EMISSIONS OF DIOXINS IN THE NETHERLANDS

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SUMMARY

In 1989, high dioxin concentrations (compared to the nationwide background concentration) were found in cow’s milk originating from cows grazing in the surroundings of a number of municipal solid waste (MSW) incinerators.

As dioxin emissions of only some incinerators were known, commission was given to have emission measurements conducted at all Dutch MSW incinerators \(^1\). Measurements on sources other than MSW incinerators had only been carried out on a restricted scale. An inventory of possible dioxin sources was made in co-operation with the Regional Inspectorates of Public Health for Environmental Protection. On the basis of the results of this inventory, additional measurements on sources not previously measured were conducted in the period 1991-1992. The measurement results, partly supplemented with data from the literature, were then elaborated into a total estimate of the dioxin emission in the Netherlands in 1991. This estimate is surveyed in the table below.

As far as possible, one or more measurements have been carried out on installations which are considered representative for the process category. Measurements were carried out on more installations for process categories in which higher contributions were expected than for categories in which lower contributions were expected. By doing so, the estimate of the emission from the most significant sources (and therefore the larger part of the total emission) is the most accurate.

From the set-up of the investigation and the depth of the inventory, it can be concluded that the estimate of the total emission in the Netherlands (as presented in the table below) gives a reasonable reflection of the real emission.

In total, the emission into the air in 1991 was 484 g l-TEQ. Emissions from (accidental) fires have not been included. Of that total, the MSW incinerators emit the largest quantity, i.e. 80% of the total. The remainder of the estimated yearly emission is distributed over 16 process categories, the most significant of which are: sintering processes (5.4% of the total), the (former) use of wood preservatives (5.2%), the incineration of hazardous waste (3.3%) and wood combustion (maximum 2.5%). The estimated yearly emission of each of the remaining process categories amounts to less than 1% of the total emission in the Netherlands.

Sintering processes and the incineration of hazardous waste are process categories for which measurements were carried out on various installations.

Few data on wood combustion and the former use of wood preservatives are available. For these process categories, only an indication of the yearly emission has been given. No estimate has been given of emissions as a result of (accidental) fires, because of insufficient data being available. The information available, however, shows that fires are a source that cannot be neglected.

The quantities of dioxins bound to the residues of incineration processes are often much larger than the quantities emitted into the air. For MSW incinerators it is estimated that three times as many dioxins are removed via the residues as via emission into the air (situation 1991). For all the process categories taken together, the emission via residues (as far as is known) is 1050 g l-TEQ yr\(^{-1}\). The emission to surface waters is about 3 g l-TEQ yr\(^{-1}\) (fires excluded).

---

\(^1\) Slob et al. reported on this (1992).
Estimated dioxin emissions into the air in 1991 and expected emissions in the year 2000

<table>
<thead>
<tr>
<th>Process category</th>
<th>EMISSION 1991 [g I-TEQ yr(^{-1})](^2)</th>
<th>EMISSION 2000 (^1) [g I-TEQ yr(^{-1})](^2)</th>
</tr>
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<tbody>
<tr>
<td>Municipal solid waste incineration</td>
<td>382</td>
<td>2 - 4</td>
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<tr>
<td>Incineration of hazardous wastes</td>
<td>16</td>
<td>1.7</td>
</tr>
<tr>
<td>Incineration of landfill, biogas and sludge</td>
<td>0.3</td>
<td>1.5</td>
</tr>
<tr>
<td>Cable and electromotor burning e.d.</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Waste incineration at hospitals</td>
<td>2.1</td>
<td>0</td>
</tr>
<tr>
<td>Asphalt-mixing installations (^3)</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Oil combustion</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Coal combustion</td>
<td>3.7</td>
<td>3.7</td>
</tr>
<tr>
<td>Wood combustion (^4)</td>
<td>12</td>
<td>9</td>
</tr>
<tr>
<td>Crematorio</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Fires</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>Various high-temperature processes</td>
<td>2.7</td>
<td>2.7</td>
</tr>
<tr>
<td>Traffic</td>
<td>7.0</td>
<td>0.2 - 5</td>
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<td>Sintering processes</td>
<td>26</td>
<td>3</td>
</tr>
<tr>
<td>Metal industry</td>
<td>4.0</td>
<td>4.0</td>
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<tr>
<td>Chemical production processes (^3)</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Use of wood preservatives</td>
<td>25</td>
<td>20</td>
</tr>
<tr>
<td>Total (fires excluded)</td>
<td>484</td>
<td>max.5.8</td>
</tr>
</tbody>
</table>

\(^1\) The emission estimate in the year 2000 (with the exception of MSW incinerators) does not account for the growth or a shift in certain categories.

\(^2\) The number of the given figures is no indication of certainty; values lower than 10 are rounded off to the first decimal place.

\(^3\) Emission as a result of heat generation is included in the energy generators concerned.

\(^4\) Much uncertainty as to the emission factors; additional research is recommended.

If, and to what extent, humans are exposed to dioxins depends on the way in which emitted dioxins are dispersed in the environment. The major route of exposure is food consumption, especially through milk and dairy products. Based on a recently conducted dispersement study, a chain model has been developed. With this model, a quantitative relation between dioxin emissions and dioxin concentrations in cow’s milk can be given. Calculations using this model have shown that in none of the investigated industrial sources the level is expected to exceed the standard set for milk (set in 1989 at 6 pg I-TEQ g\(^{-1}\) milk fat).

Besides the standard for cow’s milk, an emission standard of 0.1 ng I-TEQ m\(^3\) for incineration processes to protect the environment has been included in the Incineration Directive (RV89). This
requirement is based on the principle of best technical means. For MSW incinerators, the RV89 has meanwhile been replaced by the "Incineration Decree" (Statute Book 1993, 36).

On the basis of the then available data, the total 1989 emission in the Netherlands was estimated to be 960 g I-TEQ. Since then, a number of MSW incinerators, hospital waste incinerators, and cable-burning installations have been closed. Furthermore, emission-restricting measures have been introduced with some MSW incinerators and secondary metal-working processes. Particularly as a result of these measures, the total emission in the Netherlands has been reduced to an estimated 484 g I-TEQ for 1991. In the coming years, dioxin emissions will further decrease due to measures resulting from current developments.

For the year 2000 therefore, the expected total yearly emission in the Netherlands will be about 58 g I-TEQ. The emission from MSW incinerators will decrease from 790 g I-TEQ in 1989 and the 382 I-TEQ estimated for 1991 to a maximum of 4 g I-TEQ in 2000 (depending on the quantity of waste to be incinerated by that time). Besides the estimate for 1991, the table also shows the expected distribution of emissions over the different process categories in the year 2000, provided that measures that have now been started are continued.

From the survey it can be seen that the former use of wood preservatives will, in the future, probably be the largest source. One has to keep in mind that at the moment the emission from this source is relatively low, compared to the present total emission in the country. It is difficult to carry out measurements to establish the emission from this source more accurately. Moreover, the emission will slowly decrease because of this prohibition of pentachlorophenol in wood preservatives. Therefore, additional research is not recommended.

Although the estimate of the dioxin emission from wood combustion is not certain, it is thought that probably wood combustion will be the second largest source in the future. To confirm the real level of the emission from wood combustion, additional research is recommended. Only then it will be possible to give a more certain pronouncement about the size of this source. In order to check how, and to what extent, dioxins are formed in fires, it is desirable to measure also the dioxin emissions of open fires with different fuel compositions.

In order to prevent a future shift of dioxin emissions into the air to emissions via residues and surface waters, process-integrated measures are generally preferred to end-of-pipe techniques.

When in the year 2000 the dioxin emissions in the Netherlands have been reduced to about 58 g I-TEQ yr\(^{-1}\), the background deposition will have dropped from an averaged 8 ng I-TEQ m\(^{-2}\) yr\(^{-1}\) to about 4 ng I-TEQ m\(^{-2}\) yr\(^{-1}\), assuming that the contribution from foreign sources will remain the same. Because of this decrease, the background concentration of dioxins in cow's milk will also further decrease and will be largely dependent on emissions from foreign sources. One may, however, expect that these will also decrease in the future. In the surroundings of a source, the local deposition will be increased when compared to the background deposition. According to the model calculations, nowhere in the Netherlands (with the exception of the Lijckebaet area) the dioxin standard for cow's milk is currently exceeded. By driving back the emission, the dioxin concentration in cow's milk will be further decreased compared to the standard. It is expected that this year (1993) the standard will no longer be exceeded in the Lijckebaet area.
1. INTRODUCTION

During the course of 1989 it was ascertained that samples of milk coming from the Rijnmond area (Lickebaart polder) contained high concentrations of polychlorodibeno-p-dioxins (PCDDs) and polychlorodibenzofurans (PCDFs), called dioxins for short. The concentrations exceeded the standard for milk of 6 pg l-TEQ g⁻¹ of fat.

Municipal solid waste (MSW) incinerators were known as significant dioxin sources, but dioxin emissions from only a few installations were actually known. Thus, TNO was commissioned to conduct emission measurements at all MSW incinerators, as well as to analyze milk samples from the surroundings. Furthermore, insufficient knowledge was available on the emissions from other possible sources of dioxins, so research in that area was also necessary.

The subsequent investigation into sources, distribution and risks of dioxins was co-ordinated by the Interdepartmental Co-ordination Commission on Dioxins, consisting of representatives from the Ministries of Housing, Physical Planning and the Environment (VROM), Welfare, Health and Cultural Affairs (WVC), and Agriculture, Nature Management and Fisheries (LNV), and from the RIVM.

Inventory studies on the emissions of other sources and the total dioxin emissions in the Netherlands were carried out (Bremmer and Hesselink, 1991; Bremmer, 1991). In 1990/1991, TNO carried out emission measurements at MSW incinerators, while RIVM did milk analyses. TNO and RIVM published a common report (Slob et al., 1992) with respect to the results, the distribution calculations and the relation between emission and concentrations of dioxins in milk. Additionally, emission measurements were carried out on waste incineration plants near hospitals (TNO/RIVM 1990/1991; Bremmer et al., in preparation).

The above-mentioned inventory studies led to a survey of process categories (other than waste incineration and hospital waste incineration) which could be sources of dioxin emissions. The selection criterion in drawing up this survey was an elevated temperature in the presence of organic matter, oxygen and chlorine (bromated dioxins were not included into this investigation). These criteria have been further motivated in Appendix 1, which also contains a general introduction into dioxins. The survey of the process categories for which dioxin emissions were deemed possible is included in Table 1.

It appeared that insufficient knowledge on a number of the selected process categories was available; thus it was not possible to give a sufficiently accurate quantification of the emissions caused by these categories. VROM then decided to commission TNO to conduct dioxin emission measurements on some 40 plants or processes to be selected, in order to be able to complete the inventory. The selection proposals were made by RIVM. The measurement results were worked out by TNO and RIVM to reach an estimate of the emissions of dioxins occurring in the whole of the Netherlands. The emission research, hereafter to be called the project "Measurements at Other Sources" (MOB), started mid-1991 and was recently finished. The execution of the project was supervised by a committee.

The present report describes the execution and the results of the MOB research. In addition, an overall survey is given of the available knowledge on the dioxin sources and the estimated size of the total dioxin emission in the Netherlands into the air, water and soil. The report can be regarded as a completion of the total emission inventory research and as an updating of the working document "Bronnen van dioxinen in Nederland" (Sources of Dioxins in the Netherlands) published by RIVM in 1991 (Bremmer, 1991).
The report has been divided into 23 chapters. Chapter 2 describes how the MOB programme was carried out. Chapters 3 to 19 describe the data obtained on the selected process categories (one process category per chapter).

A distinction was made between the emission data obtained within the scope of the MOB project, and emission data originating from other measurements in the Netherlands (including the above-mentioned investigations into MSW incinerators and waste incineration installations at hospitals). In those cases where the authors thought that information from public documentation could contribute to a better insight into the Dutch situation, this literature was also included in the description. Each chapter concludes with an evaluation.

Table 1  Process categories for which dioxin emissions can be expected (in the Netherlands)

<table>
<thead>
<tr>
<th>Process category</th>
<th>Chapter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Incineration of municipal solid waste</td>
<td>3</td>
</tr>
<tr>
<td>Incineration of hazardous wastes</td>
<td>4</td>
</tr>
<tr>
<td>Incineration of landfill, biogas and sludge</td>
<td>5</td>
</tr>
<tr>
<td>Cable and electromotor burning</td>
<td>6</td>
</tr>
<tr>
<td>Waste incineration at hospitals</td>
<td>7</td>
</tr>
<tr>
<td>Asphalt-mixing installations</td>
<td>8</td>
</tr>
<tr>
<td>Oil combustion</td>
<td>9</td>
</tr>
<tr>
<td>Coal combustion</td>
<td>10</td>
</tr>
<tr>
<td>Wood combustion</td>
<td>11</td>
</tr>
<tr>
<td>Crematoria</td>
<td>12</td>
</tr>
<tr>
<td>Fires</td>
<td>13</td>
</tr>
<tr>
<td>Various high-temperature processes</td>
<td>14</td>
</tr>
<tr>
<td>Traffic</td>
<td>15</td>
</tr>
<tr>
<td>Sintering processes</td>
<td>16</td>
</tr>
<tr>
<td>Metal industry</td>
<td>17</td>
</tr>
<tr>
<td>Chemical production processes</td>
<td>18</td>
</tr>
<tr>
<td>Use of wood preservatives</td>
<td>19</td>
</tr>
</tbody>
</table>

In Chapter 20, all data stated in the previous chapters has been combined to give an overall picture of the dioxin emissions occurring in the Netherlands. An expectation of the dioxin emission for the year 2000 has also been included in Chapter 20. Further, Chapter 20 considers the comparison of the analysis results with each other and the relations among the occurrence of the different compounds (congeners). Chapter 21 renders the conclusions and the recommendations resulting from the research, while Chapters 22 and 23 contain the bibliography and a list of concepts and abbreviations used, respectively.
The majority of processes can be well categorized under the selected chapter divisions. In a number of cases, a certain process can be categorized under various chapters. For example, an asphalt-mixing installation that is fired with spent oil can be categorized under Chapter 8 as well as under Chapter 9; the combustion of coal in a blast furnace is suitable for insertion in both Chapter 10 and Chapter 17. To prevent double counts, we have chosen to have the dioxin emission of these processes included in only one chapter. The process is then, however, mentioned in both chapters.

In this investigation, the dioxin concentrations are expressed in toxicity equivalents (I-TEQ), on the basis of internationally accepted toxicity equivalence factors (I-TEF). For further explanation, the reader is referred to Appendix 1 (Explanation of Dioxins).
2. CARRYING OUT MOB RESEARCH

2.1 General

Support committee
As already stated in the Introduction, the carrying out of the MOB project was guided by a support committee consisting of representatives of VROM, the Interprovincial Consultation (IPO) and RIVM. TNO was in charge of the secretariat of the committee. The principal tasks of the support committee were:
- to make agreements by which the desired confidentiality was guaranteed;
- to select the sources to be measured and to define a measuring programme;
- to guide the investigation and its reporting;
- to advise about actions to be taken as a consequence of the results obtained.

The meetings of the support committee were also attended by the executor of the project and by representatives of the corporate sector, i.e. the Association for the Dutch Chemical Industry (VNCI), the Federation of Enterprises in the Metal, Electronics and Electrical Industries and Associated Branches (FME), and the Environment and Physical Planning Agency of the Council of Dutch Employers' Organizations VNO and NCW (BMRO). These representatives acted as mediators in obtaining the co-operation of the companies involved. The composition of the support committee and the participants to the meetings are recorded in Appendix 2. The support committee held nine meetings.

Procedures
From the process categories (see Introduction) to be investigated, the support committee, at the suggestion of RIVM, selected installations at which emission measurements had to be carried out. The (expected) representativeness of the installation(s) for the process category concerned was an important selection criterion (in addition to practical possibilities of carrying out measurements, etc.). After the first contact had been made with the company by a representative of the corporate sector, a visit was paid to the company and further arrangements were made on the measurements to be conducted.

A description of the procedures that were followed in carrying out the measurements and reporting has been included in the "Informatiebulletin Meten Overige Bronnen (MOB) ten behoeve van de voorlichting aan de bedrijven" (MOB Information Bulletin for Companies). Appendix 3 gives the English translation of this leaflet.

At this stage it should be stated that all companies rendered assistance in the carrying out of the project on a voluntary basis and in a very positive way.

Time schedule
The support committee met for the first time at the end of April 1991 to make arrangements for carrying out the project. The final measurements within the framework of the said commission were carried out in the spring of 1992. Meanwhile it had appeared that additional information was needed for a number of processes, which led to the commission by the Chief Inspectorate of Public Health for Environmental Protection (HIMH) to TNO for a limited follow-up measuring programme. This follow-up programme ran up to December 1992.
2.2 Measurement Programme

The aim was to record the emissions of as many installations as possible within the available financial budget. Thus preference was given to measurements conducted at many installations on a one-day (one dioxin sample), above measurements conducted at a smaller number of installations during a longer period of time. Only if a measurement result was relatively high or deviated so much from what was expected, thus raising doubts as to its representativeness, was a second measurement at the same or a comparable installation to be carried out in order to add to the reliability of the measurement result.

The support committee established a basic measurement programme; which would lead to data being obtained on the dioxin emissions, as well as to information about the process conditions (that is, process control, Cl\(^{-}\) concentration in flue gases and the completeness of the incineration) and the variations in it.

This basic measurement programme consisted of measuring the following variables of a installation’s flue gases:
- the flow rate (once or a few times);
- the concentration of O\(_2\), CO\(_2\), CO, C\(_x\)H\(_y\) (continuous recording);
- the temperature (continuous recording);
- the concentration of gaseous inorganic chlorides (two samples of approximately two hours);
- the dioxin concentration (one sample of approximately six hours).

As the measurement results had to be extrapolated to annually averaged emissions, an agreement was reached with the plant’s owner or manager that the factory operation during the measurement would be as "normal" as possible. Wherever possible, the plant manager recorded the most important installation data. This data, as well as annual production data, number of hours of operation, etc., were put at the disposal of TNO.

2.3 Measuring Methods

The measurements were always carried out in accordance with the instructions issued in the "Integrally Updated Version of the 1989 Incineration Directive" (VROM, 1992). The relevant pages from this report have been included in Appendix 4. The measurement methods used are similar to those used in the emission investigations at MSW incinerators (Slob et al., 1992) and waste incinerators at hospitals (Bremmer et al., in preparation). Appendix 4 also gives a description of the measuring and sampling techniques used.

2.4 Accuracy of Established Dioxin Emissions

In establishing the annual dioxin emissions by a process category (starting from the results of the MOB measurements), a number of factors determining the inaccuracy of these results are considered. These factors can be distinguished into:

a. The inaccuracy attached to the dioxin measurement.
   Using the dilution method, this inaccuracy can, under normal conditions, be set at less than 30%. This value can be regarded as a good result for this technique. Further information about the way in which the value of this inaccuracy was determined has been included in Appendix 5.

b. The inaccuracy attached to the extrapolation of the measurement result to a process, in accordance with the annual emission per process category.
In order to convert measurement results into an annual emission per process category, two extrapolations are needed, i.e.:
- extrapolation of the measurement result to the annual emission of the process in which the measurement was carried out;
- extrapolation of the annual emission of the measured processes to the annual emission of the process category.

The inaccuracy as a result of the extrapolations mentioned in b. depends on the representativeness of the process in which measurements were taken (or the process conditions during the measurement) and the possible variations within the process category. Naturally, the inaccuracy also depends on the number of times that measurements were carried out in one process and the number of processes within the process category concerned. This inaccuracy will often be larger than that attached to the measurement itself (see a.). Because of this, it is not possible to give a numerical indication of the final accuracy. However, a general indication of the inaccuracy attached to the extrapolations will be given in the summarizing table in Chapter 20 (Table 20.1).

In order to restrict the inaccuracy of the finally calculated nationwide annual emissions, most measurements were carried out on those process categories that could cause the largest dioxin emissions. Where high measurements resulted, the number of measurements was expanded (see 2.2). Further, in calculating the annual emissions not only were MOB results used, but also literature data and measurement results obtained in other frameworks. Although the thus calculated annual nationwide emission (the final aim of this report) can be regarded as reasonably accurate, the annual emissions per process category as derived from the measurements should be interpreted with great care. This is specifically true for the process categories that have only a small contribution to the total emission in the Netherlands.

It will be clear that the results obtained may not be used for establishing the emission of an individual installation; the variations that can occur within one process category are too large to do this.

Finally, within this scope, it should be mentioned that in a number of cases it was quite difficult to define representative process conditions of a installation where measurements were carried out. In such a case, when setting the process conditions, a "worst case" approach was followed, starting from "normal" conditions. The consequence of this approach is that if there are doubts as to the representativeness of a calculated annual emission this emission can be considered a high estimate. Should the occasion arise, this is explicitly stated.
3. INCINERATION OF MUNICIPAL SOLID WASTE

3.1 General

Incineration of municipal solid waste (MSW) is an important source of dioxins. These dioxins leave the installation together with the flue gases and the residues (slag, ESP ash, flue gas cleaning residue, effluent).

Within the framework of a general investigation of dioxins in the Netherlands, TNO was commissioned by VROM to carry out an investigation in which the emissions via the stack gases of all Dutch MSW incinerators (1990) were measured. The stack gas emissions mentioned in this chapter were derived from the results of this investigation.

The dioxin emissions via the residues were determined on the basis of data from the literature and recently reported results of measurements on residues of Dutch MSW incinerators.

3.2 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.

All furnaces in Dutch MSW incinerators are grate furnaces. Various types of grate furnaces are currently being used. Through a chute, the waste is dosed onto the moving grate where it is incinerated. The flue gases, having yielded their heat in a steam or water boiler (there are still a few installations where the temperature is decreased by water injection), are subsequently cleaned. All incineration lines in the Netherlands are equipped with an electrostatic precipitator which collects 99% or more of the fly ash as "ESP ash". In order to form compounds with acid components, lime is injected before the electrostatic precipitator in the installations in Amsterdam-North, The Hague and ROTEB. In addition to an electrostatic precipitator, the installation at Alkmaar has also been equipped with a fabric filter. Lime and activated carbon are injected before this fabric filter. The installations of Philips, GEVUDO, AVIRA and ARN have been equipped with wet scrubbers, in addition to electrostatic precipitators. The stacks of the installations are between 49 and 110 metres high.

In one of the incineration lines of GEVUDO, the flue gases are led to a multiple-hearth furnace, in which purification sludge is incinerated. The dioxin emission as a result of this sludge incineration is also included in this chapter. This sludge incineration furnace will be put out of operation in the course of 1993.

Currently, the flue gas purification of various installations is strongly expanded in order to meet the "Incineration Decree" (Statute Book, 1993, 36). This decree states that the dioxin concentration in the stack gases should be less than 0.1 ng I-TEQ m\(^{-3}\) (ind. 11% O\(_2\)). The decree applies to new installations (permit granted on or after 1 April 1990), starting 21 February 1993. Existing MSW incinerators (permit granted before 1 April 1990) should meet the emission requirements set in the decree from 1 January 1995. In granting or changing the permit of existing MSW incinerators, the authorities may deviate from the emission requirement of 0.1 ng I-TEQ m\(^{-3}\), up to a maximum of 0.4 ng I-TEQ m\(^{-3}\).
3.3 Measurement Results and Emissions via Flue Gases

Table 3.1 gives the average dioxin emissions per MSW incinerator, as estimated by the end of 1991. The emission data have been derived from the report on the emission investigation held at MSW incinerators in 1990 (Slob et al., 1992). Table 3.1 shows that the dioxin emission by MSW incinerators was 382 g I-TEQ yr\(^{-1}\) at the end of 1991. The dioxin concentration of the stack gases of the MSW incinerators ranged between 1 and 92 ng I-TEQ m\(^{-3}\) (ind. 11% O\(_2\)).

If all the above-mentioned MSW incinerators meet the requirements of the "Incineration Decree", their combined emission will not exceed 1.5 g I-TEQ yr\(^{-1}\). Concerning the increase in incineration capacity in the coming year, there are a number of scenarios in use. RIVM, for instance, assumes an incineration capacity of 7,100 ktonne yr\(^{-1}\) in the year 2000 (RIVM, 1991). The policy scenario of the Consultative Body for Waste (Afval Overleg Orgaan, AOO) arrives at 5,200 ktonne yr\(^{-1}\) (AOO, 1992). With the RIVM scenario, the dioxin emission by MSW incinerators in the year 2000 will remain below 4 g I-TEQ yr\(^{-1}\) (Liem et al., 1993). A dioxin emission of 2.5 g I-TEQ yr\(^{-1}\) has been calculated on the basis of the AOO scenario.

Table 3.1 Estimated dioxin emission per MSW incinerator (situation end 1991)

<table>
<thead>
<tr>
<th>Installation</th>
<th>Waste throughput (^{2}) [ktonne yr(^{-1})]</th>
<th>Dioxin emission (I-TEQ) [μg tonne(^{-1})]</th>
<th>[g yr(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkmaar</td>
<td>112 (^{6})</td>
<td>7 (^{4})</td>
<td>0.8</td>
</tr>
<tr>
<td>Amsterdam-North</td>
<td>521 (^{3})</td>
<td>28</td>
<td>15</td>
</tr>
<tr>
<td>The Hague</td>
<td>45</td>
<td></td>
<td>15</td>
</tr>
<tr>
<td>AVR</td>
<td>331</td>
<td>262</td>
<td>234</td>
</tr>
<tr>
<td>ROTEB</td>
<td>895</td>
<td>277</td>
<td>92</td>
</tr>
<tr>
<td>Philips (^{1})</td>
<td>331</td>
<td>43</td>
<td>1.2</td>
</tr>
<tr>
<td>Roosendaal</td>
<td>27</td>
<td>42</td>
<td>0.8</td>
</tr>
<tr>
<td>GEVUDO</td>
<td>19</td>
<td>81</td>
<td>12 (^{7})</td>
</tr>
<tr>
<td>AVIRA</td>
<td>148</td>
<td>27</td>
<td>8.0</td>
</tr>
<tr>
<td>ARN (^{1})</td>
<td>296</td>
<td>40</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>382</td>
</tr>
</tbody>
</table>

\(^{1}\) Incineration of RDF.
\(^{2}\) VVAV, 1992.
\(^{3}\) Information given by Amsterdam-North.
\(^{5}\) 1990 Emission factors (Slob et al., 1992).
\(^{6}\) Incineration re-started in the course of 1991; waste throughput over 1990 is 112 ktonnes.
\(^{7}\) Including the dioxin emission from the sludge incineration furnace.

