TNO Institute of Environmental and Energy Technology

Laan van Westenenk 501
P.O. Box 342
7300 AH Apeldoorn
The Netherlands

Telex 39395 tnoap nl
Phone +31 55 49 34 93
Fax +31 55 41 98 37

TNO-report

'Sources of dioxin emissions into the air in Western Europe

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Author
J.W. Wormgoor

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Summary

Starting around the middle of the eighties, research on the formation and fate of the highly toxic dioxins has received increased attention. Improvements in analytical techniques allowed for the separate quantification of the different congeners at very low detection limits in various matrices.
Many processes with a potential for dioxin formation have been investigated since then.

In this report, published data has been used to provide information about dioxin emissions into the air of the known source categories, in six European countries.

It is currently not possible, due to the complicated reaction mechanisms involved in the formation of dioxins, to predict emission rates theoretically. The observed variation of dioxin emissions from comparable processes can be very large. Thus, extrapolation of data, established at a specific installation, to a different (almost) similar installation is not possible at present.
For this reason, the accuracy of an inventory like this one, is dependent on the availability and accuracy of measured (and published) emission data and production figures of processes. In this survey, comprising Germany, Denmark, France, The Netherlands, Great Britain and Sweden, the completeness of these data is at present insufficient, to accurately calculate total national emissions of dioxins into the atmosphere. However the available specific emission data, for a large part established in German, Dutch and Swedish investigations, does provide a reasonable view on the relative contribution of the various source categories considered.

In the following table, latest data published in literature are presented. It should be emphasised that data from the different countries have not been established on a common basis and do not refer to the same year. Because of recent improvements of various processes and termination of others (after the reference year), the figures will not fully represent the current situation.

Table S.1 Published data on sources of dioxin emissions into the atmosphere

Country:	D	DK	F	GB	NL	S
Category	Total emission into the air, g I-TEq/a					
MSW inc.	5.4-432	34	834	8.4-486	382	5
Haz.waste inc.	0.5-22	4	17	0.17-8	6	2-6
Landf.gas inc.	0.24-2.4				0.06	
Sludge inc.	0.01-1.1	0.5	0.4		0.46	
Cable inc.	0				1.5	
Hosp. waste	5.4	14	28	47	1	2-6
Asphalt prod.				1.5	0.3	
Oil comb.	0.5-27	0.01-0.02[1)]		1.9	1.0	
Coal comb.	3.7-34.1		0.02	32	28	1
Wood comb.	1.6-4.3[2)]	0.4[3)]		2-4	12	
Crematoria					0.2	
High Temp.proc.					2.7	2.7-4
Road traffic	10		16		<6	5-15
Sinter proc.	250-800	0			26	[4)]
Steel ind.	1.3-19	12[3)]	10		2.8	2-19[5)]
Non-Fe metal ind.	38-380				1.2	4.5
Chemical ind.					0.5	
Pesticides					<25	

1) Eadon TEq
2) Domestic use only
3) Nordic TEq
4) Included in steel ind.
5) Preliminary data

Investigations on dioxin emissions have for a large part been focussed on various types of waste incineration, and particularly on municipal waste incineration. Indeed, the emission levels from old incinerators made this category the main source. Although the exact formation mechanisms of dioxins in these installations is not yet completely clear, technologies to reduce the emissions into the atmosphere by about two orders of magnitude have been developed. In countries where the emission standards require application of these technologies, the role of municipal waste incineration as a dioxin source, will be greatly reduced. At present a transition to improved installations is taking place.

Because of inadequate process control, or even complete lack of control, combustion processes like cable smouldering and 'traditional' hospital waste incineration, show very high specific emissions. The scale of these processes is usually small; however locally their contribution to emissions can be high.

This same effect plays a role for domestic heating appliances, specially those fired with coal or wood. Although the specific emission levels are not extremely high, the total amount of fuel burned this way and the location of the sources cause this category not to be negligible.

Emissions from road traffic, which may have been considerable in the past, are expected to decrease further because of the reduced use of leaded petrol containing chlorinated scavengers.

A number of categories presented in this survey might be characterised as relatively less important sources, because the specific emission level is low, and/or the scale of these processes is small. This generally applies to fossil fuel fired power plants, use of landfill gas, incineration of sewage sludge and most high temperature industrial processes.

Processes related to the metal industry are relatively important. This specialy concerns sintering processes, and the secondary metal industry.

An important secondary source is evaporation of dioxins from wood (formerly) treated with dioxin containing preservatives (PCP).

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1 Introduction

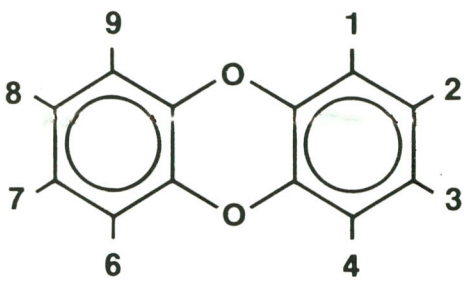
Polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF), generally referred to as dioxins, have never been produced intentionally. However, these highly toxic substances are generated as trace contaminants in a variety of thermal and industrial processes. Because of their chemical, physical and biological stability they are ubiquitous in the environment.

Because dioxins are accumulated in the food chain, especially in fatty materials (as for instance cow's milk and human milk) the exposure of human consumers to these products is enhanced. In some instances, the maximum tolerable daily intake level, which so far has not been established exactly, might even be passed.
While the harmful effects of dioxins have not been completely quantified yet, it is generally accepted that preventing production and emission of dioxins is highly desirable. As a first step, it is therefore required to identify the various sources and rank these according to their relative importance.
In a number of countries a national inventory of sources has been made or is in preparation. It is the general view that the main sources are known by now, but that the mechanisms and parameters involved in the generation of dioxins are not always completely understood yet. As a consequence, specific emission data of many processes are to a large extent uncertain.
In this report the latest published data of national inventories of emissions of dioxins into the atmosphere in Denmark, France, Germany, The Netherlands, Sweden and the United Kingdom, are presented.

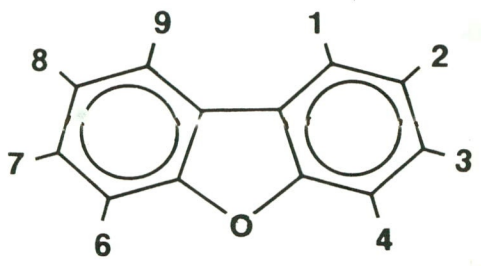
2 General

2.1 Chemical composition

Dioxins is the collective name for polychlorinated dibenzo-p-dioxins (PCDD's) and polychlorinated-dibenzofurans (PCDF's), often abbreviated to PCDD/F's.
The basic structure of a dibenzo-p-dioxin and dibenzofuran, two benzene rings interconnected by two respectively one oxygen bridge, is presented below. At one or more of the places indicated with 1, 2, 3, 4, 6, 7, 8 and 9, a hydrogen atom has been substituted with a chlorine atom, thus making it possible to form a total of 75 PCDDs and 135 PCDFs. This produces a total of 210 different 'congeners'.



Dibenzo-para-dioxin



Dibenzofuran

The most toxic congener is 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD). However, the various congeners mutually show great differences in toxicity. It appears that only the 17 congeners that have been substituted with a chlorine atom on the 2,3,7 **and** 8 place have a significant toxicity. These 17 congeners (the 'dirty seventeen') all have obtained a so-called 'toxicity equivalence factor' (TEF) stating the congener's toxicity compared with 2,3,7,8-TCDD.

Various TEF schemes have been used in various countries in the past and several are still being used. In 1988 an international joint venture, chaired by the NATO/CCMS, reached consensus about the so-called International ('I-TEF') scheme (Van Zorge et al., 1989). This scheme only regards the seventeen 2,3,7,8 chlorine-substituted dioxins and furans as 2,3,7,8-TCDD-related compounds (see Table 2.1).

Multiplying the concentration of a 2,3,7,8-TCDD-related compound with the I-TEF involved, produces the concentration expressed in 2,3,7,8-TCDD Toxic Equivalents (I-TEq) of that congener. By adding all I-TEqs of the compounds in a mixture, the

entire mixture is expressed in I-TEq and can be assessed as a quantity of 2,3,7,8-TCDD.

Table 2.1 Toxicity Equivalence Factors of the 17 dioxins and furans

Congener	I-TEF
dioxins	1
2378 - TCDD	0.5
12378 - PCDD	0.1
123478 - HxCDD	0.1
123678 - HxCDD	0.1
123789 - HxCDD	0.01
1234678 - HpCDD	0.001
octa - CDD	
furans	
2378 - TCDF	0.1
12378 - PCDF	0.05
23478 - PCDF	0.5
123478 - HxCDF	0.1
123678 - HxCDF	0.1
123789 - HxCDF	0.1
234678 - HxCDF	0.1
1234678 - HpCDF	0.01
1234789 - HpCDF	0.01
octa - CDF	0.001

Dioxins can be formed not only with chlorine, but also with bromine. Brominated dioxins or mixed chlorine/bromine dioxins could arise in the same way as chlorinated dioxins. Bromine occurs much less general than chlorine (the bromine concentration in domestic waste, for example, is less than 1% of the chlorine concentration). In general, brominated dioxin emissions will therefore be much lower than the emissions of chlorinated dioxins. For this reason, as well as for reasons of an analytical-technical nature (there are about 5,000 mixed chlorinated/brominated dioxins), the investigation of brominated dioxins did not get high priority, they will not be considered in this report. Also the 'planary' PCBs (77, 126 and 169), that are closely related to dioxins, from a chemical and toxicological point of view, will not be considered.

2.2 Properties

At ambient temperature the higher chlorinated dioxins are colourless crystalline solids. Vapour pressures of TCDD and OCDD are resp. $<4.5 .10^{-6}$ and $<8.7.10^{-7}$ Pa at 25 °C [Fiedler et al., 1990]. According to this same source, water solubility is low, data between 8 and 200 ng/L for TCDD and between 0.4 and 0.97 ng/L for OCDD are reported. Solubility in oils, fats and organic solvents is high. Specially the higher chlorinated species are extremely lipophilic and will therefore strongly accumulate in organic matrices and when present in the environment, they will usually be adsorbed on solid particles. Lower chlorinated dioxins will preferably

be transported in the gaseous phase, and can therefore be transported over long distances.
If oxygen is present, dioxins will be stable up to temperatures of 700 °C. In the atmosphere dioxins will be subject to photochemical degradation. However if the dioxins are adsorbed to solids, or have entered into the soil, this process is slowed down considerably or even stopped.
Concerning toxicity many questions are still open. Ingestion is generally the pathway for over 95% of human exposure. Recommended ADI (acceptable daily intake) levels in different countries show some variation. For instance, in Germany the recognised value of precaution is 1 pg I-TEq/kg body weight per day, the intervention level is 10 pg I-TEq/kg.day. The World Health Organisation recommends an ADI of 10 pg I-TEq/kg.day. The estimated present average exposure in Germany is 2 pg I-TEq/kg.day [Schulz, 1993].

3 Dioxins in the environment

To assess the impact of the present emission sources on the environment, a comparison can be made with the 'natural' background level. This is possible by comparing the present environmental concentrations, with many antropogenic sources (industrial and combustion processes) with that of the pre-industrial era, or by comparing heavily industrialised areas with rural or remote areas.
The soil is the most important sink for dioxins entering the environment. Dioxin concentrations in UK (semi rural) archived soil samples taken since 1846, show a steady increase, starting around the turn of the century. Since then the level rose from around 30 ng ΣPCDD/F to 90 ng ∑PCDD/F per kg of soil in 1986 (the 1986 level corresponds to 1.6 ng I-TEq/kg) [Kjeller et al., 1991). The increasing trend was found for all different congener groups. The only possible pathway for the dioxin input to this area is atmospheric deposition.
In parallel to the soil samples, in the same investigation, dioxin concentrations in archived herbage samples, covering almost the same period, and originating from a comparable site have been analysed for dioxin concentration and congener distribution. The results confirm the conclusions drawn from the soil data with bulked samples from 1960-1970 and 1979-1988 showing concentrations 7 to 8 times higher than the 1891-1900 sample. The concentration tends to decrease again since the beginning of the 1970's (apart from an incidental peak of HxCDD's in the early eighties). Another finding is that the ratio of PCDF / PCDD changed from 60/40 in the herbage samples before 1930-1940, to 30/70 in the later samples. A possible explanation might be the dominance of dioxins derived from the combustion of wood and fossil fuels in this first period and a larger post world war contribution of other processes, like the production and use of chlorinated organic chemicals in the UK (PCP, 2,4,5-T) or also the use of leaded fuels (declining after 1973).

An investigation in Baden-Würtemberg (D) established a background level in soil of 0.8 ng BGA-TEq/kg[1)], with levels of 3.4 ng BGA-TEq/kg in urban areas and 8.4 ng BGA/TEq/kg in heavily industrialised areas [ATV-Arbeitsgruppe 7.03, 1994). In North Rhine Westfalia, it was also concluded that levels in urban areas (50% < 5 ng, 90% < 10 ng BGA-TEq/kg) are roughly two times as high as the levels in rural areas.

In soil samples taken from a an ancient Roman site in Germany, dating back to the period around the year 50, that has not been disturbed nor contaminated since then, dioxin levels up to 2,0 ng I-TEq/kg have been found [Hartmann et al., 1992].

Locally, concentrations in soil may be severely contaminated by (former) activities. In the neighbourhood of a former wire scrap incinerator, concentrations between 13,000 and 300 ng I-TEq/kg have been measured, compared to a background level of 4.8 ng I-TEq /kg, measured at a distance of 2 km, [Hülster et al., 1993].

There is evidence for long range transport of dioxins, e.g. the variation of dioxin concentration measured at a location in Sweden has been shown to be dependent on the direction of the wind. In periods when the sampled air originated from areas in Europe with higher dioxin emissions, observed concentrations were higher and the congener profiles varied. By comparison with known source profiles, air samples from

1) BGA: German Federal Health Office

the north could be identified with the background profile. In these samples higher chlorinated congeners dominated [Tysklind 1993].

