denmark (who is currently not a member of this IEA task) and The United Kingdom have done comprehensive and very well documented work in this field. In general it must be stated that most countries in this investigation have done a good job documenting and quantifying the amount dioxin that is emitted from different sources to the air. There are however, uncertainties connected to the estimates due to sampling procedures (e.g. short time sampling performed under good operating conditions, as opposed to long term sampling that also includes periods with unstable operating conditions) and lack of measurements. Long-term sampling or comprehensive dioxin sampling is expensive and therefore not used unless required.

Several conclusions can be drawn from this study:

- Since 1990 the overall emissions of dioxins to air have been reduced substantially. In UK the total emissions of dioxins to air were reduced from 1142 g I-TEQ/year in 1990 to 345 g I-TEQ/year in 1999. In Norway the corresponding numbers were 131 g I-TEQ in 1990 and 34 g I-TEQ in 2000.
- MSW combustion has had a drastic reduction in emissions of dioxins to air the last 10-15 years. The introduction of more and more complex flue gas cleaning systems have reduced the emissions of dioxins although the cleaning systems were intended for other pollutants than dioxins. Improved furnace design also contributes to lower dioxin emissions. The introduction of dedicated dioxin abatement equipment has taken the emissions down to a level below the new EU regulation limit of 0.1 ng/Nm³.
- The Danish study on concentration of dioxins in the flue gas depending on different flue gas cleaning systems with or without dioxin abatement, states that the concentration for systems with now dioxin abatement varies from 2.3 ng/Nm³ (wet system) to 0.2 ng/Nm³ (semidry system). Systems with dioxin abatement have typically a concentration of 0.04 ng/Nm³. The potential reduction of dioxins when introducing a dioxin abatement system is hence dependent upon the flue gas system that is currently being used.
- The share of total dioxin emissions to air caused by MSW combustion plants have been reduced substantially due to the introduction of more comprehensive flue gas cleaning systems. In 1990 in the UK MSW combustion contributed with a 52% share of the total emissions. In 1999 the corresponding number was 1%.
- As an example of the efficiency of flue gas cleaning and dioxin abatement equipment on the emission of dioxins the FREVAR plant in Norway demonstrated above 99% efficiency after installing both a wet flue gas cleaning equipment for acid components and heavy metals and dioxin abatement equipment (activated carbon)
- After 2006 the new EU regulations on dioxin emissions will be enforced for all MSW combustion plants in the European Union and many industrialized countries around the world will have the same requirements. In order to reduce the total exposure of dioxins efforts should be focused on sources with a greater potential for reduction than that of MSW combustion.

KEYWORDS

| | | |
|--------------------------|----------------|---------------|
| SELECTED BY AUTHOR(S) | MSW Combustion | Air pollution |
| | Dioxins | |

TABLE OF CONTENTS

| | Page |
|---|------|
| 1 INTRODUCTION..... | 3 |
| 1.1 DIOXINS AND FURANS – STRUCTURE AND COMPOSITION..... | 3 |
| 1.2 SOURCES OF DIOXINS..... | 3 |
| 1.3 TOXICOLOGICAL ASPECTS OF POLYCHLORINATED DIBENZO-P- DIOXINS AND DIBENZOFURANS..... | 4 |
| 1.4 DIOXINS AND WASTE COMBUSTION..... | 4 |
| 1.5 FORMATION OF DIOXINS IN A MSW COMBUSTION PLANT..... | 5 |
| 1.6 DEVELOPMENT OF EMISSION REGULATIONS FOR MSW COMBUSTION PLANTS IN NORWAY..... | 6 |
| 2 DIOXIN EMISSIONS TO AIR..... | 7 |
| 2.1 TOXIC EQUIVALENCY AND TERMINOLOGY..... | 8 |
| 2.2 UNITED KINGDOM..... | 8 |
| 2.3 NORWAY..... | 10 |
| 2.4 FINLAND..... | 12 |
| 2.5 DENMARK..... | 13 |
| 2.6 SWEDEN..... | 17 |
| 2.7 THE NETHERLANDS..... | 18 |
| 3 REFERENCES..... | 21 |

1 INTRODUCTION

The objective of this work is to give an overview of the dioxins issue in general and in Municipal Solid Waste (MSW) combustion especially. Dioxin emission data to air from MSW combustion plants for several member countries in the IEA are presented in this report. In some countries a comparison between sources of dioxin emission to air is also given. An overview of the chemical structure and composition, sources, toxicological aspects, the dioxin issue in MSW combustion, development in emission regulations for MSW combustion and emission data are presented in this report. Data are gathered through questionnaires distributed to the members of IEA Task 36. Information presented in sections 1.1 and 1.2 is found in a EU report on dioxins [1].

1.1 Dioxins and furans – structure and composition

The term "dioxin" is often used to denote a family of compounds known chemically as polychlorinated dibenzo-para-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). Each compound comprises two aromatic („benzene“) rings interconnected by oxygen atoms. In the case of PCDDs, two oxygen bridges join the rings, whereas in the PCDFs, a carbon bond and an oxygen bridge connect the rings. Figure 1 depicts the basic structural formula of PCDDs and PCDFs, together with the numbering convention at the positions on the benzene rings where chlorine or other halogen atoms can be substituted.

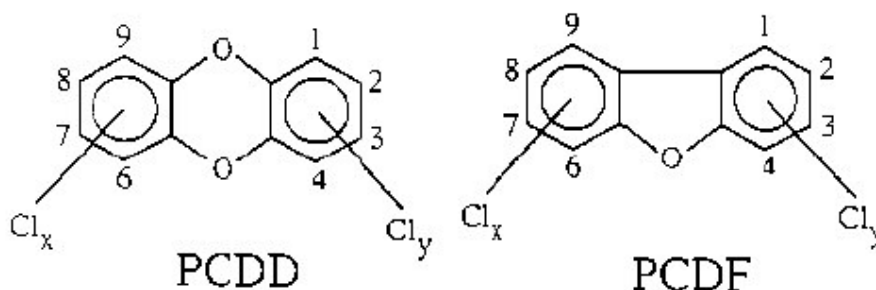


Figure 1. Chemical structures of PCDDs and PCDFs.

Beside the polychlorinated compounds also dioxins and furans substituted by bromine are of certain interest. Particularly, fuel additives in leaded gasoline („scavengers“) and flame-retarding agents in plastics may form precursors of (partly) brominated dioxins and furans (PBDD/Fs).