3.4 Emissions via Residues

Beside the flue gases emitted through the stack, solid residues are being released during the incineration of domestic waste in the form of slags and ESP ash. Further purification of the stack gases results in flue gas purification residues (for example, sludge from the wet scrubbers) and possibly effluent of the wash water. Many of the dioxins are bound to these residues and discharged with them.
3.4.1 Slags

Little is known about the dioxin concentration of slags originating from MSW incinerators. In slags from German MSW incinerators, dioxin concentrations of 80 pg I-TEQ g\(^{-1}\) (Schmidt-Tegge, 1990) and 7.2 pg I-TEQ g\(^{-1}\) (Bamberg, 1992) were found. During a recent investigation into dioxins in ESP ash, slags and sludge of Dutch MSW incinerators, a dioxin concentration of on average 17.3 pg I-TEQ g\(^{-1}\) (d.m.) was found (at a dry matter concentration of 75.8 to 83.2%). The concentrations varied between 5 and 31 pg I-TEQ g\(^{-1}\) (d.m.) (four measurements; Matthijisen et al., 1993). For the time being, the above-mentioned average of 17.3 pg I-TEQ g\(^{-1}\) (d.m.) is used in the current inventory. At a rate of slags of about 490 ktonne yr\(^{-1}\) (d.m.), this means that in the Netherlands approximately 8.5 g I-TEQ yr\(^{-1}\) is discharged together with slags (Matthijisen et al., 1993). MSW incinerator slag is mainly used as embankment fill (Anthonissen, 1991).

3.4.2 ESP ash

In the former Federal Republic Germany, a large number (about 50) of determinations of dioxins were carried out on ESP ash (Hagenmaier et al., 1990). On average, a concentration of 13 ng I-TEQ g\(^{-1}\) was found. At five Dutch MSW incinerators (8 samples) values between 0.53 and 24.0 ng I-TEQ g\(^{-1}\) (d.m.) were found (Matthijisen et al., 1993). The average dioxin concentration was 12.2 ng I-TEQ g\(^{-1}\) of ESP ash (d.m.). At one of these five installations, an earlier investigation (Hesseling, 1992) found a dioxin concentration in ESP ash that corresponded well with the concentration found by Matthijisen et al. (1993).

At the end of 1991, about 2.76 million tonnes yr\(^{-1}\) of domestic and industrial wastes were processed in MSW incinerators in the Netherlands (see Table 3.1). This resulted in about 83.2 ktonne yr\(^{-1}\) (d.m.) of ESP ash (at dry matter concentrations of 99.4 to 100%). At a concentration of 12.2 ng I-TEQ g\(^{-1}\) (d.m.) this means a total of about 1,020 g I-TEQ yr\(^{-1}\) (Matthijisen et al., 1993) being discharged with the ESP ash. Approximately 35% of the produced quantity of ESP ash (about 29,000 tonnes yr\(^{-1}\) (d.m.)) are used as a filler in preparing asphalt; the remainder is dumped under ICM criteria (Anthonissen, 1991).

By applying ESP ash in asphalt, about 350 g I-TEQ of dioxins end up every year in asphalt (29,000 tonnes yr\(^{-1}\}; 12.2 ng I-TEQ g\(^{-1}\)). The wear and tear of asphalt roads is about 13,500 tonnes of asphalt per year (Slooff et al., 1992). At an asphalt production of 7.4 million tonnes per year (including recycling; see Chapter 8), we can calculate that approximately 0.6 g I-TEQ per year can be released from asphalt roads as a result of this wear and tear. The top layers have a lifetime of about 15 years (VWB-Asphalt, 1992). As ESP ash has been applied as a road filling material for only eight years, the dispersion via this route will currently amount to only half the above-mentioned quantity.

3.4.3 Flue gas cleaning residues

Flue gas cleaning residues are the solid residues that are left as a result of the flue gas cleaning after the electrostatic precipitator. The application of wet scrubbers causes particularly sludges to arise; in the case of "dry" flue gas cleaning, a residue is obtained, the main constituent of which is lime.

Dioxin concentrations from 3.2 to 69 ng I-TEQ g\(^{-1}\) d.m. were found in the sludge of wet scrubbers (four measurements). On average, 12.2 ng I-TEQ g\(^{-1}\) d.m. were found. The dry matter concentrations of the sludge varied from 31.9 to 49.3% (Matthijisen et al., 1993). In another investigation (Hesseling, 1992) conducted at one of the two MSW incinerators from the above investigation, a dioxin concentration of the same order as that found by Matthijisen et al. was
established in sludge of a wet scrubber. On the basis of the assumption that the sludge production at MSW incinerators with a wet scrubber is proportionate to the waste throughput, we calculated that approximately 851 tonnes of sludge (d.m.) are produced in the Netherlands. At an average dioxin concentration of 12.2 ng I-TEQ g \(^{-1}\) of sludge, this means that a total of approximately 10.4 g I-TEQ per year is discharged with the sludge at MSW incinerators with a wet scrubber (situation end 1991). As far as it is known, sludge of wet scrubbers is dumped under ICM criteria. The quantity of fabric filter ash that is being released at the MSW incinerator in Alkmaar is 1,600 tonnes yr\(^{-1}\). The filter ash is dumped (C3 storage facility). The dioxin concentration of the filter ash is not known (NV Huisvuilcentrale N.H., 1993). On the basis of the process conditions, it is assumed that the dioxin concentration is less than that in the ESP ash of that same installation.

3.4.4 Effluent

At two MSW incinerators with wet scrubbers, 0.79 and 3.43 pg I-TEQ l\(^{-1}\), respectively, were found in the effluent (two determinations; on average 1.87 pg I-TEQ l\(^{-1}\)). Approximately 119,000 m\(^3\) of waste water are discharged at these two MSW incinerators per year (Matthijsen et al., 1993). Starting from the assumption that the effluent at MSW incinerators is proportionate to the waste throughput, this means a total water quantity of about 175,000 m\(^3\) (in 1991). On the basis of the average dioxin concentration of 1.87 pg I-TEQ l\(^{-1}\) found at these two MSW incinerators we calculated that, at the four installations that are equipped with wet scrubbers, a total of about 0.33 mg I-TEQ yr\(^{-1}\) is being discharged with the effluent.

3.5 Summary

Table 3.2 summarizes the various data concerning the dioxin emissions of MSW incinerators.

Table 3.2 Data of dioxin emissions by Municipal Solid Waste incinerators (1991)

<table>
<thead>
<tr>
<th>Emission via</th>
<th>Quantity yr(^{-1})</th>
<th>Emission factor</th>
<th>PCDD/F emission yr(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flue gases</td>
<td>2760 kt waste</td>
<td>138 µg I-TEQ t(^{-1}) waste (^1)</td>
<td>382 g I-TEQ (^3)</td>
</tr>
<tr>
<td>ESP ash</td>
<td>83.2 kt (d.m.)</td>
<td>12.2 µg I-TEQ t(^{-1}) ESP ash (d.m.)</td>
<td>1,020 g I-TEQ (^2)</td>
</tr>
<tr>
<td>Slags</td>
<td>490 kt (d.m.)</td>
<td>17.3 µg I-TEQ t(^{-1}) slags (d.m.)</td>
<td>8.5 g I-TEQ</td>
</tr>
<tr>
<td>Sludge of wet scrubbers</td>
<td>851 t (d.m.)</td>
<td>12.2 mg I-TEQ t(^{-1}) sludge (d.m.)</td>
<td>10.4 g I-TEQ</td>
</tr>
<tr>
<td>Effluent</td>
<td>175,000 m(^3)</td>
<td>1.87 ng I-TEQ m(^{-3}) waste water</td>
<td>0.0003 g I-TEQ</td>
</tr>
</tbody>
</table>

\(^1\) Average value; per MSW incinerator, this emission factor ranges between 7 and 277 µg I-TEQ tonne\(^{-1}\) (see Table 3.1)

\(^2\) As a consequence of the use of ESP ash in asphalt for roads and the wear and tear of the road surface about 0.6 g I-TEQ is emitted yearly into the environment in an uncontrolled way.

\(^3\) Including the dioxin emission of the sludge incineration furnace of GEVUDO
3.6 Future

As far as the future situation is concerned, we can state that the flue gas cleaning in various MSW incinerators will be strongly expanded in order to be able to meet the emission standards set in the "Incineration Decree" (see also section 3.2). A total annual dioxin emission of 2.5 to 4 g l-TEQ is expected for the year 2000. However, because of the expansions, the quantity of flue gas cleaning residues will increase. But through improved incineration conditions, the dioxin concentration of the various residues is expected to decrease. To what extent this will happen is still difficult to forecast.
4. INCINERATION OF HAZARDOUS WASTES

4.1 General

"Hazardous waste" in this chapter includes:
- Any substance that has been designated as such according to the Chemical Waste Act. In contrast to what is stated in this Act, no exception is made here for substances that are processed within the company itself.
- Chlorine containing gaseous waste streams, such as process and ventilation gases.

4.2 Process Description

4.2.1 Types of furnaces

The furnaces that are used in the Netherlands for incinerating hazardous wastes can be categorized into:
- rotary kilns;
- liquid-injection furnaces;
- thermal after burners;
- fluid bed furnaces;
- fixed grate furnaces.

Rotary kilns
Rotary kilns are suited for (mixtures of) solid, pasty and liquid waste streams. The kiln consists of a cylindrical, slowly revolving drum that is lined inside with firebrick. The longitudinal axis is slightly sloping, so that the waste slowly descends through the kiln, as it rotates. This rotation results in the waste being mixed well, simultaneously providing a continuously renewed contact between the waste and the warm kiln walls. There is always a combustion chamber behind the rotary kiln to incinerate the combustion gases. Sometimes still burnable liquid waste is injected into this combustion chamber. Kiln temperatures range from 800 to 1300 °C, incineration temperatures from 900 to 1300 °C.

Liquid-injection furnaces
Liquid waste is burnt via burners in liquid-injection furnaces in chambers lined inside with firebrick, at temperatures of usually 1000 °C and higher. In a number of cases, fuel is added to reach the desired temperature. In some industries, gaseous waste substances are also injected into the furnace, in which case the liquid-injection furnace also serves as a thermal after burner.

Thermal after burners
Thermal after-burning is a waste gas purification technique in which the (in this case: chlorine containing) contaminants present are oxidized (burned) at high temperatures. These after burners usually consist of combustion chambers that are lined inside with firebrick, in which the gas stream to be incinerated is brought to a high temperature using burners that are fired with support fuel (or sometimes with liquid waste, see above). The incineration temperatures vary between 750 and 1200 °C. The incineration of gaseous wastes in existing (steam or hot-water) boilers is also reckoned under thermal after-burning.

Catalytic after burners for hazardous wastes (operating with a catalyst and at lower temperatures) were not found in the inventory.
Fluid bed furnaces
In fluid bed furnaces, inert granular particles are brought in suspension (fluidization) by an upward flow of air. The (solid or liquid) waste substances to be incinerated are dosed into the hot bed material where they are incinerated. Low-temperature burning (no higher than about 900 °C) is essential, otherwise the bed material may sinter. Fluid bed furnaces can also be applied to burning coatings (e.g. paint) off materials at lower temperatures (400-600 °C).

Fixed grate furnaces
Fixed grate furnaces consist of a chamber lined with firebrick; in this chamber, waste substances are usually incinerated on a grate in a batch process. Air is usually supplied in stages. A substoichiometric amount of air is admitted through the grate. The waste deaerates and the remaining char is incinerated. The discharging gases are incinerated after the supply of secondary air. This process is also (incorrectly) indicated as pyrolysis combustion. Fixed grate furnaces are mostly used for the recovery of metals from waste (e.g. photographic film materials). The temperature in the combustion chamber is on average 600 - 1000 °C, the after-burning temperature is about 1000 °C.

4.2.2 Flue gas treatment

As already explained in Appendix 1, important factors in the forming of dioxins are not only the incineration process, but also the conditions prevailing between the furnace and the stack.

The methods used for flue gas treatment differ strongly. In a number of cases, the flue gases are emitted into the atmosphere, without being cleaned and cooled. Possible dioxin formation no longer takes place then behind the furnace (what subsequently happens in the plume is not known).

Another variant is cooling the flue gases in a boiler or using an evaporation cooler. In this case, the detention time of the gases at 200 - 400 °C is such that dioxin formation is in essence possible. After the flue gases are cooled, they are usually cleaned with an electrostatic precipitator, lime injection, fabric filter, wet scrubber, or combinations thereof.

A third variant to treat the flue gases is to quench them from high temperatures down to below 200 °C. The detention time of the gases between 400 and 200 °C is then minimal. This happens especially where the process is used to recover HCl from the flue gases; after this, the flue gases pass scrubbers before being emitted.

4.3 Inventoried Processes

Twenty-five incineration installations were found of which it is assumed that dioxins can be formed on the basis of the presence of chlorine in the waste to be incinerated (Bremmer and Hesseling, 1991). Of three other installations it is not known whether chlorine is present in the waste and thus it is not known whether dioxins may be formed. Table 4.1 gives a survey of the 28 installations, arranged according to furnace type.

In 14 of the 28 installations, about 155,000 tonne yr⁻¹ of solid, liquid and gaseous chlorine containing hazardous wastes are incinerated. In the other 14 installations (thermal after burners), solely gaseous chlorine-containing products are incinerated. Only in a single case are the quantities that are incinerated in the thermal after burners known. Therefore, no estimate is given of the total quantity of waste incinerated in that way.
Table 4.1 Incinerated quantities of chlorine containing hazardous wastes per furnace type

<table>
<thead>
<tr>
<th>Furnace type</th>
<th>Number of installations</th>
<th>Waste [tonne yr(^{-1})]</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotary kiln</td>
<td>3</td>
<td>92,000</td>
<td>90,000 tonne yr(^{-1}) in two installations</td>
</tr>
<tr>
<td>Liquid-injection</td>
<td>5</td>
<td>54,000</td>
<td>44,000 tonne yr(^{-1}) in three installations, for HCl recovery</td>
</tr>
<tr>
<td>Fluid bed</td>
<td>1</td>
<td>1,400</td>
<td>-</td>
</tr>
<tr>
<td>Fixed grate</td>
<td>5</td>
<td>7,000</td>
<td>5,500 tonne yr(^{-1}) in one installation</td>
</tr>
<tr>
<td>Thermal after burner</td>
<td>14</td>
<td>not known</td>
<td>-</td>
</tr>
</tbody>
</table>

The large-scale incineration of hospital waste takes place in the incineration plants of AVR-Chemie. The dioxin emission as a result of this incineration of hospital waste is therefore included in this chapter. From the beginning of 1992, the incineration of hospital waste has also taken place in ZAVIN’s special installation in Dordrecht. Incineration of hospital waste by hospitals in their own installations will be treated separately in Chapter 7.

4.4 MOB Measurement Results

Within the framework of the MOB programme, measurements were carried out on eight installations for the incineration of hazardous wastes. Table 4.2 gives several important characteristics of the installations. It also gives a rough impression of several important characteristics of the hazardous wastes that are incinerated. It was not always possible to obtain precise information about the process conditions. In such cases, it was explicitly agreed with the plant manager that, during the measurements, the process would be operated under "normal" conditions with an average load.

Table 4.3 shows the average measurement results per installation. The PCDD/F concentration for installation 4G has been marked with "high value". The background to this is that in cases in which "normal plant operation" could not be defined very well, the process conditions were set in such a way that maximum dioxin emissions could be expected (see also section 2.4). The measured value is therefore fairly high. Table 4.3 shows that PCDD/F concentrations between 0.04 and 9.7 ng 1-TEQ m\(^{-3}\) (ind. 11% O\(_2\)) were measured in the flue gases.
<table>
<thead>
<tr>
<th>Installation no.</th>
<th>Type of furnace</th>
<th>Temperature of furnace (°C)</th>
<th>Type of flue gas treatment</th>
<th>Hours of operation per year</th>
<th>Throughput (tonnes yr(^{-1}))</th>
<th>Aggregation (^{(1)})</th>
<th>Cl concentration (wtr.)</th>
<th>Kind of waste (^{(7)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>4A</td>
<td>rotary kiln</td>
<td>800 - 850 (^{(2)})</td>
<td>quench, gas scrubber</td>
<td>7,200</td>
<td>2,000</td>
<td>s</td>
<td>~ 65%</td>
<td>solid waste of chemical industry</td>
</tr>
<tr>
<td>4B</td>
<td>liquid-injection</td>
<td>1000 - 1100</td>
<td>quench, gas scrubber</td>
<td>7,200</td>
<td>9,000</td>
<td>l</td>
<td>~ 65%</td>
<td>GKW residues</td>
</tr>
<tr>
<td>4C</td>
<td>liquid-injection</td>
<td>1000 - 1400</td>
<td>steam boiler, quench, gas scrubber</td>
<td>5,500</td>
<td>5,500</td>
<td>g + l</td>
<td>~ 30%</td>
<td>light-ends + liquid GKW residues</td>
</tr>
<tr>
<td>4D</td>
<td>after burner</td>
<td>1400 - 1600</td>
<td>quench, scrubber</td>
<td>8,000</td>
<td>33,000</td>
<td>l</td>
<td>~ 69%</td>
<td>GKW residues</td>
</tr>
<tr>
<td>4E</td>
<td>after burner</td>
<td>~ 800</td>
<td>steam boiler</td>
<td>8,760</td>
<td>6(^{(2)})</td>
<td>g</td>
<td>&lt; 30 mg m(^{-3})</td>
<td>e.g. ethylene dichloride</td>
</tr>
<tr>
<td>4F</td>
<td>fixed grate</td>
<td>~ 1000</td>
<td>lye quench, gas scrubber</td>
<td>2,040</td>
<td>-</td>
<td>g</td>
<td>n.k. (^{(4)})</td>
<td>mainly photographic residues</td>
</tr>
<tr>
<td>4G</td>
<td>after burner</td>
<td>~ 1000 (^{(5)})</td>
<td>incinerator, quench, gas scrubber</td>
<td>8,000</td>
<td>5,500</td>
<td>s + l</td>
<td>n.k.</td>
<td>waste gas, natural gas</td>
</tr>
<tr>
<td>4H</td>
<td></td>
<td>1200</td>
<td>quench, gas scrubber</td>
<td>8,000</td>
<td>-</td>
<td>g</td>
<td>n.k.</td>
<td></td>
</tr>
</tbody>
</table>

\(^{(1)}\) g = gas, l = liquid, s = solid

\(^{(2)}\) With incineration of gaseous waste streams

\(^{(3)}\) After-burning unit

\(^{(2)}\) Batch process

\(^{(4)}\) Not known

\(^{(5)}\) Beside natural gas and hydrogen also "waste gas": 10,400 GJ per year (lower heat of incineration, on average 352 kJ m\(^{-3}\) ind.)

\(^{(7)}\) GKW = chlorinated hydrocarbons
<table>
<thead>
<tr>
<th>Installation no.</th>
<th>Flue gas flow ( \text{[m}^3\text{ h}^{-1}]^3 )</th>
<th>Flue gas temp. ( \text{[°C]} )</th>
<th>( \text{O}_2 ) (vol% dry)</th>
<th>( \text{CO}_2 ) (vol% dry)</th>
<th>( \text{NO}_2 ) (µg m(^{-3}))</th>
<th>PCDD/F ( \text{[mg I-TEQ m}^3\text{ ]}^{3} )</th>
<th>Cl(^-) ( \text{[mg m}^3\text{ ]}^{2} )</th>
<th>CO ( \text{[mg m}^3\text{ ]}^{2} )</th>
<th>( \text{C}_4\text{H}_8 ) ( \text{[mg m}^3\text{ ]}^{2} )</th>
<th>Yearly emission of PCDD/F ( \text{[µg I-TEQ yr}^{-1}] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4A</td>
<td>12,100</td>
<td>38</td>
<td>13.9</td>
<td>4.0</td>
<td>63</td>
<td>9.7</td>
<td>8</td>
<td>37</td>
<td>&lt; 5</td>
<td>0.62</td>
</tr>
<tr>
<td>4B</td>
<td>5,500</td>
<td>36</td>
<td>7.7</td>
<td>16.8</td>
<td>62</td>
<td>0.4</td>
<td>405</td>
<td>15</td>
<td>&lt; 5</td>
<td>0.02</td>
</tr>
<tr>
<td>4C</td>
<td>7,800</td>
<td>40</td>
<td>5.3</td>
<td>10.9</td>
<td>92</td>
<td>7.6</td>
<td>1057</td>
<td>13</td>
<td>&lt; 5</td>
<td>0.51</td>
</tr>
<tr>
<td>4D</td>
<td>15,400</td>
<td>58</td>
<td>6.1</td>
<td>12.6</td>
<td>206</td>
<td>0.5</td>
<td>46</td>
<td>36</td>
<td>&lt; 5</td>
<td>0.09</td>
</tr>
<tr>
<td>4E</td>
<td>59,800</td>
<td>143</td>
<td>2.4</td>
<td>5.7</td>
<td>99</td>
<td>0.05</td>
<td>39</td>
<td>8</td>
<td>&lt; 5</td>
<td>0.05</td>
</tr>
<tr>
<td>4F</td>
<td>7,000</td>
<td>60</td>
<td>17.4</td>
<td>2.0</td>
<td>160</td>
<td>0.04</td>
<td>6</td>
<td>16</td>
<td>&lt; 5</td>
<td>0.0001</td>
</tr>
<tr>
<td>4G</td>
<td>13,500</td>
<td>59</td>
<td>13.3</td>
<td>3.3</td>
<td>153</td>
<td>0.9</td>
<td>30</td>
<td>810</td>
<td>≤ 174</td>
<td>0.02</td>
</tr>
<tr>
<td>4H</td>
<td>19,000</td>
<td>49</td>
<td>14.7</td>
<td>3.3</td>
<td>100</td>
<td>0.21</td>
<td>8</td>
<td>9</td>
<td>&lt; 5</td>
<td>0.02</td>
</tr>
</tbody>
</table>

\(^{1}\) Refers to dry flue gases under standard conditions
\(^{2}\) Refers to dry flue gases under standard conditions, converted to 11% \( \text{O}_2 \)
\(^{3}\) Reasonably high because of plant operation chosen
4.5 Measurement Results Outside MOB Framework

4.5.1 Flue gas emissions

In 1991, two rotary kilns (DTOs) were operational at AVR-Chemie for the processing of hazardous wastes: DTO 7 and DTO 8. Outside the MOB framework, measurements were conducted on both DTOs. DTO 7 (installation 4J) was drastically modified at the end of 1991. The electrostatic precipitator was replaced by a fabric filter (installation 4J6). Lime and activated carbon are now being injected before this fabric filter.

Six analyses were carried out on the flue gases of three after burners at one installation from which halogenated solvents and chloroparaffins are released. Of halogenated solvents and chloroparaffins, 360 tonnes are annually released there in a drying process; they are sucked off and incinerated (installation 4K).

At another company dioxins were measured in the flue gases of an installation in which laundry waste sludge is incinerated (installation 4L). This waste sludge originates in the chemical cleaning of textiles that are contaminated with edible oils and fats, for example. Perchloroethylene and methylene chloride are used as detergents. Both substances are largely recovered in order to be reused.

At installation 4M, dioxins were measured in a sample of fly ash, taken in order to determine the particle concentration. This sampling differs in a number of essential points from the sampling methods that are currently used for dioxins. The results of this measurement must therefore be considered indicative.

In Table 4.4 the important characteristics of the installations and of the waste substances incinerated in them are shown. Table 4.5 shows the measurement results per installation. This table also states the annual emissions calculated from the measurement results.
<table>
<thead>
<tr>
<th>Installation no.</th>
<th>Type of furnace</th>
<th>Type of flue gas treatment</th>
<th>Hours of operation per year</th>
<th>Throughout (tonne yr(^{-1}))</th>
<th>Aggregation (\text{m}^3)</th>
<th>CI concentration (sv.)</th>
<th>Kind of waste</th>
<th>Literature source</th>
</tr>
</thead>
<tbody>
<tr>
<td>41</td>
<td>rotary kiln</td>
<td>ESP, gas scrubber</td>
<td>8,000</td>
<td>45,000</td>
<td>s+i</td>
<td>&lt;5</td>
<td>normal plant operation</td>
<td>(Kuippen, 1992)</td>
</tr>
<tr>
<td>41(_a)</td>
<td>rotary kiln</td>
<td>ESP</td>
<td>8,000</td>
<td>45,000</td>
<td>s+i</td>
<td>&lt;5</td>
<td>normal plant operation</td>
<td>(Poot, 1990)</td>
</tr>
<tr>
<td>41(_b)</td>
<td>rotary kiln</td>
<td>fabric filter</td>
<td>8,000</td>
<td>45,000</td>
<td>s+i</td>
<td>&lt;5</td>
<td>normal plant operation</td>
<td>(Koch, 1992)</td>
</tr>
<tr>
<td>4K(_a)</td>
<td>after burner</td>
<td>n/a</td>
<td>-</td>
<td>-</td>
<td>g</td>
<td>-</td>
<td>halogen-containing</td>
<td>confidential, 1991</td>
</tr>
<tr>
<td>4K(_b)</td>
<td>after burner</td>
<td>n/a</td>
<td>-</td>
<td>360 (^2)</td>
<td>g</td>
<td>-</td>
<td>solvents and chlorine</td>
<td>confidential, 1991</td>
</tr>
<tr>
<td>4K(_c)</td>
<td>after burner</td>
<td>n/a</td>
<td>-</td>
<td>-</td>
<td>g</td>
<td>-</td>
<td></td>
<td>confidential, 1991</td>
</tr>
<tr>
<td>4L</td>
<td>liquid-inj.</td>
<td>fabric filter, gas scrubber</td>
<td>8,000</td>
<td>-</td>
<td>l</td>
<td>1.7</td>
<td>laundry waste sludge</td>
<td>confidential, 1991</td>
</tr>
<tr>
<td>4M</td>
<td>fluid bed</td>
<td>fabric filter, gas scrubber</td>
<td>8,000</td>
<td>1,400</td>
<td>l</td>
<td>-</td>
<td>metal recovery unit</td>
<td>confidential, 1991</td>
</tr>
</tbody>
</table>

\(^1\) g = gas, l = liquid, s = solid
\(^2\) Total for three after burners
Table 4.5 Measurement results of incineration for hazardous wastes, measured outside MGB framework

| Installation no | Flue gas flow \( [\text{m}^3 \text{h}^{-1}] \) | Flue gas temp \( [\text{°C}] \) | \( \text{O}_2 \) [vol% dry] | \( \text{CO}_2 \) [vol% dry] | \( \text{H}_2\text{O} \) [g m\(^{-3}\)] | PCDD/F [ng I-TEQ m\(^{-3}\)] | Cl\(^-\) [ng m\(^{-3}\)] | CO [ng m\(^{-3}\)] | \( \text{C}_4\text{H}_8 \) [ng m\(^{-3}\)] | Annual emissions of PCDD/F [g I-TEQ yr\(^{-1}\)] |
|----------------|----------------------------------|--------------------------------|-----------------|-----------------|-----------------|------------------|----------------|----------------|----------------|----------------|-----------------|
| 4L             | 48,600                           | 63                             | 9.9             | 8.7             | 217             | 34               | 30             | <5             | 14             | 30             | <5              | 4               |
| 4L\_a          | 64,400                           | 222                            | 14.1            | 5.9             | 408             | 26.8            | 360            | 120            | 2.5            | 120            | 2.5             | 10              |
| 4L\_b          | 59,900                           | 180                            | 11.1            | 5.7             | 482             | 0.31             | 25             | <5             | 4.2            | 4.2            | 4.2             | 0.2             |
| 4K\_a          |                                  |                                |                 |                 |                 | 0.0007           |                |                |                |                | 0.0007          | 0.0007          |
| 4K\_b          |                                  |                                |                 |                 |                 | 0.0006           |                |                |                |                | 0.0006          | 0.0006          |
| 4K\_c          |                                  |                                |                 |                 |                 | 0.003            |                |                |                |                | 0.003           | 0.003           |
| 4L             | 1,210                            | 34                             | 2.4             |                 | 91              | 4.2              |                |                |                |                | 4.2             | 0.1             |
| 4M             | 3,890                            | 53.8                           | 15.7            |                 | 140             | < 1.3            |                |                |                |                | < 1.3           | < 0.02          |

1) Refers to dry flue gases under standard conditions
2) Refers to dry flue gases under standard conditions, converted to 11% \( \text{O}_2 \)
3) Indication, see text - Chapter 4.5.1
4) Insufficient information available
4.5.2 Emissions via residues

Recent measurement data about dioxin concentrations in slag, sludge, ESP ash and fabric filter ash are not available. The quantities of solid residues are known only in a few cases. However, some measurement data are available for the emissions to water. Because of the confidentiality of this data, they will not be mentioned individually, but will be used in the evaluation to estimate the total emission to water. The wash water of a number of processes with wet scrubbers is processed or reused. In those processes, emission to water does not take place.