Measurements of dioxin concentrations in ambient air in The Netherlands showed a background level in an urban area in the western part of the country between 10 and 15 fg I-TEq/m^3 [Bolt et al., 1993]. Air arriving from the North Sea contained about 5 fg I-TEq/m^3. In the neighbourhood of a large MSW incinerator, emitting (at that time) around 250 g I-TEq per year, concentrations ranged between 15±5 fg I-TEq/m^3 and 125±25 fg I-TEq/m^3, the high values found in the downstream airmasses.
The yearly average of the dioxin immision concentration in West Germany is around 10 fg I-TEq/m^3 in the rural areas and above 100 fg I-TEq/m^3 in urban areas. An average background concentration of 24 fg I-TEq/m^3 has been determined in the summer of 1990 [Bröker et al., 1994]. The corresponding average deposition is between 10 and 15 pg I-TEq/m^2 per day.

In samples from sediments in large lakes and river estuaries, a strong increase of the PCDD/F concentration, above the depth corresponding to the year 1940, has been observed. Older sediment layers contained considerably lower or non-detectable concentrations. The results of PCA modelling indicated that the congener and isomer fingerprint patterns in surficial sediments were similar to those found in municipal sewage sludge, municipal solid waste incinerator fly ash, pentachlorophenol, sodium pentachlorate, soils from metal reclamation plants, combustion engines, and pulp and paper mill black liquor recovery plants [Wenning, 1993].

From the examples given above, it can be concluded that current concentration levels of PCDD/F in various environmental compartments are considerably higher than the natural background level. Apparently the increase has started around the beginning of the century and may have stopped and turned into a slight decrease somewhere around the beginning of the last decade.

3.1 Sources

Traditionally the sources of dioxins are divided intro three main categories: industrial sources, combustion processes and secondary sources. Secondary sources contain dioxins generated in an earlier process, that may be (slowly) released to the environment (e.g. sewage sludge, red copper slag, waste disposal sites).
The available data on the emissions from several of these sources have to be treated with great care, as the available data may be quite uncertain and not representative for a source category.

Dioxins are not commercially manufactured and have no applications either. Yet they can be formed as undesired by-products in a number of processes:

1. In combustion processes in which both chlorine and a carbon source are present; a number of metal compounds (specifically copper and maybe iron also) act as a catalyst here. The dioxins are partly emitted into the air and partly bound to combustion residues;

2. In processes in which precursors (compounds from which dioxins can simply be generated) or compounds from which precursors can be formed, are heated to above 150 °C, in the presence of chlorine. This happens for example during production and processing or at the use of chlorophenols, chlorobenzenes, HCH, PCBs, but also at the oxichlorination of ethene. In such processes, the dioxins can be emitted to water or air or can end up in the waste;

3. In sintering processes, in melting/founding and at the recovery of metals in the presence of organic material and a chlorine source, a metal-cutting liquid or chlorine gas (magnesium production);

4. In processes in which activated chlorine is used for the bleaching of cellulotic raw materials, such as paper, cardboard and their products.

Processes as described under 4 have not been considered in this report, because they are not expected to cause emission of dioxins into the atmosphere.

In the three other categories, there are four important process conditions that make the forming of dioxins possible:
- temperature between 200 and 800 °C (ideal range between 200 and 400 °C);
- presence of chlorine;
- presence of organic (specifically aromatic) matter;
- presence of oxygen (in basic material or surroundings).

Three possible mechanisms have been proposed to explain the presence of dioxins in the emissions of (combustion) processes:
- dioxins present in the process input are not completely destroyed;
- production from related chlorinated precursors;
- formation from chemically unrelated compounds via de novo synthesis.

In principle, all production processes in which chlorine and a carbon source are used in combination at a temperature above 200 °C are potential dioxin sources. Therefore, at the selection of processes to be considered, these factors (increased temperature, presence of organic matter, oxygen and chlorine) were used as criteria.

4 National inventories of sources of dioxin emissions into the air

4.1 General

Since it was recognised that dioxins are formed in many different processes, not only these processes have been investigated, but also national inventories, listing calculated emissions from the known sources, have been composed. Characteristic for these surveys is a large margin of uncertainty, because specific emission data of processes appear to vary over a wide range and it is usually also complicated to collect the required production data of these processes.

In this inventory, attention is focused on sources of emissions of dioxins to the air in six Western European countries. Emissions with waste water and in process residues have not been considered.

In order to make the inventory as complete and up to date as possible, information from reports, that exist only in draft version, had to be used. This limited the extent to which all reported data could be used, because some data might be subject to change, e.g., from the report, that Her Majesty's Inspectorate of Pollution in Great Britain is preparing [HMIP, 1995], only the production data of various processes are incorporated. Emissions from the various sources might be calculated from specific emission data of similar sources to be found in the literature. It is outside the scope of this inventory to make this step.
The opposite is more or less the case with regard to the German situation. Although some information concerning the scale on which particular processes take place in Germany can be found in the literature [Hutzinger et al., 1993], many more source categories have been recently investigated. The final report containing the collected results of these investigations will be published shortly. Data presented here, have been taken from the (latest) draft of this report [LIS, 1993]. It is unlikely that reported data will be significantly different in the final report.
The Danish EPA is preparing a survey of dioxin emissions in Denmark, based on the results of investigations that have been conducted in the past. Some of the collected data, like those from municipal waste incineration have been measured between 5 and 10 years ago [Miljoprojekt nr. 117, 1989], so these will no longer adequately represent the current situation. From the EPA report, at present only a summary is available, this has been used as the main reference concerning the situation in Denmark [Miljostyrelsen, 1994].
Dioxin emission data from France are scarce. Measurements that have been carried out are mostly confidential and are not published. The main (and only) document that was available concerning dioxin emissions [Bouscaren, 1992], uses mainly foreign measurement data for the calculations and presents a limited number of sources.
Based on measurements in the period 1990-1992 at installations, representing the known/suspected sources, the so-called MOB programme, a comprehensive survey of dioxin sources in The Netherlands has been made [Bremmer, 1994]. These data are presented here, although e.g. emission levels of municipal waste incinerators, will presently be considerably lower, because of improved technologies.
In the Swedish Dioxin Survey many potential sources, among which many industrial processes have been assessed [Lexen et al., 1991]. Part of the measured data, e.g. at

municipal waste incinerators are no longer representative for the actual situation. At present a survey, presenting all known sources of dioxin emissions in Sweden is in preparation (to be completed around the middle of 1995). Some results, already calculated in this framework, are incorporated in this report.

Because the references, mentioned above, are the main basis for the data given in this report, it will not be noted specifically every time they have been used. Unless it might raise confusion, only the additional references will be mentioned explicitly.
The reference year for the presented data is usually not mentioned, unless it is known that these data have been subject to significant change in recent years, like in case of waste incineration or dioxin emissions related to traffic.

It is common practice to express PCDD/F concentrations as (International) Toxic Equivalent mass/Nm^3, where N(ormal) stands for 0 °C, 1013 mbar, and 11% O_2. Wherever possible, data have been converted to these units. Especially the O_2 percentage that has been used in calculations is not always clear, in case of doubt it has been assumed, that the conversion to 11% has already been incorporated.

In the following chapters, the known sources that are relevant with regard to PCDD/F emissions to the atmosphere will be presented. General information and data for each source will be given and also, if these figures have been found in literature, the emission figures related to these sources in the respective countries.

4.2 Incineration of municipal solid waste

4.2.1 Process Description

Domestic and comparable industrial waste and bulky waste are incinerated in MSW incinerators (municipal solid waste incinerators). A municipal solid waste incinerator consists of one or several 'incineration lines'. An incineration line is understood to mean the combination of furnace, boiler, flue gas cleaning and stack. Several lines may have a common stack.

Most incinerators in Europe apply one of the various grate-type furnaces. Through a chute, the waste is dosed onto the moving grate where it is combusted. At present most installations apply heat recovery in a boiler where steam or hot water is produced, there are still some plants where the temperature is decreased by water injection. The flue gases are subsequently cleaned before being released to the atmosphere. All flue gas cleaning systems consist at least of a particulate control system, usually an electrostatic precipitator, which collects 99% or more of the fly ash as 'ESP ash'. Several systems exist for removal of acid components (HCl and H_2SO_4) and trace components like heavy metals and other particulate bound components like dioxins, from the flue gas stream. The most usual types can roughly be divided in dry, semi-dry and wet scrubbers. Ca-based components or $NaHCO_3$, sometimes with addition of activated carbon are used as adsorbent. For improved particulate control, and in all cleaning systems with a dry scrubber, fabric filters are used. In some systems fixed bed activated carbon filters are used as a final cleaning stage. Catalytic convertors, initially added for NO_x reduction, have shown to reduce dioxins as well, and are now also applied for this purpose (with increased catalyst volume).

Incineration of municipal waste has first been recognised as a source of dioxin emissions in 1977 [Olie et al., 1977]. In the second half of the eighties in several countries large campaigns to monitor dioxin concentrations in the flue gas of incinerators (and in the solid residues) have been carried out. These campaigns were also aiming at a better understanding of the formation mechanism, to be able to design installations with reduced emissions. Because repeatable experiments with waste in large scale commercial installations, e.g. to investigate the effect of changing waste composition, appear to be quite complicated, most conclusions have to be based on statistical considerations, and have a large margin of uncertainty.
From a German investigation it is concluded that differences of a factor 2 in figures of dioxin emission with the flue gas, found in this programme, are not significant [Johnke et al., 1992].

In an investigation comprising 48 measurements on 17 municipal waste incineration lines in The Netherlands [Brem et al., 1992], parameters having a high correlation with dioxin emissions were identified. Apparently a distinction had to be made between older installations with an ESP only, and newer units with an ESP and a wet scrubber.
In the first group, independent parameters having a significant effect on dioxin emissions were:
- carbon content in the filter ash
- peaks in CO concentration
- dust concentration in the flue gas
- moisture content in the flue gas

For the group of installations with dechlorination of the flue gases, two independent parameters were found:
- carbon content in the filter ash
- combustion chamber temperature

It is concluded that apparently primary measures, affecting above parameters, can be applied to reduce dioxin emissions.

4.2.2 Measured emission data

Apart from numerous separately reported emission measurements a number of national surveys has been carried out and reported.

Between 1985 and 1990 systematic investigations were conducted at waste incinerators throughout the Federal Republic of Germany within the framework of a National Dioxin Measurement Programme [Greiner et al., 1991; Johnke et al., 1992]. A total of 11 plants with 15 incineration units participated in this programme, that was mainly focusing on the mechanisms of PCDD/F formation in the plants and on ways to reduce these emissions. Concentration levels measured in the cleaned flue gas ranged from 0.2 to 63 ng I-TEq/m^3 with an geometric average of 5 ng (89 measurements).
Current emission standards limit the emission via the flue gas of new installations to 0.1 ng I-TEq/Nm^3. Existing installations will have to comply with this same standard in 1995.

In the period 1985 to 1988 a PCDD/F research programme has been conducted in Denmark, involving over 200 analyses of dioxin emissions of 12 incinerators. It has

been estimated from the results of this study that the average PCDD/F emission into the air from municipal waste incineration is 4 ng N-TEq/m^3. This brings the total figure related to MSW incineration in Denmark (1.7 Mtonne) to 34 g N-TEq/year.

In 1990 PCDD/F emissions of all 12 MSW incinerators in operation in The Netherlands by then have been measured [Slob et al., 1993]. Three of these were closed in that same year. The concentration in the flue gas of the remaining installations ranged from 2.2 to 92 ng I-TEq/m^3, with an average value of 18 ng I-TEq/m^3. The calculated yearly emission to the air of these installations, with a troughput in 1989 of 3.1 Mtonne, based on these figures, is 411 g I-TEq.
Current emission standards limit the emission via the flue gas of new installations (post 1989) to 0.1 ng I-TEq/Nm^3. Existing installations will have to comply with this same standard in 1995 (some exceptions may be allowed up to a maximum of 0.4 ng I-TEq/Nm^3).

Measurements of PCDD/F emissions of 15 Swedish waste to energy installations, conducted in 1985 showed that for most installations levels were between 5 and 50 ng E-TEq/Nm^3, with 3 installations below 5 ng and 1 installation above 100 ng [Bergvall, 87]. Total emissions to the air from waste incineration (1.45 Mtonne in 1989) were 25 g E-TEq/year.
In 1987 in Sweden new standards were adopted, to be achieved in 1992, limiting the yearly average emission in the flue gas to 2 ng N-TEq/m^3 for existing plants and 0.1 ng for new plants.

In the UK, in 1989 annually 2.5 Mtonnes of municipal waste were burned in 37 incinerators of various types and designs [HMIP, 89]. Testing of 13 units resulted in an emission range of 8.4-486 ng I-TEq/m^3.

Based on the results of these measurements, and the revision of emission standards, development of abatement technologies has been accelerated and sometimes older installations have been closed down.
In the current design of new incinerators much attention is paid to proper control of the combustion process. This includes sufficiently high temperature levels and mixing and residence time of the combustion gases that guarantee complete combustion. The effectiveness of these designs is confirmed by measurements of the dioxin concentration in the uncleaned flue gas of the latest, optimized waste incinerators, where levels in the order of magnitude of 1 ng I-TEq/Nm^3 are state of the art.
Because of the above developments, the differences in emission of presently operating incinerators is very large. Installations adapted to comply with the most severe standards will have a concentration level in the cleaned flue gas < 0.1 ng I-TEQ/Nm^3, while older installations may show levels that are far above 10 ng I-TEQ/ Nm^3.

4.2.3 National inventories

Forced by more stringent standards, in recent years, the emission characteristics of MSW installations have been drastically improved by more sophisticated process control, retrofitting extensive flue gas cleaning systems to existing installations and by building new ones. Therefore, in most countries the emissions to the air from this source have continuously been decreasing during the last years. Because published figures are mostly based on inventories from years ago,

it is difficult to use these data as a basis for an inventory in a more recent year. Therefore, in Table 4.2.1, three different figures are given:

A. the figure for the year 1993, based on a uniform calculation procedure used by Rijpkema (see below).
B. the most recent figure/range found in literature.
C. the figure calculated on basis of compliance with the present emission standards (also for existing installations).