1.2 Sources of dioxins

Not being produced intentionally for any purpose PCDD/Fs are formed as by-products in a number of chemical processes (e.g. production of chlorophenols) as well as in almost every combustion process in presence of precursor compounds containing carbon, oxygen, hydrogen and halogen atoms. Therefore, PCDD/Fs are being emitted by various sources in differing amounts and mass flows. Even small changes in the design of the equipment or process or a switch to a different substance that is entered into the process may result in considerable alterations of the dioxins concentrations in the waste gas, wastewater or solid residues. The literature frequently distinguishes between primary and secondary sources of dioxins. According to this distinction, which is quite uncommon in air pollution control, a source entering dioxins, which formed during a process, into the environment at a later time and/or at a site that differs from the site of development with waste water or residual matter belong into the category of secondary sources. For example, anthropogenic PCDD/F that are prevented from being emitted by waste gas cleaning processes may remain in absorbents and still get into the food chain and increase human intake if they are not destroyed.

1.3 Toxicological Aspects of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans

The toxicological aspects of polychlorinated dibenzo-p-dioxins and dibenzofurans have been discussed in detail in several reports [1,2,3] and therefore only a very brief overview will be given in this report.

Of all 75 dioxins and 135 furans the toxicity of very few of these substances has been studied in greater detail. The most extensive studies concentrated on the most toxic congener: 2,3,7,8-tetrachlorodibenzodioxin (2,3,7,8-TCDD). That dioxins and furans are highly toxic has been confirmed with different test on animals. As little as 5 mg/kg body weight of 2,3,7,8-TCDD is enough to kill a hamster. When it comes to the effect on human beings, it has been documented that relatively small doses of dioxins can cause chronic effects such as reduced weight, reduced immune defense, lower testosterone level and skin damage. Dioxins can also cause a malformation and/or cancer in liver and intestines. ‘At risk’ individuals have been defined as those people consuming higher than average amounts of fatty foods, particularly fatty fish and fish products, but also meats and dairy products. Such high level consumers (95 or 97.5 percentile) have been exposed to around 3.1 pg I-TEQ/kg bw/day in the Netherlands and 1.7-2.6 pg ITEQ/kg bw/day in the United Kingdom. Once again, when PCBs are also taken into account, the exposure of such individuals is likely to exceed the WHO recommended TDI, of 1-4 pg TEQ/kg bw/day. In Norway the daily intake of dioxins is about half of the recommended daily maximum intake. Almost our entire intake of dioxins is via food and especially food with a high fat content.

1.4 Dioxins and waste combustion

Information in section 1.4 and 1.5 is gathered solely from Vehlow’s report waste combustion and the dioxin issue [4]. In Europe the preferred combustion technology is mass burning, that means the combustion of untreated waste on a grate. The scheme of a typical plant is shown in Figure 2. Combustion temperatures have to exceed 800 - 850 °C. The air consumption is approx. 4 500 m³/Mg of waste. In most countries a boiler is implemented to cool the flue gas down to approx. 200 °C and to recover the energy.

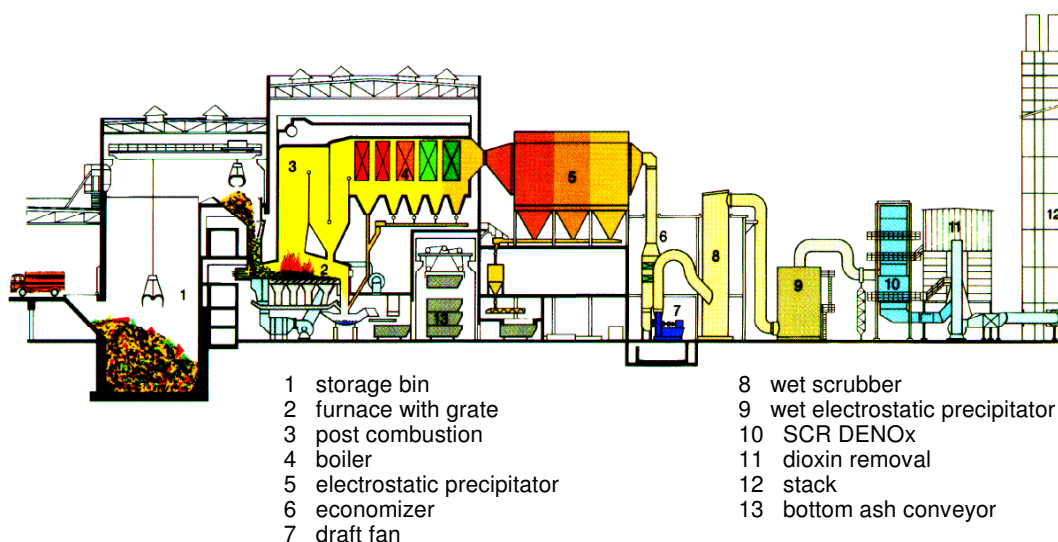


Figure 2. Municipal solid waste combustion facility.

The first step in air pollution control (APC) is mainly the dedusting by means of an electrostatic precipitator (ESP). Sometimes a fabric filter (FF) is used. The chemical, adsorptive and/or catalytic cleaning devices follow the dust precipitation.

The different scrubbing technologies implemented today are distinguished by the amount and quality of residues only. In principle their efficiency resembles each other. For wet scrubbing at least two-stage systems with a first acid step for hydrohalogen and Hg removal and a neutral step for SO₂ abatement are typically used. The advantage is the stoichiometric and hence chemicals saving operation mode and the potential of easy recovery of components such as HCl, HF, Hg or gypsum. The disadvantage is the discharge of water, which has to be cleaned or evaporated.

Dry or semi-dry processes use mainly Ca(OH)₂ or CaCO₃ to precipitate acid gases as Ca salts. For the effective removal of Hg the temperature should be kept < 150 °C and charcoal should be added, too. Dry processes use simple technology. The amount of residues - soluble salts contaminated by heavy metals and organics - is higher than in the case of wet scrubbing.

For NO abatement SNCR technologies are sometimes used. The common DENOx system, however, is a catalyst at the back end of the APC system. In Germany often a charcoal injection system is installed directly upstream of the stack as a polishing step for Hg and dioxins.