4.6 Evaluation

4.6.1 Emissions via flue gases

Rotary kilns
Dioxin measurements were conducted at all three rotary kilns that were operational at the end of 1991 (4A, 4I and 4J) and incinerated chlorine containing hazardous wastes. The emission measured in 1992 (see 4Jb in Table 4.5) has not been included in the calculation of the total emission of installation 4J, as this report considers the situation at the end of 1991. Therefore, the total dioxin emission of rotary kilns (end 1991) is the sum of the annual emissions of the installations 4A, 4I and 4J, i.e. 15 g I-TEQ yr\(^{-1}\). This emission includes the dioxin emission as a result of the incineration of hospital waste at AVR-Chemie.

Liquid-injection furnaces
The dioxin emission of four of the five liquid-injection furnaces was measured. The installation at which no measurements were carried out is more or less identical to installation 4C (see Table 4.2), while it also combusts the same kind of waste. On the basis of the emission data stated in the Tables 4.3 and 4.5, the dioxin emission by this type of furnace was 1.2 g I-TEQ yr\(^{-1}\).

Fluid bed furnaces
One dioxin measurement was carried out at the fluid bed installation (4M). The calculated annual emission is < 0.02 g I-TEQ. This figure should be regarded as an indicative value (see section 4.5.1).

Fixed grate furnaces
A dioxin measurement was carried out at the largest of the five fixed grate furnaces (installation 4G). It is assumed that the emission factor for dioxin at the other four (small) installations is 10 times larger than at the large installation where the dioxin measurement was carried out (rough estimate). On the basis of the annual emission and the waste throughput of installation 4G, as well as the total waste throughput of these small installations (see Table 4.1), it was calculated that the total emission at the incineration of hazardous wastes in fixed grate furnaces is 0.07 g I-TEQ per year.

Thermal after burners
The dioxin emission was determined for four installations (4E, 4F, 4H and 4K) of the 14 inventoried after burners. The quantities of waste substances or the quantities of flue gases are known for only a few installations.

Installation 4E is by far the largest in the Netherlands. During the measurements, installation 4H was operated under conditions that are favourable for dioxin formation. It is assumed that the emissions of 4F and 4K (which are significantly lower) are more representative of the other
installations. On the basis of the above, the total dioxin emission by incinerators was put at about 0.2 g I-TEQ per year.

4.6.2 Emissions via residues

No recent information is available with respect to the quantities of dioxins in solid residues (slag, sludge, ESP ash and fabric filter ash). On the basis of process data and confidential measurement data of dioxin emissions to water, it is estimated that 0.5 - 1 g I-TEQ is emitted to water.

4.7 Summary

Table 4.8 summarizes the data on the dioxin emissions via the flue gases.

Table 4.8 Dioxin emissions via flue gases at the incineration of hazardous wastes

<table>
<thead>
<tr>
<th>Type of furnace</th>
<th>Number of installations</th>
<th>Waste throughput [tonne yr(^{-1})]</th>
<th>PCDD/F emission [g I-TEQ yr(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotary kiln</td>
<td>3</td>
<td>92,000</td>
<td>15 (^{1)})</td>
</tr>
<tr>
<td>Liquid-injection</td>
<td>5</td>
<td>54,000</td>
<td>1.2</td>
</tr>
<tr>
<td>Fluid bed</td>
<td>1</td>
<td>1,400</td>
<td>&lt; 0.02</td>
</tr>
<tr>
<td>Fixed grate</td>
<td>5</td>
<td>7,000</td>
<td>0.07</td>
</tr>
<tr>
<td>Thermal after burner</td>
<td>14</td>
<td>not known</td>
<td>about 0.2</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>28</strong></td>
<td></td>
<td><strong>16</strong></td>
</tr>
</tbody>
</table>

\(^{1)}\text{Including the dioxin emission as a result of the incineration of hospital waste at AVR-Chemie.}

The quantities of dioxins that are discharged with the solid residues are not known. The dioxin emission to surface waters is estimated at 0.8 g I-TEQ yr\(^{-1}\).

4.8 Future

The following should be stated concerning the future situation: in order to be able to meet the requirements set in the 1989 Incineration Directive (RV'89), the rotary kilns (installations 4A, 4I and 4J) will have to be modified. The flue gas cleaning of installation 4J was drastically modified at the end of 1991 (effective as of early 1992). The electrostatic precipitator (installation 4J\(_a\)) was replaced by a fabric filter (installation 4J\(_b\)). Lime and activated carbon are now injected for this fabric filter. After these modifications, TNO carried out one more measurement in 1992 (Table 4.5, 4J\(_b\)). The annual emission of dioxins decreased from 10 to 0.2 g I-TEQ because of the modification.

In the summer of 1992, a third rotary kiln (DTO-9) became operational at AVR-Chemie for the incineration of hazardous wastes. This installation was designed to meet the 1989 Incineration Directive (RV'89), i.e. 0.1 ng I-TEQ m\(^{-3}\) ind. at 11% O\(_2\).
Once all rotary kilns have been modified and meet the 1989 Incineration Directive (< 0.1 ng m\(^{-3}\)), the total annual emission of these kilns will be about 0.2 g l-TEQ (on the basis of an emission reduction in proportion to the mentioned concentrations; the 1992 data have been used for installation 4J). The total dioxin emission at the incineration of hazardous wastes will then be 1.7 g l-TEQ per year.
5. INCINERATION OF LANDFILL GAS, BIOGAS AND SLUDGE

5.1 General

This chapter considers the following flows:
- Landfill gas: This gas is released from the organic fraction of landfilled (domestic) waste. It consists mainly of CO$_2$ and CH$_4$.
- Biogas: Biogas here means gas that is being released during the anaerobic sludge digestion in sewage treatment plants.
- Sewage sludge: Sludge coming from sewage treatment plants.
- Industrial sludge: Sludge coming from industrial production processes and wet scrubbers, in as far as they contain chlorine.

5.2 Process Description

Incineration of landfill gas and biogas
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 some cases, landfill gas or biogas is used 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. A top flare consists of a "flare pipe" on which the "flare tip" (burner) is found. In order to guarantee that the gases blown off are always incinerated in a flame, pilot flame burners, which are near the "flare tip", are fed with natural gas or a similar fuel. The pilot flames are continuously in operation.

Gas engines are sometimes equipped with a "de-NO$_x$" unit in order to reduce the emission of nitrogen oxides. It is obvious that no flue gas cleaning is used in flares.

Sometimes after cleaning (to < 5 mg Cl m$^{-3}$), landfill gas or biogas is added to the natural gas network. During the cleaning, halogenated and higher hydrocarbons are removed from the gas using activated carbon. The hydrocarbons that are released at the regeneration of this carbon are flared.

Sludge incineration
The incineration of sludge in the Netherlands happens mainly in fluid bed furnaces (see Chapter 4 for a description), possibly in combination with other substances. In one case in the Netherlands, use is made of a multiple-hearth furnace. This furnace is part of one of the incineration lines of the GEVUDO MSW incinerator in Dordrecht. A multiple-hearth furnace consists of a cylinder with several storeys; these storeys have holes in the floor. In the centre, there is an axis with rakers. The sludge is pumped into the furnace at the top. The rakers cause the sludge to move through the holes down to the lower storeys. The sludge will dry in the upper storeys, while it is incinerated in the lower ones at temperatures from 800 to 1000 °C. The combustion residue will cool down in the bottom storeys. In the present situation, flue gases from the MSW incinerator will flow through the GEVUDO plant. The emissions have therefore been included in Chapter 3.
5.3 Inventoried Processes

Incineration of landfill gas
Approximately 74 million m$^3$ of landfill gas was extracted in the Netherlands in 1991. About 22 million m$^3$ of this quantity was flared, while the remaining 52 million m$^3$ was used:
- in incineration (untreated) in a brick kiln, for instance, and a kiln for electrodes (14 million m$^3$);
- in incineration (untreated) in gas engines for electricity generation (16 million m$^3$);
- for reprocessing to the quality of natural gas (22 million m$^3$).
So, a total of 52 million m$^3$ of untreated landfill gas is incinerated (Oonk et al., 1993).

Incineration of biogas
Gas obtained at the anaerobic digestion of sewage sludge is usually incinerated in gas engines. Seven biogas-fired engines were inventoried. On the basis of the inventory conducted in 1990 it is estimated that approximately 60 million m$^3$ of biogas are incinerated per year (Bremmer and Hesseling, 1991).

Incineration of sludge
In the Netherlands, sewage sludge is incinerated in three installations. One of them is connected to the GEVUDO MSW incinerator in Dordrecht (see 5.2; the dioxin emission has been included in Chapter 3). The other two installations are fluid bed furnaces, one equipped with an electrostatic precipitator and the other with a wet scrubber for flue gas cleaning. These two installations together incinerate about 6,000 tonnes of sludge per year (on the basis of dry matter) (internal company information; RIMH North Brabant, 1993).

The GEVUDO multiple-hearth furnace was to have fall into disuse during 1993. From then on, sludge incineration was to take place in a fluid bed furnace at DRSH Zuiveringsslib N.V. The sewage sludge of the Province of South Holland will be incinerated in this installation (with a capacity of 45,000 tonnes of dry matter per year).

In the Netherlands, the incineration of (chlorine containing) industrial sludge takes place mainly in two installations (both fluid bed furnaces). The one installation has a throughput of 7,850 tons (d.m.) per year (see Chapter 5.4), the other of 45,000 tonnes (d.m.) per year (see Table 5.4). The latter specifically incinerates sludge from a papermill. Furthermore, there is an experimental incineration plant, as well as a plant that works intermittently. The total quantity of sludge incinerated in these two installations is estimated to be only 100 tonne d.m. yr$^{-1}$ (Bremmer and Hesseling, 1991).

In the Netherlands, a total of 462,000 tonnes of sludge are released per year (on the basis of dry matter). Of this, 282,000 tonnes are sewage sludge, while the remaining 180,000 tonnes are industrial sludge (Duvoort-van Engers, 1991; RIVM, 1992).

5.4 MOB Measurement Results

Within the MOB framework, measurements were taken at one sludge incineration plant. In a fluid bed furnace, this installation incinerates industrial sludge from the flocculation/flotation units of the water treatment plant of a refinery, as well as sludge filter cake of the primary treatment and the bioreactors of the central water treatment. The flue gases are subsequently treated in an electrostatic precipitator, a quenching tower, and an absorption tower.

When interpreting the measurement results (Table 5.1), one should take into account that the results were collected during two measurement periods, as the plant broke down during the
measurement. The way of firing and the emissions of CO, C\textsubscript{x}H\textsubscript{y} and Cl\textsuperscript{-} differed strongly in the two measurement periods. No distinction can be made as to the dioxin emission, as the sampling took place on one filter. If it is assumed that all dioxins were emitted during the first part of the measurement (i.e. during the period of high Cl\textsuperscript{-} concentrations), this means a maximum dioxin concentration of about 1 ng I-TEQ m\textsuperscript{-3} (ind. at 11% O\textsubscript{2}) for this process.

Table 5.1 Data and measurement results of sludge incineration, measured within MOB framework

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Installation 5A measurement 1</th>
<th>Installation 5A measurement 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of furnace</td>
<td>fluid bed</td>
<td>electrostatic precipitator, quenching, cooler, absorption, tower</td>
</tr>
<tr>
<td>Flue gas treatment</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sludge throughput (d.m.)</td>
<td>[tonne yr\textsuperscript{-1}]</td>
<td>7,850</td>
</tr>
<tr>
<td>hours of operation per year</td>
<td></td>
<td>about 7,200</td>
</tr>
<tr>
<td>Flue gas flow \textsuperscript{1)}</td>
<td>11.30</td>
<td>11.60</td>
</tr>
<tr>
<td>Flue gas temperature \textsuperscript{2)}</td>
<td>19</td>
<td>19</td>
</tr>
<tr>
<td>\textsuperscript{O}{\textsubscript{2}} \textsuperscript{2)}</td>
<td>12.2</td>
<td>12.8</td>
</tr>
<tr>
<td>\textsuperscript{CO}{\textsubscript{2}} \textsuperscript{2)}</td>
<td>6.2</td>
<td>5.8</td>
</tr>
<tr>
<td>\textsuperscript{H}{\textsubscript{2}O} \textsuperscript{1)}</td>
<td>42</td>
<td>21</td>
</tr>
<tr>
<td>PCDD/F \textsuperscript{2)}</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Cl\textsuperscript{-} \textsuperscript{2)}</td>
<td>209</td>
<td>1</td>
</tr>
<tr>
<td>CO \textsuperscript{2)}</td>
<td>99</td>
<td>31</td>
</tr>
<tr>
<td>C\textsubscript{x}H\textsubscript{y} \textsuperscript{2)}</td>
<td>7</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Yearly emission of PCDD/F \textsuperscript{3)}</td>
<td>0.025</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{1)} Refers to dry flue gases under standard conditions
\textsuperscript{2)} Refers to dry flue gases under standard conditions, converted to 11% O\textsubscript{2}
\textsuperscript{3)} Calculated on the basis of measured concentration, measured average flue gas flow and hours of operation on a yearly basis

5.5 Measurement Results Outside the MOB Framework

Incineration of landfill gas
Outside the MOB framework, measurements were taken at a gas engine and a flare. In both installations, untreated landfill gas was incinerated. Table 5.2 states the results of these measurements. Insufficient data was available to calculate annual emissions. The emission factors needed, however, can be calculated from the results (see section 5.7).
Table 5.2 Data and measurement results for landfill gas incineration measured outside the MOB framework (confidential literature source)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>5B</th>
<th>5C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of installation</td>
<td>gas engine</td>
<td>flare</td>
</tr>
<tr>
<td>Consumption of landfill gas [m³ h⁻¹]</td>
<td>200</td>
<td>600</td>
</tr>
<tr>
<td>Flue gas treatment</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>Flue gas flow [m³ h⁻¹]</td>
<td>790¹</td>
<td>about 10,000³</td>
</tr>
<tr>
<td>Flue gas temperature [°C]</td>
<td>530</td>
<td>about 1,000⁵</td>
</tr>
<tr>
<td>O₂ [vol % dry]</td>
<td>3.0</td>
<td>16.4⁴</td>
</tr>
<tr>
<td>H₂O [g m⁻³]</td>
<td>160</td>
<td>5.5⁵</td>
</tr>
<tr>
<td>PCDD/F [ng l-TEQ m⁻³]</td>
<td>0.07²</td>
<td>0.022⁴</td>
</tr>
<tr>
<td>PCDD/F emission [ng l-TEQ h⁻¹]</td>
<td>105</td>
<td>220</td>
</tr>
</tbody>
</table>

¹) Refers to dry flue gases under standard conditions
²) Refers to dry flue gases under standard conditions, converted to 11% O₂
³) According to company statement; Refers to wet flue gases under standard conditions
⁴) Refers to wet flue gases (under standard conditions)
⁵) Moisture content could not be determined

Incineration of sewage sludge
Measurement data is available for the incineration of sewage sludge in one of the two fluid bed furnaces. Table 5.3 states the results. Calculation of the annual emissions was not possible. However, the emission factors needed can be calculated from the results (see section 5.7).

Table 5.3 Data and measurement results for incineration of sewage sludge measured outside the MOB framework (confidential literature source)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Installation 5D</th>
<th>Measurement 1</th>
<th>Measurement 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of oven</td>
<td>fluid bed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flue gas treatment</td>
<td></td>
<td>cyclone and wet scrubber</td>
<td></td>
</tr>
<tr>
<td>Sludge throughput [kg h⁻¹]</td>
<td></td>
<td>260</td>
<td></td>
</tr>
<tr>
<td>Flue gas flow [m³ h⁻¹]</td>
<td>9,700</td>
<td>9,500</td>
<td></td>
</tr>
<tr>
<td>Flue gas temperature [°C]</td>
<td>60</td>
<td>57</td>
<td></td>
</tr>
<tr>
<td>O₂ [vol % dry]</td>
<td>8.5</td>
<td>9.7</td>
<td></td>
</tr>
<tr>
<td>H₂O [g m⁻³]</td>
<td>111</td>
<td>129</td>
<td></td>
</tr>
<tr>
<td>PCDD/F [ng l-TEQ m⁻³]</td>
<td>0.11</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>PCDD/F emission [ng l-TEQ h⁻¹]</td>
<td>900</td>
<td>1.5</td>
<td></td>
</tr>
</tbody>
</table>

¹) Refers to dry flue gases under standard conditions
²) Refers to dry flue gases under standard conditions, converted to 11% O₂
Incineration of industrial sludge
Measurement results of the incineration of sludge from a paper mill (measured outside MOB framework) are available. Some data and measurement results are stated in Table 5.4.

Table 5.4 Data and measurement results for incineration of industrial sludge measured outside the MOB framework (confidential literature source)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Installation 5E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of furnace</td>
<td>fluid bed</td>
</tr>
<tr>
<td>Flue gas treatment</td>
<td>steam boiler</td>
</tr>
<tr>
<td></td>
<td>limestone in bed, cyclone and fabric filter</td>
</tr>
<tr>
<td>Sludge throughput (d.m.)</td>
<td>[tonne yr(^{-1})] 45,000</td>
</tr>
<tr>
<td>Hours of operation per year</td>
<td>8,000</td>
</tr>
<tr>
<td>Flue gas flow</td>
<td>([m^3 \text{ h}^{-1}]) 31,500</td>
</tr>
<tr>
<td>Flue gas temperature</td>
<td>([\degree \text{C}]) 183</td>
</tr>
<tr>
<td>(O_2)</td>
<td>[vol % dry] 8.9</td>
</tr>
<tr>
<td>(CO_2)</td>
<td>[vol % dry] 10.3</td>
</tr>
<tr>
<td>(H_2O)</td>
<td>[g m(^{-3})] 238</td>
</tr>
<tr>
<td>PCDD/F</td>
<td>[ng I-TEQ m(^{-3})] 0.6</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>[mg m(^{-3})] 77</td>
</tr>
<tr>
<td>CO</td>
<td>[mg m(^{-3})] 38</td>
</tr>
<tr>
<td>(C_xH_y)</td>
<td>[mg m(^{-3})] 2</td>
</tr>
<tr>
<td>Yearly emission of PCDD/F</td>
<td>[g I-TEQ yr(^{-1})] 0.18</td>
</tr>
</tbody>
</table>

\(^1\) Refers to dry flue gases under standard conditions
\(^2\) Refers to dry flue gases under standard conditions, converted to 11% \(O_2\)

5.6 Data from the Literature

The following dioxin concentrations were determined at three places in the flame of a flare for the incineration of biogas (Scheiner et al., 1992):
- top 0.0034 ng I-TEQ m\(^{-3}\)
- middle 0.013 ng I-TEQ m\(^{-3}\)
- bottom 0.014 ng I-TEQ m\(^{-3}\).
5.7 Evaluation

Incineration of landfill and biogas
From the results of Table 5.2, emission factors were calculated for the incineration of untreated landfill gas in a gas engine and a flare, i.e. 0.5 and 0.4 ng I-TEQ/m³ of landfill gas, respectively. As the emission factors are practically the same, one emission factor of 0.5 ng I-TEQ m⁻³ of landfill gas is taken for the incineration of untreated landfill gas.

No Dutch measurement data of the incineration of biogas are available. From data form the literature (see Chapter 5.6) it appears that the dioxin concentration in the flue gases of flares in which biogas is incinerated is in the same order of magnitude as in the incineration of landfill gas (see Table 5.2). Therefore, the same emission factor is used for the incineration of biogas as for landfill gas.

In the Netherlands, a total of 112 million m³ of landfill gas and biogas are incinerated each year without being treated (see Chapter 5.3). This brings about a dioxin emission of about 0.06 g I-TEQ per year.

Incineration of sewage sludge
From the data of Table 5.3, an average emission factor of about 5 µg I-TEQ tonnes of sludge was calculated for the incineration of sewage sludge. Annually (1991) 6,000 tonnes of sludge are being incinerated (see section 5.3), causing an annual dioxin emission of approximately 0.03 g I-TEQ.

It should be noted that as of January 1993 sludge will no longer be incinerated in one of the two installations for sewage sludge incineration. As of that date, about 5,000 tonnes of sludge will still be incinerated yearly. In the course of 1993 this will increase to 50,000 tonne yr⁻¹, when the installation at DRSH becomes operational.

Incineration of industrial sludge
The dioxin emission of the two most important plants for the incineration of industrial sludge is, in total, 0.205 g I-TEQ per year (see Tables 5.1 and 5.4). From the data stated in these two tables, an average emission factor of about 4 µg I-TEQ per tonne was calculated for sludge incineration. On the basis of this emission factor, the dioxin emission of the two small installations (throughput estimated at about 100 tonnes yr⁻¹) is only 0.0004 g I-TEQ yr⁻¹. The total dioxin emission as a result of industrial sludge incineration is 0.21 g I-TEQ yr⁻¹.

Dioxins in residues
Data of dioxins in cyclone ash, fabric filter ash and ESP ash are not available. In view of the dioxin emissions into the air, it is assumed that the dioxin concentrations are lower than those in the ESP ash of MSW incinerators. Data of dioxin emissions to water is not available. In view of the measured dioxin emissions into the air and of the process conditions, it is likely that the emission to water is no more than 0.1 ng I-TEQ yr⁻¹.

Dioxins in sludge
A total of 462,000 tonnes of sludge (including sewage and industrial sludge) are released in the Netherlands. A recent investigation shows that sewage sludge contains on average 26 µg I-TEQ tonnes of sludge (d.m.) (TAUW, in preparation). On the basis of this analysis result, a total of 12 g I-TEQ of dioxins are annually discharged with the sludge. In 1988 (Duvoort-van Engers, 1991), this quantity of sludge was used as follows: 22% agriculture, 14% compost/black earth, 55% dumping, 2.6% incineration and 6.6% various.
5.8 Summary

The dioxin emissions as a result of the incineration of landfill gas, biogas and sludge are summarized in Table 5.5.

Table 5.5 Dioxin emissions in the incineration of landfill gas, biogas and sludge (1991 situation)

<table>
<thead>
<tr>
<th>Kind of process</th>
<th>Quantity per year</th>
<th>Emission factor</th>
<th>PCDD/F emission</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>[g I-TEQ yr⁻¹]</td>
</tr>
<tr>
<td>Incineration of:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>untreated landfill gas</td>
<td>52 million m³</td>
<td>0.5 ng I-TEQ m⁻³</td>
<td>0.03</td>
</tr>
<tr>
<td>untreated biogas</td>
<td>60 million m³</td>
<td>0.5 ng I-TEQ m⁻³</td>
<td>0.03</td>
</tr>
<tr>
<td>sewage sludge ¹)</td>
<td>6,000 tonnes (d.m.)</td>
<td>5 µg I-TEQ t⁻¹</td>
<td>0.03</td>
</tr>
<tr>
<td>industrial sludge ¹)</td>
<td>53,000 tonnes (d.m.)</td>
<td>4 µg I-TEQ t⁻¹</td>
<td>0.21</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>0.30 ²)</td>
</tr>
</tbody>
</table>

¹) The Dutch sludge production was 282,000 tonnes of sewage sludge and 180,000 tonnes of industrial sludge; with this sludge, about 12 g I-TEQ of dioxins are discharged annually.

²) The dioxin emission of the sludge incineration furnace at GEVUDO in Dordrecht has been included in Chapter 3.

The emission to water as a result of the incineration of landfill gas, biogas and sludge is negligible. Insufficient data is available on the quantities bound to residues.

5.9 Future

With respect to the situation in the year 2000, it is estimated that a total of about 300,000 tonnes (d.m.) of purification sludge (including sewage and industrial sludge) will be incinerated per year (Nagelhout and Van Lohuizen, 1992). Assuming the above calculated emission factor of 5 µg I-TEQ per tonne of sludge (d.m.), this leads to an annual emission into the air of 1.5 g I-TEQ in the year 2000.
6. BURNING OF CABLES, ELECTROMOTORS, ETC.

6.1 General

This chapter will consider:
- the legal burning of cables;
- the illegal burning of cables;
- the burning of electromotors.

The burning of brake blocks (a process comparable to cable burning) will also be dealt with in this chapter. The cables that are legally burnt are the so-called greasy underground cables (armoured paper lead cables). Plastic-insulated cables are usually shredded. Illegal burning specifically involves cables from cars and from building and demolition waste.

6.2 Process Description

Burning of cables
Cable burning is the process in which copper and lead are recovered by burning the insulating material from 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).

The burning is done batchwise in simple furnaces. In the furnace, the possibly pre-shredded 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 off. After the process, the copper core and the steel strip (of cable armouring) are scooped from the furnace with the combustion residue. The gases arising from the burning are incinerated at temperatures of 800 °C or higher, and then emitted.

In the one, still operational, legal cable burner (see Chapter 6.3), the burning takes place in a furnace that is lined inside with firebrick. The flue gases are cleaned in a thermal after burner and a wet scrubber.