In 1993, emissions of European municipal waste incinerators have been inventoried, based on the characteristics of the individual installations, that have been collected [Rijpkema, 1993]. Assumptions in the calculations have been:

- 1 tonne of waste corresponds to 5140 Nm^3 of flue gas (air factor 1.8)
- For installations not complying with the standard of 0.1 ng, but equipped with a dry, semi-dry or with wet scrubbers, the emission level is 8 ng I-TEq/Nm^3, or 15 ng I-TEq/Nm^3 if there is no flue gas cleaning system or dust removal only.

Table 4.2.1 Dioxin emissions of municipal solid waste incineration

Country	Process input [ktonne/a]	PCDD/F emission into the air			
		Concentration flue gases [ng I-TEq/-m^3][1)]	Annual emission [g I-TEq]		
			A	B	C
D	9000	0.1-8	312	5.4-432[2)]	5.4
DK	1760	8-15	56	34[3)]	
F	8400	8-15	550	834[4)]	
GB	2400	15	180	8.4-486[5)]	13
NL	2700	0.1-15	78	382[6)]	1.6
S	1500	8-15	69	5[7)]	0.8

1) under standard conditions
2) Hutzinger et al., 1993
3) Danish EPA
4) Bouscaren, 1992
5) Bremmer et al., 1994
6) HMIP, 1989
7) Swedish EPA, 1995, to be published

4.3 Hazardous waste incineration

4.3.1 Process description

This waste category includes all substances, that because of their harmful chemical composition require carefully controlled high temperature incineration. The waste may be solid, pasty, liquid or gaseous.
The most common types of incinerators for this purpose are rotary kilns, liquid injection furnaces, after burners and to a lesser extent fluid bed furnaces or fixed grate furnaces.
The flue gases of these installations may be discharged to the atmosphere without cooling, or after passing through a boiler, usually combined with a flue gas cleaning system, or after cooling by quenching, mostly combined with a scrubber.

Depending on the type of installation and the applied flue gas cleaning system, dioxin emissions can vary over a wide range.

4.3.2 Measured emission data

In the Dutch survey [Bremmer et al., 1994], e.g. the figures for a specific rotary kiln change from 27 to 0.3 ng I-TEq/m^3 after the replacement of the ESP by a fabric filter with injection of lime and activated carbon (1992). This improvement is equivalent to a reduction of the specific emission from 200 µg/ton to 2 µg/ton.
For the other type of hazardous waste incineration presented in the same report, emission figures vary considerably, ranging from 0.6 pg I-TEq/m^3 for an afterburner in which halogen containing solvents and chloroparaffins are destroyed, to 7.6 ng I-TEq/m^3 for a furnace in which liquid and gaseous chlorinated hydrocarbons are incinerated.
Totalising and averaging the known figures for the year 1991, the specific dioxin emission from incineration of hazardous waste in The Netherlands is 110 µg I-TEq/ton. After the retrofit of a new flue gas cleaning systems on the rotary kiln furnaces, the specific emission will be reduced to 10 µg/ton. This will be realised in 1994.

Jones et al., 1993 report emission data from eleven European installations that, apart from one exception in case of an old installation, range from 0.06 to 5.8 Ng I/TEq/m^3, the average value being around 1.6 ng I-TEq/m^3. Some of these installations burn PCB or PCB containing material.

4.3.3 National inventories

Fiedler et al., 1992 estimate the specific emission of dioxins from hazardous waste incineration in Germany to be between 0.1 and 4.5 ng I-TEq/Nm^3. With an assumed 6000 Nm^3 flue gas per tonne of waste, and 800,000 tonnes/year being incinerated in Germany, this corresponds to a range from 0.5-22.5 g. In Germany also, the newly adapted emission standard is 0.1 ng I-TEq/Nm^3, meaning that in the near future the lower limit of this range will be met.

Hagenmaier et al., 1990, calculated a total emission from hazardous waste incineration of 1 g I-TEq, based on an estimated input of 200,000 tonne/year and a specific flue gas emission of 0.5 ng I-TEq/m^3.

In the Danish EPA survey figures are given for the year 1985. The total amount generated then was 135,000 tonnes, of which 80,000 tonnes has been exported. Specific emissions are estimated to be 30 microg I-TEq/tonne, resulting in a total of 4 g for all generated hazardous waste.

In GB, presently 290 ktonnes of hazardous waste is incinerated annually, [HMIP, 1995]. Of this total around 140 ktonnes is incinerated in large public installations and the rest in industrial installations, mainly in the chemical industry. It was reported earlier [HMIP, 1989], that there are around 60 of these industrial installations. No specific information on these installations and their emissions is published. The new emission standard in GB is 1 ng I-TEq/m^3, with a goal of reaching 0.1 ng. The estimated GB emission from this source is calculated with the same data as used for Germany.

In the Dutch inventory, a total emission in 1991 of 16 g has been calculated. By the retrofit of a new flue gas cleaning system on the first of the large rotary kilns in 1992, this has already been reduced to 6 g annually. After completing the retrofit programme of all large rotary kilns, the total emission via the flue gas of the hazardous waste incinerators will be further reduced to 1.7 g I-TEq/year.

Table 4.3.1 Dioxin emissions of hazardous waste incineration

Country	Process input [ktonne/a]	PCDD/F emission into the air		
		Concentration flue gases [ng I-TEq/-m^3]	Emission factor [µg I-TEq/-tonne of input]	Annual emission [g I-TEq]
D	800	0.1-4.5	0.6-27	0.5-22
DK	135		30	4
F	570		30	17
GB	290	0.1-4.5	0.6-27	0.17-8
NL (1992)	155		39	6
S (1989)	30			2-6

4.4 Incineration of landfill gas and biogas and sludge

4.4.1 Process description

Landfill gas and biogas are increasingly being collected and incinerated. The reason for this is that the incineration of the gas causes less environmental pollution than when it is emitted without precautions being taken. Incineration in

practice takes places with and without energy utilization. Energy utilization often takes place in a reciprocating engine (gas engine), that drives a generator for the production of electricity. In other cases, landfill gas or biogas is used in a boiler for the production of hot water or steam, or in a process.

Incineration without energy utilization takes place in 'flares', at which the gas is incinerated in a free flame in the open atmosphere. Small 'top flares' (up to about 30 m high) are used for landfill gas and biogas.

Sometimes after cleaning (to < 5 mg Cl/m^3), landfill gas or biogas is added to the public natural gas grid. By cleaning, halogenated and higher hydrocarbons are removed from the gas using activated carbon. The hydrocarbons that are released at the regeneration are flared.

Most sludge is generated in sewage water cleaning stations, other sources are industrial processes.
The incineration of sludge usually is done in fluidized bed furnaces, possibly in combination with other substances. Another technology that can be applied is the multiple-hearth furnace.
Possibly in some national inventories, incineration of industrial sludge is incorporated in the incineration of industrial (hazardous) waste.

4.4.2 Measured emission data

From two measurements in The Netherlands respectively at a gas engine and a flare, it was concluded that for the incineration of untreated landfill gas, an emission factor of 0.5 ng I-TEq/m^3 of gas can be used. The emission factor for biogas was assumed to be equal.

From results of a confidential measurement, an average emission factor of about 5 µg I-TEq/tonne of sludge was calculated for the incineration of sewage sludge.

From measurements at two fluidised bed incinerators of industrial sludge, an average emission factor of about 4 µg I-TEq/tonne was calculated.

The results of measurements of dioxin emissions at the incineration of landfill gas, biogas and sludge in The Netherlands are summarized in Table 4.4.1.

Table 4.4.1 Dioxin emissions at the incineration of landfill gas, biogas and sludge in The Netherlands (1991 situation)

Incineration process	Quantity per year	Emission factor	PCDD/F emission [g I-TEq/year]
untreated landfill gas	52 million m^3	0.5 ng I-TEq/m^3	0.03
untreated biogas	60 million m^3	0.5 ng I-TEq/m^3	0.03
sewage sludge	51,000 tonnes (d.s.)	5 µg I-TEq/ton	0.25
industrial sludge	53,000 tonnes (d.s.)	4 µg I-TEq/ton	0.21
Total			0.52

From the German measurement programme, measurements at 6 landfill gas fired furnaces and over 20 gas engines are reported. The emission concentrations in the flue gas of the furnaces are typically (far) below 0.05 ng I-TEq/m^3 with a highest value of 0.28 ng I-TEq/m^3. With only one exception (0.2 ng), all results of the gas engine measurements are significantly below 0.1 ng I-TEq/m^3.

For the calculation of the British emissions from landfill gas, additional measured data are included [Mitchell et al., 1993], extending the estimated emission range down to 0.01 ng I-TEq/m^3.

4.4.3 National inventories

Landfill gas and Biogas
Approximately 74 million m^3 of landfill gas were extracted in The Netherlands in 1991. About 22 million m^3 of this quantity were flared. Of the rest 14 million m^3 were used for heating purposes, 16 million m^3 were used (untreated) in gas engines for electricity generation and 22 million m^3 were processed to natural gas quality (Oonk et al., 1993).
Gas that is obtained at the anaerobic digestion of sewage sludge is often incinerated in gas engines. Based on an inventory conducted in 1990 it is estimated that approximately 60 million m^3 of biogas are incinerated per year (Bremmer and Hesseling, 1991).

Sludge
In The Netherlands, sewage sludge is incinerated in three fluidised bed furnaces with a total capacity of 51,000 tonnes (d.s.)/year.
The incineration of (chlorine containing) industrial sludge mainly takes place in two fluidized bed furnaces, with a throughput of resp. 7,850 and 45,000 tonnes (d.s.) per year. The latter specifically incinerates sludge from a papermill. Furthermore, there are two very small incinerators with a total throughput of 100 tonnes d.s./year (Bremmer and Hesseling, 1991).
In The Netherlands, a total of 282,000 tonnes sewage sludge, and 180,000 tonnes industrial sludge are released annually (Duvoort-Van Engers, 1991; RIVM, 1992).

Table 4.4.2 Dioxin emissions of incineration of landfillgas, biogas and sewage sludge

Country	Process input [ktonne/a]	PCDD/F emission into the air		
		Concentration flue gases [ng I-TEq/-m^3]	Emission factor [µg I-TEq/-tonne of input]	Annual emission [g I-TEq]
D sludge		0.01-1		0.01-1.1[1)]
gas		0.1-1		0.24-2.4[1)]
DK sludge	250		2	0.5
F sludge	140	0.5	3	0.4
gas				
GB sludge	77			
gas	470			
NL sludge	104		4-5	0.46
gas	111.10^6 m^3		0.5 ng/m^3	0.06
S sludge				
gas				

1) Hutzinger et al., 1993

4.5 Burning of cables, electromotors, etc.

4.5.1 Process description

Cable burning is the process in which copper and lead are recovered by burning the insulating material of electricity and electronics cables. In this process, all ingredients for the forming of dioxins are present, i.e. carbon (sheath), chlorine (PVC or mould-resistant agents), and a catalyst (copper).
Because of the highly polluting character of cable burning it is prohibited in some countries (a.o. Germany).
The cables that are legally burnt are so-called greasy underground cables (armoured paper lead cables). Plastic-insulated cables are usually shreddered. Illegal burning specifically involves cables from cars and from building and demolition waste.

The burning is done batch-wise in simple furnaces. In the furnace, the possibly pre-shreddered cables are set afire (using oil or gas). The combustible substances present (grease, oil, paper, jute, and the like) then keep the fire going. The lead present melts and is drained. After the process, the copper core and the steel strip (of cable armouring) are scooped from the furnace with the combustion residue. The gases arisen at the burning are incinerated at temperatures of 800 °C or higher, and then emitted, sometimes via a scrubber.

If cables are burnt illegally, this is usually done in a very primitive way. The cables are set afire either on the ground or in a cask. By placing the stake on a small elevation or by making holes in the bottom of the cask, the lead can run off and be collected.

A process related to cable burning is the burning of windings of electric motors, brake blocks, and the like. These processes are also carried out in a furnace at 300 to 400 °C, with incineration of the generated gases. The furnace temperature is usually set by a separate burner and not by the burning of the material itself.

4.5.2 Measured emission data

Table 4.5.1 Results of measurements at cable burners and at a plant for burning electric motors in The Netherlands (confidential literature source)

Type of material	PCDD/F concentration in flue gases [ng I-TEq/m^3][1)]	PCDD/F emission [µg I-TEq/tonne input]
underground cables	0.6 - 1.0	3.7 - 6.4
underground cables, cables containing PVC	1.9 - 3.2	7.4 - 14
stripped cable[2)]	3.8	21
partly stripped cable[3)]	254	2,280
electric motors	1.3	3.3

1) referred to dry flue gases under standard conditions, converted to 11% O_2
2) cable without lead, scrap and bitumen; just copper core with grease and (greasy) paper
3) cable with lead, without scrap and bitumen; this cable was generally burnt.

Results of earlier measurements by Bröker et al., 1986, cited in the French survey, show concentration levels up to 120 ng I-TEq/m^3. The average is estimated to be 30 ng I-TEq/m^3, corresponding to an emission factor of 45 µg/tonne.

4.5.3 National inventories

Table 4.5.2 Dioxin emissions of burning of cables and electric motors

Country	Process input [tonne/a]	PCDD/D emission into the air		
		Concentration flue gases [ng I-TEq/-m^3]	Emission factor [µg I-TEq/-tonne of input]	Annual emission [g I-TEq]
D	0[1)]			0
DK	-			-
F			45	
NL	approx. 4500		3.3 - 500[2)]	1.5
S				
GB				

1) prohibited
2) the high figure is estimated for illegal calbe burning

4.6 Hospital waste

4.6.1 Process description

Hospital waste can be distinguished into general waste, similar to municipal solid waste and specific waste containing pathological material. Because of this last fraction, it is very usual for hospitals to have their own waste incinerator. Characteristic for these installations is a small scale and batch wise operation. Generally the construction principle is a pyrolysis furnace with an incineration chamber and no flue gas cleaning system. Consequently the specific emissions of these installations are relatively high.
Because of the poor emission characteristics, there is a tendency to close the small traditional installations and use more sophisticated larger (centralised) installations or burn the hospital waste in rotary kiln hazardous waste installations.