1.5 Formation of dioxins in a MSW combustion plant

Since all chemical reactions are controlled by equilibrium, a complete transformation into one direction is impossible in most cases, the more so in a heterogeneous process like waste incineration. As has been addressed already, the carbon content of the waste cannot totally be converted into CO₂ and minor amounts of products of incomplete combustion such as CO, PAH, or soot particles are found in the flue gases. The particulate carbon is known to be involved in the formation of low-volatile and toxic organic compounds, especially of PCDD and PCDF. Tests in laboratory and in full scale waste incineration plants revealed that particulate carbon, chlorides and Cu compounds - as catalyst - in the fly ashes and an oxygen surplus in the atmosphere are the basic materials for the formation of these compounds. The major controlling reaction is a de novo synthesis by means of a heterogeneous oxichlorination of the particulate carbon, which occurs in fly ashes deposited at the adequate temperature level. The same formation route was detected for chlorinated benzenes and phenols.

The original publications stated a temperature window of 250 - 450 °C for the PCDD/PCDF formation. The back end of the boiler hence was identified as the major breeding zone. More scrutine on-line investigations were performed at the TAMARA test incinerator by parallel raw gas sampling with one PTFE plane filter kept at 180 and the other one kept at temperatures between 150 and 240 °C. The total loads of organics analysed in the gas phase and in the filter ash were always standardised to the reference sampling. The results give evidence of a threshold temperature for the formation of low volatile organic compounds of approx. 200 °C.

The dioxins and phenols form easier than the furans and benzenes. These findings imply an upper operation temperature for any dedusting device of approx. 200 °C in order to prevent further breeding.

In the mid eighties in old incineration plants raw gas concentration of up to some 10 or even 100 ng(TE)/m³ were found. The high load of particulate carbon in the fly ashes cared for an almost total adsorption of the PCDD/PCDF in this matrix. The in-depth knowledge of the formation reaction caused a drastic reduction of this level by simple primary or head-end measures during the last years - e.g. improved burnout by adequate combustion control, appropriate cleaning of the boiler. A state-of-the-art plant is generating approx. 1 ng(TE)/m³ or less.

The improvement in combustion control resulted in PCDD/PCDF concentrations in bottom ashes in the order of 1 - 2 ng/kg. This is the typical level found in German so-called 'unloaded' soils.

In modern installations the low PCDD/PCDF levels go along with low concentrations in particulate C, too, and a great fraction of the PCDD/PCDF stays in the gas phase. The gaseous PCDD/PCDF can be adsorbed on charcoal in a bed filter or in an injection system or they can be destroyed by oxidizing catalysts, which are often combined with DENOX catalysts.

All these abatement techniques are installed downstream of the APC system and require a heating of the flue gas. Other attempts aim for a destruction by injecting H₂O₂ as oxidizing agent into the raw gas between boiler and filter. In view of early intervention this technology is most promising. The process requires a fabric filter for dedusting which has in addition the advantage to remove - with the exception of Hg - all thermally mobile heavy metals from the flue gas stream. If the Hg is to be removed at this position, too, small amounts of charcoal can be injected upstream of the FF. In this case the charcoal will adsorb and remove also the PCDD/PCDF and the addition of H₂O₂ is not necessary.

A balancing of PCDD/PCDF levels in all mass streams of a modern waste incinerator documents that this waste treatment technology represents an impressive sink for organic compounds. Published data give indication that the PCDD/PCDF contamination of municipal solid waste is in the order of 50 mg(TE)/Mg. For a combustion plant burning 300 000 Mg/y of waste this means an annual input of approx. 15 g(TE)/y. A rough estimate of a dioxin balance on the basis of the above given numbers is shown in Figure 3. There is no other waste treatment technology, which can compete with this destruction potential. Levels analysed in the bottom ashes of 1 - 2 ng(TE)/kg are similar to those found in surface soils and do not prevent a utilisation of this material e.g. in road construction. The contamination in the APC residues can be destroyed by means of thermal treatment processes such as the 3R Process.

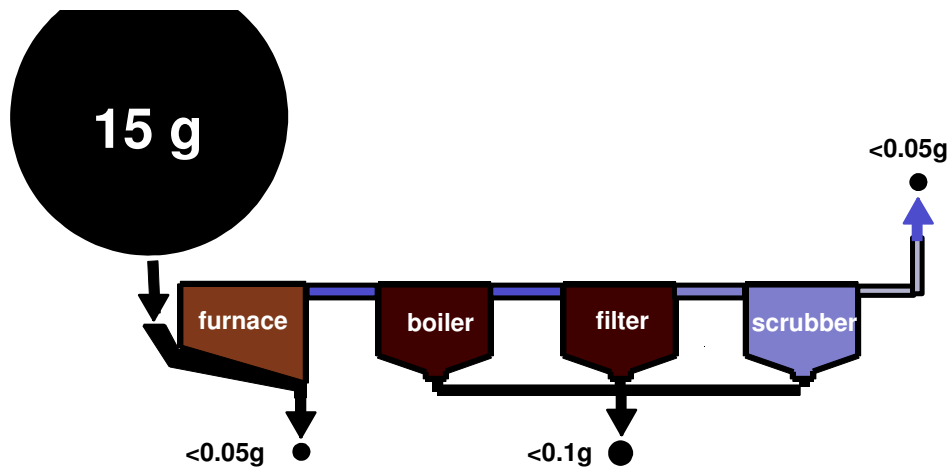


Figure 3. PCDD/PCDF balance for a 300 000 Mg/y MSWI (data in toxic equivalents (TE))

1.6 Development of emission regulations for MSW combustion plants in Norway

Dioxin emissions are dependent upon the type of flue gas equipment used. Flue gas cleaning measures that are designed for reducing the level of acid gases and heavy metals also have an effect on the emissions of dioxins. In addition to this, dedicated flue gas cleaning for dioxins will of course reduce the emissions to a level below the new EU regulation. In order to cope with increasingly strict emissions different types of flue gas cleaning equipment may be used (wet, semidry and dry systems). The effect of different flue gas cleaning systems will be discussed in section 2. In order to illustrate the development for emission regulations for emissions to air,

Heimdal Varmesentral (HVS) in Trondheim Norway can be used as an example. Table 1, shows the emission regulations development for HVS from 1983 until they have to comply with the new EU regulations in 2006. The table also shows typical emissions for HVS. In 1983 when HVS got its first licence, the only air emission regulated was particulate emissions. During the 90's the emission regulations have become much stricter. More and more species have been included and stricter emission limits have been enforced. The number of components has increased from 1 in 1983 to 21 in 2006.