In the illegal burning of cables, there is usually no installation at issue. 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.

Burning of electromotors and the like
Processes related to cable burning are the burning of electromotor windings, the burning of coatings of instruments, the burning of 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. Particularly in the burning of electromotors, temperature control is important, as the motors should keep their original form. Therefore, the process control of electromotor burning is better monitored than that of cable burning.
6.3 Inventoried Processes

The annually released quantity of armoured paper lead cables is estimated to be 8,265 tonnes. This quantity is mainly discharged by the electricity supply companies, which account for 50% of it. In addition to the quantities that are annually released by the Dutch dischargers, a multiple of the above-mentioned quantity of cable residues is probably imported. Export of cable residues could also be an issue (Helm, 1992).

Legal cable burning
Currently, there is still one cable burner operating in the Netherlands. This is a relatively modern installation (see 6.2), compared with the closed installations at which measurements were taken outside MOB framework (see section 6.4). Several hundreds of tonnes of cables are processed yearly in this still operative installation. The combustion residue is transported to Belgium for further upgrading; the sludge of the wet scrubber is stored in casks in the meantime. The installation is operative about eight days a month. The company now has to submit a plan for emission reduction (from 1 January 1993) (Province of Gelderland, 1992a).

Illegal cable burning
On the basis of data obtained from provincial authorities in the provinces where most of the illegal cable burning is done, it is assumed that the quantity of cables being illegally burnt in the Netherlands is now about 3,000 tonnes per year (Province of Gelderland, 1992a; Province of North Brabant, 1993; Province of Limburg, 1992; Province of Overijssel, 1993). Probably few underground cables are burnt illegally, but the principal part of illegal burning involves small lots of cables originating from cars, and from building and demolition waste.

Burning of electromotors and the like
An inventory was made of two companies where electromotors are burnt. The installations of these companies can burn about 1,500 kg of material daily. Furthermore, one additional company inventoried burnt brake blocks (production loss) (Province of Gelderland, 1992b). The installation of this company is operative about one week every month. Data on quantities annually being processed in these three companies are not known.

6.4 Measurement Results Outside the MOB Framework

Outside the MOB framework, measurements were carried out at two cable burning companies; these companies have meanwhile been closed down. Furthermore, there are measurement results available of a TNO investigation into a plant for burning electromotors. The results of these measurements are shown in Table 6.1.
Table 6.1 Results of measurements at cable burners and at an installation for burning electromotors (confidential literature source)

<table>
<thead>
<tr>
<th>Type of company</th>
<th>PCDD/F concentration in flue gases [ng I-TEQ m⁻³]</th>
<th>PCDD/F emission [µg I-TEQ tonne⁻¹ input]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cable burner:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>underground cables</td>
<td>0.6 - 1.0</td>
<td>3.7 - 6.4</td>
</tr>
<tr>
<td>underground cables, cables containing PVC</td>
<td>1.9 - 3.2</td>
<td>7.4 - 14</td>
</tr>
<tr>
<td>Cable burner:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>stripped cable ²)</td>
<td>3.8</td>
<td>21</td>
</tr>
<tr>
<td>partly stripped cable ³)</td>
<td>254</td>
<td>2,280</td>
</tr>
<tr>
<td>Installation for burning electromotors</td>
<td>1.3</td>
<td>3.3</td>
</tr>
</tbody>
</table>

1) Refers to dry flue gases under standard conditions, converted to 11% O₂
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.

6.5 Data from the Literature

An investigation into the dioxin concentration of the soil was carried out at seven sites where the soil was suspected of being contaminated with dioxins (Liem et al., 1991). These suspicions were based on the illegal burning of cables and cars. Strongly increased dioxin concentrations were found. A total of 20 samples were analyzed. The dioxin concentrations in the soil ranged between 60 and 98,000 ng I-TEQ kg⁻¹ of dry matter.

6.6 Evaluation

Legal cable burning
The cable burners measured outside the MOB framework have all been closed down. The emission factors determined at these companies strongly vary from 4 to 2,280 µg I-TEQ tonne⁻¹ (see Table 6.1). The cable burner still operating has an installation that is relatively modern, compared with the closed plants. On the basis of the emission factors mentioned, however, it is not possible to give a correct estimate of the dioxin emission of this company, also in view of the fact that the quantity of cables being processed is not known either. It is expected that the emission factor of this company will not exceed several dozens of µg I-TEQ tonne⁻¹. Assuming an emission factor of 40 µg I-TEQ tonne⁻¹ and an (also assumed) processing of 500 tonnes per year, we calculated an emission of 0.02 g I-TEQ yr⁻¹.

Illegal cable burning
No emission factors are known for the illegal burning of cables. In view of the emission factors stated in Table 6.1, we estimated an emission factor of 500 µg I-TEQ tonne⁻¹ for illegal burning. At an (estimated) processing of 3,000 tonnes of cables per year (see Chapter 6.3), the annual dioxin emission is 1.5 g I-TEQ.
Burning of electromotors and the like
A value of 3.3 $\mu$g I-TEQ tonne$^{-1}$ of input is used as emission factor for burning electromotors (see Table 6.1). Assuming that $1,500 \text{ kg}$ are being processed daily in each installation for 250 days per year, the dioxin emission for the two installations will be about 0.0025 g I-TEQ per year.

The installation for burning brake blocks is identical to that for burning electromotors. Therefore, it is assumed (also considering the composition of the materials to be burnt) that the dioxin emission (per time unit) is of the same order as that of an installation for the burning of electromotors. The installation is operative for about 60 days per year (one week per month). Assuming that the daily waste throughput is identical to that of electromotors, the annual emission is less than 0.001 g I-TEQ. The annual dioxin emission for the installations involved will therefore be less than 0.0035 g I-TEQ.

Residues
Data on the quantities of residues that are released at the burning of cables and such like are not known. The majority of the residues is released in the illegal burning of cables. At the illegal burning sites, dioxin concentrations up to 98,000 ng I-TEQ/kg d.m. were found in soil material. Therefore, it is recommended to give first priority to measures in the area of maintenance, and, where necessary, decontamination of the soil.

### 6.7 Summary

Table 6.2 summarizes the estimated dioxin emissions into the air in the burning of cables, electromotors, etc. The emissions have been estimated on the basis of many assumptions. Further investigation is necessary for a more accurate estimate than the dioxin emissions mentioned here.

<table>
<thead>
<tr>
<th>Type of plant</th>
<th>Processed quantity [tonne yr$^{-1}$]</th>
<th>Emission factor $[\mu$g I-TEQ tonne$^{-1}$ of waste]</th>
<th>PCDD/F emission [g I-TEQ yr$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cable burning plants:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>legal</td>
<td>500</td>
<td>40 $^{1)}$</td>
<td>0.02 $^{1)}$</td>
</tr>
<tr>
<td>illegal</td>
<td>3,000</td>
<td>500 $^{1)}$</td>
<td>1.5 $^{1)}$</td>
</tr>
<tr>
<td>Installations for burning</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>electromotors and the like</td>
<td>about 800</td>
<td>3.3</td>
<td>&lt;0.0035</td>
</tr>
<tr>
<td>Total</td>
<td>about 4,300</td>
<td></td>
<td>1.5</td>
</tr>
</tbody>
</table>

$^{1)}$Indication; see section 6.5.

Insufficient information is available on quantities and concentrations in residues.
7. WASTE INCINERATION AT HOSPITALS

7.1 General

Hospital waste can be distinguished into "specific hospital waste" and "other hospital waste". Specific hospital waste includes human anatomic remains and organ parts, waste contaminated with bacteria, viruses and fungi, and larger quantities of blood. Specific hospital waste has been designated as hazardous waste in the Indication Decree on Hazardous Wastes (BACA), starting 1 March 1992. Other hospital waste includes non-contaminated waste that is similar to domestic waste.

Most of the specific hospital waste released in the Netherlands is incinerated on a large scale in a furnace for hazardous waste incineration, and in a special installation for hospital waste incineration. Other hospital waste is usually discharged as industrial waste.

A number of hospitals incinerate hospital waste in their own incinerators. This chapter will only discuss the emissions of these installations. It is based on a recently completed investigation into the dioxin emissions of hospital waste incinerators (Bremmer et al., in preparation). The emissions released at the above-mentioned large-scale installations have been included in Chapter 4 (Incineration of Hazardous Wastes).

7.2 Process Description

As a rule, the waste incinerators at hospitals consist of a pyrolysis furnace with an incineration chamber. In the pyrolysis furnace, the waste is degased and the remaining char is incinerated. Burn-out of the generated gases occurs in the after-burning chamber. In both parts of the process, the temperature is regulated by way of burners. The installations are operated batchwise. In general, there is no additional flue gas cleaning: energy recovery is usually not done.

The installations at the hospitals are operated only during the day. At start-up, the furnace is heated using the available support burners and, if required, the burning of domestic hospital waste. Every day, after the last charge of waste has been dosed, the furnaces are kept at temperature for another 1-2.5 hours using the burners. Subsequently, the furnace is cooled by leading ambient air through it for a number of hours.

7.3 Inventoried Processes

The dioxin emissions of four hospital waste incinerators, including the two largest installations, were established from November 1990 to May 1991 (Bremmer et al., in preparation). Following the results of that investigation, seven hospitals closed down their waste incinerators, including the installations at which measurements were conducted.

On 31 December 1991, 18 hospital waste incinerators were still operating. An annual total of 675 tonnes of hospital waste were incinerated there:
- Two hospitals incinerate a total of 650 tonnes per year of specific waste, combined with other hospital waste;
- Sixteen hospitals incinerate a total of 25 tonnes of specific hospital waste, with quantities varying per installation from 40 kg to 2.5 tonnes per year.
7.4 Measurement Results Outside the MOB Framework

As mentioned above, measurements into the dioxin emissions were conducted at the incinerators of four hospitals. The results of these investigations have been summarized in Table 7.1.

Table 7.1 Data and measurement results of hospital waste incinerators

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Installation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>7A</td>
</tr>
<tr>
<td>Number of furnaces</td>
<td>1</td>
</tr>
<tr>
<td>Operating hours per year</td>
<td>2,100</td>
</tr>
<tr>
<td>Incinerated waste (1)</td>
<td>[tonne yr(^{-1})]</td>
</tr>
<tr>
<td>Flue gas treatment</td>
<td>no</td>
</tr>
<tr>
<td>Energy recovery</td>
<td>yes</td>
</tr>
<tr>
<td>Flue gas flow (1)</td>
<td>(\text{[m}^3\ \text{h}^{-1}])</td>
</tr>
<tr>
<td>Flue gas temperature (1)</td>
<td>(^{\circ}\text{C})</td>
</tr>
<tr>
<td>(\text{O}_2)</td>
<td>(\text{[vol % dry]})</td>
</tr>
<tr>
<td>(\text{CO}_2)</td>
<td>(\text{[vol % dry]})</td>
</tr>
<tr>
<td>(\text{H}_2\text{O})</td>
<td></td>
</tr>
<tr>
<td>(\text{PCDD/F} 3)</td>
<td>(\text{[ng I-TEQ m}^{-3})</td>
</tr>
<tr>
<td>Cl(^{-})</td>
<td>(\text{[mg m}^{-3})</td>
</tr>
<tr>
<td>CO</td>
<td>(\text{[mg m}^{-3})</td>
</tr>
<tr>
<td>(\text{C}_x\text{H}_y)</td>
<td>(\text{[mg m}^{-3})</td>
</tr>
<tr>
<td>Yearly emission of (\text{PCDD/F})</td>
<td>(\text{[g I-TEQ yr}^{-1}]</td>
</tr>
</tbody>
</table>

\(^1\) Refers to dry flue gases under standard conditions  
\(^2\) Refers to dry flue gases under standard conditions, converted to 11\% \(\text{O}_2\)  
\(^3\) Averages of two measurements  
\(^4\) Situation August 1991

The emissions presented in Table 7.1 only refer to the periods during which waste was actually incinerated in the furnaces. During the intervening periods (i.e. during cooling), clearly increased emissions of CO and \(\text{C}_x\text{H}_y\) were sometimes measured. Therefore, it is to be expected that the PCDD/F emissions will also occur during these periods. The emissions of CO, \(\text{C}_x\text{H}_y\) and PCDD/F can therefore be considered to be (low) indications.

7.5 Evaluation

The investigation shows that the large installations (7B and 7D) emitted about 0.8 mg I-TEQ per tonne of waste. The two medium-sized installations (7A and 7C) emitted about 3 mg I-TEQ per tonne of waste.

No dioxin emissions from the small installations are known. Considering the composition of the waste (only specific hospital waste) and the process conditions at these installations, it is assumed
that the dioxin concentrations (and thus the emission factors) are higher than those at the installations (7A and 7C) where measurements were actually conducted.

The following emission factors were assumed to calculate the dioxin emission by the hospital waste incinerators in use (see section 7.3):
- 3 mg I-TEQ per tonne of waste for the two medium-sized installations (as determined at installations 7A and 7C);
- 5 mg I-TEQ per tonne of waste for the small installations (a somewhat higher factor than for installations 7A and 7C).

On the basis of these emission factors and the quantities of waste mentioned in section 7.3, the dioxin emission in the Netherlands as a result of waste incineration at hospitals amounts to 2.1 g I-TEQ per year for the situation on 31 December 1991.

### 7.6 Summary

Table 7.2 summarizes the data with respect to dioxin emissions by hospital waste incinerators.

<table>
<thead>
<tr>
<th>Installation</th>
<th>Quantity of waste</th>
<th>Emission factor</th>
<th>PCDD/F emission</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 installations of medium-size (10 - 500 tonnes of waste per year)</td>
<td>650</td>
<td>3 (^1) I-TEQ tonne(^{-1})</td>
<td>2 (^1) I-TEQ yr(^{-1})</td>
</tr>
<tr>
<td>16 installations of small (2 installations) (&lt; 2.5 tonnes of waste per year)</td>
<td>25</td>
<td>5</td>
<td>0.1</td>
</tr>
<tr>
<td>Total (18 installations)</td>
<td>675</td>
<td></td>
<td>2.1 (^1) I-TEQ yr(^{-1})</td>
</tr>
</tbody>
</table>

\(^1\) Low estimates (see section 7.4)

Data on the occurrence of dioxins in bottom ash are not known. Considering the process conditions and the extent to which dioxins occur in MSW incinerators (Chapter 3), it is assumed that only small quantities of dioxins occur in bottom ash.

### 7.7 Future

In January 1993, one medium-sized and several small hospital waste incinerators were still operating (VROM, 1993). This means an emission of approximately 1 g I-TEQ per year for the situation in January 1993. It is assumed that all installations that are still operating now will be closed in 2000. Therefore, the emission in 2000 is put at 0.
8. ASPHALT-MIXING INSTALLATIONS

8.1 General

Asphalt consists of a mixture of gravel or granite chippings, sand, filler and bitumen. The composition depends on the requirements set on the asphalt and although figures can vary substantially per case is roughly:

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>gravel or granite chippings</td>
<td>about 55%</td>
</tr>
<tr>
<td>sand</td>
<td>about 35%</td>
</tr>
<tr>
<td>filler</td>
<td>about 5%</td>
</tr>
<tr>
<td>bitumen</td>
<td>about 5%</td>
</tr>
</tbody>
</table>

In principle, old asphalt can be easily reused. After heating the old asphalt and mixing it with minerals and bitumen, it can be used again. Filler consists of pulverized limestone or a mixture of it with ESP ash of MSW incinerators or power plants, mineral stone powder and/or slaked lime.

8.2 Process Description

The components (see 8.1) are heated and mixed in order to compose the asphalt. This process takes place in asphalt-mixing installations. We can distinguish the following three types of asphalt-mixing installations:

- Batchwise mixing installation
  Here gravel, sand and filler are dried and heated in a direct-fired counterflow rotary drum. After the drum, the hot minerals (180-190 °C) are put in intermediate storage. The various components are subsequently mixed in the mixer with hot bitumen to obtain asphalt. This system has only restricted possibilities for processing old asphalt (maximum 10 - 20% of the installation’s capacity).

- Drum mixing installation
  In a drum mixing installation, gravel and sand are fed, close to the burner, into a directly fired parallel flow rotary drum, and subsequently dried and heated. At the end of the drum, filler and bitumen are added and mixed to obtain asphalt. With this system, a maximum of 50% asphalt can be processed by dosing it into the drum at a temperature of 300-400 °C. Research is being done on improving this system.

- Batchwise mixing installation with parallel system for recycling
  The batchwise mixing installation with parallel drum was introduced to be able to process more old asphalt. This system is increasingly being built these days. Old asphalt is heated in an individual recycling drum to about 150 °C with flue gases that have been mixed with ambient air to a temperature of 300-400 °C. Parallel to this recycling drum, the minerals (sand and gravel/granite chippings) are dried and heated in the "main drum" to a temperature of about 220 °C. The flue gases leaving the recycling drum are led along the main burner of the main drum for incineration. The old asphalt (from the recycling drum; about 180 °C), the minerals (from the main drum; about 220 °C) and new bitumen (from the hot storage tank; about 180 °C) are mixed in a mixer to obtain new asphalt. In principle, up to 100% old asphalt can be recycled with this system.
In approximately 80% of the asphalt-mixing installations, the flue gases are cleaned with fabric filters. In the other installations, wet dust arrestors are used. In the case of wet scrubbers, the water is discharged via a sedimentation basin.

8.3 Inventoried Processes

The companies associated with the trade association Vereniging tot Bevordering van Werken in Asfalt (Association to Promote Working in Asphalt) (VBW Asfalt) possess 72 asphalt-mixing installations. This figure concerns around 95% of the asphalt-mixing installations in the Netherlands. The installations of the companies associated with VBW Asfalt can be distinguished into:

- 56 batchwise mixing installations;
- 4 drum mixing installations;
- 12 batchwise mixing installations with parallel drum.

Of the companies that are not associated with VBW Asfalt, at least one has a batchwise mixing installation with parallel drum (VBW Asfalt, 1992).

Approximately 7.4 million tonnes of asphalt were produced in the Netherlands in 1991 (VBW Asfalt, 1992).

In asphalt-mixing installations, 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 installations also have provisions for lignite-firing.

8.4 MOB Measurement Results

Within MOB framework, measurements were conducted at an asphalt-mixing installation of the "batchwise mixing installation with parallel drum" type. The installation, first operating in 1991, can be fired with both oil and natural gas. The installation is equipped with a flue gas cleaning unit, consisting of cyclones and a fabric filter. The target recycling percentage is 50%. During the measurements, 46% old asphalt was reused. The filler used did not contain ESP ash from MSW incinerators.

Table 8.1 states the results of the measurements and the principal characteristics of the installation.
Table 8.1 Data and measurement results of the asphalt-mixing installation measured within the MOB framework

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Installation 8A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of installation</td>
<td>batchwise mixing with parallel drum</td>
</tr>
<tr>
<td></td>
<td>cyclone/fabric filter</td>
</tr>
<tr>
<td>Fuel during measurement</td>
<td>natural gas</td>
</tr>
<tr>
<td>Production per year [tonne]</td>
<td>150,000</td>
</tr>
<tr>
<td>Process Temperature of recycling drum [°C]</td>
<td>150</td>
</tr>
<tr>
<td>Process temperature of main drum [°C]</td>
<td>150 - 190</td>
</tr>
<tr>
<td>Flue gas flow in stack [m^3 h^-1]</td>
<td>40,400</td>
</tr>
<tr>
<td>Flue gas temperature [°C]</td>
<td>116</td>
</tr>
<tr>
<td>O_2 [vol % dry]</td>
<td>16.8</td>
</tr>
<tr>
<td>CO_2 [vol % dry]</td>
<td>2.8</td>
</tr>
<tr>
<td>H_2O [g m^-3]</td>
<td>151</td>
</tr>
<tr>
<td>PCDD/F [ng I-TEQ m^-3]</td>
<td>0.45</td>
</tr>
<tr>
<td>Cl^- [mg m^-3]</td>
<td>21</td>
</tr>
<tr>
<td>CO [mg m^-3]</td>
<td>817</td>
</tr>
<tr>
<td>C_x H_y [mg m^-3]</td>
<td>46</td>
</tr>
<tr>
<td>Yearly PCDD/F emission [g I-TEQ yr^-1]</td>
<td>0.007</td>
</tr>
</tbody>
</table>

1) Refers to dry flue gases under standard conditions
2) Refers to dry flue gases under standard conditions, converted to 11% O_2

8.5 Evaluation

Of the asphalt raw materials it is particularly the bitumen that contains organic compounds from which, with chlorine, dioxins can be formed. At the recycling of old asphalt, the organic substances will generally remain longer in the temperature range between 200 and 400 °C, causing a possibly higher emission of dioxins than in the production of new asphalt.

From the data in Table 8.1, we can calculate that the dioxin emission of the batchwise mixing installation with parallel drum was 47 ng I-TEQ per tonne of asphalt. Starting from this determination and an asphalt production of 7.4 million tonnes in the Netherlands in 1991, we calculated that the dioxin emissions into the air caused by asphalt-mixing installations in 1991 were about 0.3 g I-TEQ per year. The estimate obtained in this way may be fairly high, considering the fact that this estimate is based on a measurement at an installation that recycles old asphalt (see above).

Besides, the calculated estimate concerns natural gas-fired asphalt-mixing installations (see Table 8.1). Additional emissions that occur as a result of oil or lignite being used as fuel will be included in the Chapters 9 and 10.
No data is available on the quantities and the dioxin concentrations in fabric filter ash and sludge. In view of the dioxin emissions into the air and because the wet scrubbers are equipped with a sedimentation basin (the dioxins remain behind in the sludge), it is assumed that the dioxin emission to water is, in any case, less than 0.1 g I-TEQ per year.

8.6 Summary

Table 8.2 summarizes the estimated dioxin emissions of asphalt-mixing installations.

Table 8.2 Data of dioxin emissions from asphalt-mixing installations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Asphalt-mixing installations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of asphalt-mixing installations</td>
<td>about 75</td>
</tr>
<tr>
<td>PCDD/F emission per tonne of asphalt</td>
<td>[ng I-TEQ tonne(^{-1})] 47 2(^{2})</td>
</tr>
<tr>
<td>Asphalt production in 1991</td>
<td>[tonne yr(^{-1})] 7.4*10^6</td>
</tr>
<tr>
<td>PCDD/F emission per year (1991)</td>
<td>[g I-TEQ yr(^{-1})] 0.3 2(^{2})</td>
</tr>
</tbody>
</table>

1\(^{1}\) The dioxin emissions as a result of the firing of oil or lignite have not been included; see Chapter 9 or 10 for these emissions.

2\(^{2}\) As the estimate is based on measurement at a installation that recycles old asphalt, it is a fairly high one.

The quantity of discharged dioxins that are bound to residues is not known. The dioxin emission to water is less than 0.1 g I-TEQ per year.
9. OIL COMBUSTION

9.1 General

Various kinds of oil can be distinguished. Oils are used not only as fuel, but also for lubrication, cooling, indirect heating and hydraulics. The oil degrades and/or becomes dirty in the last few applications so it must be replaced. The oil used is denoted as "spent oil". A part of this spent oil can be used as a fuel. Particularly as a result of the pollutants that occur in the oil, dioxins can be formed in that use.

The oil which is produced to be used as a fuel will be denoted further in this chapter as "non-polluted oil". At first it was assumed that no dioxins (or only negligible quantities of dioxins) were emitted during the combustion (in e.g. power stations) of non-polluted oil (with low chlorine concentrations). Within the framework of the MOB investigation, therefore, measurements were only conducted at installations that burn spent oil.

In road traffic, however, dioxin emissions from the use of non-polluted oil have been observed. When emission measurements were conducted on a ship, it showed that dioxins were also present in its exhaust gases (this ship used gas oil with a non-demonstrable chlorine concentration as fuel).

Therefore, this chapter will not only go into the combustion of spent oil, but also of non-polluted oil, as well as of petroleum products in refineries. The processes considered involve combustion installations both on land and in shipping. The emissions as a result of road traffic will be treated in Chapter 15.

9.2 Process Description

In the combustion of oil, a rough distinction can be made between 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 in Chapter 15).

To generate heat/steam, oil is burned in various types of burners. They can be distinguished roughly into "evaporating burners" and "atomizing burners". Evaporation takes place in evaporating burners on a flat dish into which the oil to be burnt is dosed. The evaporated oil incinerates above the dish. These burners are available only in small capacities (< 50-100 kW thermal) and occur exclusively in stoves. In atomizing burners, the oil is sprayed into the furnace via an atomizer. Atomization can be reached by pressing the oil under high pressure (20-40 bar) through small holes (pressure jet atomizers) or by using devices (such as air atomizers and steam atomizers). These burners are available within a large range of capacities. Because of the centrifugal force in rotary cup burners, the oil is atomized via a quickly rotating head. The advantage of this technique is the insensitivity for clogging. The latter burners usually have larger capacities (> 500 kW thermal).

In generating heat/steam, flue gas cleaning (dust arrestors) is used only if the process that uses the generated heat/steam makes this necessary, as is the case in asphalt mixing installations, 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 ocean-going vessels. These applications have no flue gas cleaning.
9.3 Inventoried Processes

9.3.1 Spent oil

In 1988, about 100,000 tonnes of spent oil were released (Nieuwenhuis et al., 1990). The way in which this quantity was processed is shown in Table 9.1.

Table 9.1 Removal of spent oil (1988)

<table>
<thead>
<tr>
<th>Removal</th>
<th>Quantity [tonne]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Collection via licensees and processing</td>
<td>about 53,000</td>
</tr>
<tr>
<td>substitute fuel</td>
<td></td>
</tr>
<tr>
<td>Collection as (small) hazardous waste</td>
<td>about 15,000</td>
</tr>
<tr>
<td>Incineration without reprocessing</td>
<td>about 10,000</td>
</tr>
<tr>
<td>Illegal marketing</td>
<td>about 10,000</td>
</tr>
<tr>
<td>Discharge</td>
<td>about 12,000</td>
</tr>
</tbody>
</table>

For the year 1991, the following provides information on the incineration of spent oil:

- The quantity of spent oil that was collected and processed (i.e. partly cleaned through centrifugation) into substitute fuel, was about 61,000 m³ (VROM, 1992a), or about 55,000 tonnes. Approximately 11,000 tonnes of this was used as fuel on land by service stations, market gardeners, asphalt mixing installations, brickyards, dry cleaners, and machine works (VROM, 1992b). The remaining 44,000 tonnes were mixed ("blended") with heavy fuel oil (about 2%) to be applied in shipping (specifically ocean-going shipping).
- In 1988, about 10,000 tonnes of unprocessed spent oil were legally incinerated (see Table 9.1). A rough inventory made within the framework of this project showed that many companies have meanwhile stopped the incineration of this oil. The 1991 consumption is estimated to be roughly 3,000 tonnes. The illegally incinerated quantity is equated with that of 1988, i.e. 10,000 tonnes. The total quantity of unprocessed spent oil that was incinerated in 1991 (both illegally, see Table 9.1, and legally) is therefore estimated to be 13,000 tonnes.