4.6.2 Measured emission data

Measurements in traditional installations in The Netherlands gave emission figures above 70 ng I-TEq/m^3, resulting in calculated specific emissions of 0.8 mg I-TEq/tonne for the large installations, 3 mg I-TEq/tonne for the medium sized installations and 5 mg I-TEq/tonne for the smallest installations. With one medium size and several small size traditional installations still in operation at the beginning of 1993, the total dioxin emission was calculated to be around 1 g I-TEq per year [Bremmer et al., 1994].

Fiedler et al., 1993 estimate a specific emission value of 18 ng I-TEq/m^3, corresponding to 108 µg/tonne.

Cains et al., 1993 report measured data of 5 different installations under various operating conditions, resulting in emissions via the flue gas between 2.5 and 700 ng I-TEq/ kg feed, with an average of 177 ng (or 106 ng if the highest figure, measured under poor combustion conditions, is left out).

4.6.3 National inventories

Table 4.6.1 Dioxin emissions of hospital waste incineration

Country	Process input [ktonne/a]	PCDD/F emission into the air		
		Concentration flue gases [ng I-TEq/-m^3]	Emission factor [µg I-TEq/-tonne of input]	Annual emission [g I-TE]
D	50	18	108	5.4
DK	16.8		800	14
F	175	15	160	28
GB	260		180	47
NL (1993)	0.7		0.6-500	1
S (1989)	30		60-200	2-6

4.7 Asphalt mixing plants

4.7.1 Process description

Asphalt consists of a mixture of gravel or granite chippings, sand, filler and bitumen. Filler may consist of pulverized limestone or a mixture of it with ESP ash of MSW incinerators or power stations, mineral stone powder and/or slaked lime. Old asphalt can re-used by heating it and mixing it with minerals and bitumen.

The components are heated and mixed in order to compose the asphalt. This process takes place in asphalt mixing plants, of which three types can be distinguished:
- the batchwise mixing installation, consisting of a direct-fired counterflow rotary drum heater, an intermediate storage and a mixer. Only 10-20% old asphalt can be processed.
- the continuous mixing installation, in which the mixing takes place in the direct-fired parallel flow rotary drum heater. With this system, a maximum of 50% asphalt can be processed by dosing it into the drum with a temperature of 300-400 °C.
- Batchwise mixing installation with parallel system for recycling.

Old asphalt is heated in a separate recycling drum parallel to the main drum in which virgin material is fed and in which the flue gases of the recycling drum are incinerated. The two flows are mixed with hot bitumen in a separate mixer. In principle, up to 100% old asphalt can be recycled with this system.

In approximately 80% of the asphalt mixing plants, the flue gases are cleaned with fabric filters. In the other installations, wet dust arresters are used. In the last case, the water is discharged via a sedimentation basin.

4.7.2 Measured emission data

Measurements at one German installation of 177 tonne/h, operating with 50% re-used asphalt have been performed [LIS, 1993]. The measured concentration, after the fabric filter, varied from 0.01 to 0.03 ng I-TEq/m^3 (2-6 ng/tonne).

In The Netherlands emissions were measured at a similar installation, fired with natural gas. An emission of 47 ng I-TEq/tonne was calculated.

4.7.3 National inventories

Approximately 7.4 million tonnes of asphalt were produced in The Netherlands in 1991 (VBW Asfalt, 1992).
In asphalt mixing plants, mainly natural gas is used as a fuel. Other fuels that are used include oil, light fuel oil, gas oil, heavy fuel oil, and occasionally spent oil. Six plants also have provisions for lignite-firing.

Table 4.7.1 Dioxin emissions of asphalt mixing installations

Country	Process input [ktonne/a]	PCDD/F emission into the air		
		Concentration flue gases [ng I-TEq/-m^3]	Emission factor [ng I-TEq/-tonne of input]	Annual emission [g I-TEq]
D				
DK				
F				
GB	33,000		47	1.5
NL	7,400	0.45	47	0.3
S				

4.8 Oil combustion

4.8.1 Process description

Various kinds of oil can be distinguished. Oils are not only used as fuel, but also for lubrication, cooling, indirect heating and hydraulics. The oil degrades and/or becomes contaminated in the last few applications so it must be replaced. The oil used is denoted as 'spent oil'. Part of this spent oil is used as a fuel. Particularly as a result of the pollutants that occur in the oil, dioxins can be formed in that use. For certain applications spent oil is cleaned before use, involving removal of solids (but not the chlorine containing components).

The oil which is produced to be used as a fuel (with low chlorine concentrations) will be denoted further in this chapter as 'fuel oil'.
Applications of fuel oil to be considered are the generation of heat/steam (stoves, boilers, drying processes) and the generation of power in diesel engines in shipping (other forms of traffic will be dealt with elsewhere).
In generating heat/steam, flue gas cleaning (dust arresters) are used only if the process that uses the generated heat/steam makes this necessary, as is the case for asphalt mixing plants, and the like.

Oil is also used extensively as fuel for marine engines. Light oil types (gas oil) are mainly applied in inland navigation, while heavy fuel oil is mainly used by sea-going vessels. These applications have no flue gas cleaning.

4.8.2 Measured emission data

Fuel oil

The dioxin concentrations of the flue gases of a low-speed two-stroke ship's diesel engine were shown to be below the detection limit (MAN, B&W, 1989?).

In the former Federal Republic of Germany, dioxin concentrations were determined in soot of coal-fired and oil-fired central heating boilers and stoves. Coal-fired units were found to contain at least five times as many dioxins in the soot as oil-fired ones (Thoma, 1988).

Hutzinger et al., 1992 present specific emission figures for home heating with oil of 0.024 ng I-TEq/m^3 and an annual consumption in Germany of 43 Mtonnes.

At two measurements conducted at a power station that was fired with heavy fuel oil (Hagenmaier and Beisling, 1989), no dioxins were shown (< 0.001 ng/m^3 for the individual congeners).
In the German dioxin survey [LIS, 1993], emission levels between 0.003 and 0.02 ng I-TEq/m^3 are reported.

Measured emissions of ships engines [Compaan et al., 1992, Danton and Reynolds, 1991a and 1991b) are shown in table 4.8.1. Based on these data an average emission factor of 0.4 microg I-TEq/tonne of fuel is taken for ocean going vessels in port and a factor of 1 microg I-TEq/tonne of fuel for inland navigation.

Table 4.8.1 Concentrations of organic chlorine in fuel, and dioxin concentration in the exhaust gases of marine engines

Type of ship	Fuel	Cl concentration in fuel [mg/kg]	PCDD/F concentration in flue gases [ng I-TEq/m^3][1)]
Ferry	heavy fuel oil	11	0.1 and 0.2
Container ship	gas oil	1.2	0.002 and 0.2
Rhine barge	gas oil	< 2	0.012 and 0.04

1) under operational conditions at 300 Kelvin (ferry 14.7% O_2, Rhine barge 13% O_2, container ship not known)

Spent oil

Table 4.8.2 shows results of measurements at 3 installations fired with spent oil.

Table 4.8.2 Total chlorine concentration of the fuel and dioxin emission of 3 installations

Burner	Fuel	Total chlorine concentration of fuel[1)] [mg/kg]	Emission factor [µg I-TEq/tonne of fuel]
atomiser	unprocessed spent oil	about 35	2
rotary cup	solvents and oil[2)]	about 340	4.8
rotary cup	processed spent oil	about 240	6.0

1) calculated from the chlorine concentration of the flue gases and the process parameters
2) is equated here with spent oil

On the basis of Table 4.8.2, a value of 4 µg I-TEq per tonne of oil is set as average emission factor for the combustion of spent oil on land.

4.8.3 National inventories

The data concerning the dioxin emissions in The Netherlands as a result of the combustion of oil have been summarized in Table 4.8.3.

Table 4.8.3 Data of dioxin emissions from oil combustion in The Netherlands (1991)

Emission source	Fuel	Consumption [ktonne/year]	Emission factor [µg I-TEq/tonne]	PCDD/F emission [g I-TEq/year]
installations on land	spent oil	24	4	0.1
seagoing vessels (in port)	heavy fuel oil[1)]	30.4	4	0.1
inland navigation	gas oil	531	1	0.5
installations on land:	fuel oil			
small-scale		560	0.5	0.3
large-scale		48	< 0.001[2)]	< 0.001
refineries		351,000	< 0.001[2)]	< 0.004
Total		1,193		1.0

1) if necessary, blended with spent oil
2) indicative

Table 4.8.4 Dioxin emissions of oil combustion

Country	Process input [ktonne/a]	PCDD/F emission into the air		
		Concentration flue gases [ng I-TEq/-m^3]	Emission factor [µg I-TEq/-tonne of input]	Annual emission [g I-TEq]
D			15-80	0.5-2.7
DK	35 large scale 40 small scale		0.13-0.17[1)]	0.01-0.02[1)]
F				
GB	40 large scale		2	0.08
	360 small scale		5	1.8
NL	1193		0.001-4	1.0
S				

1) Eadon-TEq

4.9 Combustion of coal and lignite

4.9.1 Process description

The largest application of combustion of coal is in power plants. Coal is also used, to a lesser extent, in industrial steam boilers, cement kilns and in some countries

also for (domestic) heating purposes. The most significant ways of combustion are pulverized-coal burning (power stations, cement kilns, steam boilers) and chain grate stoker combustion (steam boilers, grass drying plants). Other types used are the screw conveyor stoker, the fluidized bed furnace and the grate furnace. The small scale domestic installations apply a fixed grate.
Depending on its availability and costs, lignite will in principle be used for the same purposes and in the same way as coal.
In general it may be stated, that the control of the combustion process is very good for the large scale installations, specially the pulverised coal systems, and the fluidised bed systems, resulting in a relatively complete and clean combustion. Also the flue gas cleaning systems, of which specially the particulate control is important with respect to the reduction of dioxin emissions to the atmosphere, will usually be more efficient for the large scale installations.

4.9.2 Measured emission data

Table 4.9.1 Dioxin emissions of various British coal firing installations [CRE, 1994]

Type	Size	Operating mode, %MCR	PCDD/F ng I-TEq/Nm^3	PCDD/F ng I-TEq/kg
domestic open fire		N.A.		
- bituminous			0.75	5.7
- anthracite			0.08	2.1
- smokeless			0.25	4.7
domestic underfeed	17.5 kWth	100	0.08	1.5
underfeed	150	85	0.09	1.1
gravity feed	700	100	0.09	0.74
Recpr. grate cyclone	1000	100	0.05	0.54
underfeed	1.4 MWth	100	0.10	1.68
top feed grate, cyclone	4.6	100	0.014	0.20
tipping grate	5	80	0.008	0.15
travelling grate	5	100	0.034	0.57
			0.023	0.39
AFBC, multi cyclone	19		0.004	0.05
CFBC, bag filter	36	28	0.001	0.01
CFBC, ESP	43	100	0.007	0.07
pulverised Fuel-Cement kiln, ESP	90		0.004	0.06
pulverised fuel, ESP	380	100	0.031	0.25
pulverised fuel, ESP	500		0.005	0.06

Using data, derived from these measurements, the emissions from coal firing in GB are estimated to be as shown in the next table (coal consumption figures 1992).

Table 4.9.2 Dioxin emissions in the UK from various coal fired categories

Sector	Coal consumption k tonnes/year	Specific emission µg I-TEq/ tonne	PCDD/F g I-TEq/year
Domestic	5300	4	23
Industrial/commercial	8800	0.45	4
Power generation	77000	0.06	5
Total	91100		32

A different source [Sloss et al., 1993] gives somewhat deviating figures, namely 0.2 to 1.6 µg I-TEq/tonne for installations with a thermal rating above 3 MW.

In a German investigation of emissions of domestic heating installations [Bröker et al., 1994], the results shown in Table 4.9.3 are reported.

Table 4.9.3 Comparison of specific dioxin emissions of various fuels

Fuel	Spec. emission ng I-TEq/kg
natural gas	0.051 (/m^3)
light fuel oil	0.017 (/l)
anthracite	0.124
coke	0.522
lignite briquets	0.125
egg coal	0.356
wood	0.53-0.94
wood (open fire)	0.19-1.1

German measurements of power stations also show low specific emissions of dioxins into the air. The installations at which measurements have been taken generally have a flue gas desulphurization system and often a catalytic Denox system. Some of the measured data [LIS, 1993] are assembled in Table 4.9.4.

Because the levels measured for the different congeners are often quite close to the detection limit, the uncertainty of the data is relatively high.

Table 4.9.4 Dioxin emissions into the air of various large German coal and lignite firing installations

Size	Flue gas flow 1000 Nm^3/h	PCDD/F conc. pg I-TEq/m^3	PCDD/F µg I-TEq/tonne
150 MWth	200	3-4	0.03-0.04
775 MWth	986	<3	<0.03
523 MWe	1270	<2	<0.02
63 MWth	68	9	0.09
254 MWth	380	4	0.04
254 MWth	360	18	0.18
280 MWth, lignite	440	<2	<0.02

It may be concluded from the results presented in Table 4.9.4, that for the German coal fired powerplants average dioxin emissions are around 0.1 µg I-TEq/tonne. Measurements at powerplants co-firing up to 10% different other materials like waste oil, paper waste, sewage sludge, liquid waste and soot show results in the same order of magnitude.

Two measurements in The Netherlands showed specific emission data of 0.02 ng I-TEq/Nm^3 and 0.16 ng I-TEq/Nm^3 for resp a 518 MWe powerplant and a 15 MWth industrial plant (corresponding to resp. 0.35 and 1.6 µg I-TEq/tonne).