Table 1. Development of emission regulations for HVS Norway.

| Components | Emission regulations and emissions at HVS (Norway) | | | | |
|--|--|------|---------------------------------|-------------|--------------------------|
| | [mg/Nm ³ @11vol% O ₂ , dry] | | | | |
| | 1983 | 1990 | 1995 | 2006 (2002) | Emissions at HVS 1999 |
| Particulate Matter (PM ₁₀) | 100 | 30 | 30 | 10 | 16 |
| Hg | - | 0.1 | 0.05 | 0.05 | 0.007 |
| Cd+Tl | - | - | 0.05 ^c | 0.05 | 0.001 ^c |
| Pb+Cr+Cu+Mn+Sb +As+Co+Ni+V+Sn | - | - | 5 (Pb+Cu+Cr+Mn) og 1 (Ni+As) | 0.5 | 0.05 ^d |
| CO | - | 100 | 100 | 50 | <50 |
| HF | - | - | 2 | 1 | 0.09 |
| HCl | - | 100 | 50 | 10 | 0.8 |
| TOC | - | - | 20 | 10 | 3.2 |
| NO _x (as NO ₂) | - | - | - | 200 | ~300 ^b |
| SO _x (as SO ₂) | - | 300 | 300 | 50 | 228 |
| Dioxins ^a | - | 2 | 2 | 0.1 | 1.13 |

^a ng/Nm³ 2,3,7,8 TCDD-ekvivalenter (Nordisk standard)

^b Measurements performed by TEV over longer time periods (months)

^c Only Cd

^d Only Pb, Cu, Cr, Mn

Only heavy metals mentioned in parentheses applies for 1995

In order to give an example of the efficiency of retrofitting an existing plant with new flue gas cleaning system to comply with the new emission regulations on dioxins, the FREVAR plant in Norway is chosen. FREVAR burns 78 000 tons/year of MSW. The FREVAR plant has retrofitted their plant with injection of activated carbon, wet scrubber and a bag house filter. Before retrofitting (late 80's), the concentration of dioxins in the flue gas were 15,8 ng/Nm³@11 vol.%O₂ dry. After installing all the above-mentioned flue gas cleaning equipment, the emissions were reduced to 0,004 ng/Nm³ (i.e. indicating an efficiency of above 99%).

2 DIOXIN EMISSIONS TO AIR

Emission data of dioxins to air for MSW combustion plants in Great Britain, The Netherlands, Norway, Sweden, Finland and Denmark are presented in this section. In some cases a comparison between the different sources of emissions is also given. Since there is several ways of report dioxin emission data, a brief discussion of the different methods is also included.

2.1 Toxic equivalency and terminology

Dioxins and dioxin-like PCBs are families of structurally related compounds. Dioxins and dioxin-like PCBs are never found as individual congeners but occur as complex mixtures with only some congeners exhibiting 2,3,7,8-TCDD-like toxicity. In order to simplify the handling of data on these compounds and to give a single measure of the toxicity of a sample, various systems for weighting the amounts of individual congeners in a mixture have been used. These ‘toxic equivalency’ schemes provide a series of factors that are applied to the measured concentrations of each congener of interest to give a measure of overall toxicity of a mixture. The toxic equivalent concentration (TEQ) is broadly the amount of 2,3,7,8-TCDD that would give the same overall effect.

The most widely used system until recently was that proposed by the North Atlantic Treaty Organisation, Committee on Challenges to Modern Society (NATO/CCMS) in 1988 which gives factors for the 17 dioxin and furan congeners with 2,3,7,8-TCDD-like toxicity. The results are often quoted as I-TEQ to denote International Toxic Equivalent.

Several systems of toxic equivalence factors (TEFs) have been compiled for the ‘dioxin-like’ PCBs. The most widely used, and that adopted by the UK in 1997, was recommended by the World Health Organisation (WHO) European Centre for Environment and Health/International Program for Chemical Safety (ECEH/IPCS) task force in 1994.

In 1997 the WHO held an expert meeting that proposed a revised scheme of TEFs for dioxins and dioxin-like PCBs⁴. This scheme was adopted in the UK by COT and is likely to be more widely adopted internationally. This new WHO-TEF scheme differs slightly from the I-TEF scheme for dioxins and from the previous scheme for PCBs.

In this report the International Toxic Equivalent, I-TEQ, is used.

2.2 United Kingdom

United Kingdom presented in October 2002 a comprehensive study in a report called “Dioxins and dioxin-like PCBs in the UK environment” [2]. The emissions from MSW combustion and a comparison between different sources are presented in this report.

Figure 4 shows how the contribution to overall emissions from the different source sectors has changed between 1990 and 1999. Interestingly one can observe that the contribution from MSW incineration reduced its share drastically from 52% in 1990 to only 1% in 1999. The reason for this major change in emission of dioxins is due to the enforcement of process control (i.e. flue gas cleaning equipment). Figure 5 shows overall trends in releases from each major source category and how total releases of dioxins to air have reduced since 1990. The overall impact of control measures is hard to assess with accuracy but it has been estimated that overall UK emissions have been reduced by around 70% between 1990 and 1999.