The chlorine concentration of both processed and unprocessed spent oil is mainly between 100 and 200 mg kg⁻¹ (VROM, 1992b).

The 1990 fuel consumption (fuel oil and gas oil) of inland shipping is estimated to be 30,400 tonnes per year (Van Uffelen et al., 1990).
9.3.2 Non-polluted oil

The following information was obtained on the use of non-polluted oil:
- The quantity of non-polluted oil that is used in small-sized installations (in industry, greenhouses, construction and for domestic use) was 560,000 tonnes in 1990 (calculated from: CBS, 1991).
- The 1990 oil consumption in large-sized installations (electricity and heat-producing installations) was 42,000 tonnes of heavy fuel oil and 6,300 tonnes of gas/diesel/fuel oil (CBS, 1991).
- The 1988 consumption of gas oil by inland navigation vessels in the Netherlands was 531,000 tonnes (CBS, 1991).
- The 1990 consumption of petroleum raw materials and petroleum products for energy generation in refineries was 3.53 million tonnes (CBS, 1991).

9.4 MOB Measurement Results

Within the MOB framework, measurements were conducted at the following three incinerators fired with spent oil:
- a garage stove;
- a hot-water boiler;
- a steam boiler.

The garage stove was fired with unprocessed spent oil (lubricating oil from diesel engines). The heat was used to heat the working accommodation.

The hot-water boiler was fired with the organic fraction (chlorine- and sulphur-poor) that is separated from the rinse water; this rinse water originates in the cleaning of oil tanks and tankers. The boiler installation is used to warm up a water supply (to about 90 °C) using thermal oil as transfer medium.

The steam boiler was fired with processed spent oil. The steam is used in a production process for making conserves, for example.

Table 9.1 presents the results of the measurements and the principal characteristics of the installations. The results show that all three installations were well tuned up during the measurements (low CO and C\textsubscript{x}H\textsubscript{y} concentrations of the flue gases).
Table 9.2 Data and measurement results of the combustion of spent oil measured within the MOB framework

<table>
<thead>
<tr>
<th>Parameter</th>
<th>9A</th>
<th>Installations</th>
<th>9B 3)</th>
<th>9C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of burner</td>
<td>atomizer</td>
<td>rotary cup burner</td>
<td>rotary cup burner</td>
<td></td>
</tr>
<tr>
<td>Flue gas cleaning</td>
<td>none</td>
<td>none</td>
<td>none</td>
<td></td>
</tr>
<tr>
<td>Origin of oil</td>
<td>diesel engines</td>
<td>org. phases of</td>
<td>processed by collector</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(lubricating oil)</td>
<td>rinse water of tank cleaning</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fuel consumption</td>
<td>9,060 kg yr⁻¹</td>
<td>460 m³ yr⁻¹</td>
<td>350 tonnes yr⁻¹</td>
<td></td>
</tr>
<tr>
<td>Working hours per year</td>
<td>460</td>
<td>not known</td>
<td>2,000</td>
<td></td>
</tr>
<tr>
<td>Flue gas flow</td>
<td>[m³ h⁻¹] ¹)</td>
<td>275</td>
<td>6,300</td>
<td>2,100</td>
</tr>
<tr>
<td>Flue gas temperature</td>
<td>[°C]</td>
<td>373</td>
<td>308</td>
<td>303</td>
</tr>
<tr>
<td>O₂</td>
<td>[vol % dry]</td>
<td>4.8</td>
<td>10.5</td>
<td>3.1</td>
</tr>
<tr>
<td>C₂O₂</td>
<td>[vol % dry]</td>
<td>11.8</td>
<td>8.1</td>
<td>13.0</td>
</tr>
<tr>
<td>H₂O</td>
<td>[g m⁻³] ¹)</td>
<td>83</td>
<td>72</td>
<td>118</td>
</tr>
<tr>
<td>PCDD/F</td>
<td>[ng l-TEQ m⁻³]</td>
<td>0.1</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>²)</td>
<td>1.5</td>
<td>14</td>
<td>9</td>
</tr>
<tr>
<td>CO</td>
<td>[mg m⁻³] ²)</td>
<td>8.3</td>
<td>8.1</td>
<td>8</td>
</tr>
<tr>
<td>CₓHᵧ</td>
<td>[mg m⁻³] ²)</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Yearly PCDD/F emission</td>
<td>[g l-TEQ yr⁻¹]</td>
<td>0.00002</td>
<td>0.002</td>
<td>0.002</td>
</tr>
</tbody>
</table>

¹) Refers to dry flue gases under standard conditions
²) Refers to dry flue gases under standard conditions, converted to 11% O₂
³) Data referred to one of the two boilers

9.5 Measurement Results Outside the MOB Framework

The Insurance Company of Lloyds Register commissioned an investigation into the composition of the exhaust gases of ships. As part of this investigation, TNO measured the concentration of organic micropollutants in these exhaust gases (such as PAHs, nitro-PAHs, PCBs, HCBs and dioxins), with additional funds from the Ministries of Transport and Public Works (V&W), and of Housing, Physical Planning and Environment (VROM). The total organic chlorine concentration (TOCl) in the fuel was also determined.

The above-mentioned measurements were conducted in duplicate on a ferry sailing between Hull and Europoort, on a Rhine barge, and on a container ship (Compaan et al., 1992, Danton and Reynolds, 1991a and 1991b). The most significant results for dioxins are summarized in Table 9.3.
Table 9.3 Concentrations of organic chlorine in fuel and dioxin concentration in the exhaust gases of ship engines

<table>
<thead>
<tr>
<th>Type of ship</th>
<th>Fuel</th>
<th>TOCl concentration in fuel [mg kg⁻¹]</th>
<th>PCDD/F concentration in flue gases [ng I-TEQ m⁻³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferry</td>
<td>heavy fuel oil</td>
<td>11</td>
<td>0.1 and 0.2</td>
</tr>
<tr>
<td>Container ship</td>
<td>gas oil</td>
<td>1.2</td>
<td>0.002 and 0.2</td>
</tr>
<tr>
<td>Rhine barge</td>
<td>gas oil</td>
<td>&lt; 2</td>
<td>0.012 and 0.04</td>
</tr>
</tbody>
</table>

1) Under operational conditions at 300 Kelvin (ferry 14.7%O₂, Rhine barge 13% O₂, container ship not known)

9.6 Data from the Literature

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

In the former Federal Republic of Germany, dioxin concentrations were determined in the 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 in the oil-fired ones (Thoma, 1988).

In 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 ind. for the individual congeners).

9.7 Evaluation

9.7.1 Spent oil

Table 9.4 states the type of spent oil, the calculated total chlorine concentration in the oil, and the dioxin emission via the flue gases for the installations measured within the MOB framework.

Table 9.4 Total chlorine concentration of the fuel and dioxin emission from the installations measured within the MOB framework

<table>
<thead>
<tr>
<th>Process</th>
<th>Fuel</th>
<th>Total chlorine concentration of fuel [mg kg⁻¹]</th>
<th>Emission factor [µg I-TEQ per tonne of fuel]</th>
</tr>
</thead>
<tbody>
<tr>
<td>9A</td>
<td>unprocessed spent oil</td>
<td>about 35</td>
<td>2</td>
</tr>
<tr>
<td>9B</td>
<td>solvents and oil</td>
<td>about 340</td>
<td>4.8</td>
</tr>
<tr>
<td>9C</td>
<td>processed spent oil</td>
<td>about 240</td>
<td>6.0</td>
</tr>
</tbody>
</table>

1) Calculated from the chlorine concentration of the flue gases and the process parameters

2) Is equated here with spent oil
It is not possible to derive from Table 9.4 a relation between the chlorine concentration of the fuel and the emission factor for dioxins. In this respect it should be stated that the processing of spent oil only involves the removal of solids, and not the removal of chlorine-containing components. On the basis of Table 9.4, a value of 4 $\mu$g I-TEQ per tonne of oil is set as an average emission factor for the combustion of spent oil on land. In section 9.3.1, the total quantity of spent oil incinerated in 1991 was estimated to be 24,000 tonnes per year (11,000 tonnes processed, 13,000 tonnes unprocessed). From this data, an annual dioxin emission of 0.1 g I-TEQ follows for this application.

From the dioxin emissions measured on a ferry (fired with possibly blended heavy fuel oil; see Table 9.3), an emission factor of 3.2-6.5 $\mu$g I-TEQ per tonne of fuel can be calculated for this type of sources. In this we use a flue gas quantity of 10-12 m$^3$ (ind., at 0% O$_2$) per kg of oil, and the measured oxygen concentration. At the gas oil-fired container ship, one time an emission factor of the same order of magnitude as for heavy oil was determined, and another time it was a factor of 100 lower. On the basis of the above factors, an average emission factor of 4 $\mu$g I-TEQ per tonne of fuel can be taken for ocean-going vessels in port. This factor is in the same order of magnitude as that of spent oil. This data combined with the fuel consumption of ocean-going vessels in port (30,400 tonnes per year) produces an emission for this category of sources of 0.1 g I-TEQ per year.

9.7.2 Non-polluted oil

In the emissions of the ships that use gas oil as fuel, dioxin concentrations between 0.002 and 0.2 ng I-TEQ m$^{-3}$ were measured (see 9.5, Table 9.3). A cause for this large difference cannot be given with the available information. From the measurement results in Table 9.3 an average emission factor for inland navigation of 1 $\mu$g I-TEQ per tonne of fuel can be estimated. When we put the 1991 gas oil used by inland navigation at the same level as the 1988 consumption (531,000 tonnes, see 9.3.2), a dioxin emission from these sources of about 0.5 g I-TEQ per year follows.

Hardly anything is known of the emissions as a result of the combustion of non-polluted oil in relatively small-scale installations. An emission factor of maximally 0.5 $\mu$g I-TEQ per tonne is estimated here, on the basis of the following considerations:

- The emission factor for small-scale industrial coal-fired installations is about 4.2 $\mu$g I-TEQ per tonne of fuel (see Chapter 10.5). Five times as many dioxins were found in the soot of coal-fired installations as in the soot of oil-fired installations (Thoma, 1988).
- The emission factor of gas oil combustion in shipping is about 1 $\mu$g I-TEQ per tonne of fuel (see above).
- The emission factor of diesel engines in traffic is about 0.03 $\mu$g I-TEQ per tonne of fuel (see Chapter 15).

Starting from the estimated emission factor of 0.5 $\mu$g I-TEQ per tonne of fuel and a total oil consumption of 560,000 tonnes in 1990, a dioxin emission of maximally 0.3 I-TEQ per year was calculated for these small-scale installations.

The total oil consumption in large-scale installations was about 48,000 tonnes per year. According to the literature (see 9.6), no detectable quantities of dioxins were measured at these sources. A very rough calculation shows that the annual emission from these sources is less than 0.001 g I-TEQ. No data is known of the dioxin emissions at refineries. It is assumed that, just as with the above-mentioned large-scale installations, no detectable quantities of dioxins will be found either in the heat generation at refineries. At a total consumption of 3.51 million tonnes per year, this means (very roughly converted) an annual dioxin emission of less than 0.004 g I-TEQ.
9.8 Summary

The data for the dioxin emissions from the combustion of oil have been summarized in Table 9.5.

Table 9.5 Data of dioxin emissions for oil combustion (1991)

<table>
<thead>
<tr>
<th>Emission source</th>
<th>Fuel</th>
<th>Consumption [tonne yr(^{-1})]</th>
<th>Emission factor [(\mu g) I-TEQ tonne(^{-1})]</th>
<th>PCDD/F emission [g I-TEQ yr(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Installations on land</td>
<td>spent oil</td>
<td>24,000</td>
<td>4</td>
<td>0.1</td>
</tr>
<tr>
<td>Ocean-going vessels</td>
<td>heavy fuel oil(^1)</td>
<td>30,400</td>
<td>4</td>
<td>0.1</td>
</tr>
<tr>
<td>(in port)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inland navigation</td>
<td>gas oil</td>
<td>531,000</td>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>Installations on land:</td>
<td>non-polluted oil</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Small-scale</td>
<td></td>
<td>560,000</td>
<td>0.5</td>
<td>0.3</td>
</tr>
<tr>
<td>Large-scale</td>
<td></td>
<td>48,000</td>
<td>&lt; 0.001(^2)</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>Refineries</td>
<td></td>
<td>3.51*10(^6)</td>
<td>&lt; 0.001(^2)</td>
<td>&lt; 0.004</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>1,193,000</td>
<td></td>
<td>1.0</td>
</tr>
</tbody>
</table>

\(^1\) If necessary, blended with spent oil
\(^2\) Indicative

9.9 Emission on the North Sea

Although the dioxin emissions on the North Sea are not part of the Dutch emissions, they are briefly mentioned here as part of the emitted emissions will be deposited in the Netherlands.

The data on oil consumption in the North Sea show strong variations. Bremmes and Melhus (1990) estimate that 1.56*10\(^6\) tonnes per year of heavy fuel oil and 0.49*10\(^6\) tonnes per year of gas oil are used. The "Dienst Getijdewateren" (Tidal Waters Division) (1992) estimates the total oil consumption on the North Sea to be 3.5-6.5*10\(^6\) tonnes per year. Starting from the above-mentioned data, the dioxin emission on the North Sea will at least be smaller than 40 g I-TEQ per year (worst case). A more realistic estimate appears to be a dioxin emission of 15 g I-TEQ per year, which starts from an emission factor of 4 \(\mu g\) I-TEQ per tonne of fuel and a total fuel consumption on the North Sea of 4*10\(^6\) tonnes per year.

Considering the small number of measurements and the differences between the measurements (see Table 9.3), these figures should be seen as orders of magnitude.
10. COMBUSTION OF COAL AND LIGNITE

10.1 Process Description

The combustion of coal is mainly applied in power plants. Coal is also burned, to a limited extent, in a number of grass drying plants, cement kilns, and industrial steam boilers. The most significant combustion methods are pulverized-coal combustion (power plants, cement kilns, steam boilers) and chain grate stoker combustion (steam boilers, grass drying plants). Combustion of lignite takes place on a limited scale in the Netherlands (see section 10.2), and virtually exclusively in pulverized-coal burners.

Pulverized-coal burners
In order to be burned in pulverized-coal burners, the coal is first pulverized and, if required, dried. The pulverized coal, together with part of the combustion air, is blown into the furnace via injection burners. De-aeration, ignition, and combustion take place while suspended. The combustion time of the particles is short and comparable to that of oil-fired and gas-fired installations. In water-tube boilers, the energy is converted into steam (in power plants about 540 °C, 185 bar; in industrial steam boilers often at lower conditions) or used for direct drying or heating. The flue gases always receive additional treatment in a dust arrestor (e.g. an electrostatic precipitator) and, if required, in a flue gas desulphurization unit.

Chain grate stokers
Chain grate stokers are mainly applied in grass drying plants. With a constant layer thickness, coal (e.g. nuts # 5) is dumped from a silo onto the grate. The grate (a conveyor belt) moves the coal slowly through the furnace. Primary air is blown through the grate, with secondary air above it. At the end of the grate, the combustion residue falls into a slag silo. The boiler capacity is controlled by way of the fuel and air supplies. The flue gases are led into a rotary drier into which the grass is dosed. After drying, the grass is led to the product cyclone where the dried product is separated. The flue gases are subsequently emitted without further additional cleaning.

Ways of combustion other than the above-mentioned ones (such as the screw conveyor stoker@, the fluid bed furnace and the grate furnace) hardly ever occur in the Netherlands. These processes will therefore not be further described here.

10.2 Inventoried Processes

Coal
Table 10.1 summarizes the use of coal in the Netherlands. The data is based on CBS statements in PJ (CBS, 1991) and a conversion factor of 27 MJ kg⁻¹ of coal (KEMA, 1992).

In the Netherlands, there are five coal-fired power plants. In 1991, 7.67 million tonnes of coal (compared to 8.63 million tonnes in 1990) were burned by these installations and by heat and power generation in industry (SEP/VEEN, 1992).
Table 10.1 Consumption of coal in the Netherlands (1990)

<table>
<thead>
<tr>
<th>Kind of application</th>
<th>Consumption [10^6 tonne]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Public and company power plants</td>
<td>8.63</td>
</tr>
<tr>
<td>Industrial and domestic use for energetic purposes, excluding the base metal industry 2)</td>
<td>0.55</td>
</tr>
<tr>
<td>Coke production 1)</td>
<td>4.09</td>
</tr>
<tr>
<td>Base metal industry 1)</td>
<td>0.72</td>
</tr>
<tr>
<td><strong>Total (1990)</strong></td>
<td><strong>13.99</strong></td>
</tr>
</tbody>
</table>

1) Will be discussed in Chapter 17: Metal Industry

2) Includes industries such as grass drying plants, market gardening, and a shell lime-combustion plant.

Lignite
Lignite is used as fuel in, for example, about six asphalt mixing plants, a manure drying plant, and a cement factory. The quantity of lignite that is annually consumed in the Netherlands is probably in the order of magnitude of 0.05 million tonnes.

10.3 MOB Measurement Results

Within the MOB framework, measurements were conducted at two coal-fired plants. Selected were a large-scale power plant for the production of electricity and a grass drying plant, representative of a small-scale combustion installation.

In the power plant, two pulverized coal-fired production units for electricity with a net electric potential of 2 x 518 MW are set up. The flue gases are led to two stacks via four ducts (two per production unit). Each of these ducts is equipped with an electrostatic precipitator, followed by a desulphurization unit (wet scrubber). The measurements were conducted in one of the four ducts, after the wet scrubber and before the stack. In interpreting the measurement data, one should note that these are the result of a measurement in one duct.

The grass drying plant operates a coal-fired combustion unit of the 'chain grate stoker' type. The combustion unit supplies the heat for two rotary driers in which the grass is dried. To this end, the product to be processed is brought into direct contact with the flue gases. Behind the rotary drier, the dried product is separated from the flue gases in a cyclone for coarse products, followed by a multi-cyclone. The flue gases are emitted without further additional cleaning. The measurements were conducted in the horizontal duct after the multi-cyclone and before the stack.

Table 10.2 presents the results of the measurements and the principal characteristics of the plants. In the calculated total annual emission of the power plant, one may assume that the production unit in which no measurements were conducted has the same emission of PCDD/F as the measured unit.
### Table 10.2 Data and measurement results of coal combustion measured within MOB framework

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Plant</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10A 4)</td>
<td>10B 4)</td>
<td></td>
</tr>
<tr>
<td>Type of combustion</td>
<td>pulverized coal</td>
<td>chain grate</td>
<td></td>
</tr>
<tr>
<td>Flue gas treatment</td>
<td>ESP, flue gas</td>
<td>cyclones for</td>
<td></td>
</tr>
<tr>
<td></td>
<td>desulphurization</td>
<td>products</td>
<td></td>
</tr>
<tr>
<td>Operating hours per year 3)</td>
<td>7,700</td>
<td>3,900</td>
<td></td>
</tr>
<tr>
<td>Coal consumption per year</td>
<td>[tonne]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1,330,000</td>
<td>8,100</td>
<td></td>
</tr>
<tr>
<td>Flue gas flow</td>
<td>[m³/h] 1)</td>
<td>1,730,400</td>
<td>50,400</td>
</tr>
<tr>
<td>Flue gas temperature</td>
<td>[°C]</td>
<td>94</td>
<td>116</td>
</tr>
<tr>
<td>O₂</td>
<td>[vol % dry]</td>
<td>5.5</td>
<td>15.4</td>
</tr>
<tr>
<td>CO₂</td>
<td>[vol % dry]</td>
<td>13.2</td>
<td>4.7</td>
</tr>
<tr>
<td>H₂O</td>
<td>[g m⁻³] 1)</td>
<td>88</td>
<td>365</td>
</tr>
<tr>
<td>PCDD/F</td>
<td>[ng I-TEQ m⁻³] 2)</td>
<td>0.02</td>
<td>0.16</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>[mg m⁻³] 2)</td>
<td>2.9</td>
<td>1.9</td>
</tr>
<tr>
<td>CO</td>
<td>[mg m⁻³] 2)</td>
<td>28</td>
<td>859</td>
</tr>
<tr>
<td>CₓHᵧ</td>
<td>[mg m⁻³] 2)</td>
<td>&lt;5</td>
<td>113</td>
</tr>
<tr>
<td>Yearly emission of PCDD/F</td>
<td>[g I-TEQ yr⁻¹]</td>
<td>0.46</td>
<td>0.01</td>
</tr>
</tbody>
</table>

1) Refers to dry flue gases under standard conditions  
2) Refers to dry flue gases under standard conditions, converted to 11% O₂  
3) Company statement  
4) Data referred to one of the two production units  
5) The not rounded off annual emission of 0.013 g I-TEQ is used to calculate the emission factor.

### 10.4 Data from the Literature

**Power plants**  
In Germany (Hagenmaier and Beising, 1989), no dioxins were shown in the flue gases (< 0.001 ng m⁻³ (ind.) for individual congeners) of three coal-fired power plants (6 measurements) and at one lignite-fired power plant (2 measurements). More recently, Hagenmaier (1991) stated that measurements showed that the dioxin emission at coal-fired power plants is in the order of 0.01 ng TEQ m⁻³ (TEQ in accordance to BGA). Nielsen and Blinksbjerg (1989) found no dioxins (<0.031 ng TEQ m⁻³, TEQ in accordance to Edon) in a coal-fired power plant (80 MW). The dioxin emission by coal-fired power plants in the United Kingdom is estimated to be 1.3 kg yr⁻¹ (sum PCDD/F).

**Industry and private households**  
The dioxin emission from coal-firing in private households and industry is estimated to be 5.1 and 7.7 kg yr⁻¹ (sum PCDD/F), respectively (Harrad et al., 1992).
10.5 Evaluation

The dioxin emission of the power plant measured within MOB framework was 0.35 µg I-TEQ per tonne of coal. The dioxin emission of the measured grass drying plant was 1.6 µg I-TEQ per tonne of coal.

From German data from the literature (Hagenmaier, 1991), an emission of approximately 0.1 µg I-TEQ tonne per year of coal is estimated for coal-fired power plants (assumptions: 10 m³ flue gas per kg of coal, 1 TEQ in accordance with BGA = 1 I-TEQ).

Conversion of the English emission data produces the following emission factors in µg I-TEQ tonne per year of coal:
- power plants 0.16 µg I-TEQ tonne⁻¹;
- heat and power generation in industry 4.2 µg I-TEQ tonne⁻¹;
- private households 9.6 µg I-TEQ tonne⁻¹.

Here, use was made of the published data on the annual coal consumption in England (power plants 80*10⁶ tonnes, industry 12*10⁶ tonnes, households 8*10⁶ tonnes; Department of Environment, 1989). To convert total PCDD/F into I-TEQ, a conversion factor of 0.01 was applied.

The emission factors determined within the MOB framework are of the same order of magnitude as the factors that were calculated from the data from the literature. The emission factors for domestic use of coal are probably higher (see above) than the emission factors obtained in the MOB measurements. Domestic use of coal, however, hardly occurs any more in the Netherlands (4% of use stated in Table 10.1; CBS, 1991). Therefore, the following emission factors obtained within the MOB framework are used to estimate the emissions in the Netherlands:
- Public and company power plants 0.35 µg I-TEQ tonne per year of coal;
- Industrial and domestic use for energetic purposes (excluding base metal) 1.6 µg I-TEQ tonne per year of coal.
It is further assumed that the emission factor for lignite-firing is also 1.6 µg I-TEQ/tonne.

On the basis of these emission factors and the coal consumption as stated in section 10.2, the following dioxin emissions were calculated:
- Public and company power plants 2.7 g I-TEQ yr⁻¹;
- Industrial and domestic use for energetic purposes (excluding base metal) 0.9 g I-TEQ yr⁻¹;
- Combustion of lignite 0.1 g I-TEQ yr⁻¹.

Considering the dioxin concentrations in the emissions into the air, it is assumed that only very small quantities of dioxin will occur in ESP ash.
10.6 Summary

Table 10.3 summarizes the various data on the dioxin emissions as a result of the combustion of coal and lignite.

Table 10.3 Data of dioxin emissions in the combustion of coal and lignite (1991) \(^1\)

<table>
<thead>
<tr>
<th>Application</th>
<th>Coal consumption ([10^6 \text{ tonne yr}^{-1}])</th>
<th>Emission factor ([\mu \text{g I-TEQ tonne}^{-1}])</th>
<th>PCDD/F emission ([\text{g I-TEQ yr}^{-1}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Public and company power plants</td>
<td>7.67</td>
<td>0.35</td>
<td>2.7</td>
</tr>
<tr>
<td>Industrial and domestic use for energetic purposes</td>
<td>0.55 (^2)</td>
<td>1.6</td>
<td>0.9</td>
</tr>
<tr>
<td>Lignite combustion</td>
<td>0.05</td>
<td>1.6</td>
<td>0.1</td>
</tr>
<tr>
<td>Total emission per year (1991)</td>
<td></td>
<td></td>
<td>3.7</td>
</tr>
</tbody>
</table>

\(^1\) The emissions connected to the use of coal in blast furnaces and coke factories are included in Chapter 17.
\(^2\) The 1991 coal consumption for this application was equated with the 1990 consumption.

The quantity of dioxins that is discharged with residues is small (i.e. < 0.1 g I-TEQ yr\(^{-1}\)), just like the emission to water.
11. WOOD COMBUSTION

11.1 General

In wood combustion, one can distinguish between domestic combustion and industrial combustion. These two subjects are individually discussed below.

11.2 Process Description

11.2.1 Domestic combustion

Equipment for combustion wood on a domestic scale (< about 20 kW thermal) can be classified into fireplaces (or open hearths), built-in stoves and individual, metal wood-burning stoves (tile stoves are very rare in the Netherlands). An open hearth is a fireplace for wood that cannot be closed by way of doors, slides or something similar. Built-in stoves are built in the fireplace and can be closed. Wood-burning stoves are meant here to be individual, closed heating equipment. A further description of the various types is given by Okken (Okken et al., 1992). All these appliances are hand-fired. Although some stoves are equipped with a catalyst, it can be generally stated that there is no flue gas cleaning whatsoever.

11.2.2 Industrial combustion

A considerable number of systems are available for combustion wood in industry. These systems can be distinguished into hand-fired and automatically fired installations.

Hand-fired installations
Hand-fired installations are hand-filled and manually regulated. These installations have a thermal capacity of usually less than 0.1 MW (0.1 MW equals about 25 kg of wood per hour). Practically all installations are equipped with a fixed grate, comparable with a domestic wood-burning stove. They are mainly used for heating air or water. Flue gas cleaning hardly ever occurs in these installations.