4.9.3 National inventories

Table 4.9.5 Dioxin emissions of coal and lignite combustion

Country	Process input [Mtonne/a]	Emission factor [µg I-TEq/-tonne of input]	Annual PCDD/F emission [g I-TEq]
D	coal 40	domestic 0.1-0.5	0.9-6.1[1]
	lignite 100	power 0.02-0.2	2.8-28
DK	11	[2]	-
F	17 (industry)	0.001	0.02
GB (CRE, 1994)	77 (power)	0.06	5
	8.8 (industry)	0.45	4
	5.3 (domestic)	4	23
NL	7.7 (power)	0.35	27
	0.55 (industry)	1.6	0.9
	0.05 (domestic)	1.6	0.1
S			1

[1] Bröker et al., 1994
[2] below detection limit of 0.001 ng/m^3 per isomer

4.10 Wood combustion

4.10.1 Process description

Wood combustion can be divided in domestic and industrial combustion. Domestic combustion, which can be subdivided in (open) fire places and stoves, is characterised by a small scale, hand fired operation and the absence of flue gas cleaning.
Industrial combustors above 100 kW are usually automatically controlled, these are mainly used for production of steam or hot water. In countries that do not have a large wood production industry, the size of the installations is mostly less than 5 MW. The wood fired in underfeed stokers, screw conveyor stokers or grate stoker systems, is mostly waste wood from industries that use wood in their products (timber, construction, furniture). The flue gas cleaning system, if present at all, is generally restricted to a cyclone for dust removal. In the Nordic countries larger installations do exist, firing woodchips, sometimes in fluidised bed systems.

4.10.2 Measured emission data

In an investigation in Denmark 4 different stoves (3.5-9.2 kW), with 3 types of clean wood have been tested at 2 operating conditions [Vikelsøe et al., 1993]. It was concluded that the emissions depended on the stove type, the mode of operation and also on the type of wood. Spruce emissions were more than twice the emissions of birch and beech. In 2 of the stoves optimal combustion conditions corresponded to significantly higher dioxin emissions. The average emission for all experiments with three of the stoves is around 5 ng/Nm^3, the average of all data of the 4th stove is around 35 ng/Nm^3. Based on these results and the quantity of the various fuels sold, the calculated annual emission of stoves in Denmark is 0.4 g Nordic TEQ. This is considerably lower than an earlier estimation based on different experiments, [Vikelsøe et al. 1991] which are now considered to have given less reliable results.

German measurements on commercial industrial installations and some test installations between 50 kW and 25 MW (over 50 measurements), fired with different fuels, ranging from untreated wood to chipboard with various Cl containing additives, show results in a wide range.
The highest value using untreated wood was observed at a 50 kW manually charged stove (0.99 ng I-TEq/m^3), the other results were between 0.007 and 0.27 ng I-TEq/m^3.
Typical data for firing of uncoated chipboard (after flue gas cleaning) were around 0.1 ng I-TEq/m^3, with some results as low as 0.02 and a maximum value of 0.9.
In case of PVC coated or $(NH_4)Cl$ or $(NH_4)SO_4$ hardened chipboard levels might raise to around 4 ng I-TEq/m^3. It is not quite clear if this is the direct effect of the increased Cl content only, because combustion quality was also poorer with these fuels (high CO).
Similar effects are also illustrated by the results of measurements at a test installation (flue gas flow 250 m^3/h) consisting of a pyrolyser and a cyclone burner as shown in Table 4.10.1.

Table 4.10.1 Effect of wood type and additives on emission of dioxins to the air

Fuel type	PCDD/F emission ng I-TEq/m^3	Cl content in fuel %	PCDD/F content in fuel
untreated wood	0.04 0.03	0.004 0.006	0.0005
PVC coated chipboard	0.04 0.32	0.30 0.31	0.002
PCP/Lindan treated wood	0.64 0.23	1.0 1.2	0.35
demolition wood	0.12 0.17	0.10 0.08	0.067 0.26

Experiments in a fluidised bed installation, equipped with a wet scrubber showed concentrations in the stack gas around 0.1 ng I-TEq/m^3 in case untreated wood or demolition wood was fired and 1-4 ng I-TEq/m^3 in case of firing of waste wood (old furniture, painted wood etc.)

Bröker et al., 1994, report emission ranges of 0.53 to 0.94 and 0.2 to 1.1 µg I-TEq/ tonne of wood for domestic stoves respectively open fires.

In the MOB programme in The Netherlands, three industrial installations, with capacities from 0.3 to 3.5 MW, burning wood with plastics and glue or wood with PUR-foam, have been investigated. All installations were equipped with cyclones. The dioxin concentration in the flue gas ranged from 0.4 to 1.0 ng I-TEq/Nm^3.
From measurements at a stove for domestic use, firing clean wood at three different loads (13,17 and 23 kW), emission factors between 1.0 and 3.3 µg/tonne of wood are reported. The highest levels were observed at full load, the lowest at intermediate load.

Bremmer et al., 1994, conclude that the range of emission factors of wood combustion is from 1 µg I-TEq/tonne for industrial firing of clean wood (with flue gas cleaning) up to an estimated 500 µg I-TEq/tonne for firing of PCP contaminated wood in domestic fire places.

4.10.3 National inventories

Table 4.10.2 Dioxin emissions of wood combustion

Country	Process input [ktonne/a]	Emission factor [µg I-TEq/-tonne of input]	Annual PCDD/F emission [g I-TEq]
D	4300 (domestic) industrial	0.2-1.1 0.02 - 4	1.6 - 4.3
DK			0.4[1]
F			
GB	200 industrial 900 domestic	10 - 20[2]	2 - 4
NL	1236	1 - 500	12
S			

1) N-TEq
2) Caines et al., 1994

4.11 Crematoria

4.11.1 Process description

A crematory furnace consists of a refractory chamber in which the mortal remains to be cremated are placed. In the so-called 'cold type' furnaces, the coffin is placed inside at a temperature of about 300 °C. In the 'hot types', the temperature is 800 °C or higher.
After placing the coffin inside the furnace, the temperature of the chamber of the 'cold' furnace is increased to 800-900 °C, using a burner, and maintained at that level. The gases flowing out of the chamber are incinerated in an afterburner at a temperature of about 850 °C. In the cold types, the process lasts for 2-2.5 hours, in the hot types 1.2-1.5 hours.

As the oxygen demand of the cremation process varies, the air supply in the furnace is regulated according to an adjustable pre-set time schedule. Control of the afterburners is often based on temperature, with a pre-set gas/air ratio. More modern systems control this air supply using an oxygen meter in the flue gases.

A distinction can be made into the following flue gas discharge systems:
1. Discharge into the atmosphere without cooling.
2. Cooling of the flue gases by mixing with ambient air to a temperature between 200-350 °C, before being emitted.
3. Additional cooling to about 150 °C in an indirect air cooler, and dust removal in a fabric filter.

4.11.2 Measured emission data

Jager et al., 1992 found a dioxin emission of 28 µg I-TEq/cremation.

Caines et al., 1994 report a measured emission range from 25 to 70 ng I-TEq/kg, corresponding to approx. 2-5 µg I-TEq/cremation.

From two measurements in the MOB programme in The Netherlands, an average emission of 4 µg I-TEq/cremation was concluded.

4.11.3 National inventories

Table 4.11.1 Dioxin emissions of crematoria

Country	Number of cremations/a	PCDD/F emission into the air		
		Concentration flue gases [ng I-TEq/-m^3] [1])	Emission factor [µg I-TEq/-cremation]	Annual emission [g I-TEq]
D			28	
DK				
F				
GB			2-5	
NL	60000		4	0.2
S				

4.12 Fires

4.12.1 Description

This chapter concerns dioxin emissions that can occur at fires of and in buildings, cars, forests, etc.
Fires can be described as uncontrolled combustion processes. The fuel and oxygen supply and the mixing are determined by the fire itself and its surroundings. At a fire, usually insufficient air is available near to the seat of fire to get proper combustion. At some distance from the seat of fire however, the combustion gases are mixed very quickly with an abundance of air, so they are cooled down rapidly and burn-out is poor. Because of these effects, emissions occur (including those of incompletely burnt components) that are high compared with those of controlled combustion. In addition to the mentioned 'poor' combustion, the presence of chlorine is also important for the forming of dioxins. Chlorine by nature already occurs in building materials, such as wood. Many buildings also contain PVC, a significant source of chlorine.

Apart from fires that are registered one way or another, like fires of buildings, ships, cars, containers, forests, chimneys, etc., quite a number of materials are burnt in so-called 'open fires', particularly in rural areas by private persons and (agrarian) companies. In The Netherlands there are an estimated three of these non-registered fires per town per day, on average. On an annual basis, this means about 75,000 non-registered fires for the whole of The Netherlands on top of the around 40,000 registered fires.

4.12.2 Literature data

Useful emission factors concerning the dioxin concentrations in the flue gases, combustion residues, and soil samples in the surroundings of fires, are not given in the literature and cannot be deduced from that data either. There are some examples of fires where dioxin measurements in flue gases and residues have been carried out.

After a fire in a carpet factory, during which a storage room with 200 tonnes of PVC and 500 tonnes of (PVC containing) carpeting burnt out completely, a large number of deposition measurements were conducted in the surroundings. On the basis of these deposition measurements, the dioxin emission as a result of the fire was estimated to be less than 3 mg I-TEq (Marklund et al., 1989).

Binder, 1994 describes experiences with some fires in which PVC has been involved. Emissions into the air have been registered in two of these cases. In a fire in a warehouse in Mülheim 340 t PVC and 150 t PE were involved. The established contamination of flue gas dust was 1.5 ng I-TEq/m^3. At a fire of a plastic storage in Lengerich (1500 t in total, of which 500 t PVC) the first measurements in the flue gases showed levels of 5 ng I-TEq/ m^3, later measurements were considerably lower. Soil samples taken in the area around fires, also confirmed that dioxin emissions with the flue gas had hardly increase the concentration of dioxins in the soil of the effected area.

4.12.3 Evaluation

There is a general lack of data from which the dioxin emissions occurring at fires can be calculated. From the data of Marklund (see section 13.4) an emission factor can be calculated; this factor is around 4 µg I-TEq/tonne of burnt material (a relatively high percentage of plastics/PVC was involved here). However, it cannot be stated in which way this factor can be used for other fires. In order to calculate/ estimate the dioxin emissions on the basis of such an emission factor, the quantities and type of material that are combusted must be known, which is usually not the case.

Reliable estimations of the dioxin emissions at fires can therefore not be given. Actually, from the available data concerning 'industrial' fires, like these described above, it appears that these are probably a dioxin source of relatively little importance.

4.13 Various high-temperature processes

4.13.1 General

In this category, a number of high-temperature processes of a different nature are collected, at which dioxin emissions can be expected on the basis of the process conditions (from the process and/or from the raw materials).

4.13.2 Process Description

Thermal soil cleaning

Soil contaminated with more or less volatile organic compounds can be cleaned in a thermal way. To this end, the soil is heated in a rotary kiln or a tubular kiln. The temperature at which the soil is treated depends on the nature of the components to be removed and is maximally 650 °C. The heating in the kiln can be either direct or indirect. In order to prevent premature ignition of the vapours being released, the O_2 concentration in the kiln is kept at a low level (via burner settings or nitrogen dosing).

The gas flow that leaves the rotary or tubular kiln contains both evaporated components and dust from the soil. This gas flow is dedusted at high temperature in a (multi)cyclone, after which the organic compounds present are destroyed in an afterburner before being released to the atmosphere (sometimes after scrubbing). Depending on the nature of the components, the temperature in the afterburner is controlled at 800 - 1200 °C.

Manufacture of insulating bricks and tiles

Insulating bricks and tiles derive their characteristics from the fact that specific combustible substances (i.e. carbon-containing slate and wood saw dust) are mixed through the clay. During the baking, the combustible constituents are combusted.

Ceramics are formed from the raw materials (clay, slate, fly ash from power stations, sawdust), and are first pre-dried by bringing them in direct contact with the hot flue gases of the kiln. Baking takes place in a tunnel kiln in three phases: pre-heating (at 400-600 °C), firing (about 1000 °C) and after-firing. After reduction of the temperature to around 180 °C the flue gas is passed through the drying zone and discharged into the atmosphere.

Drying of fly ash

Part of the fly ash that is produced in municipal solid waste incinerators is used in road building as a filler in asphalt. The fly ash is mixed here with substances such as marl, mining stone, etc. During the process, the fly ash is usually moistened to prevent dust. Before processing it is then dried again. The drying is done in two ways:

- in an air separator that is operated with flue gases of a lignite or natural gas fired installation. By mixing the flue gases with ambient air, these are cooled to 500-600 °C, before being brought into contact with the fly ash;
- in a direct-fired countercurrent rotary drier, with the flame of the burner being in the drum.

After the drying process, the flue gases are cleaned with fabric filters, and if required with a cyclone as pre-cleaning device.

Production of cement

Cement is produced by binding dried limestone with various additives, like: pyrite ash, fly ash of coal-fired power stations, sandy clay and filter ash from the ESP in the process. The obtained mixture is ground and then heated in a clinker kiln (a long rotary kiln) to a maximum temperature of 1450 °C. Next, the obtained material is cooled with ambient air. Coal, petroleum coke, lignite and heavy fuel oil are normal fuels in this process. But because of the high temperature and long residence time, that guarantee complete destruction of organic material, various secondary fuels are also used, like shredded tires, spent oil, RDF and distillation residues.
The flue gases of the clinker kiln pass the marl drier and an electrostatic precipitator before being emitted.

Manufacture of rockwool

During the manufacture of rockwool, volcanic rocks (basalt, diabase) and briquettes that consist of cement and recycled process waste are melted in a cupola kiln at a temperature of approximately 1500 °C. The melted stone is continuously drained from the bottom of the cupola kiln, and then spun to rockwool fibres. The melting temperature is reached by combusting coke in the cupola kiln. The combustion gases leave the top of the cupola kiln to an afterburner at a temperature of about 170 °C. Flue gases from the afterburner, are emitted into the atmosphere via two heat exchangers and a fabric filter.

Manufacture of glass

At the manufacture of glass, a mixture of sand and (dependent on the type of glass) lime, sodium carbonate, dolomite, clay or feldspar, while adding other oxides, are melted at high temperatures (1400-1550 °C) to a viscous, flowing mass. In addition to these raw materials, recycled glass is also applied as a raw material. Chloride occurs in the manufacturing process as a result of NaCl contamination of the sodium carbonate.

4.13.3 Measured emission data

In the Dutch MOB programme, emission measurements were conducted at the following processes:
- manufacture of insulating bricks (two installations);
- fly ash drying (two plants);
- cement manufacture;
- rockwool manufacture.

The results of these measurements, as well as several measurements at a soil cleaning installation are presented in Table 4.13.1. Because of the confidential nature of the data, the installations are presented anonymously.