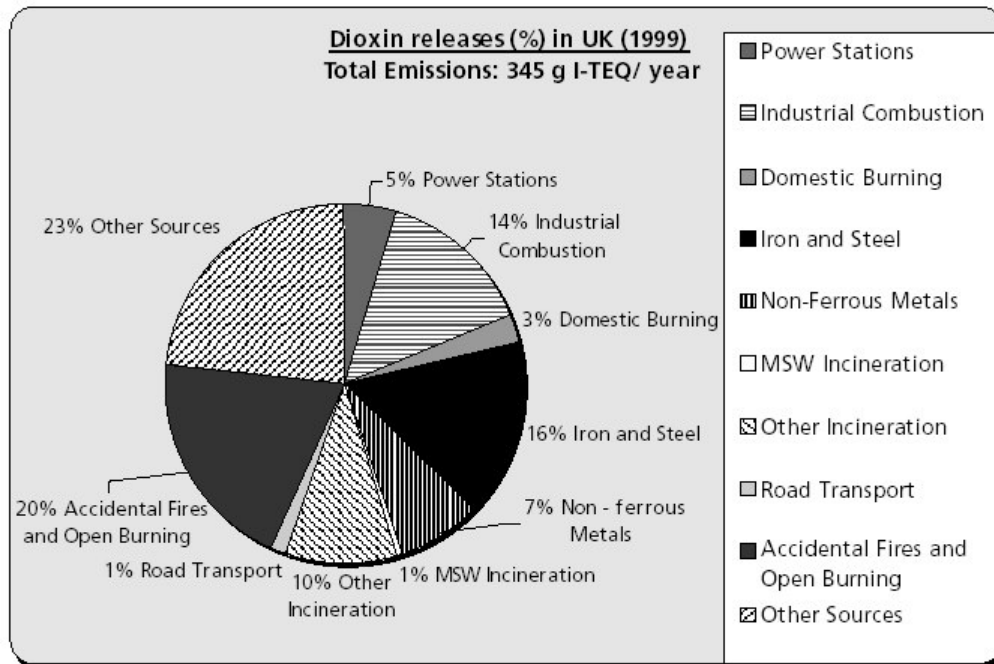
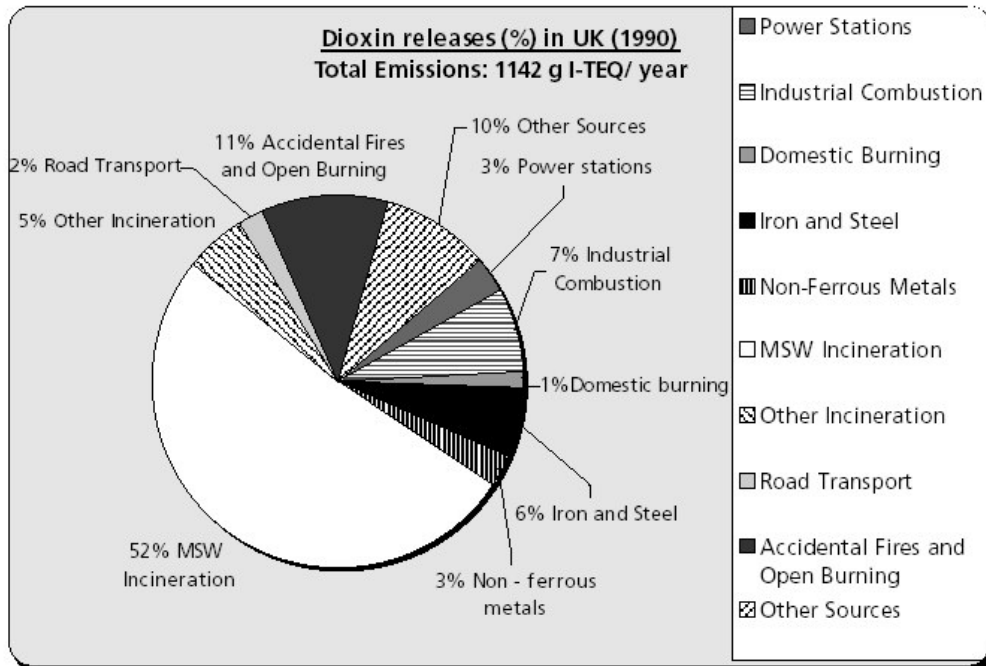


Figure 4. UK dioxin emissions to air (1990 and 1999).

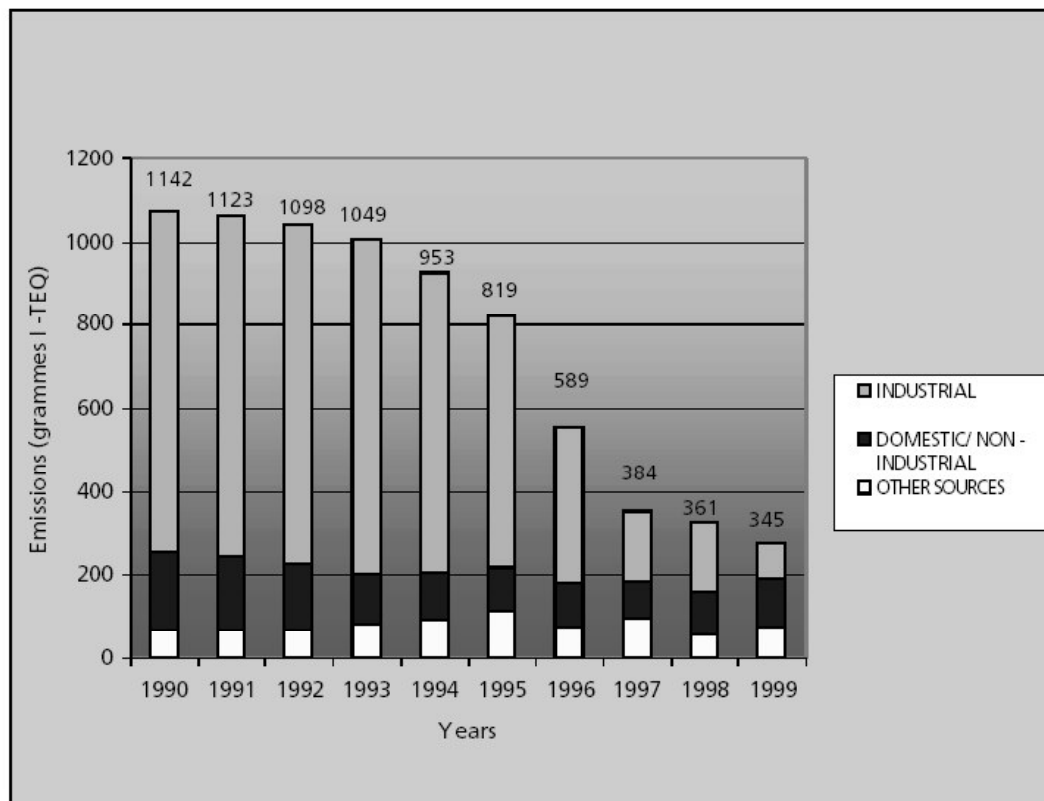


Figure 5. Trends in dioxins emissions to air in UK (grammes I-TEQ per year).

2.3 Norway

Data for Norway are gathered from a report given by Statistics Norway [5]. In Norway the total emission of dioxins to air was 34 grams I-TEQ in 2000. This is 74% less than in 1990 and approximately half of that in 1995. The major reduction dioxin emissions since 1990 are caused by the shut down of a larger metal industry plant and introduction of stricter emission requirements. 1995 is the basis year for the governments target for a substantial reduction of the dioxin emissions in Norway. Figure 6 shows the historic data on emission of dioxin to air in Norway. In 2000 62% of the total emissions came from stationary combustion, whereas industrial processes and mobile combustion (transportation) constituted 23 and 15%, respectively. The most important sources for dioxin emissions to air in Norway today are the metal industry, navigation, combustion of wood waste in industry and woodstoves. Uncontrolled combustion such as house fires and straw combustion is also important. Figure 7 shows the historic data on dioxin emissions to air from different stationary sources. The reductions seen for MSW combustion are due to closing down small combustion plants with relatively high emissions and stricter emission regulations. However, the emissions for MSW combustion in Norway are going to be even lower once all combustion plants comply with the new EU regulations by 2006.