Automatically fired installations
In automatically fired installations, the fuel supply (and often also the air supply) is controlled automatically, e.g. via a thermostat or the return water temperature. On/off switching often takes place. Thermal capacities are more than 0.1 MW, and practically always less than 5 MW. There are various types of installations available. By far the most common system in the Netherlands is the underfeed stoker. The following systems are also found: screw conveyor stokers, pulverized fuel burners with fixed grates, and two-stage combustion installations. The various systems are described below in short.

- Underfeed stokers:
  In underfeed stokers, the fuel is screwed along the bottom of the combustion container. In this container, the fuel is propelled up in the form of a cone. Forced underfire air is supplied through tuyères in the container. Above the level where the burning off occurs, overfire air is supplied, which should provide a complete combustion of CO and volatile components.
- Screw conveyor stokers:
  In screw conveyor stokers, the fuel is screwed by one or more revolving worms in the furnace. These worms are found all through the furnace. Underfire air is supplied along the blades on the worm. Above the burner bed, overfire air is supplied to help complete the burning of the gases. While still burning, the fuel is screwed by the worms to the end of the furnace, where the ash is tapped.

- Pulverized fuel burners with fixed grates:
  In pulverized fuel burners, the fuel is pneumatically brought into the furnace. A part of the transport air is utilized as combustion air. The wood combusts partly in suspension. The coarser particles fall on a grate where they undergo further combustion.

- Staged combustion systems:
  In staged combustion, the supplied fuel is firstly de-aerated on a grate. The heat needed for this is supplied by the burning of the char that remains after de-aeration. To this end, a substoichiometric amount of air is supplied through the grate. The combustible gases that arise from the de-aeration undergo after-burning, together with the flue gases of the coal burning, by a supply of overfire air.

Automatically fired installations are used for heating air or water and for generating steam. If flue gas cleaning is at all present, it is restricted in general to a cyclone or multi-cyclone. In one case, a fabric filter has been installed. In newly installed units that fall within the current Nuisance Act, a dust emission of 50 mg/m³ ind. or less is often required. It is therefore expected that good dust cleaning equipment will be increasingly installed in these installations.

11.3  Inventoried Processes

11.3.1  Domestic combustion

Estimates as to the number of appliances available in the Netherlands for domestic combustion of wood and the annual wood consumption that goes with it are given by Okken (Okken et al., 1992) and Slob (Slob and Steenwinkel, 1992, in prep.). The various estimates are not the same, but give the same order of magnitude. The quantities stated in Table 11.1 are taken as an average estimate.

<table>
<thead>
<tr>
<th>Type of installation</th>
<th>Number</th>
<th>Fuel consumption [tonne yr⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fireplaces</td>
<td>565,000</td>
<td>320,000</td>
</tr>
<tr>
<td>Built-in stoves</td>
<td>130,000</td>
<td>180,000</td>
</tr>
<tr>
<td>Wood-burning stoves</td>
<td>235,000</td>
<td>550,000</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>930,000</td>
<td>1,050,000</td>
</tr>
</tbody>
</table>

57
Only estimates can be made as to what fuels are burnt in what quantities in this class of installations.

Estimated subdivision according to type of fuel
From the above data from the literature (Okken, and Slob and Steenwinkel), a subdivision of the estimated total fuel consumption stated in Table 11.1. was made as follows:
- 80% clean wood : 840,000 tonnes
- 16% possibly polluted wood \(^2\): 168,000 tonnes \(^3\)
- 4% other (coal, lignite, peat) : 42,000 tonnes

Paper pallets, synthetics, empty milk containers, leather, rubber, etc. are very seldom used as fuel for wood-burning stoves (< 1%).

Estimate of the quantities of fuel according to type of fuel and type of installation
For this estimate, it is of importance, within the framework of the dioxin problem, to know what part of the polluted wood contains pentachlorophenol (PCP). It is known that pallets and demolition wood from after the Second World War may have undergone preservation with PCP (PCP was used in the Netherlands from 1950 to 1989). Wood that has been treated with PCP cannot be recognized as such, as PCP is colourless and can be overpainted. Data of PCP concentrations of the burnt polluted wood are not available. It is estimated here that about 6% of the burnt polluted wood contains PCP (this estimation is made as follows: polluted wood that is combusted on a domestic scale consists of about 40% demolition wood, 40% pallets, and 20% other material. On the basis of data occurring in Chapter 19, approximately 8% of the quantity of demolition wood and pallets are considered to be polluted with PCP).

It is assumed that:
- the remaining fuels (coal, lignite and the like) are combusted only in wood-burning stoves and built-in stoves;
- in fireplaces 5% and in wood-burning stoves (including built-in stoves) 22% of the wood consumption consists of polluted wood.

On the basis of the above, the following subdivision of the consumptions stated in Table 11.2 can be made according to type of fuel and type of installation:

- fireplaces (565,000 installations):
  - 304,000 tonnes of clean wood,
  - 16,000 tonnes of possibly polluted wood, about 1,000 tonnes of which (6%, see above) have been polluted with PCP;

- wood-burning stoves and built-in stoves (365,000 installations altogether):
  - 537,000 tonnes of clean wood,
  - 151,000 tonnes of possibly polluted wood, 9,000 tons of which (6%, see above) have been polluted with PCP,
  - 42,000 tonnes of other fuels (coal, lignite and the like).

The dioxin emissions as a result of the combustion of the 42,000 tonnes of other fuels have already been included in Chapter 10 (Combustion of coal and lignite).

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\(^2\) Painted, impregnated, glued and the like

\(^3\) Of this, 40% is demolition wood, 40% pallets and 20% other
11.3.2 Industrial combustion

Recently an inventory was carried out into the small-scale burning of clean waste wood in the Netherlands (Sulilatu, 1992). The figures below have been derived from this inventory. It is estimated that in the Netherlands 148,000 tonnes per year of clean waste wood and about 80,000 tonnes per year of polluted waste wood are combusted in industrial installations (polluted: impregnated with specifically creosote oil and other impregnating salts, painted, glued, chipboard, and the like).

At the moment there is no clear survey of the number and the type of installations in which polluted waste wood is combusted. A rough inventory indicates several dozens of installations with a thermal capacity of about 0.2 to 10 MW. These installations are usually equipped with a cyclone or a multi-cyclone as flue gas cleaning device.

Thanks to the above-mentioned inventory, more is known about the installations in which clean waste wood is combusted. This information is rendered in short below.

Hand-fired installations
There are about 630 hand-fired installations with a total installed thermal capacity of about 32 MW. This results to an average capacity of about 50 kW per installation. The total installed thermal capacity of 32 MW is about 15% of the total installed capacity of industrial wood-burning installations. Hand-fired installations are mainly found in single-owner carpenters shops, small wood-processing industries, such as clog shops, and at market gardens and nurseries.

Automatically fired installations
Automatically fired wood-burning installations occur in the wood/furniture trade, the food industry (smokehouses) and at market gardens. Their total number is about 270. The larger part, about 220, have a thermal capacity ranging between 0.1 and 1 MW. The total installed thermal capacity is about 186 MW, which boils down to an average capacity of about 0.690 MW per installation. The installations can be roughly divided as follows among the various systems (100% ≈ 270 installations):

- Pulverized fuel burners with fixed grate: about 18%
- Underfeed stoker: about 70%
- Screw conveyor stoker: about 8%
- Two-stage combustion: about 4%

About 10% of the number of combustion installations for clean waste wood have been equipped with a cyclone or multi-cyclone as a flue gas cleaning installation. As flue gas cleaning is only used with the relatively large installations, the quantity of clean wood that is combusted in installations with flue gas cleaning is considerable; this quantity is over 70% of the total quantity of clean wood. Only one system with a fabric filter was inventoried. The other systems are not equipped with any flue gas cleaning.

A number of wood combustion installations are used in smokehouses. The information on this is not univocal. Therefore, the different process control at smokehouses has not been taken into account in this chapter.

The inventoried and estimated data concerning industrial wood combustion installations and quantities of wood combusted in them have been summarized in Table 11.2. In this respect, this report assumes that 5,000 tonnes of polluted waste wood (of a total of 80,000 tonnes) are
combusted in industrial installations without flue gas cleaning. It is to be expected that in industrial installations, wood (old pallets) that are polluted with PCP are also combusted. Data on this, however, are not available. It is assumed, therefore, that (just as with domestic combustion) 6% of the combusted quantity of polluted wood contain PCP (see section 11.3.1).

Table 11.2 Data on industrial wood combustion installations

<table>
<thead>
<tr>
<th>Kind of installation</th>
<th>Number</th>
<th>Total capacity installed (thermal)</th>
<th>Wood consumption¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[-]</td>
<td>[MW]</td>
<td>[%]</td>
</tr>
<tr>
<td><strong>Combustion of clean wood</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>hand-fired without flue gas cleaning</td>
<td>630</td>
<td>32</td>
<td>15</td>
</tr>
<tr>
<td>automatic without flue gas cleaning</td>
<td>about 185</td>
<td>33</td>
<td>15</td>
</tr>
<tr>
<td>automatic with flue gas cleaning</td>
<td>about 85</td>
<td>153</td>
<td>70</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>900</td>
<td>218</td>
<td>100</td>
</tr>
<tr>
<td><strong>Combustion of polluted wood</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>automatic/hand-fired without flue gas cleaning</td>
<td>no detailed information available</td>
<td>5,000</td>
<td></td>
</tr>
<tr>
<td>automatic with flue gas cleaning</td>
<td>no detailed information available</td>
<td>75,000</td>
<td></td>
</tr>
</tbody>
</table>

¹) On the basis of installed thermal capacity and 3,000 full-load hours per year.

11.4 MOB Measurement Results

Within the MOB framework, emission measurements were carried out at three (automatically fired) industrial wood combustion installations. This involved two underfeed stokers and one stoker with staged combustion. The underfeed stokers were selected because these are used mostly; the stoker with two-staged combustion was selected because this system is considered to be a promising technology for the future. In none of the three installations was completely clean wood combusted. In one underfeed stoker, the wood waste came from the construction of wooden roof panels; it was polluted with insulation material and similar. In the other two stokers, the waste came from the furniture industry, thus also contained glue residues, veneering, etc. As far as it is known, the waste wood did not contain PCP. Further details of the installations and the measurement results have been included in Table 11.3.
Table 11.3  Data and measurement results from wood combustion installations measured within the MOB framework

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Installation</th>
<th></th>
<th>Installation</th>
<th></th>
<th>Installation</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>11A</td>
<td>11B</td>
<td>11C</td>
<td></td>
<td>11A</td>
<td>11B</td>
</tr>
<tr>
<td>Type</td>
<td>underfeed stoker</td>
<td>underfeed stoker</td>
<td>staged combustion</td>
<td></td>
<td>underfeed stoker</td>
<td>underfeed stoker</td>
</tr>
<tr>
<td>Nominal capacity</td>
<td>[kW]</td>
<td>3,480</td>
<td>2,350</td>
<td>291</td>
<td>3,480</td>
<td>2,350</td>
</tr>
<tr>
<td>Flue gas treatment</td>
<td>multi-cyclone</td>
<td>multi-cyclone</td>
<td>cyclone</td>
<td></td>
<td>multi-cyclone</td>
<td>multi-cyclone</td>
</tr>
<tr>
<td>Fuel composition</td>
<td>wood with plastics and glue</td>
<td></td>
<td>wood with insulation material (PUR)</td>
<td></td>
<td>wood with plastics and glue</td>
<td></td>
</tr>
<tr>
<td>Fuel consumption</td>
<td>[tonne yr⁻¹]</td>
<td>580</td>
<td>500</td>
<td>150</td>
<td>580</td>
<td>500</td>
</tr>
<tr>
<td>Heating season</td>
<td>[h yr⁻¹]</td>
<td>about 5,080</td>
<td>5,800</td>
<td>?</td>
<td>about 5,080</td>
<td>5,800</td>
</tr>
<tr>
<td>Switch on/off</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
<td></td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>Flue gas flow</td>
<td>[m³h⁻¹] ¹</td>
<td>3,400 ⁶</td>
<td>9,500</td>
<td>740</td>
<td>3,400 ⁶</td>
<td>9,500</td>
</tr>
<tr>
<td>Flue gas temperature</td>
<td>[°C]</td>
<td>95</td>
<td>119</td>
<td>164</td>
<td>95</td>
<td>119</td>
</tr>
<tr>
<td>O₂</td>
<td>[vol % dry]</td>
<td>15.8</td>
<td>17.3</td>
<td>12.3</td>
<td>15.8</td>
<td>17.3</td>
</tr>
<tr>
<td>CO₂</td>
<td>[vol % dry]</td>
<td>4.5</td>
<td>3.7</td>
<td>8.5</td>
<td>4.5</td>
<td>3.7</td>
</tr>
<tr>
<td>H₂O</td>
<td>[g m⁻³] ¹</td>
<td>104</td>
<td>83</td>
<td>55</td>
<td>104</td>
<td>83</td>
</tr>
<tr>
<td>PCDD/F</td>
<td>[ng I-TEQ m⁻³] ²</td>
<td>0.4</td>
<td>0.5 - 0.9</td>
<td>1.0</td>
<td>0.4</td>
<td>0.5 - 0.9</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>[mg m⁻³] ²</td>
<td>21</td>
<td>349</td>
<td>39</td>
<td>21</td>
<td>349</td>
</tr>
<tr>
<td>CO</td>
<td>[mg m⁻³] ²</td>
<td>4,920</td>
<td>390</td>
<td>1,252</td>
<td>4,920</td>
<td>390</td>
</tr>
<tr>
<td>C₅H₇</td>
<td>[mg m⁻³] ²</td>
<td>430</td>
<td>5</td>
<td>5</td>
<td>430</td>
<td>5</td>
</tr>
<tr>
<td>Annual emission of PCDD/F</td>
<td>[g I-TEQ/year]</td>
<td>0.002</td>
<td>0.002 - 0.004</td>
<td>0.001</td>
<td>0.002</td>
<td>0.002 - 0.004</td>
</tr>
</tbody>
</table>

1) Refers to dry flue gases under standard conditions
2) Refers to dry flue gases under standard conditions, converted to 11% O₂
3) During the measurements
4) Will probably no longer contain CFCs in 1993
5) Period that installation is "standby"; actual working hours considerably fewer
6) When boiler is in operation

A sample of soot was also scraped from the inside of the stack of installation 11B and subsequently analyzed. The PCDD/F content of the soot was 0.2 ng I-TEQ per gramme.

11.5  Results of Measurements Outside the MOB Framework

Commissioned by VROM and outside MOB framework, TNO conducted emission measurements at a wood-burning stove and a fireplace.

Wood-burning stove
Emission measurements were conducted for an individual, cast-iron wood-burning stove with a combustion chamber lined with fire refractory clay. The stove is of a type that is common in the Netherlands. The maximum load of the stove was 23 kW. The way of firing during the
measurements was in agreement with the draft test procedure issued for wood-burning stoves by the Vereniging Haard en Rookkanaal (Association for Fireplaces and Stacks) (VHR) on 25 June 1992. Measurements were conducted at three loads (i.e. maximum, average and minimum) using clean wood as a fuel. Further details and measurement results are included in Table 11.4.

Table 11.4 Measurement results 1) of emission measurements for wood-burning stoves measured outside the MOB framework

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Load [kW]</th>
<th>23</th>
<th>17</th>
<th>13</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel consumption</td>
<td>[kg/h]</td>
<td>4.6</td>
<td>3.4</td>
<td>2.6</td>
</tr>
<tr>
<td>(clean wood, dry)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flue gas temperature</td>
<td>[°C]</td>
<td>337</td>
<td>238</td>
<td>193</td>
</tr>
<tr>
<td>O₂</td>
<td>[vol % dry]</td>
<td>8.4</td>
<td>7.3</td>
<td>7.3</td>
</tr>
<tr>
<td>CO₂</td>
<td>[vol % dry]</td>
<td>11.7</td>
<td>12.1</td>
<td>12.3</td>
</tr>
<tr>
<td>CO</td>
<td>[mg m⁻³]</td>
<td>&gt;6,800</td>
<td>&gt;10,660</td>
<td>&gt;12,100</td>
</tr>
<tr>
<td>CₓHᵧ</td>
<td>[mg m⁻³]</td>
<td>1,480</td>
<td>&gt;2,870</td>
<td>&gt;1,800</td>
</tr>
<tr>
<td>PCDD/F</td>
<td>[ng I-TEQ m⁻³]</td>
<td>0.26 - 0.36</td>
<td>0.12 - 0.19</td>
<td>0.31 - 0.32</td>
</tr>
<tr>
<td>Emission factor PCDD/F</td>
<td>[µg I-TEQ tonne⁻¹ of wood]</td>
<td>2.4 - 3.3</td>
<td>1.0 - 1.6</td>
<td>2.5 - 2.6</td>
</tr>
</tbody>
</table>

1) Average during test run
2) Refers to dry flue gases under standard conditions

Fireplace

Measurements for two ways of burning were conducted at a fireplace of a type that is common in the Netherlands. In one case, the burning took place on a grate; in the other, on a flat floor. The firing conditions were also pursuant to the draft procedure made by the VHR (see above). Further data and the measurement results are presented in Table 11.5.

Table 11.5 Measurement results 1) of emission measurements at a fireplace measured outside the MOB framework

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Ways of burning</th>
<th>on a grate</th>
<th>on the floor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel consumption</td>
<td>[kg/h]</td>
<td>5.7</td>
<td>5.1</td>
</tr>
<tr>
<td>(clean wood, dry)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Load</td>
<td>[kW]</td>
<td>29</td>
<td>26</td>
</tr>
<tr>
<td>Flue gas temperature</td>
<td>[°C]</td>
<td>375</td>
<td>346</td>
</tr>
<tr>
<td>O₂</td>
<td>[vol % dry]</td>
<td>16.3</td>
<td>16.3</td>
</tr>
<tr>
<td>CO₂</td>
<td>[vol % dry]</td>
<td>4.7</td>
<td>4.8</td>
</tr>
<tr>
<td>CO</td>
<td>[mg m⁻³] ²</td>
<td>1,560</td>
<td>1,450</td>
</tr>
<tr>
<td>PCDD/F</td>
<td>[ng I-TEQ m⁻³] ²</td>
<td>1.2</td>
<td>0.5</td>
</tr>
<tr>
<td>Emission factor of PCDD/F</td>
<td>[µg I-TEQ tonne⁻¹ of wood]</td>
<td>28.5</td>
<td>13.0</td>
</tr>
</tbody>
</table>

1) Average during test run
2) Refers to dry flue gases under standard conditions
11.6 Data from the Literature

In soot from chimneys of domestic heating systems in the former Federal Republic of Germany, the following average concentrations were found (Thoma, 1988): wood/coal stove: 0.9 ng 1-TEQ g\(^{-1}\), wood (central heating): 15 ng 1-TEQ g\(^{-1}\), wood-burning stove 7.5 ng 1-TEQ g\(^{-1}\).

Vikelsoe investigated the dioxin emission of a wood-burning stove in which different types of fuels were burned (Vikelsoe et al., 1991; Denmark, 1990). The analysis method used was the so-called "sum determination". In the burning of wood briquettes, he found an emission factor of about 300 µg 1-TEQ per tonne, in the burning of wood impregnated with PCP a factor of about 6,500 µg 1-TEQ per tonne (these values have been estimated on the basis of the data presented by Vikelsoe). During repeat measurements, however, he found considerably lower values (for pieces of wreckage). The test conditions are insufficiently known.

Bröker recently published results of dioxin emission measurements conducted on domestic heating equipment (Bröker et al., 1992). For a wood-burning stove, an emission factor of 0.7 - 1.2 µg 1-TEQ per tonne was determined, for a fireplace the same factor was determined: 0.7 - 1.2 µg 1-TEQ per tonne. The equipment was operated in practical situations, burning beechwood logs.

11.7 Evaluation

11.7.1 General

At least four types of combustion installations (or equipment) should be distinguished in calculating the emissions as a consequence of wood burning, i.e.:
- industrial installations with flue gas cleaning;
- industrial installations without flue gas cleaning;
- wood-burning stoves (including built-in stoves);
- fireplaces.

Furthermore, a distinction should be made between three types of wood:
- clean wood;
- polluted wood without PCP;
- polluted wood with PCP.

In this way, twelve combinations will arise for which an emission factor must be determined and the relevant fuel quantities should be known.

Certainly when considering the large number of installations or equipment installed, there is very little known about dioxin emissions at wood combustion. From the results of the MOB measurements, an emission factor can be calculated for the industrial combustion (with flue gas cleaning) of polluted wood without PCP. From experiments done by TNO (outside MOB framework), emission factors can be derived for domestic combustion of clean wood in wood-burning stoves and fireplaces. These latter factors, however, were obtained under laboratory conditions; there is still insufficient insight into their relation to actual practice. In the scanty literature about this subject (see 11.6), only very varying indications can be obtained on emissions. Table 11.6 gives a schematic indication as to the installation/fuel combinations for which some information is available.
Table 11.6 Available information on emission factors for wood combustion ¹)

<table>
<thead>
<tr>
<th>Type of wood</th>
<th>Industrial installations</th>
<th>Wood-burning stoves</th>
<th>Fireplaces</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>without flue gas cleaning</td>
<td>with flue gas cleaning</td>
<td></td>
</tr>
<tr>
<td>Clean wood</td>
<td>-</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Polluted wood:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>without PCP</td>
<td>-</td>
<td>x</td>
<td>-</td>
</tr>
<tr>
<td>with PCP</td>
<td>-</td>
<td>-</td>
<td>o²)</td>
</tr>
</tbody>
</table>

¹) x = Information on the basis of measurements; - = no information; o = information from the literature
²) Only qualitative information

In order to be able to give an estimate of the order of magnitude of the PCDD/F emissions by wood combustion in the Netherlands on the basis of the existing data, the following assumptions were made:

- The emission factors for industrial installations without flue gas cleaning and those for wood-burning stoves are equated. Because half (referring to capacity, see Table 11.1) of the industrial installations is fired automatically without flue gas cleaning, this assumption will probably mean an overestimation of the emissions of this category.
- The emission factors for industrial wood combustion installations have been correlated to the dust emission. For installations with flue gas cleaning (cyclones) this dust emission is roughly a factor of 4 less than for installations without flue gas cleaning. As the dioxins are mainly bound to small dust particles (retention efficiency small for cyclones), it is assumed that the dioxin emission at installations with flue gas cleaning is a factor of two less than with installations without flue gas cleaning.
- The relation between the emission factors for fireplaces and wood-burning stoves is the same for all types of wood.
- The emission factors of wood-burning stoves and fireplaces measured under laboratory conditions agree with those measured in practical situations.

11.7.2 Emission factors

Industrial installations with flue gas cleaning, polluted wood without PCP
From the MOB measurement results (Table 11.3), it can be calculated that the emission factor for dioxins of the underfeed stokers was 3 µg I-TEQ per tonne of wood and on average 6 µg I-TEQ per tonne of wood. For the two-stage combustor, an emission factor can be calculated of 7 µg I-TEQ per tonne of wood. On average, the emission factor for polluted wood without PCP then amounts to 5 µg I-TEQ per tonne of wood (using a cyclone as flue gas cleaning).
Wood-burning stoves, clean wood
From Table 11.4, an average emission factor of 2.2 µg I-TEQ per tonne is derived for the combustion of clean wood in a wood-burning stove. At an average load, the dioxin emission appears to be the smallest. This value is in agreement with the value found by Bröker (see under 11.6). For the time being, the average factor mentioned is assumed.

Fireplaces, clean wood
The subdivision of the number of fireplaces according to the burning method (on a grate or sheet) is not known. Therefore, for the time being, the average of the factors mentioned in Table 11.5 is taken as the emission factor for the combustion of clean wood in a fireplace, i.e. 20 µg I-TEQ per tonne. The emission factor obtained in this way is considerably higher than the one reported by Bröker (see under 11.6). The cause of the difference cannot be indicated because of the limited data. For the time being, this investigation assumes the average value measured outside MOB framework.

Wood-burning stoves, wood polluted with PCP
The only information available on the emission by combustion PCP-treated wood in wood-burning stoves comes from Vikelsoe (see section 11.6). For the combustion of clean wood in a wood-burning stove, Vikelsoe found an emission factor that is 135 times higher than the average found by Bröker (see 11.6) and in the investigation carried out outside the MOB framework (Table 11.4). Based on the assumption that this relation also applies to the combustion of wood polluted with PCP in a wood-burning stove, an emission factor is assumed for this type of wood (6500 µg I-TEQ per tonne; see 11.6) which is a factor of 135 less (i.e. around 50 µg I-TEQ per tonne of wood).

The above-mentioned emission factors, combined with the assumptions stated in 11.7.1, have led to the survey of emission factors, as presented in Table 11.7.

<table>
<thead>
<tr>
<th>Type of wood</th>
<th>Industrial installations</th>
<th>Wood-burning stoves</th>
<th>Fireplaces</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>without flue gas cleaning</td>
<td>with flue gas cleaning</td>
<td></td>
</tr>
<tr>
<td>Clean wood</td>
<td>2.2 4)</td>
<td>1 4)</td>
<td>2.2 2)</td>
</tr>
<tr>
<td>Polluted wood</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>without PCP</td>
<td>10 4)</td>
<td>5 1)</td>
<td>10 4)</td>
</tr>
<tr>
<td>with PCP</td>
<td>50 4)</td>
<td>25 4)</td>
<td>50 3)</td>
</tr>
</tbody>
</table>

1) Determined in a practical situation
2) Determined under laboratory conditions
3) Rough estimate on the basis of the literature (see 11.7.2)
4) Rough estimate, see assumptions under 11.7.1
5) Great uncertainties; see remarks under 11.7.2
11.7.3 Dioxin concentrations of soot

The dioxin concentration of soot from the stack of installation 11B was 0.2 ng I-TEQ g\(^{-1}\) (see 11.4). This is considerably lower than the values reported by Thoma (1-15 ng I-TEQ g\(^{-1}\) of soot, see 11.5). Thoma’s measurements, however, concerned domestic installations, while the measurements conducted within the MOB framework were carried out at an industrial installation. These differences confirm the assumption (see 11.7.1) that the emission of industrial wood combustion installations with flue gas cleaning will be lower than that of equipment for domestic wood combustion. As the history of the investigated soot samples is not known, no quantitative assessment can be given as to the significance of the analysis results. No data are available on the dioxin concentrations of ash.

11.8 Summary

On the basis of the wood consumption in 11.3 and the emission factors in 11.7.2, the total dioxin emission as a consequence of wood combustion in the Netherlands was calculated. The results and the various data are summarized in Table 11.8. Once again it is explicitly stated that these data and emissions must be regarded as rough estimates in view of the many assumptions that have been made.