Table 4.13.1 Results of measurements to high-temperature processes measured within MOB programme in The Netherlands

Installation no.	Flue gas flow [m^3/h][1)]	Flue gas temperature [°C]	PCDD/F [ng I-TEq/m^3][2)]	Cl^- [mg/m^3][2)]	CO [mg/m^3][2)]	Yearly emission of PCDD/F [g I-TEq/year]
A	179,700	138	0.44	1.5	238	0.95
B	65,700	231	2.5	0.9	13,200	0.4
C	19,700	174	0.77	<2.3	26	0.03
D	29,500	112	19.5	3.8	5,000	0.25
E	27,100	221	0.045	51	158	0.04[4)]
F	89,900	77	0.4	19[3)]	30	0.003
G	9000		0.02-0.08	2.7-12	12-83	0.005

1) referred to dry flue gases under standard conditions
2) referred to dry flue gases under standard conditions, converted to 11% O_2; the accuracy of the concentration at 11% O_2 is small at the high measured O_2 concentration
3) average of the individual values: 2, 3 and 51 mg/m^3
4) concerns dioxin emission of entire plant (other results concern one production line).

From the results of the measurements at an installation for *thermal soil cleaning* an emission factor of 0.07 µg I-TEq/tonne of treated soil was calculated for this type of process.

A large number of measurements has been carried out in a German survey [LIS, 1993] on cement- lime- and tile- kilns.
The 10 cement kilns in this survey, with capacities from 1100 to 3150 tonne/day, are fired with coal, mostly in combination with different fuel mixtures. Fuels included in these mixtures contained various portions of respectively spent oil (in one case contaminated with up to 1000 ppm PCB), lignite, landfill gas and up to 50% tires. All kilns were equipped with an ESP for dust removal.

With one exception (0.24 ng I-TEq/m^3), all measured dioxin concentrations in the clean flue gas were generally significantly lower than 0.1 ng I-TEq/m^3, with most of the 54 results < 0.035 ng I-TEq/m^3.
Also 4 measurements are reported concerning the concentration of dioxins in the cement clinker-product, with most data < 1 ng BGA-TEq/kg and a maximum value of 2.3 ng BGA-TEq/kg.

Reported data on two lime burning kilns both equipped with a fabric filter show no effect of the applied fuel (respectively fuel oil and spent oil). Concentrations measured in the clean flue gas vary from 0.008 to 0.046 ng I-TEq/m^3.

Also flue gases of 10 tile burning kilns, fired with natural gas or with fuel oil, and with different tile additives, have been measured. With exception of one result (out of 17), showing a concentration of 0.34 ng I-TEq/m^3, all other data are (far) below 0.1 ng I-TEq/m^3, mostly in the pg-range. On the other hand, sometimes additional measures like afterburners are required to get to the required level.

4.13.4 National inventories

About 350,000 tonnes of soil were cleaned in this way in The Netherlands in 1991 (Bremmer; 1994). The manufacture of insulating bricks takes place in three Dutch installations. Fly ash drying is done in two installations, while both cement and rockwool are manufactured in just one installation.
In The Netherlands, there are nine companies where glass, glass fibre or glass wool is being manufactured. The glass production in The Netherlands is approximately 980,000 tonnes per year (Loos, 1992).
On the basis of their use of chlorine containing components and the application of a 'high' temperature, the inventory also includes one company that manufactures siliconcarbide, and one rubber plant (compression at 400 °C).

The emissions of the various processes in The Netherlands mentioned in this chapter have been summarized in Table 4.13.3.

Table 4.13.2 Dioxin emissions at high-temperature processes in The Netherlands

Process	Emission factor [µg I-TEq/tonne]	PCDD/F emission [g I-TEq/year]
Thermal soil cleaning: 350,000 tonnes/year	0.07	0.03
Other processes:	not applicable	1.7
according to measurements:		
according to estimate:	not applicable	1
Total		2.7

Table 4.13.3 Dioxin emissions of ceramic and other high temperature processes

Country	Process input [ktonne/a]	PCDD/F emission into the air		
		Concentration flue gases [ng I-TEq/-m^3]	Emission factor [µg I-TEq/-tonne of input]	Annual emission [g I-TEq]
D		0.03-0.3		
DK				
F				
GB	25,400			
NL				2.7
S				2.7-4[1)]

[1)] Swedish EPA, 1994, preliminary

4.14 Dioxin emissions of traffic

4.14.1 General

Various methods have been applied to establish specific emissions of cars running on different fuels, with or without catalytic converter.
In the so-called tunnel experiments [Oehme et al., 1991], an average figure for the emission of the cars driving through a tunnel tube is calculated from the difference in concentration at air inlet and air outlet side. Monitoring the varying number of cars and the type (passenger or heavy duty), allow for an estimation of the specific emissions for both types of cars. At the time of the experiment, the percentage of unleaded fuel (in Norway) was 25-30% of the total fuel consumption. It is calculated that average passenger car emissions vary from 0.04 to 0.52 ng N-TEq/km and average heavy duty vehicle emissions vary from 0.72 to 9.5 ng N-TEq/km. The low values have been measured for the traffic on the declining lanes, the high values on the inclining lanes (3.5%).

A different procedure for the determination of emissions of cars is direct measurement at the exhaust, while the car is performing a load cycle on a dynamo meter [Hagenmaier et al., 1990; Schwind et al., 1991]. The results of the investigation of Schwind et al. are reported in BGA-TEq. To make these data comparable to the other data in this report, conversion data based on figures in the report of Hagenmaier et al. (giving both data), have been used. The measurements at representative loads give the following results (BGA data in parentheses):

	ng I-TEq/litre
leaded petrol:	0.53 (0.74)
unleaded petrol:	0.07 (0.09)
petrol, cat. conv.:	0.02 (0.02)
diesel:	0.06 (0.050

The large difference between the data for leaded and unleaded petrol are apparently mainly due to the scavengers (dichloroethane and dibromoethane) in the leaded fuel, corresponding to a Cl-content of 70 mg/kg resp. a Br-content of 76 mg/kg.
With the above data, the total emission of road-traffic in (Western)Germany in 1990 is estimated to be 13 g BGA-TEq/year (approx. 10 g I-TEq/year), of which around 75% is produced by cars using leaded petrol. Due to the ban of chlorinated scavengers and the increase of the number of cars with a catalytic convertor, this figure will drop considerably.

4.14.2 National inventories

Table 4.14.1 Dioxin emissions of traffic

Country	Process input [10^9 km/a]	Emission factor [ng I-TEq/litre of fuel]	Annual PCDD/F emission [g I-TEq]
D (1990)		0.02-0.53	10
DK	31		
F (1990)		0.02-1,0	16
GB	270		
NL	98	0.007-1.1	<6
S			5-15

4.15 Sintering processes

4.15.1 Process description

In sintering processes, a mixture of various substances is coalesced at high temperatures. The aim of a sintering process may be to obtain a marketable product (e.g. artificial gravel), or to produce a material of such a size and strength that it can be used as a raw material in certain production processes. The basic material may consist of ores, admixtures, and/or waste substances, usually mixed with a solid fuel.

Sintering processes are used in various industries. It is used on a very large scale in the preparation of the feedstock for the blast furnaces for the production of iron (from a mixture of iron ore, coke and admixtures).
The mixed material is transported on a grate, where in the first stage, the top layer is ignited. By drawing air through the layer, the combustion is sustained and the combustion front travels slowly down through the layer. Considered as a combustion process, control possibilities are limited to the airflow and indirectly to the composition of the mixture.

Cleaning of the flue gases generated during the process is done in different ways, depending mainly on the (particulate) emission limits. Dry systems (cyclones plus ESP or bagfilters) or wet scrubber systems can be used.

In The Netherlands four large-scale sintering processes are known.

- The production of artificial gravel from fly ash of power stations and pulverized coal. In this production, a mixture of fly ash and pulverized coal is granulated, with water as binding agent. The granules are sintered in a sintering machine that is fired on spent oil, at a temperature of maximally 1100 °C. The flue gases are cleaned by a bag filter.

- The sintering of iron ore, coke and admixtures, including waste substances, in a sintering machine. The mixture is ignited with coke oven gas. The sintering temperature is 1000 - 1200 °C. The flue gases are cleaned with cyclones.

- The sintering of iron ore with bentonite and coke. The iron ore is ground and mixed with the other substances. The mixture is processed into granules using water. These granules are heated in a sintering machine, mostly with coke oven gas, to about 1100 °C. The flue gases are cleaned in wet scrubbers.

- For phosphate production, phosphate ore, clay and return material are granulated and sintered in a sintering machine at 1000 - 1200 °C. The fuel used is phosphor oven gas. The flue gases are washed twice with water (to remove fluoride, dust and sulphur dioxide), after which the flue gases are emitted.

4.15.2 Measured emission data

In a German iron ore sintering installation, 1.9 ng I-TEq/m^3 was measured in the cleaned flue gas after the ESP (flue gas flow 1 Mm^3/h) [LIS, 1993).

According to Lahl, 1993, in Western Europe 40 (iron ore) sintering plants are in operation, with a total flue gas flow of 25.4 million m^3/hour (including countries are A, B, SF, F and D). He assumes a PCDD/F concentration in the clean flue gas of 3-10 ng I-TEq/Nm^3, resulting in total emissions of more than 1 kg/year from these plants.

Bröker et al., 1993 reports first results from an investigation at 76 industrial installations in North Rhine Westfalia. Results from installations with an emission level above 1 ng I-TEq/m^3 are shown in Table 4.15.1.

Table 4.15.1 Emissions to the atmosphere of some industrial installations

Installation	PCDD/F emission	
	ng I-TEq/m^3	mg I-TEq/hour
hot briquetting of recycling material	70	3.7
sintering of recycling material	47	13
sintering iron ore	43	29
sintering iron ore	12	5.8
secondary Sn-smelter	5.9	0.09
sintering iron ore	1.9	2.0
workhall ventilation sintering inst.	0.62	0.27
workhall ventilation sintering inst.	0.01	0.002

Apart from the height of the emission level of the above installations, this table also shows, that emissions from ventilation systems related to these processes may be significant.

Emission levels measured in the MOB programme in The Netherlands show approximately the same level as presented in Table 4.15.1. In the flue gas of two iron ore sintering installations 6.8 resp 4.5 ng I-TEq/Nm^3 was measured. In the flue gas of a fly ash sintering installation, fired with spent oil and equipped with a fabric filter, 0.12 ng I-TEq/Nm^3 was observed.

In the Swedish dioxin survey, the concentration measured in the flue gas of an iron ore sinter plant was 0.75 ng N-TEq/m^3 (not corrected to 11% O_2).

4.15.3 National inventories

Table 4.15.2 Dioxin emissions of sintering processes

Country	Process input [tonne/a]	PCDD/F emission into the air		
		Concentration flue gases [ng I-TEq/-m^3]	Off gas flow [Mm^3/h]	Annual emission [g I-TEq]
D		3-10	10.2	250-800
DK	0			0
F			7.5	
GB	13.5[1)]		5.9	
NL		6.5	0.35	26
S				[2)]

1) steel industry only
2) incorporated in metal industry

4.16 Metal industry

4.16.1 General

This chapter discusses the dioxin emissions of the following sectors of the metal industry:
- the base metal industry;
- the secondary iron and steel industry;
- the non-ferrous metal industry.

4.16.2 Process description base metal industry

Coke production
Coke is produced by de-gassing coal at high temperature in *'coke ovens'*. Coke ovens consist of a large number of *'rooms'* built side by side. The ovens are indirectly heated to about 1000 °C with gas that is released during the process.
Emissions at the production of coke particularly occur when the rooms are being charged and emptied and the coke is being quenched. The vapours that are being released during charging are usually discharged via an afterburner and a venturi scrubber or a fabric filter. Vapours escaping during discharging also pass a wet scrubber or fabric filter. The gases and vapours released during quenching of the coke from 1000 °C to ambient temperature, using a large amount of water, are emitted without cleaning.

Blast furnaces
In a blast furnace, pig iron is produced from iron ore, simultaneously generating blast furnace gas. The furnace is filled with a mixture of sinters or pellets, slag, coke and admixtures. Hot air (generated in the *'hot blast stoves'*), that are fired with blast furnace gas, enriched with coke oven gas) is fed at the bottom of the blast furnace. The coke is combusted, the iron oxides in the iron ore are reduced, generating pig iron and a molten slag. Pig iron and slag are then tapped. The gases drawn off at the runout are cleaned in a bag filter. The collected dust is re-used in the sintering plant. The hot slag is quenched with water.

The blast furnace gas is cleaned in order to make it suitable as a fuelgas. The dust collected in the first dry cleaning stage is re-used in the sintering process, and so is the coarse fraction of the sludge that is obtained in the second stage wet cleaning. The fine fraction of this sludge (that contains most of the zinc and lead) is stored. This cleaned blast furnace gas may be enriched with coke oven gas.

Oxygen steel process
In the oxygen steel process, the carbon content of the pig iron is decreased and pollutants (silicon, manganese, phosphorus and sulphur) are removed. These substances are oxidized by blowing oxygen into the liquid iron bath. Dust in the released gases is removed in a (wet) pre-separator, followed by additional cleaning with a venturi scrubber.

In addition to this primary dust formation, secondary dust is generated during the charging and runout of pig iron and steel, respectively. To capture this dust, the converter is connected to a second exhaust system with a bag filter. All solids captured in the cleaning systems are re-used in the sintering plant.

4.16.3 Measured emission data base metal industry.

Within the Dutch MOB programme, measurements were conducted at one coke plant, with a capacity of 670 ktonnes per year.
In the waste water of the scrubber of the charging car and the scrubber of the ejection machine, around 80 ng I-TEq/m^3 was measured, from which an annual emission into the air from these units, of 0.002 µg I-TEq/tonne of coal was calculated.
In flue gases of the quenching tower 0.23 µg I-TEq/tonne of coal was measured, corresponding to an annual emission into the air of 0.2 g I-TEq.
On the basis of confidential measurement results, it is estimated that the annual emission related to the primary iron and steel industry, apart from coke production (and sintering) in The Netherlands is in the order of 0.5 g I-TEq.