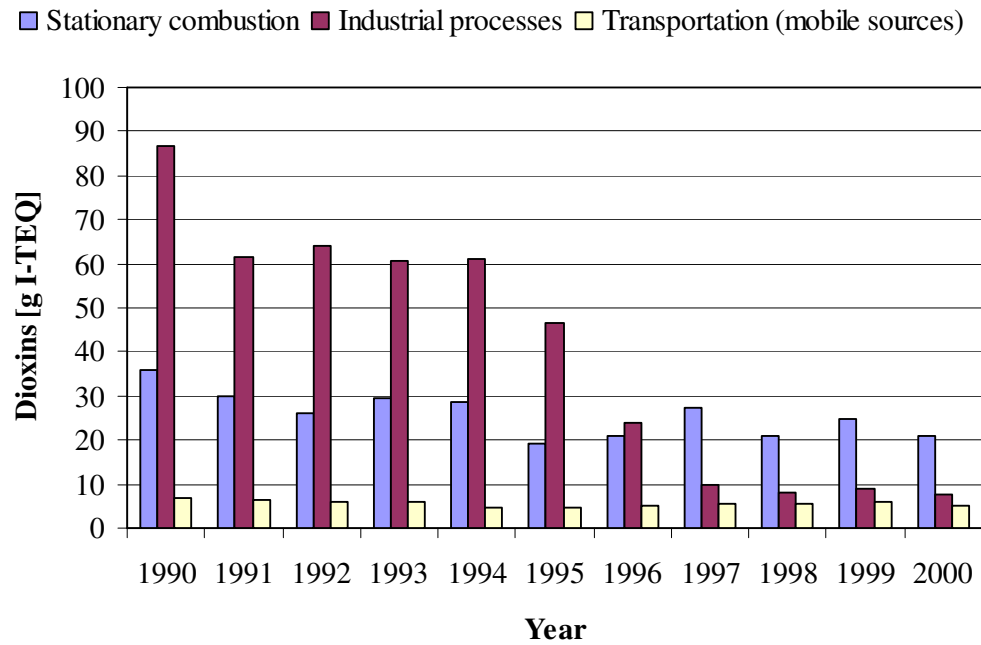


Figure 6. Historic data on dioxin emissions to air in Norway.

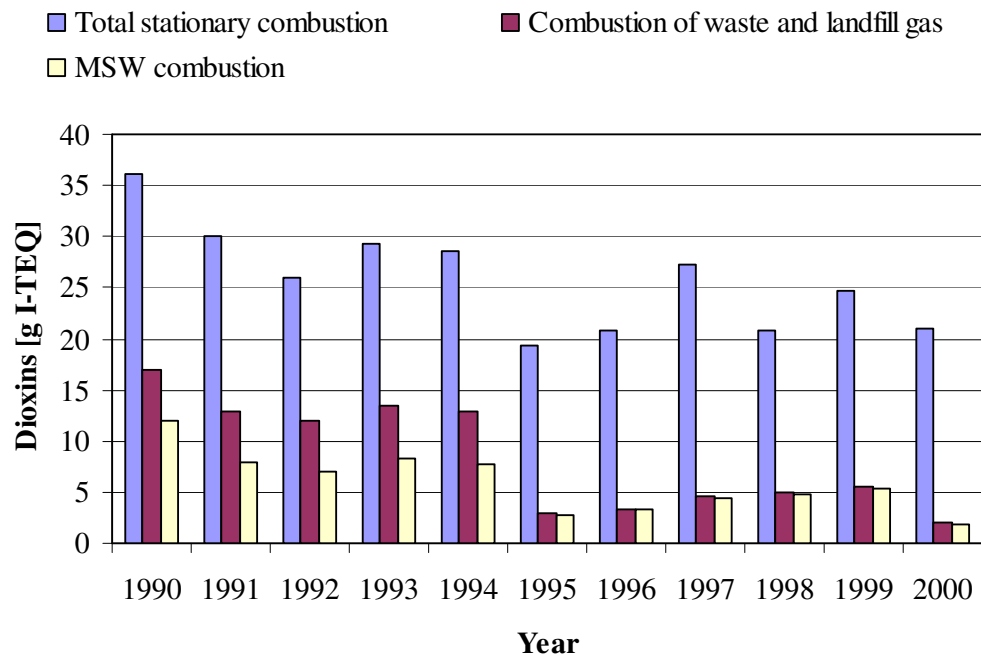


Figure 7. Historic data on dioxin emissions to air from different stationary sources.

2.4 Finland

The emissions of PCDD/PCDF from sources in Finland are between 100 and 200 g TEQ per year. Major sources are waste incineration, sintering processes, steel industry, and wood combustion [6].

Table 2. Estimated annual PCDD/PCDF releases into air (1999).

| Source | g TEQ/year |
|---|------------|
| Asphalt mixing installations | 0.5-1 |
| By-products of chlorinated substances manufacture | <1 |
| Cable incineration | <1 |
| Chemical industry | <1 |
| Coal combustion | 2 |
| Contaminated pesticides | <1 |
| Forest/grass fire | <1 |
| Fuel combustion | 20-30 |
| High temperature processes | NA |
| Wastes incineration | 30-80 |
| Industrial processes | NA |
| Ironworks | NA |
| Landfill gas incineration | NA |
| Non-Fe metal industry oil combustion | 5-15 |
| Other contaminated chemicals (e.g. PCB's) | NA |
| Pesticides | Very low |
| Sintering processes | 15-20 |
| Sludge incineration | 1 |
| Steel industry | 5-10 |
| Traffic emissions | 1-10 |
| Transportation | 0.5-2 |
| Hazardous waste incineration | 0.3 |
| Municipal waste incineration | 1-5 |
| Medical waste incineration | 2-5 |
| Wood combustion | 10-20 |

2.5 Denmark

Data presented for Denmark are collected from Danish EPA [3]. 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 I-TEQ/Nm³. 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-TEQ/Nm³. 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). Table 3 indicates 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.