Considering the size of the various (estimated) emissions from wood combustion, further investigation is recommended. This investigation will particularly have to aim at:
- the representativeness of the dioxin emissions measured so far in the domestic combustion of clean wood;
- the quantities of polluted wood (with or without PCP) burned in the various installations/equipment;
- the emissions that occur from the combustion of polluted wood, both into the air and via ash residue, specifically with domestic combustion;
- the possibilities of reducing the dioxin emission from wood combustion (e.g. by improved combustion conditions);
- making an inventory of smokehouses occurring in the Netherlands, and the emissions occurring at these installations.
Table 11.8  Data of dioxin emissions from the combustion of wood (1991)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Number of installations</th>
<th>Wood consumption [tonne yr(^{-1})]</th>
<th>Emission factor [(\mu)g 1-TEQ per tonne of wood]</th>
<th>PCDD/F emission [g 1-TEQ yr(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Industrial combustion without flue gas cleaning:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clean wood</td>
<td>about 815</td>
<td>44,000</td>
<td>2.2</td>
<td>0.1</td>
</tr>
<tr>
<td>Polluted wood</td>
<td>not known</td>
<td>4,700</td>
<td>10</td>
<td>}</td>
</tr>
<tr>
<td>- without PCP</td>
<td>not known</td>
<td>300</td>
<td>50</td>
<td>} 0.1</td>
</tr>
<tr>
<td>- with PCP</td>
<td>not known</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Industrial combustion with flue gas cleaning:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clean wood</td>
<td>about 85</td>
<td>104,000</td>
<td>1</td>
<td>0.1</td>
</tr>
<tr>
<td>Polluted wood</td>
<td>not known</td>
<td>71,000</td>
<td>5</td>
<td>0.4</td>
</tr>
<tr>
<td>- without PCP</td>
<td>not known</td>
<td>4,000</td>
<td>25</td>
<td>0.1</td>
</tr>
<tr>
<td>- with PCP</td>
<td>not known</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Domestic combustion (^1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wood-burning stoves (incl. built-in stoves):</td>
<td>365,000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clean wood</td>
<td>537,000</td>
<td>2.2</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>Polluted wood</td>
<td>142,000</td>
<td>10</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>- without PCP</td>
<td>9,000</td>
<td>50</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>- with PCP</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fireplaces (^2):</td>
<td>565,000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clean wood</td>
<td>304,000</td>
<td>20</td>
<td>6.1</td>
<td></td>
</tr>
<tr>
<td>Polluted wood</td>
<td>15,000</td>
<td>100</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>- without PCP</td>
<td>1,000</td>
<td>500</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>- with PCP</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>1,236,000</td>
<td></td>
<td>12.0</td>
<td></td>
</tr>
</tbody>
</table>

\(^1\) The dioxin emission as a result of the burning of coal etc. in stoves has been included in Chapter 10.

\(^2\) Great uncertainties; see remarks under 11.7.2

Nothing is known about the quantities of residues and the dioxin concentrations occurring in them.

11.9 Future

When, through good information and training, all polluted wood that is used in domestic combustion is replaced by clean wood, a total dioxin emission of about 9 g 1-TEQ will remain in the year 2000, at an otherwise constant consumption. This emission concerns both industrial and domestic combustion. This estimate, however, still depends on the results of the investigation recommended for this.
12. CREMATORIA

12.1 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 "warm 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 kept at that temperature. For the "warm" furnace, the burner is, in essence, not needed further, as the process is sustained. The gases flowing out of the chamber are incinerated in an after burner at a temperature of about 850 °C. In the cold types, the process lasts for 2-2.5 hours, in the warm types 1.2-1.5 hours.

The oxygen demand of the cremation process varies during the process; particularly at the disintegration of the coffin, the air demand is greatest. The air supply in the furnace is regulated according to an adjustable time schedule (usually a choice can be made between three variants). The after burners are often still regulated as to temperature, in which process the gas/air ratio has been pre-set. More modern systems regulate the air supply in the after burners using an oxygen meter in the flue gases.

As far as the route that the flue gases pass after the after burner is concerned, a distinction can be made into the following three systems:
1. The flue gases are brought into the atmosphere without cooling.
2. The draught is regulated using an air blast by which the flue gases are cooled with ambient air to a temperature between 200-350 °C, before being emitted.
3. The flue gases are cooled as under 2, followed by further cooling to about 150 °C in an indirect air cooler. Subsequently, they pass a fabric filter in which the dust carried along is collected.

12.2 Inventoried Processes

There are 43 crematoria in the Netherlands. The number of cremations in 1991 was 59,143. About a quarter of the crematory furnaces are of the cold type, the remaining three-quarters of the warm type. Particularly the furnaces in small crematoria are of the cold type.

All crematory furnaces have been equipped with an after burner. In 5-10 crematoria, specifically those with furnaces of the cold type, the flue gases are emitted without cooling into the air. In about 30 crematoria, the flue gases are cooled with ambient air to 200-350 °C after the after burner, and then emitted. The furnaces of five crematoria have been equipped with a fabric filter (CVN, 1992; TNO, 1992).
12.3 MOB Measurement Results

Within the MOB framework, measurements were carried out at two installations, one of the cold type and one of the warm type. The flue gases of the cold type were emitted without cooling, those of the warm type were emitted after dilution with ambient air to about 220 °C. In both installations, the measurements were conducted for three or four processes. The results are stated in Table 12.1. The concentrations of particularly CO and C\textsubscript{x}H\textsubscript{y} were found, on average, to be somewhat higher for the warm process than for the cold one. For a considerable part of the time, however, the concentrations of these components were below the detection limit of the analysis device involved. The accuracy of the calculated averages is therefore limited.

Table 12.1 Data and measurement results from cremation processes measured within the MOB framework

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Installation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>12A</td>
</tr>
<tr>
<td></td>
<td>12B</td>
</tr>
<tr>
<td>Type of furnace</td>
<td>cold after-burning</td>
</tr>
<tr>
<td>Flue gas treatment</td>
<td></td>
</tr>
<tr>
<td>Processes per year</td>
<td>850</td>
</tr>
<tr>
<td>Operating hours per year</td>
<td>2,125</td>
</tr>
<tr>
<td>Flue gas flow [m\textsuperscript{3} h\textsuperscript{-1}]\textsuperscript{1)}</td>
<td>750</td>
</tr>
<tr>
<td>Flue gas temperature [°C]</td>
<td>730</td>
</tr>
<tr>
<td>O\textsubscript{2} [vol % dry]</td>
<td>11.7</td>
</tr>
<tr>
<td>CO\textsubscript{2} [vol % dry]</td>
<td>6.3</td>
</tr>
<tr>
<td>H\textsubscript{2}O [g m\textsuperscript{-3}]\textsuperscript{1)}</td>
<td>95</td>
</tr>
<tr>
<td>PCDD/F [ng I-TEQ m\textsuperscript{-3}]\textsuperscript{2)}</td>
<td>1.6</td>
</tr>
<tr>
<td>Cl\textsuperscript{-} [mg m\textsuperscript{-3}]\textsuperscript{2)}</td>
<td>43</td>
</tr>
<tr>
<td>CO [mg m\textsuperscript{-3}]\textsuperscript{2)}</td>
<td>38</td>
</tr>
<tr>
<td>C\textsubscript{x}H\textsubscript{y} [mg m\textsuperscript{-3}]\textsuperscript{2)}</td>
<td>6</td>
</tr>
<tr>
<td>Yearly emission of PCDD/F [g I-TEQ yr\textsuperscript{-1}]</td>
<td>0.002</td>
</tr>
</tbody>
</table>

\textsuperscript{1)} Refers to dry flue gases under standard conditions
\textsuperscript{2)} Refers to dry flue gases under standard conditions, converted to 11% O\textsubscript{2}

12.4 Data from the Literature

At a crematorium in (former) West Berlin, a dioxin emission of 8 ng I-TEQ m\textsuperscript{-3} was found. An average of 3,500 m\textsuperscript{3} of flue gas was emitted per body. This would lead to a dioxin emission of 28 μg I-TEQ per body (Jager et al., 1992).
12.5 Evaluation

From the figures of Table 12.1 (not rounded up or down), it was calculated that the dioxin emission per body was 2.4 μg I-TEQ for crematory furnace 12A (flue gases not cooled) and 4.9 μg I-TEQ for crematory furnace 12B (flue gases cooled with outside air). At the incineration of urban waste in municipal solid waste incinerators, it was shown that dioxins are particularly formed after the incineration in the furnace at temperatures between 200 and 500 °C. It turns out that at crematory furnace 12B, where the flue gases pass through this temperature range, most of the dioxins do indeed arise.

When flue gas treatment using a fabric filter is applied, the flue gases are further indirectly cooled to 150 °C after being mixed with air. Because of this further cooling and the efficient dust collection in fabric filters, the emission of dioxins of such installations is probably lower than those of 12A and 12B.

It is assumed that when applying a fabric filter the emission of dioxins is smaller than 1 μg I-TEQ per body. There is no data known for the dioxin concentration of the collected dust. The quantity of collected dust is about 75 g per body (TNO, 1993). In total, probably less than 1 tonne of filter ash is collected per year by the five crematoria that have furnaces equipped with fabric filters. It is assumed that the dioxin concentration in the filter ash is not higher than that in the fabric filter ash of the secondary non-ferrous industry (3 - 17.8 ng I-TEQ g⁻¹; see Chapter 17). The total quantity of dioxins discharged with fabric filter ash of crematoria is, therefore, less than 0.02 g I-TEQ per year.

At the (West) Berlin crematorium, the dioxin emission is 5 to 10 times higher than the emissions measured in this investigation. As process data of the Berlin crematorium are lacking, no cause can be given for this difference.

From the number of different types of crematory furnaces and the dioxin emissions measured here, it can be calculated that the average emission per body is about 4 μg I-TEQ. The total dioxin emission of crematoria in 1991 then boils down to about 0.2 g I-TEQ. No account is taken here of the five crematoria which are equipped with both an after-burner and a fabric filter (and thus have a lower emission factor).

12.6 Summary

The dioxin emissions of crematoria have been summarized in Table 12.2.

Table 12.2 Data of dioxin emissions from crematoria

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of crematoria</td>
<td>43</td>
</tr>
<tr>
<td>PCDD/F emission per body</td>
<td>[μg I-TEQ]</td>
</tr>
<tr>
<td>Number of cremations in 1991</td>
<td>59,143</td>
</tr>
<tr>
<td>PCDD/F emission per year (1991)</td>
<td>[g I-TEQ yr⁻¹]</td>
</tr>
</tbody>
</table>

The quantity of dioxin remaining in the residue is less than 0.02 g I-TEQ per year.
13. FIRES

13.1 General

This chapter includes data about dioxin emissions that can occur at fires (of and in buildings, cars, forests, etc.). In the inventory of processes (Bremmer and Hesseling, 1991), flares were also included in this process category. However, in the twelve flares that were inventoried, no chlorine containing substances were incinerated (not including the burning off of landfill gas and biogas). Therefore, flares will not be discussed further in this chapter. The dioxin emissions as a result of the combustion of landfill gas and biogas have been dealt with in Chapter 5.

13.2 Process Description

Fires can be described as uncontrolled combustion processes. The fuel and oxygen supplies 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 good burning. At some distance from the seat of fire, the combustion gases, however, are mixed very quickly with a great overmeasure of air, so that the flue gases have been cooled before a good burn-out can take place. Because of these effects, emissions occur (including those of incompletely burnt components) which are high compared with the emissions of controlled incineration. In addition to the mentioned "poor" combustion, the presence of chlorine is also important for the forming of dioxins. Chlorine already occurs naturally in building materials, such as wood. Practically all Dutch buildings also contain PVC, a significant source of chlorine.

13.3 Inventoried Processes

The number of registered fires in the Netherlands was 40,095 in 1990. The subdivision according to a number of categories is as follows (CBS, 1992):
- buildings: 11,940
- containers, cars, ships: 10,803
- forest, heathland, dune, road, ground fires and fires alongside roadsides: 9,744
- chimney fires: 2,229
- other: 5,379

In addition to these registered fires, quite a number of materials are burnt in so-called 'open fires", particularly in the country by private persons and (agrarian) companies. 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.

13.4 Data from the Literature

In the working document (Bremmer, 1991), a literature study was reported on fires as to the dioxin concentrations of the flue gases, combustion residues, and soil samples in the surroundings of fires. Usable emission factors are not given in the literature and cannot be deduced from that data either.

Several important data from the literature are given below.
Emissions into the air
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).

Dioxin in combustion residues (ash and soot)
A large number of dioxin determinations were conducted in ash residue and soot, particularly for fires in which PVC material was involved.

In an investigation of 200 residues of fires (in which PVC was involved), dioxins were shown in 90% of the samples; the dioxin levels varied from picogrammes I-TEQ per gramme to nanogrammes I-TEQ per gramme. In the combustion residues of a fire (a room in which drums with PVC were stored) dioxin concentrations up to 28 ng I-TEQ g\(^{-1}\) were shown (Funcke et al., 1988). According to the authors, this fire was representative of the above investigation. The values found are in the same order of magnitude as the dioxin concentrations of ESP ash of MSW incinerators (see section 3.4.2).

After a fire in a university building (PVC not specifically present), dioxin concentrations of 0.04 - 7 ng TEQ g\(^{-1}\) (TEQ in accordance to EPA; Deutsch and Goldfarb, 1988) were found in soot samples.

13.5 Evaluation

Emissions into the air
Real data from which the dioxin emissions occurring at fires can be calculated is hardly available. Only from the data of Markland (see section 13.4) an emission factor can be calculated; this factor is around 4 \(\mu\)g I-TEQ per tonne of burnt material (a relatively high percentage of plastics/PVC was at issue here). However, it cannot be stated in which way this factor can be used for the fires stated in the inventory. The kinds of materials that are burned will, for that matter, differ strongly. In order to calculate/estimate the dioxin emissions on the basis of such an emission factor, the quantities combusted must be known, which is not the case here.

Reliable estimations of the dioxin emissions at fires can therefore not be given. Actually, from the available data it appears that fires could be a dioxin source not to be ignored.

Dioxin in combustion residues (ash and soot)
Of combustion residues (ash/soot), data is only available on the dioxin concentrations, and not on the quantities of these residues. Estimates of the quantities of dioxins that remain on the sites of fires or are somehow discharged cannot be given either.

Recommendation
On the basis of the above, it is recommended to carry out additional investigation into the dioxin emissions from fires. Special attention should be paid in this respect to the effect of the substances involved in a fire on the occurring emissions of toxic components. Considering the dioxin concentrations given in literature of combustion residues (ash/soot), it is important to also include these in the investigation.
14. VARIOUS HIGH-TEMPERATURE PROCESSES

14.1 General

In this chapter, different high-temperature processes from which dioxin emissions can be expected on the basis of the process conditions (from the process and/or from the raw materials) will be discussed. Section 14.2 will give process descriptions of four of these processes. Within the MOB framework, emission measurements were conducted at six installations.

Of the processes dealt with in this chapter, only a small number of installations (or in one case only one installation) are available in the Netherlands. This means these companies could be easily recognized. In order to prevent this easy recognition, the information presented in this chapter is generally mentioned just roughly; emissions will not be given for individual processes where this is not necessary.

14.2 Process Description

14.2.1 Thermal soil cleaning

Soil contaminated with more or less volatile organic compounds can be cleaned thermally. 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 O₂ 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 a high temperature in a (multi-)cyclone, after which the organic compounds present are destroyed in an after burner. Depending on the nature of the components, the temperature in the after burner is set at 800 - 1200 °C.

The gases leaving the after burner are emitted into the atmosphere. This can happen without heat recovery and flue gas cleaning, but also with heat recovery and subsequent wet scrubbing of the flue gases in a venturi washer, for instance.

14.2.2 Manufacture of insulating bricks

Insulating bricks derive their insulating characteristic from the fact that these bricks have open spaces. This is achieved by mixing combustible substances (i.e. carbon-containing slate and wood sawdust) through the clay. During the baking, the combustible constituents burn up, leaving behind holes in the bricks.

Bricks are formed from the raw materials, clay, slate, fly ash from power plants, sawdust, and subsequently loaded on a cart. The bricks are firstly pre-dried by bringing them in direct contact with the warm flue gases of the kiln (see below). After drying, the bricks are baked in a kiln. The process can be divided into three parts: the pre-firing zone, the firing, and the after-firing zone. During pre-firing, the combustible parts of the raw materials are ignited at a temperature of 400-600 °C. During firing, the bricks are baked at about 1000 °C, while the burn-out takes place during after-firing. Finally, the bricks are cooled in a cooling chamber.
The process mostly takes place in a continuously operating tunnel kiln, in which the bricks pass the various process steps in a tunnel. Sometimes a much smaller tunnel than usual is employed; this tunnel is not explicitly separated from the three above-mentioned zones.

The flue gases generated during baking are mixed, if necessary, with ambient air, until a temperature of about 180 °C is reached. The flue gas flow now arising is led through drying sheds in which the formed bricks are dried (see above). Subsequently, the flue gases are emitted without further additional cleaning.

14.2.3 Drying of fly ash

Part of the fly ash that is produced in Dutch municipal solid waste incinerators is used in roadbuilding as a filler in asphalt (see also section 3.3). 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 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.

The production of filler is strongly seasonally bound as a result of its use in the production of asphalt. The installations operate only during a part of the period March-November.

14.2.4 Production of cement

Cement is made by binding limestone with various additives. The extracted limestone (marl) is firstly dried with flue gases from the clinker kiln (see below). Subsequently the following products are added to the dried limestone: pyrite ash, fly ash from coal-fired power plants, sandy clay and filter ash from the electrostatic precipitator present (see below). The mixture obtained is ground. The resulting powder is heated in a clinker kiln (a long rotary kiln) to a maximum temperature of 1450 °C. Next, the material obtained is cooled with ambient air. Petroleum coke, lignite, high-sulphurous oil and glycol bottom residues (distillation residues) are used as fuels. The flue gases of the clinker kiln subsequently pass the marl drier and an electrostatic precipitator before being emitted.

14.2.5 Manufacture of rockwool

In the manufacture of rockwool, volcanic rocks (basalt, diabase) and briquettes that consist of cement and return waste from the manufacturing companies are melted in a cupola kiln. The melting process takes place at a temperature of approximately 1500 °C. The melted stone is continuously drained at 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 required combustion air is brought, in counterflow, into contact with the raw materials and the coke. The combustion gases are then led via the top of the cupola kiln to an after burner at a temperature of about 170 °C. From the after burner, the flue gases are emitted into the atmosphere via two heat exchangers and a fabric filter.
14.2.6 Manufacture of glass

In the manufacture of glass, a mixture of sand (SiO₂ 70 - 74%) and (depending on the type of glass) lime (CaCO₃, 5 - 12%), sodium carbonate (Na₂CO₃ 12 - 16%), dolomite (MgCO₃·CaCO₃), clay or feldspar (Al₂O₃ carriers), 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 used as a raw material. Chloride occurs in the manufacturing process as a result of NaCl pollution in sodium carbonate.

14.3 Inventoried Processes

Twenty-three installations with high-temperature processes have been inventoried. Thermal soil cleaning takes places in five installations. About 350,000 tonnes of soil were cleaned in this way in the Netherlands in 1991 (RIVM, 1993). 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 its use of chlorine-containing components and the application of a "high" temperature, one company that manufactures siliconcarbide, and one rubber plant (compression at 400 °C) are included in the inventory.

14.4 MOB Measurement Results

Within the MOB framework, emission measurements were conducted for the following processes:
- manufacture of insulating bricks (two installations);
- fly ash drying (two plants);
- cement manufacture;
- rockwool manufacture.

The results of the measurements conducted, as well as several process data, are shown in Table 14.1. As already mentioned in section 14.1, the information is kept brief because of the easy recognition of the installations.
<table>
<thead>
<tr>
<th>Installation no.</th>
<th>Working hours per year</th>
<th>Flue gas flow [m³ h⁻¹] ¹</th>
<th>Flue gas temperature [°C]</th>
<th>O₂ [vol% dry]</th>
<th>CO₂ [vol% dry]</th>
<th>H₂O [g m⁻³] ¹</th>
<th>PCDD/F [ng I-TEQ m⁻³] ²</th>
<th>Cl⁻ [mg m⁻³] ²</th>
<th>CO [mg m⁻³] ²</th>
<th>CₓHᵧ</th>
<th>Yearly emission of PCDD/F [g I-TEQ yr⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>14A</td>
<td>7,000</td>
<td>179,700</td>
<td>138</td>
<td>8.3</td>
<td>20.7</td>
<td>172</td>
<td>0.44</td>
<td>1.5</td>
<td>238</td>
<td>11</td>
<td>0.95</td>
</tr>
<tr>
<td>14B</td>
<td>8,760</td>
<td>65,700</td>
<td>231</td>
<td>18.0</td>
<td>2.7</td>
<td>38</td>
<td>2.5</td>
<td>0.9</td>
<td>13,200</td>
<td>941</td>
<td>0.4</td>
</tr>
<tr>
<td>14C</td>
<td>8,760</td>
<td>19,700</td>
<td>174</td>
<td>18.7</td>
<td>0.1</td>
<td>22</td>
<td>0.77</td>
<td>&lt;2.3</td>
<td>26</td>
<td>&lt;22</td>
<td>0.03</td>
</tr>
<tr>
<td>14D</td>
<td>1,500</td>
<td>29,500</td>
<td>112</td>
<td>18.6</td>
<td>1.8</td>
<td>102</td>
<td>19.5</td>
<td>3.8</td>
<td>5,000</td>
<td>584</td>
<td>0.25</td>
</tr>
<tr>
<td>14E</td>
<td>7,500</td>
<td>27,100</td>
<td>221</td>
<td>13.0</td>
<td>8.1</td>
<td>43</td>
<td>0.045</td>
<td>51</td>
<td>158</td>
<td>&lt;5</td>
<td>0.04 ⁴</td>
</tr>
<tr>
<td>14F</td>
<td>500</td>
<td>89,900</td>
<td>77</td>
<td>19.5</td>
<td>1.1</td>
<td>103</td>
<td>0.4</td>
<td>19 ³</td>
<td>30</td>
<td>7</td>
<td>0.003</td>
</tr>
</tbody>
</table>

¹) Refers to dry flue gases under standard conditions  
²) Refers to dry flue gases under standard conditions, converted to 11% O₂;  
³) The accuracy of the concentration at 11% O₂ is small at the high measured O₂ concentration  
⁴) 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).
14.5 Measurement Results Outside the MOB Framework

Outside the MOB framework, measurements were conducted at a thermal soil cleaning installation. The measurements were conducted for five days during the processing of four lots of soil. Table 14.2 presents several data and the measurement results, as well as the minimum and maximum daily averaged values.

Table 14.2 Data and measurement results from a thermal soil cleaning installation, measured outside MOB framework

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Installation 14G</th>
</tr>
</thead>
<tbody>
<tr>
<td>fuel</td>
<td>rotary kiln: diesel oil after burner: gas after burner and gas scrubber</td>
</tr>
<tr>
<td>Flue gas cleaning</td>
<td></td>
</tr>
<tr>
<td>Throughput</td>
<td>75,000</td>
</tr>
<tr>
<td>Operating hours per year</td>
<td>7,500</td>
</tr>
<tr>
<td>Flue gas flow</td>
<td></td>
</tr>
<tr>
<td>[m$^3$ h$^{-1}$]</td>
<td>9,000</td>
</tr>
<tr>
<td>O$_2$</td>
<td></td>
</tr>
<tr>
<td>[vol % dry]</td>
<td>4.4 - 6.6</td>
</tr>
<tr>
<td>H$_2$O</td>
<td></td>
</tr>
<tr>
<td>[g m$^{-3}$]</td>
<td>720 - 920</td>
</tr>
<tr>
<td>PCDD/F</td>
<td></td>
</tr>
<tr>
<td>[ng I-TEQ m$^{-3}$]</td>
<td>0.020 - 0.082</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td></td>
</tr>
<tr>
<td>[mg m$^{-3}$]</td>
<td>2.7 - 12</td>
</tr>
<tr>
<td>CO</td>
<td></td>
</tr>
<tr>
<td>[mg m$^{-3}$]</td>
<td>12 - 83</td>
</tr>
<tr>
<td>C$_x$H$_y$</td>
<td></td>
</tr>
<tr>
<td>[mg m$^{-3}$]</td>
<td>&lt; 3</td>
</tr>
<tr>
<td>Yearly emission of PCDD/F</td>
<td></td>
</tr>
<tr>
<td>[g I-TEQ yr$^{-1}$]</td>
<td>0.005</td>
</tr>
</tbody>
</table>

1) Refers to dry flue gases under standard conditions
2) Refers to dry flue gases under standard conditions, converted to 11% O$_2$

14.6 Evaluation

From the results of the measurements at an installation for thermal soil cleaning (Table 14.2) an emission factor of 0.07 μg I-TEQ/tonne of treated soil was calculated for this type of process. In the Netherlands in 1991, a total of 350,000 tonnes of soil underwent thermal cleaning (in five installations), so the dioxin emission on the basis of this emission factor is around 0.03 g I-TEQ per year.

The emissions of the installations measured within the MOB framework have not been stated per type of process, for reasons of confidentiality. It suffices to state the total dioxin emission of these installations on the basis of the measurement results presented in Table 14.1. This emission is around 1.7 g I-TEQ per year.
The annual dioxin emission is roughly estimated for the other installations mentioned in the inventory (see Section 14.3) in which no dioxin measurements were conducted (within or outside MOB framework) or for which no data from the literature is known. This estimate is based on the processes where measurements were indeed conducted, as well as on the type and size of the process, the process conditions, and the type of flue gas cleaning, in as far as these are present.

Since, for example, the conditions for the production of glass and rockwool are practically comparable (both are melting processes with comparable temperatures), the same emission factor as for the production of rockwool was taken to indicate the emission at glass manufacture. This produces an emission of around 1 g I-TEQ per year for these other processes.

The total dioxin emission of the high-temperature processes is therefore estimated to be 2.73 g I-TEQ per year.

No data on ESP ash and fabric filter ash as to quantities and dioxin concentrations is available. Several thermal soil cleaning installations are equipped with a wet scrubber. As far as it is known, the wash water is internally circulated or discharged after a purification step. Considering the dioxin emissions of thermal soil cleaners into the air, it is assumed that the emission to water is in any case smaller than 0.1 g I-TEQ per year.

14.7 Summary

The emissions of the various processes mentioned in this chapter have been summarized in Table 14.3.