In Germany, some measurements were carried out at hot blast stoves of a blast furnace and at the cleaned ventilation air from the tapping area from the same furnaces [LIS, 1993]. For a 600 tonne/day installation a total of around 90 ng I-TEq/tonne was measured, for a 9000 tonne/day installation this was around 30 ng I-TEq/tonne.

4.16.4 Process description secondary iron and steel industry

In this branch of industry, mainly iron and steel scrap is used as feed material. This scrap is melted in special furnaces. The three most important types of melting furnaces are: the cupola furnace, the electric furnace and the rotary furnace.

Cupola furnace
The cupola furnace is a continuously operating shaft kiln melting unit, charged via an opening in the side wall. In addition to the emissions of dust (coming from coke, feed material and refractory lining), there are also gaseous emissions. These mainly consist of CO and SO_2, and, for a small part, of pyrolysis products that come from the feed material. The hot gases from cupola furnaces are usually cleaned in a dry scrubber especially designed for this purpose sometimes after being incinerated first. The hot gases must first be cooled to this end, using heat exchangers.

Electric furnace
The electric furnace is a discontinuously operating melting unit. Usually, an indirect arc is used in the smaller furnaces, while a direct arc is used in the larger ones. The majority of substances are released during the charging stage of the furnace. When using clean sheet steel, only some dust and several gaseous compounds (usually CO) will be released. For contaminated scrap, the emission will be larger. In addition to arc-furnaces, 'induction kilns' are also used.

Rotary kiln
The rotary kiln is also a discontinuously operating melting unit. The rotating drum and its charge are heated by an oil burner (low-sulphur oil). A fabric filter is used for flue gas cleaning.

4.16.5 Measured emission data secondary iron and steel industry

Within the Dutch MOB programme, emission measurements were conducted at an electric direct arc-furnace for production of high-grade steel from scrap. The dioxin content in the ventilation air after the fabric filter was 0.04 ng I-TEq/m^3.
Including dioxins emitted with the dust, escaping through the roof caps, the total emission into the air of this company, processing around 230 ktonnes year, is approximately 1 g I-TEq/year.

At an iron foundry, no dioxins could be shown in the ventilation air (no cleaning; dioxin concentration < 0.09 ng I-TEq/m^3; flow rate of ventilation air not known; Rodenburg et al., 1991). In this foundry, scrap iron was melted in induction furnaces at a temperature of 1500 °C (scrap iron, clean engine blocks, brake drums and the like, however no chips).

In the German survey [LIS, 1993], measurements at various different installations with different operating conditions are reported.
In the flue gas of an oxygen converter (600,000 Nm^3/h), equipped with a fabric filter, 0.018 to 0.089 ng I-TEq/m^3 has been observed. Apparently it had no effect if the scrap being treated in the converter contained plastics.
A converter charged with pig iron (flue gas flow 570,000 Nm^3/h) showed concentrations between 0.004 and 0.033 ng I-TEq/m^3.
Results of a number of measurements at 4 different electric arc furnaces, all equipped with a fabric filter, are assembled in Table 4.16.1.

Table 4.16.1 Emission data of 4 electric arc furnaces

Input	Capacity	PCDD/F conc. ng I-TEq/m^3	Flue gas flow 1000 Nm^3/h	PCDD/F ng I-TEq/ tonne
new steel scrap+ MSW scrap		3.6 (in raw gas)	220	
+shredder scrap		0.099 (in raw gas)		
+cutting scrap		0.19 (in raw gas)		
60% clean+40% contaminated scrap	500 kt/a	0.7-2.3 (no pre-heating) 5.6;9.2 (pre-heating)	68	570;1900 4600;7500
cuttings, sheet, cast iron, demolition scrap		0.013;2.9;0.2 0.013 (after optimization	76;45 650	
scrap, used metal		0.93 0.5 (no pre-heating) 1.04 (pre-heating)	940,000	

A cupola furnace with a capacity of 38/tonne/h, showed a concentration in the flue gas (O_2 content 12%) of 0.048 ng I-TEq/m^3 at processing of steelscrap and cast iron (equivalent to 75 ng/tonne), while a second unit with the same capacity only emitted between 1 and 6 ng I-TEq/tonne, with a much lower O_2 concentration of 2%.

At a rotating heating kiln, operated at 250 °C, for drying of oil covered metal chips, equipped with an afterburner, no dioxin emissions were detected.

Measurements at two shredder installations, where the largest part of the input consisted of wrecked cars, resulted in concentration figures between 0.1 and 0.4 ng I-TEq/m^3 of off gas (after cleaning), corresponding to 0.1 to 0.6 µg/tonne.

Tysklind et al., 1989 report the following emission concentrations in the cleaned flue gas of electric arc furnaces, depending of the type of metal charged (µg I-TEq/tonne):

scrap metal with cutting oils	1.0
scrap metal with PVC	20
scrap metal without chlorine	0.7
scrap metal with calcium chloride	0.2

In the Swedish dioxin survey, at an induction oven for the casting of iron, 0.02 ng N-TEq/m^3 was measured.

French estimates of emissions are based on foreign measurements, limited to the secondary steel industry. Reference is made to reported data from Antonson et al., 1989 (7-9 µg E-TEq/tonne), Tysklind et al., 1989 (see above) and Öberg et al., 1989 (0.2-9 µg E-TEq/tonne). A value of 2 µg I-TEq/tonne is proposed as an average.

4.16.6 Process description non ferrous metal industry

In the production of non-ferrous metals, besides virgin raw materials, more and more recycled secondary sources are used, like scrap from electronic and electric appliances (copper) and batteries (lead).
Regarding dioxin emissions, particularly copper, lead and magnesium production are relevant, because of the production rate and the importance of the emission levels.

Copper

The production of copper from virgin raw material takes place in various stages. In the first stage the ore is enriched to around 60% in a melting process. In the next two stages, this is increased to approximately 95% in a converter and subsequently to 99% in an anode-furnace. Finally, further refinery takes place by electrolysis.

Lead

The first stage in the production of lead is desulphurisation in a sinter process, followed by reduction in shaft kilns. In the so-called QSL process, these two steps can be combined in one reactor, reducing emissions. This stage is followed by a refinery process, in which various kilns may be used, to remove the elements present in the crude material, like antimon, arsenic, copper, zinc, tin and precious metals.

Magnesium

One step in the production of magnesium from ore is the chlorination of MgO to waterfree $MgCl_2$, with coke as a reducing agent at a temperature of 700-800 °C. In these conditions dioxins will be generated.

Aluminum

Normally it is not expected that dioxins will be formed in the production of primary aluminum [Bremmer et al., 1991]. Only if waste materials that might contain chlorine are co-processed, dioxin formation would be possible.

4.16.7 Measured emission data non ferrous metal industry

Copper and lead

Measurements of many German installations [LIS, 1993], show results in a wide range, from some pg to 10 ng I-TEq/m^3 of flue gas. This can be explained by the large variation in the used raw materials (mostly including secondary materials), and the variation in the processes, all having different specific flue gas flows. For the various installations taking part in the processing, 30 ng to 500 µg I-TEq/tonne can be calculated. Because of this wide range it is not possible to give representative specific emission data for the processing of copper.
The same holds for the production of lead, where the reported data are less detailed, making it even more difficult to calculate specific emission data. For the processing

of lead from batteries and scrap, in an installation equipped with a fabric filter, the measured emission with the flue gas is 128 ng I-TEq/tonne (0.022 ng I-TEq/m^3). Within the German industry, involved in processing of non ferrous metals, ways to reduce dioxin emissions are being investigated.

4.16.8 Process description secondary non-ferrous metal industry

In the secondary non ferrous metal industry the raw material, largely recycled scrap, is melted, refined and sometimes processed to an end product, e.g. by casting.
The following types of furnaces are mainly used in the secondary non-ferrous industry: the rotary kiln, the crucible furnace, the reverberatory furnace, and the multi-chamber furnace.

Rotary kiln

The rotary kiln is usually operated discontinuously. Often, polluted aluminium is melted in it, under a covering of molten salt. The fuel may be either natural gas or oil.

Crucible furnace

The crucible furnace consists of a crucible of refractory material in which the metal is melted by direct heating with a flame, or by an electric induction coil. This type of furnace is used in the recycling industry to remelt thin-walled, clean types of scrap.

Reverberatory furnace

The reverberatory furnace is basically a chamber-like room into which the scrap is fed and heated both directly and by radiation by a flame. The fuel can be both oil and natural gas. This type of furnace mostly occurs in the industry and is used for melting a large variety of relatively clean types of scrap.

Multi-chamber furnace

This type of furnace consists of two rooms of which one is heated like the reverberatory furnace, while the scrap in the other room is heated by recirculating the hot molten metal from the heated room through it. This type of furnace is mostly used for melting moderately polluted types of scrap.

The flue gases of the aluminum melting furnaces may particularly contain gaseous anorganic chlorine and fluorine substances, the off gases from the converter also gaseous chlorine. Additionally organic chlorine substances may be present from paint, oil or grease on the surface of the metal being processed.

In the mentioned furnaces, usually a fabric filter and a lime injection system, is installed for flue gas cleaning. In addition to lime, activated carbon is sometimes injected.

4.16.9 Measured emission data secondary non ferrous metal industry

From confidential reports concerning emission measurements at a Dutch aluminum smelter, two emission factors were calculated for melting 'strongly polluted' aluminium scrap [Bremmer et al., 1994). In this plant, emission measurements were conducted before and after a modification to the flue gas cleaning (in addition to lime, activated carbon is now also injected before the fabric filter). The dioxin concentrations measured in the flue gases, as well as the calculated emission factors are shown in Table 4.16.2. This table also includes emission data (from a confidential report) of a plant that produces lead from scrap. From this data, a yearly emission of 0.1 g I-TEq was calculated for this plant.

Table 4.16.2 Dioxin emissions of secondary aluminum and lead industry in The Netherlands

Type of scrap	Type of flue gas cleaning	PCDD/F emission into the air	
		Concentration flue gases [ng I-TEq/-m^3][1)]	Emission factor [µg I-TEq/-tonne of scrap]
'strongly polluted' aluminium	fabric filter with lime injection	2.9	35
	fabric filter with lime and activated coal injection	0.13	1.7
lead	fabric filter with lime injection	1.3	5

1) referred to dry flue gases under standard conditions

In Germany many measurements have been carried out at various aluminum melting furnaces [LIS, 1993]. As far as the reported data allow the calculation of specific emission data, these have been assembled in Table 4.16.3. All installations in this table are equipped with lime injection and a fabric filter.

Table 4.16.3 Table Emission data to the air of German aluminum melting furnaces

Installation type	Capacity tonne/h	Input material	PCDD/F ng I-TEq/m^3	Specific emission µg I-TEq/tonne
rotary kiln + convertor	2 x 2.5	Al scrap	0.65-1.99	5.2-16
rotary kiln	7.5	Al scrap, recycling mat.	0.86;1.22	15;22
rotary kiln+ convertor	1.25	shredder scrap, castings, chips, sheet	0.19-0.27	6.5-10
rotary kiln + convertor	3.8	Al scrap	3.6-10.7	42-130
rotary kiln	6	Al chips	7.4;9.5;9.5	94-120
2 rotary kilns+ chips drier	6+2.5	Al cont. scrap, Al chips	3.3;1.6	9.5;5
reverberatory furnace	14.3	Al scrap + molten Al	0.13;0.68	0.6-3
reverberatory furnace, optimized[1)]	14.3	Al scrap + molten Al	0.016;0.007	0.03- 0.07
multichamber furnace	2.8	Al scrap	0.19;0.19	2.8
melting and casting furnace	2	Al scrap	0.06-0.09	0.15-0.22
induction furnace	20	Al scrap Cl_2-Ar gas treatment	0.008	0.014
induction furnace	0.8	Al scrap (cuttings,chips)	0.18;0.29	4.6-6.9
various types + convertors	130	Al scrap	2.9	2.3
various types	3	Al process recycling	0.029	0.27

1) Optimization: improved input preparation, removal of contaminations

The concentration of dioxins in filterdust of the same installations is usually between 1 and 10 µg I-TEq/kg, in some cases higher.

Measurements at installations used for drying of Al chips, contaminated with cutting oils and alike, showed a significant effect of the chlorine content of the contaminants on PCDD/F emissions, ranging from 1.3 to 25 µg I-TEq/tonne.

Copper is mostly melted in shaft kilns, rotary kilns or induction furnaces. The use of strongly contaminated scrap is not possible, because of the limited possibilities for cleaning of the molten product.

In the German dioxin programme, measurements have been carried out at various installations [LIS, 1993]. Emissions in the flue gas range between 0.023 and 1.77 ng I-TEq/m^3. From some reported data specific emissions, ranging from 0.03 to 0.7 µg I-TEq/tonne can be calculated

Zinc
Measurements at hot dip galvanising installations [LIS, 1993] show concentrations in the off gas after the fabric filter, in the order of magnitude of 0.01 to 0.1 ng I-TEq/m^3. The potential for dioxin formation is confirmed by the concentration in the filterdust, which is in the range of 2 to 10 µg/kg.

4.16.10 National inventories

Of more than 30 Dutch iron foundries and smelters consulted, only a few actually processed metal cutting scrap, with attached metal working liquids. This is in agreement with the fact that the majority of the metal cutting scrap is exported (Scheepens, 1988). It is not known how many companies exclusively use clean (factory-new) scrap and/or pig iron.

Table 4.16.4 Data of dioxin emissions at the secondary non-ferrous industry in The Netherlands

Type of metal	Processed scrap [tonne/year]	Type of flue gas cleaning	Emission factor [µg I-TEq/tonne of scrap]	PCDD/F emission [g I-TEq/year]
Smelters				
brass (2 companies) slightly polluted	48,000	fabric filter	5	0.24
copper/bronze (1 company)	1,000	lime injection/ fabric filter	35	0.04
lead (1 company)	20,000	lime injection/ fabric filter	5	0.1
aluminium (2 companies) strongly polluted	46,000	injection of lime and activated carbon fabric filter	1.7	0.08
aluminium (3 companies) strongly polluted	8,000	lime injection/ fabric filter or afterburner	35	0.28
aluminium (1 company) slightly polluted	35,000	lime injection/ fabric filter	5	0.18
aluminium (2 companies) slightly polluted	27,000	none	10	0.27
Various foundries (about 45 companies)	18,500[1)]	unknown	-	-
Total				1.2

1) concerns produced product

For most countries, data to calculate the national emissions from this category are incomplete and show a considerable variation. Therefore national inventories can only be calculated to a limited extent.