The available knowledge regarding dioxin emissions from Danish waste incineration plants is also indicated in Table 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 exceeding 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. 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 are summarized in Table 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 3. Dioxin emissions to air from municipal waste incineration in Denmark 2000 - 2002.

| Flue gas cleaning process 1) | | Dioxin concentration ng I-TEQ/Nm ³ 2) | | | | Waste incinerated 1000 tonnes ³⁾ | Dioxin emission g I-TEQ/year ⁴⁾ | |
|------------------------------|---------|---|------|------|---------|--|---|----------------------------------|
| | | Mean | Min. | Max. | Samples | | Best estimate | Assumed inter-val of uncertainty |
| No dioxin abatement | Wet | 2.3 | 0.9 | 4.0 | 39 | 1.029 | 14.1 | 5.9 - 24.8 |
| | Semidry | 0.2 | 0.1 | 0.3 | 3 | 342 | 0.3 | 0.1 - 0.6 |
| | Dry | 0.4 | 0.2 | 0.6 | 17 | 117 | 0.3 | 0.1 - 0.7 |
| Dioxin abatement | | 0.04 | 0.02 | 0.1 | 33 | 1423 | 1 | 0.3 - 2.8 |
| Sum | | | | | | 2911 | 15.7 | 6.4 - 28.9 |

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

No dioxin abatement, wet: I/S FASAN, Sønderborg Kraftvarmeværk, Haderslev Kraftvarmeværk, Kolding Affaldskraftvarmeværk, åbjergværket, Knudmoseværket, I/S RENO SYD, Hammel Fjernvarmeværk, Affaldscenter Århus, I/S Fællesforbrænding, I/S Kraftvarmeværk Thisted, Aars Varmerværk, Hadsund By Fjernvarme, AVV I/S, Skagen Kraftvarmeværk, Frederikshavn Kraftvarmeværk.

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, Amagerforbrænding, 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 Nm³/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- 31% 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 \pm factor 3 of the calculated best estimate, when only two measurements are available.

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 4 summarizes 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 4 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.

Table 4. Formation of chlorinated dioxins by activities/processes in Denmark 2000 - 2002

| Activity/process | Danish investigations 1) | Formation | |
|---|-----------------------------|-----------------|------------|
| | | g I-TEQ/year | % 2) |
| <i>Manufacturing activities</i> | | | |
| - Chemicals 3) | Some-none | ? | ? |
| - Cement | Some | 0.2 - 1.4? | 0.2 |
| - Lime | Some-None | 0.001 – 0.005 | <0.1 |
| - Other high-temperature materials 4) | Some | 0.02 – 0.3 | <0.1 |
| - Steel reclamation | Good | 5.1 – 12.9 | 1.9 |
| - Aluminium reclamation | Good | 1 – 3.8 | 0.6 |
| - Other metal manufacturing 5) | Some | 0.02 – 0.4 | <0.1 |
| - Føedstuff 6) | Some | 0.004 – 0.07? | <0.1 |
| - Use of chlorine for bleaching and disinfecting | None | <0.5 | <0.1 |
| - Other industrial processes 7) | Some-none | <0.04? | <0.1? |
| <i>Manufacturing activities - subtotal</i> | | 6.3 – 19 | 2.8 |
| <i>Energy production activities</i> | | | |
| - Coal power plants | Some | 0.3 – 43? | 6.2 |
| - Other fossil fuels | None | 0.4 – 1.3 | 0.2 |
| - Biomass | Some | 0.7 – 43.8 | 6.4 |
| <i>Energy production activities – subtotal</i> | | 1.4 – 88 | 12.8 |
| <i>Miscellaneous human and natural activities</i> | | | |
| - Fires | None | 1.6 – 112 | 16.5 |
| - Traffic | None | 1.3 – 1.7 | 0.2 |
| - Crematories | Good | 0.01 - 0.1 | <0.1 |
| - Other miscellaneous activities 8) | Some | 0.09 - 0.22? | <0.1? |
| <i>Miscellaneous human and natural activities – subtotal</i> | | 3 – 114 | 16.5 |
| <i>Waste treatment and disposal activities</i> | | | |
| - Reclamation of cable scrap | Some-none | 0.00004 – 0.001 | <0.1 |
| - Shredder plants | Some | <0.001 - 0.1 | <0.1 |
| - Hazardous waste | Good | 0.9? | 0.1 |
| - Incineration of waste oil | | <0.001 - 0.2 | <0.1 |
| - Municipal solid waste | Good | 58.4– 436 | 63.3 |
| - Healthcare risk waste | Some | <0.001 - 0.4 | <0.1 |
| - Municipals landfills 9) | None | 0.7 – 27? | 3.9? |
| - Wastewater and storm water treatment/discharges | | 0.4 - 1.4 | 0.2 |
| - Sewage sludge disposal | Good – some | 1 - 1.9 | 0.3 |
| <i>Waste treatment and disposal activities – subtotal</i> | | 61 - 468 | 67.9 |
| <i>Brominated dioxin from waste treatment (not included in total)</i> | | <0.01-0.1? | |
| Total (rounded) | | 72 - 689 | 100 |

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

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

1. This column gives a brief assessment of the existing Danish investigations with the purpose of indicating on which subjects improved efforts may be relevant and to what extent others may benefit from Danish experience. The assessment is mainly related to air emission measurements, as measurements of solid waste or water discharges are scarce. The assessment uses the following terminology:

- Good: Reliable Danish investigations – estimates based solely on these investigations.

- Some: Some Danish figures are available - typically combined with literature values if available.

- None: No Danish experience 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.

2.6 Sweden

Data from Sweden has been provided by RVF (Renholdsverksforeningen, Åsa Hagelin) [7]. The total emission of dioxins to air from MSW combustion in Sweden together with specific dioxin concentration in the flue gas and amount of waste burned at each plant is given in Table 5. The new EU directives requirement of 0.1 ng/Nm^3 was enforced in Sweden in the beginning of the 90's. However, each plant has their own specific requirement in terms of dioxin emissions and this is the reason for the variations shown in Table 5.

A comparison between the different sources of dioxin emissions to air was performed in the beginning of the 90's, however, the reported numbers were found to be quite unreliable and therefore a new dioxin inventory is under progress, but will not be published before the end of 2004. A study on dioxin emissions due to residues from MSW combustion has been performed, this is not a part of the scope in this study, but should nevertheless be mentioned for those who are interested.

Table 5. Dioxin emissions to air and amount of waste burned at each plant in Sweden (2002).

| Plant | Emissions to air [ng/Nm ³ @11vol%O ₂ dry] | Amount of waste [ton] |
|----------------|--|--------------------------|
| 1 | 0,028 | 35659 |
| 2 | 0,120 | 42560 |
| 3 | 0,023 | 34738 |
| 4 | 0,028 | 34075 |
| 5 | 0,000 | 15637 |
| 6 | 0,010 | 418956 |
| 7 | 0,846 | 77472 |
| 8 | 0,028 | 11183 |
| 9 | 0,005 | 38350 |
| 10 | 0,048 | 42307 |
| 11 | 0,146 | 45498 |
| 12 | 0,011 | 23496 |
| 13 | 0,075 | 29204 |
| 14 | 0,073 | 66788 |
| 15 | 0,036 | 238890 |
| 16 | 0,011 | 37622 |
| 17 | 0,028 | 200197 |
| 18 | 0,056 | 16292 |
| 19 | 0,028 | 52599 |
| 19b | 0,028 | 119555 |
| 20 | 0,005 | 480402 |
| 21 | 0,077 | 35515 |
| 22 | 0,048 | 116240 |
| 23 | 0,028 | 132235 |
| 23b | 0,001 | 123270 |
| 24 | 0,011 | 54259 |
| 25 | 0,001 | 220403 |
| 26 | 1,000 | 47500 |
| <i>Average</i> | <i>0,028</i> | |
| <i>Total</i> | <i>1,1 grams (total emissions to air)</i> | <i>2790902</i> |

2.7 The Netherlands

In the Netherlands 100 % of the emissions of Waste combustion plants are complying with the new European legislation. This is because the current regulation has the same maximum as the new European regulation.

Historic data on emission of dioxins to air for all MSW combustion plants in The Netherlands are given in Table 6 [8].

Table 6. Historic data of dioxin emissions to air for all MSW combustion plants in The Netherlands.

| | Unit | 1996 | 1997 | 1998 | 1999 | 2000 | 2001 | 2002 |
|--------------------|------------|-------|------|------|------|------|------|------|
| PCDD/PCDF | µg/ton | 1,0 | 0,8 | 0,3 | 0,2 | 0,2 | 0,2 | 0,2 |
| Waste incineration | kton | 3 683 | 4359 | 4648 | 4824 | 4896 | 4776 | 5010 |
| Total emissions | gram I-TEQ | 3,7 | 3,5 | 1,4 | 1,0 | 1,0 | 1,0 | 1,0 |

Source: VVAV

3 CONCLUSIONS

Through a questionnaire sent out to all members of the IEA Task 36, information has been gathered about the status on dioxin emissions to air for the member countries. The data that was collected had a varying degree of detailed information. Countries like Denmark (who is currently not a member of this IEA task) and The United Kingdom have done comprehensive and very well documented work in this field. In general it must be stated that most countries in this investigation have done a good job documenting and quantifying the amount dioxin that is emitted from different sources to the air. There are however, uncertainties connected to the estimates due to sampling procedures (e.g. short time sampling performed under good operating conditions, as opposed to long term sampling that also includes periods with unstable operating conditions) and lack of measurements. Long-term sampling or comprehensive dioxin sampling is expensive and therefore not used unless required.

Several conclusions can be drawn from this study:

- Since 1990 the overall emissions of dioxins to air have been reduced substantially. In UK the total emissions of dioxins to air were reduced from 1142 g I-TEQ/year in 1990 to 345 g I-TEQ/year in 1999. In Norway the corresponding numbers were 131 g I-TEQ in 1990 and 34 g I-TEQ in 2000.
- MSW combustion has had a drastic reduction in emissions of dioxins to air the last 10-15 years. The introduction of more and more complex flue gas cleaning systems have reduced the emissions of dioxins although the cleaning systems were intended for other pollutants than dioxins. Improved furnace design also contributes to lower dioxin emissions. The introduction of dedicated dioxin abatement equipment has taken the emissions down to a level below the new EU regulation limit of 0.1 ng/Nm³.
- The Danish study on concentration of dioxins in the flue gas depending on different flue gas cleaning systems with or without dioxin abatement, states that the concentration for systems with now dioxin abatement varies from 2.3 ng/Nm³ (wet system) to 0.2 ng/Nm³ (semidry system). Systems with dioxin abatement have typically a concentration of 0.04 ng/Nm³. The potential reduction of dioxins when introducing a dioxin abatement system is hence dependent upon the flue gas system that is currently being used.
- The share of total dioxin emissions to air caused by MSW combustion plants have been reduced substantially due to the introduction of more comprehensive flue gas cleaning systems. In 1990 in the UK MSW combustion contributed with a 52% share of the total emissions. In 1999 the corresponding number was 1%.

- As an example of the efficiency of flue gas cleaning and dioxin abatement equipment on the emission of dioxins the FREVAR plant in Norway demonstrated above 99% efficiency after installing both a wet flue gas cleaning equipment for acid components and heavy metals and dioxin abatement equipment (activated carbon)
- After 2006 the new EU regulations on dioxin emissions will be enforced for all MSW combustion plants in the European Union and many industrialized countries around the world will have the same requirements. In order to reduce the total exposure of dioxins efforts should be focused on sources with a greater potential for reduction than that of MSW combustion.

4 REFERENCES

1. EU report, European Dioxin Inventory:
<http://europa.eu.int/comm/environment/dioxin/download.htm#European%20Dioxin%20Inventory>
2. Department for Food, Environment and Rural Affairs, Consultation on Dioxins and Dioxin-like PCBs in the UK Environment, Report PB 6778, October 2002.
3. Danish EPA, Environmental Project No. 811 2003, Substance Flow Analysis for Dioxins 2002.
4. Vehlow, J., KIST Europe Environmental Technology Workshop, Saarbrücken February 13 - 14, 1997, Proceedings pp. 21-30.
5. Statistics Norway, Report no. 2002/7. ISBN 82-537-5040-4. Emission of dioxins to air in Norway – Documentation of methods and results, 2002.
6. United Nations Environment Programme, “Dioxin and Furan Inventories – National and Regional Emissions of PCDD/PCDF, UNEP Chemicals, Geneva, Switzerland, 1999.
7. e-mail from Åsa Hagelin (RVF Sweden) 09.09.2003.
8. e-mail from Edwin Schokker (VVAV The Netherlands) 22.09.2003.