Table 4.16.5 Dioxin emissions of the metallurgical industry into the air

Country	Process input [ktonne/a]	PCDD/F emission into the air		
		Concentration flue gases [ng I-TEq/-m^3][1)]	Emission factor [µg I-TEq/-tonne of input]	Annual emission [g I-TEq]
D[1)]	steel	0.1-1.5		1.3-19
	non ferrous	3-30		38-380
DK[2)]	sec.steel 700	2.7		12
F	sec steel 5000		2	10
GB	coke 6400			
	sec. steel 41200			
	non ferr. 1000			
NL	base metal 4090			1.4
	sec. steel 360			1.4
	sec. non ferr. 203			1.2
S[3)]	steel			1.6-4
	sec. steel			0.4-15[4)]
	non ferrous			0.13-0.27[4)]
	sec. non ferr.			4.3

1) Hutzinger et al., 1993
2) data in N-TEq
3) De Wit, 1994, data in N-TEq
4) preliminary data

4.17 Chemical production processes

4.17.1 General

In production processes in the chemical industry, the following processes are of importance with respect to the forming of dioxins, arranged according to their significance as a possible source (NATO-CCMS, 1988; Hutzinger et al., 1989).

- Application of chlorobenzenes, and production and application of chlorophenol and chlorobenzene derivatives.
- Production of aliphatic chlorine compounds.
- Various chemical processes, e.g. the regeneration of catalyst residue.

Organic chlorine compounds can be applied as end products, but are often used as intermediate products for chemical processes or as solvents in these processes. If high temperatures (specifically > 150 °C) occur in these processes, dioxins may be formed. Part of these dioxins remain in the end products, but the larger part will end up in solid or liquid waste and/or sludge. Only a small part of the formed dioxins is emitted into the air or to water during these processes. The incineration of process waste and sludge from purification plants is discussed in chapter 4.3 and 4.4.

The quantity of dioxins remaining behind in the end products is usually small and will not be a significant source (Bremmer, 1991). The dioxin emissions as a result of the **use** of pesticides (specifically wood preservatives) will be dealt with in Chapter 4.18.

4.17.2 Process Description

Chlorophenols, chlorobenzenes and derivatives
These compounds are used in the manufacturing process of pesticides, medicine and in the production of chemical specialities, which in turn are used again as intermediate products for medicine or pesticides.

Temperatures in the production processes are mostly higher than room temperature, meaning that dioxins can be formed via condensation reactions. Dioxins are especially formed at temperatures above 150 °C in an alkaline environment. The generation of dioxins can be minimized by selecting optimum process conditions and proper process control.

The end products are purified by processes such as filtration, scrubbing, or distillation. Discharged wash water is purified via a purification installation. As far as known, the solid and liquid residues of these purification processes are always incinerated as hazardous waste. The vent gases and the ventilation gases are mostly cleaned in scrubbers or afterburners.

Sometimes chlorobenzenes are used as a solvent in a chemical process. The solvent does not always take part in the chemical process, and must ultimately be removed again, e.g. by distillation. During the process and the purification phase, dioxins may be formed.

Chlorinated aliphates
Chlorinated aliphates are applied as end products, but particularly as intermediate products for other chlorinated hydrocarbons. Initial substances for these chlorination processes are mostly unsaturated hydrocarbons or alcohols. Formation of chloroaromatics from the unsaturated compounds and, consequently, formation of dioxins is possible under the usual process conditions.

Solid and liquid wastes that are released at the manufacturing and purification processes are incinerated as hazardous wastes The vent gases and the ventilation gases are mostly purified in scrubbers and/or an afterburner, specifically in large-scale processes.

Various chemical processes
In reforming processes, dioxins can be released during the regeneration of the spent catalyst. In a reforming process, at high temperature and pressure, ordinary petrol is converted to petrol with a high octane number. Regeneration of the catalyst takes place both continuously and discontinuously. At the regeneration step, the carbon deposit on the catalyst is burnt off (temperature about 600 °C), after which the chlorine concentration of the catalyst is restored to the correct level using a chlorinated hydrocarbon (temperature about 500 °C). The flue gases from this regeneration step are usually cleaned with a gas scrubber.

Activated carbon is applied for cleaning waste water, drinking water and flue gases. In regeneration (usually 'on site'), the activated carbon is heated (with steam or hot gases), so that the adsorbed substances are desorbed. In reactivation, the carbon is heated to 800-1000 °C, restoring the pore structure required for the adsorption process. The gases released at the reactivation are incinerated in an afterburner at temperatures between 800 and 1000 °C, depending mainly on the presence of chlorine compounds.

4.17.3 Measured emission data

Chlorophenols, chlorobenzenes and derivatives
Within the Dutch MOB programme, dioxin measurements were conducted at a plant for pesticides and a plant for crop protection chemicals. The measurements were deliberately conducted at these companies, because the largest dioxin emission could be expected in these chemical processes, in view of the size of these companies, the type of raw materials, and the reaction conditions. Table 4.17.1 states the results of these measurements, and also those carried out at a plant for the regeneration of reforming-catalyst.

Table 4.17.1 Data and measurement results of chemical production processes in The Netherlands

Parameter		Installations		
		A	B	C
type of process		plant for pesticides	plant for crop protection chemicals	regeneration of catalyst
type of flue gas		vent gases	vent and ventilation gases	vent gases
flue gas cleaning		gas scrubber	gas scrubber	gas scrubber
working hours per year		7,200	8,760	8,000
flue gas flow	[m^3/h]	260	6,500	260
flue gas temperature	[°C]	22	23	46
O_2	[vol% dry]	1	20.7	1.0
yearly PCDD/F emission	[ng I-TEq/m^3]	7.2	0.02 - 0.05	8
	[g I-TEq/year]	0.013	0.001 - 0.003	0.017

Measurements carried out at various installations in the German dioxin survey have been collected in Table 4.17.2. Most of these results are measured in the flue gas of after burners used to clean the off gases of chemical installations. For that reason these might also have been categorised as hazardous waste incinerators.

Table 4.17.2 Results of dioxin emission measurements in the German chemical industry

Installation	Input	Capacity	PCDD/F concentration ng I-TEq/m^3	Flue gas flow Nm^3/h
afterburner	approx. 90% HCl	60-80 m^3/h	3.6	510
afterburner	chlorinated aliphates with HCl and toluene	HCL 60 m^3/h 40-70 g toluene/h	0.013-0.042	120
afterburner	organochlor compounds	13000 m^3/h	0.024	19600
rotating kiln	PER dist.		0.3-1.24	3120
afterburner	vinyl chloride prod.off gas		0.4	17300
incinerator	CHC off gases	450 kg/h HCl	3.6	2660
afterburner	offgas 1.2-dichlorethane prod.		0.05 (2378-TCDD)	1300
Cl-parafin reactor	parafin+Cl_2		1.7	145
Cl-parafin reactor	parafin+Cl_2	600t CP/month		

4.17.4 National inventories

Table 4.17.3 summarizes the emissions into the air in the chemical production processes in The Netherlands. The waste substances and sludges being released in these processes are incinerated.

Table 4.17.3 Dioxin emissions in chemical production processes in The Netherlands[1])

Type of process	Emissions into air [g I-TEq/year]
Chlorophenols, chlorobenzenes and derivatives	0.2
Chlorinated aliphates	0.2
Various chemical processes	0.1
Total	0.5

Apart from annual production figures of 286.5 Mtonnes of halogenated compounds in GB (1992), no data are available to calculate inventories of the other countries.

4.18 Use of pesticides, specifically wood preservatives

4.18.1 General

Small quantities of dioxins can be formed at the production of chlorine compounds that are applied *inter alia* as preservative or pesticide. Part of these dioxins remain behind in the products which then become secondary sources. Despite a ban on the application of some of these compounds, emissions can still take place through evaporation or leaching of the pesticides used in the past. The most important fields of application are (or were) the use of:

- agricultural pesticides and agents for veterinary use;

As a consequence of the application of these products, most of the dioxins will be spread over agricultural land

- pentachlorophenol as a preservative in Thomas slag;
  (limited use at present)

- pentachlorophenyllaurate as a fungicide in the textile industry;
  (banned in some countries)

Waste of products treated with pentachlorophenyllaurate will be partly incinerated, during which dioxins are largely decomposed. Another part will be dumped, because of the poor solubility in water, leaching is deemed improbable.

- pentachlorophenol as a wood preservative, particularly in the past.

Dissolved in an organic solvent, pentachlorophenol (PCP) is applied as a wood preservative. A water-soluble salt can also be made from PCP (Na-PCP). In this form, it is used as a fungicide. Because this application turns out to be a relatively important secondary source it will be treated in more detail in the next chapter.

4.18.2 Emissions by the use of PCP and Na-PCP

Although the use of PCP and salts of PCP for wood preservation and fungistasis has been banned in some countries since 1989 (e.g. in The Netherlands and Germany), it is still important as a secondary source.
PCP has been used since the fifties, particularly in exterior wall carpentry.
Na-PCP has been applied as a fungicide in recently sawn wood and also as a disinfectant of wooden floors and side shelves in the cultivation of mushrooms.

In Europe PCP is no longer produced, but in a number of countries, the use of PCP or Na-PCP has not yet been banned. Wood that is imported can therefore still have been treated with PCP or Na-PCP (company-confined information). The import of wood treated with PCP has considerably decreased in the last few years (mainly used in the packaging industry). In The Netherlands Mensink et al., 1988 showed the

presence of PCP in 55% and 38% of the samples of pallet wood and of wood for vegetable and fruit crates, respectively.

Bremmer, 1991 concluded from literature, that on average, PCP is polluted with 3 mg I-TEq/kg and Na-PCP with 0.3 mg I-TEq/kg. This holds for PCP produced before the early 1980's. Since then process improvements in the production process may have resulted in reduced dioxin concentrations in PCP.
The use of Na-PCP is limited to small quantities of imported wood that is particularly applied in products with a short lifetime. In countries where the used is banned, dioxin emissions into the air are currently no longer expected, because of the low consumption and the low dioxin concentration in Na-PCP.

4.18.3 Calculated dioxin emissions resulting from the use of Pentachlorophenyllaurate and PCP

It appears that only for The Netherlands data has been calculated concerning the emissions from these sources (apart from preliminary British data).
Based on the situation before the ban of Pentachlorophenyllaurat in The Netherlands (1992), the emission to the air is estimated to be 0.06 g I-TEq/year (and will slowly decrease).

Using the figures for the total amount of PCP, processed in wood in The Netherlands (almost 1200 tonnes), it can be estimated that this corresponds to a total quantity of 3,525 g I-TEq of dioxins. HMIP, 1992 reports a use of 250 tonnes/year in GB.
PCP evaporates slowly. According to company information, about half the PCP is still present in preserved wood after 15 years. This means a loss through evaporation of 4.5% per year. From physicochemical characteristics, such as molecular weights and vapour pressures, it is estimated that dioxins, on average, evaporate ten times slower from wood than PCP. This means a loss percentage of 0.45% per year, calculated over the quantity that remains behind in wood. Taking into account that in the course of time, part of the wood will be renewed, it is calculated with some assumptions, that the emission in 1991 was about 15 g I-TEq.

Päpke et al. (1989) investigated the relation between dioxins and PCP in air. There appeared to be no direct connection between these two parameters. At elevated dioxin concentrations in the indoor air, the average ratio PCP: dioxins (in I-TEq) was about $1 : 5 \times 10^{-6}$. In 1991, the evaporation of PCP from wood in The Netherlands was estimated to be 25 tonnes. Based on this figure an emission of 125 g I-TEq/a can be calculated.
It is emphatically pointed out that both manners of calculation indicate an order of magnitude. It is estimated that the level will not exceed 25 g I-TEq/year.

5 Conclusions

Although recently many results from measurements at potential sources of dioxins have become available, the data that are required to assess the contribution of these sources in many cases still have a large margin of uncertainty. Consequently the total emissions in each country can only be estimated.

Municipal waste incineration may at present still be the main source of dioxin emissions into the atmosphere, but by the fast introduction of improved technologies, it is expected to be reduced one or two orders of magnitude.

Because of inadequate process control, or even complete lack of control, combustion processes like cable smouldering, but also 'traditional' hospital waste incineration, show very high specific emissions. The scale of these processes is usually small, however locally their contribution to emissions can be high.

This same effect plays a role for domestic heating appliances, specially those fired with coal or wood. Although the specific emission levels are not extremely high, the total amount of fuel burned this way and the location of the sources cause this category not to be negligible.

Emissions from road traffic, which may have been considerable in the past, are expected to decrease further because of the reduced use of scavenger containing leaded petrol.

A number of categories presented in this survey might be characterised as relatively less important sources, because the specific emission level is low, and/or the scale of these processes is small. This generally applies to fossil fuel fired powerplants, use of landfill gas, incineration of sewage sludge and most high temperature industrial processes.

Processes related to the metal industry are relatively important, this specialy concerns sintering processes, and the secondary metal industry.

An important secondary source is evaporation of dioxins from wood (formerly) treated with dioxin containing preservatives (PCP).

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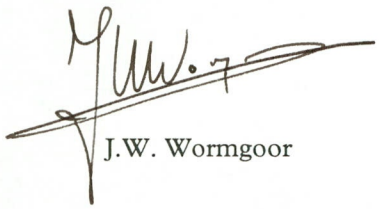
7 Authentication

Name and address of the principal
EURO CHLOR
Avenue E. Van Nieuwenhuyse, Box 2
B - 1160 Brussels

Names and functions of the cooperators
J.W. Wormgoor
Staff engineer, Dept. of Air Pollution Control
Institute of Environmental and Energy Technology TNO

Date upon which, or period in which, the research took place
August 1994 - November 1994

Signature



J.W. Wormgoor

Approved by

J. de Koning
section leader