Table 14.3 Dioxin emissions from high-temperature processes

<table>
<thead>
<tr>
<th>Process</th>
<th>Emission factor [μg I-TEQ per tonne]</th>
<th>PCDD/F emission [g I-TEQ yr⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal soil cleaning:</td>
<td>350,000 tonnes per year</td>
<td>0.07</td>
</tr>
<tr>
<td>Other processes:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>according to measurements:</td>
<td>n.a.</td>
<td>1.7</td>
</tr>
<tr>
<td>according to estimate:</td>
<td>n.a.</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

No data is known on the quantity of dioxin that is discharged with residue. The emission to water is small (< 0.1 g I-TEQ yr⁻¹).
15. TRAFFIC

15.1 General

The dioxin emissions caused by road traffic and by mobile machines\(^4\) are estimated on the basis of fuel consumption, kilometres covered and data from the literature on dioxin emissions. The dioxin emission caused by navigation was included in Chapter 9 (Oil combustion). The dioxin emission as a result of the wear and tear of asphalt roads (AVI fly ash can be used as a filler) was included in Chapter 3 (Incineration of domestic waste).

15.2 Inventoried Processes

Table 15.1 renders the consumption of petrol and diesel oil by road traffic and mobile machines.

Table 15.1 Consumption of fuel by road traffic and mobile machines in the Netherlands (1991)

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Vehicle</th>
<th>Quantity (10(^6) litre)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petrol leaded</td>
<td></td>
<td>1,817</td>
<td>CBS (1992a)</td>
</tr>
<tr>
<td>Petrol unleaded</td>
<td>without catalytic converter</td>
<td>1,076 (^1)</td>
<td>CBS (1992a)</td>
</tr>
<tr>
<td></td>
<td>with catalytic converter</td>
<td>1,627 (^1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>total (petrol unleaded)</td>
<td>2,703</td>
<td></td>
</tr>
<tr>
<td>Diesel oil</td>
<td>road traffic</td>
<td>4,070</td>
<td>CBS (1992b)</td>
</tr>
<tr>
<td></td>
<td>mobile machines</td>
<td>1,050</td>
<td>Van Walwijk and Achten (1991)</td>
</tr>
<tr>
<td></td>
<td>total (diesel oil)</td>
<td>5,120</td>
<td></td>
</tr>
</tbody>
</table>

\(^1\) Estimate, on the basis of the number of cars in the Netherlands with and without catalytic converter

The total distance covered by road traffic in the Netherlands in 1991 was 98.2*10\(^6\) km; 20.6*10\(^6\) km of this was covered by cars driving on leaded petrol (CBS, 1992b).

15.3 Data from the Literature

Dioxin emissions caused by road traffic and mobile machines have not been measured in the Netherlands. In the working document "Sources of Dioxins in the Netherlands" (Bremmer, 1991), the dioxin emission was estimated (on the basis of the then known data from the literature) at 100 pg I-TEQ km\(^{-1}\) when using leaded petrol and diesel oil, and at 1 pg I-TEQ km\(^{-1}\) when using unleaded petrol. The total emission by road traffic in 1989 was estimated at 7 g I-TEQ.

\(^4\) "Mobile machines" are understood to mean here machines, such as tractors, excavators, fork-lift trucks, etc.
In the former West Germany, an extensive investigation was made into the emission of dioxins by combustion engines (Hagenmaier et al., 1990). Quantities of halogens in the fuel and dioxin emission for various types of fuel are presented in Table 15.2. (Note the units in Table 15.2; these are expressed in pg l⁻¹, previously in pg km⁻¹). The dioxin emission from traffic was estimated at 50 g I-TEQ per year for former West Germany.

Table 15.2 Dioxin emission by traffic per type of fuel (Hagenmaier et al., 1990)

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Halogen concentration in fuel [mg kg⁻¹]</th>
<th>Dioxin emission [pg I-TEQ l⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cl⁻</td>
<td>Br⁻</td>
</tr>
<tr>
<td>Fuel leaded</td>
<td>48</td>
<td>94</td>
</tr>
<tr>
<td>Fuel unleaded</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- without catalytic converter</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>- with catalytic converter</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Diesel</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In Belgium, dioxin measurements were conducted in a tunnel (Wevers et al., 1992). From these experiments, an emission factor of 65 pg I-TEQ km⁻¹ for all road traffic collectively was calculated. The dioxin emission by road traffic in Belgium was estimated at 4 g I-TEQ per year. This emission thus does not include the emission by mobile machines.

15.4 Evaluation

The dioxin emission as a result of the road traffic in the Netherlands can be estimated by combining the quantities of fuel given for the Netherlands in Table 15.1, and the dioxin emissions per type of fuel, as found by Hagenmaier et al. (1990) (Table 15.2). The emissions then amount to:
- 2 g I-TEQ for cars driving on leaded petrol;
- 0.06 g I-TEQ for cars driving on unleaded petrol;
- 0.1 g I-TEQ for cars and mobile machines driving on diesel fuel.

According to this form of calculation, the total 1991 dioxin emission in the Netherlands is over 2 g I-TEQ.

If the emission factor of 65 pg I-TEQ/km, as found for all traffic (Wevers et al., 1992), were applied to the Dutch situation, the yearly emission would be over 6 g I-TEQ for a total distance of 98.2*10⁹ km (see above) covered by road traffic in the Netherlands. This emission does not include the emission by the mobile machines. Should this emission be included, the total 1991 emission caused by road traffic and mobile machines is about 7 g I-TEQ, on the basis of the data found by Wevers.

The two methods of approach (on the basis of the data by Hagenmaier and Wevers) produce dioxin emissions that differ by a factor of 3.5. A difference in emission factors between dioxin measurements on individual cars (Marklund et al., 1990) and tunnel experiments (Larssen et al., 1990) had already been found.
Considering the estimates in the working document (Bremmer, 1991) and on the basis of the data by Hagenmaier and Wevers, it is assumed that the 1991 dioxin emission by road traffic and mobile machines was maximally 7 g I-TEQ.

In order to be able to make the estimate given here more accurate, further investigation would be required. The question, however, remains whether a more accurate estimate can contribute to the argumentation on which the already existing attempts to restrict motor traffic are based. Also, with a view to the high costs of such an investigation and the fact that little result is expected from it, additional investigation of the dioxin emission by traffic is not recommended.

15.5 Summary

In summary, Table 15.3 presents the data concerning the dioxin emission from road traffic and mobile machines.

Table 15.3 Data on dioxin emissions from road traffic and mobile machines

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Traffic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distance covered by road traffic (1991) [km]</td>
<td>98.2*10^9</td>
</tr>
<tr>
<td>PCDD/F emission from road traffic (1991) [g I-TEQ yr^-1]</td>
<td>max. 6 1)</td>
</tr>
<tr>
<td>PCDD/F emission from road traffic and mobile machines (1991) [g I-TEQ yr^-1]</td>
<td>max. 7</td>
</tr>
</tbody>
</table>

1  ) Considering the discrepancy between the two methods of approach (i.e. those by Hagenmaier and Wevers), no emission factor is mentioned per type of fuel or per km.

15.6 Future

It is estimated that in the year 2000 approximately 80 x 10^9 km will be driven with unleaded petrol, approximately 2 x 10^9 km with leaded petrol, and approximately 19 x 10^9 km with diesel oil as fuel (RIVM, 1991). Because of the decreasing use of leaded petrol, the dioxin emission from road traffic in 2000 will be lower than in 1991. As no emission factors are available per type of fuel, the decrease according to fuel type cannot be calculated, but can be estimated only. The dioxin emission caused by road traffic and mobile machines will probably be between 0.2 and 5 g I-TEQ per year in the year 2000.
16. SINTERING PROCESSES

16.1 General

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 different industries. The sintering processes in the metal industry (i.e. the sintering of iron ore, coke and admixtures, and the palletizing of iron ore, bentonite and coke for steel production) are treated in this chapter (not in Chapter 17: Metal Industry).

16.2 Process Description

Before the sintering, the various substances are first mixed and, if desired, granulated. The mixture is then strongly heated in a sintering machine. This machine consists of a large number of waggons. These waggons that have been linked up as an endless conveyor belt are equipped with heat-resistant grates. Burners above this grate belt heat the material to the required temperature (1100 - 1200 °C). This causes the fuel in the mixture to be ignited. Air is sucked through the mixture, resulting in the flame front being moved through the sintering bed. The sintering processes are completed once the flame front has passed through the entire mixed layer and all fuel has been burnt.

Cleaning of the flue gases generated during the process is done in different ways: sometimes dedusting (cyclone or fabric filter) suffices; sometimes the flue gases are cleaned by a wet scrubber. The way of cleaning depends on the circumstances and the nature of the emissions (and on the substances to be sintered).

16.3 Inventoried Processes

As far as it is known, four large-scale sintering processes are carried out in the Netherlands:

- The production of artificial gravel from fly ash from power plants 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 fabric 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, almost always 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 phosphorus oven gas. The flue gases are washed twice with water (to remove fluoride, dust and sulphur dioxide), after which the flue gases are emitted.

16.4 MOB Measurement Results

Within the MOB framework, emission measurements were conducted at one sintering installation. The measurement results are presented in Table 16.1.

Table 16.1 Data and measurement results of a sintering process measured within the MOB framework

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Installation 16A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw material</td>
<td>ore, clay, return substances</td>
</tr>
<tr>
<td>Burner fuel</td>
<td>heating gas from installation</td>
</tr>
<tr>
<td>Flue gas cleaning</td>
<td>wet scrubbers</td>
</tr>
<tr>
<td>Operating hours per year</td>
<td>8,000 4)</td>
</tr>
<tr>
<td>Flue gas flow</td>
<td>[m³ h⁻¹] 1)</td>
</tr>
<tr>
<td>Flue gas Temperature</td>
<td>[°C]</td>
</tr>
<tr>
<td>O₂</td>
<td>[vol % dry]</td>
</tr>
<tr>
<td>CO₂</td>
<td>[vol % dry]</td>
</tr>
<tr>
<td>H₂O</td>
<td>[g m⁻³] 1)</td>
</tr>
<tr>
<td>PCDD/F</td>
<td>[ng l-TEQ m⁻³] 2)</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>[mg m⁻³] 2)</td>
</tr>
<tr>
<td>CO</td>
<td>[mg m⁻³] 2)</td>
</tr>
<tr>
<td>CₓHᵧ</td>
<td>[mg m⁻³] 2)</td>
</tr>
<tr>
<td>Yearly emission of PCDD/F</td>
<td>[g l-TEQ yr⁻¹] 3)</td>
</tr>
</tbody>
</table>

1) Refers to dry flue gases under standard conditions
2) Refers to dry flue gases under standard conditions, converted to 11% O₂
3) Total for three furnaces
4) For furnaces 1 and 2; furnace 3 is operating 2,500 hours per year.

16.5 Measurement Results Outside the MOB framework

Outside the MOB framework, measurements were conducted on two processes (16B and 16C). Process 16B is carried out in three similar installations. At two of these installations, measurements were carried out. Table 16.2 summarizes the results of these measurements, as well as the results of measurements conducted on process type 16C.
Table 16.2 Results of measurements of sintering processes outside the MOB framework

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Installation</th>
<th>16B₁</th>
<th>16B₂</th>
<th>16C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw material</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Burner fuel</td>
<td>iron ore, coke, admixtures heating gas of installation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flue gas cleaning</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Working hours per year</td>
<td></td>
<td>8,000</td>
<td></td>
<td>8,000</td>
</tr>
<tr>
<td>Flue gas flow</td>
<td>[m³ h⁻¹] ¹)</td>
<td>232,000</td>
<td>203,000</td>
<td>120,000</td>
</tr>
<tr>
<td>O₂</td>
<td>[vol % dry]</td>
<td>16.3</td>
<td>15.0</td>
<td></td>
</tr>
<tr>
<td>PCDD/F</td>
<td>[ng I-TEQ m⁻³] ²)</td>
<td>6.8</td>
<td>4.5</td>
<td>0.12</td>
</tr>
<tr>
<td>Yearly emission of PCDD/F</td>
<td>[g I-TEQ yr⁻¹] ³)</td>
<td>24 ⁴)</td>
<td></td>
<td>0.06</td>
</tr>
</tbody>
</table>

¹) Refers to dry flue gases under standard conditions
²) Refers to dry flue gases under standard conditions, converted to 11% O₂
³) Confidential information
⁴) Concerns the entire company (three installations)

16.6 Evaluation

Dioxin measurements were conducted into three of the four large-scale sintering processes in the Netherlands. According to the data in Table 16.2, the dioxin emission at installation 16B is about 24 g I-TEQ per year on average. These emissions are about 1 and 0.06 g I-TEQ per year for the installations 16A and 16C, respectively.

The dioxin emission from the process in which no measurements were taken was estimated by comparing the raw material packages, reaction conditions and type of flue gas cleaning in this process with those of the measured processes. This estimate produces a total dioxin emission of about 1 g I-TEQ per year for this installation. The total emission into the air by sintering installations then results in about 26 g I-TEQ per year.

Analysis results of dioxin emissions to water are not yet known. On the basis of process data and the measured dioxin emissions into the air, it is estimated that about 1.5 g I-TEQ is emitted to water as a result of sintering processes. This concerns two processes in which waste water is directly discharged to sea water without cleaning. Meanwhile a measurement has been taken on one of the two processes; the results, however, are not yet available. Considering the size of the estimated emission, taking a dioxin measurement on the other process as well is recommended.

The residues of the flue gas cleaning (sludge of a scrubber, cyclone ash and fabric filter ash) are used again as a raw material in the sintering process in question.
16.7 Summary

Table 16.3 summarizes the dioxin emissions of the large-scale sintering processes.

Table 16.3 Data of dioxin emissions from sintering processes

<table>
<thead>
<tr>
<th>Type of process</th>
<th>Number</th>
<th>Emissions into the air [g I-TEQ yr(^{-1})]</th>
<th>Emission to water [g I-TEQ yr(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sintering process</td>
<td>4</td>
<td>26 (^1))</td>
<td>1.5</td>
</tr>
</tbody>
</table>

\(^1\)) The contribution of one process is 24 g I-TEQ yr\(^{-1}\).

All residues are reused in the process; therefore, there is no discharge of dioxins via residues.

16.8 Future

Once the process with an emission of 24 g I-TEQ per year meets the conditions of the NER concerning this installation, the emission will diminish to about 1 g I-TEQ per year. This means that the dioxin emission into the air as a result of sintering processes will then be about 3 g I-TEQ per year.
17. METAL INDUSTRY

17.1 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 secondary non-ferrous industry.

Of the base metal industry, only the production of pig iron and steel will be discussed. The sintering processes applied in this branch of industry have been dealt with in Chapter 16. No dioxin emissions are expected from the two Dutch companies that produce primary aluminium, and at the company that produces primary zinc, considering the small chloride concentration of the raw materials. The primary production of other non-ferrous metals does not take place in the Netherlands.

17.2 Process Description

17.2.1 Base metal industry

Coke production
Coke is produced by de-aerating coal at high temperature in so-called coke ovens. Coke ovens have been set up from a large number of chambers built side by side and measuring, for example, 4 m high, 13 m deep and 0.5 m wide. The ovens are indirectly heated to about 1000 °C with gas that is released in the production of coke.

Emissions from the production of coke occur particularly when the rooms are being charged and emptied and the coke is being quenched. The rooms are charged with a charging car. This car is equipped with a device that sucks off the vapours that are being released. These vapours are then led to an after burner and a dust arrestor (venturi scrubber or fabric filter). The ejection machine also sucks off the gases being released, and leads these into the atmosphere by way of a dust arrestor (wet scrubber or fabric filter). The coke is moved to the quenching tower, and cooled from 1000 °C to ambient temperature using a large amount of water. The gases and vapours released in this are emitted without cleaning.

Blast furnaces
In a blast furnace, pig iron is produced from iron ore, simultaneously also generating blast furnace gas. The furnace is filled with a mixture of pellets, slag, coke and admixtures (pellets and slag; see Chapter 16). The charging is done via a shaft to insulate the furnace from the atmosphere. Hot air (coming from the hot blast stoves fired with blast furnace gas and enriched with coke oven gas; see below) is fed into the bottom of the furnace. The coke is combusted, generating CO₂ which is reduced to CO because of excess coke. The carbon monoxide causes the iron oxides in the iron ore to be reduced, generating pig iron and slag (melted because of the high temperature). Pig iron and slag are then tapped. The gases sucked off at the tap point are cleaned in a fabric filter. The collected dust is reused in the sintering plant. The hot slag is quenched with water; part of it is quenched to the air.

The blast furnace gas is cleaned in order to make it suitable for purposes of energetics. This gas cleaning consists of a dry pre-cleaning (on the basis of gravity) and a wet cleaning in which the
gas is also cooled. The dust collected in the dry cleaning is reused in the sintering process, and so is the coarse fraction of the sludge that is obtained in the wet cleaning. The fine fraction of this sludge (that contains most of the zinc and lead) is stored. The thus cleaned blast furnace gas is enriched with coke-oven gas. This gas mixture is used partly for the pre-heating of the combustion air of the blast furnace (hot blast stoves) and partly for electricity generation in the UNA power station (Utrecht, North Holland, Amsterdam).

Oxygen steel process
The oxygen steel process takes place in a converter. During this 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 bath with liquid iron. The oxidation products are taken up into the slag or emitted after cleaning via a chimney in the form of gases or dust particles. Coarse particles are removed in a (wet) pre-separator, followed by additional cleaning with a venturi washer.

In addition to this primary dust formation, dust formation (secondary dust) takes place during the charging and tapping of pig iron and steel, respectively. To this end, the converter is connected to a second exhaust system with a fabric filter. The collected (primary and secondary) dust as well as the sludge ("oxy-lime sludge") from the wet dust arrestors is reused in the sintering plant.

17.2.2 Secondary iron and steel industry

In this branch of industry, mainly 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 melting unit. In the shaft, coke and feed material are alternately stacked via an opening in the side wall. During the charging, the coke is ignited, causing the iron to melt and run down. In addition to the emissions of dust (coming from coke, feed material and refractory lining), there are also gaseous emissions. These consist mainly of CO and SO₂, and, for a small part, of pyrolysis products from the feed material. The hot gases from cupola furnaces are sometimes firstly incinerated and then usually cleaned in a dry scrubber especially designed for this purpose. The hot gases must first, to this end, be cooled using heat exchangers.

Electric furnace
The electric furnace is a discontinuously operating melting unit. Usually, an indirect arc is found in the smaller furnaces, while a direct arc is found in the larger ones. The majority of emissions are released when charging the furnace. The nature and quantity depend on the quantity and composition of the input. When using clean sheet steel, only some dust and several gaseous compounds (usually CO, coming from admixture (anthracite or petroleum coke)) will be released. For polluted scrap, the emission will be larger. In addition to furnaces with an arc, "induction kilns" are also used. In the Netherlands, there are two main types of these furnaces used, i.e. the induction channel furnace and the induction crucible furnace. The cleaning of the gases mostly takes place using a fabric filter (Eijsen et al., 1992).

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

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 multichamber furnace.

Rotary kiln
The rotary kiln is usually a discontinuously operating, device consisting of a horizontal cylinder that slowly rotates around its axis. Often, polluted aluminium is melted in it under a covering of melted 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 induction spiral. In order to tap the furnace, it is turned over manually or by using a hydraulic device. This type of furnace is used in the recycling industry to remelt thin-walled, clean types of scrap.

Reverberatory furnace
The reverberatory furnace is, in essence, a chamber-like room into which the scrap is fed. Above the scrap, a flame is fired with which the scrap is heated through direct contact and radiation. The fuel can be both oil and natural gas. This type of furnace is mostly found in industry and is used for melting a large variety of relatively clean types of scrap.

Multichamber furnace
This type of furnace consists of two rooms. The scrap is fed into one of the chambers. In the other room, the metal is heated using a flame, identical to the reverberatory furnace. Through a system with natural or forced convection, the warm metal is transported to the room with the scrap. By circulating the liquid metal through it, the scrap is melted. This type of furnace is mostly used for melting moderately polluted types of scrap.

In the furnaces mentioned, flue gas cleaning is usually done by way of a fabric filter with lime injection. In addition to lime, activated carbon is sometimes injected.

17.3 Inventoried Processes

17.3.1 Base metal industry

In the base metal industry, there are two companies with three coke plants. The coal consumption in these plants is in total 4.09 million tonnes per year. Further, a total of another 0.72 million tonnes of coal are used yearly in the Dutch blast furnaces as an energy carrier (see Chapter 10).

17.3.2 Secondary iron and steel industry

Thirty-nine iron and steel foundries were inventoried in the Netherlands (in 1989). A total of about 360 ktonnes of raw material are used in these foundries (the majority being scrap, the remainder pig iron). In one foundry, 230 ktonnes of scrap are processed in electric furnaces, using a fabric filter as flue gas cleaning. In the remaining 38 foundries, roughly half of the remaining quantity of raw material (about 65 ktonnes) is melted in cupola furnaces (6) and the other half in electric furnaces (number unknown). An unknown, but relatively small quantity of material, is processed in one rotary kiln (a second is under construction). In the rotary kiln and the majority of the electric and cupola furnaces, flue gas cleaning is done using a fabric filter.
In "Dioxins in the metal industry" (Rodenburg et al., 1991), more than 30 iron foundries and smelters were consulted. It appeared that 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 use clean (new) scrap and/or pig iron, exclusively.

17.3.3 Secondary non-ferrous industry

Twelve companies were inventoried that functioned mainly as smelters. Two aluminium smelters process the aluminium obtained to an end product themselves. Table 17.1 presents further production data. In eight of the companies, a fabric filter is used for flue gas cleaning, while lime (and in two companies also carbon) is also injected into the gas flow to be cleaned ("SPIN" document, Secondary non-ferrous industry, in preparation).

Further to the above-mentioned 12 smelters, there are still some 45 foundries. These foundries together produce:
- aluminium and alloys: 15,000 tonnes per year
- copper and alloys  : 2,900 tonnes per year
- other            : 650 tonnes per year

Table 17.1 Production data on smelters in secondary non-ferrous industry

<table>
<thead>
<tr>
<th>Type of metal</th>
<th>Number of companies</th>
<th>Processed scrap [tonne yr⁻¹]</th>
<th>Data of scrap ¹</th>
<th>Type of flue gas cleaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brass</td>
<td>2</td>
<td>48,000</td>
<td>slightly polluted</td>
<td>fabric filter</td>
</tr>
<tr>
<td>Copper /bronze</td>
<td>1</td>
<td>1,000</td>
<td>strongly polluted</td>
<td>lime injection, fabric filter</td>
</tr>
<tr>
<td>Lead</td>
<td>1</td>
<td>20,000</td>
<td>strongly polluted</td>
<td>lime injection, fabric filter</td>
</tr>
<tr>
<td>Aluminium</td>
<td>2</td>
<td>46,000</td>
<td>strongly polluted</td>
<td>lime and carbon injection, fabric filter</td>
</tr>
<tr>
<td>Aluminium</td>
<td>3</td>
<td>8,000</td>
<td>strongly polluted</td>
<td>lime injection, fabric filter or afterburner</td>
</tr>
<tr>
<td>Aluminium</td>
<td>1</td>
<td>35,000</td>
<td>slightly polluted</td>
<td>lime injection, fabric filter</td>
</tr>
<tr>
<td>Aluminium</td>
<td>2</td>
<td>27,000</td>
<td>slightly polluted</td>
<td>no flue gas cleaning</td>
</tr>
</tbody>
</table>

¹) "Strongly polluted" scrap is meant to be understood here as: scrap polluted with, for example, metal-working liquid, plastics, paint, oil, etc. In "slightly polluted" scrap, there are practically no pollutants (e.g.: clean, discarded products, factory scrap of non-ferrous companies).
17.4 MOB Measurement Results

17.4.1 Base metal industry (coke production)

Within the MOB framework, measurements were taken at one coke plant on the following points:
- waste water from the scrubber of the charging car;
- waste water from the scrubber of the ejection machine;
- flue gases from the quenching tower.
(It appeared that it was technically difficult to measure the emissions into the air at charging and
ejection. On the basis of the measured dioxin emissions of the scrubbers to water, an estimate was
made of the emissions into the air).

Table 17.2 presents the results of the emission measurements at the quenching tower. This table
also states the most significant production data. The results of the dioxin analyses of the two
waste-water flows and the yearly emissions calculated from it are shown in Table 17.3.

Table 17.2 Data and measurement results on coke production (quenching tower) measured within
the MOB framework

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Installation 17A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flue gas cleaning</td>
<td>none</td>
</tr>
<tr>
<td>Number of charges per year</td>
<td>51,465</td>
</tr>
<tr>
<td>Coal consumption [tonne yr(^{-1})]</td>
<td>875,000</td>
</tr>
<tr>
<td>Coke production [tonne yr(^{-1})]</td>
<td>670,000</td>
</tr>
<tr>
<td>Flue gas flow ([m^3 h^{-1}]) (^1)</td>
<td>157,000</td>
</tr>
<tr>
<td>Flue gas temperature [°C]</td>
<td>40</td>
</tr>
<tr>
<td>(O_2) [vol % dry]</td>
<td>20.9</td>
</tr>
<tr>
<td>(CO_2) [vol % dry]</td>
<td>0.1</td>
</tr>
<tr>
<td>(H_2O) [g m(^{-3})] (^1)</td>
<td>312</td>
</tr>
<tr>
<td>PCDD/F [ng l-TEQ m(^{-3})] (^2)</td>
<td>0.15 (^3)</td>
</tr>
<tr>
<td>Cl(^-) [mg m(^{-3})] (^2)</td>
<td>22</td>
</tr>
<tr>
<td>CO [mg m(^{-3})] (^2)</td>
<td>54</td>
</tr>
<tr>
<td>(C_xH_y) [mg m(^{-3})] (^2)</td>
<td>12</td>
</tr>
<tr>
<td>Yearly emission of PCDD/F [g l-TEQ yr(^{-1})]</td>
<td>0.2</td>
</tr>
</tbody>
</table>

\(^1\) Refers to dry flue gases under standard conditions
\(^2\) Refers to dry flue gases under standard conditions; not converted to 11% \(O_2\)
\(^3\) Average during 37 charges
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Installation 17A</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>charging car</td>
</tr>
<tr>
<td>Flue gas cleaning</td>
<td>after burner</td>
</tr>
<tr>
<td>Waste water per charge [m$^3$]</td>
<td>5</td>
</tr>
<tr>
<td>Number of charges per year</td>
<td></td>
</tr>
<tr>
<td>PCDD/F concentration of waste water $^1)$ [ng I-TEQ m$^{-3}$]</td>
<td>81</td>
</tr>
<tr>
<td>Yearly emission of PCDD/F via waste water [g I-TEQ yr$^{-1}$]</td>
<td>0.021 $^2)$</td>
</tr>
</tbody>
</table>

$^1$ Average of 10 charges

$^2$ On the basis of a 95% retention efficiency of the dust arrestors and the assumption that all dioxins are bound to dust, it has been calculated that the yearly emission into the air via these sources is 0.002 g I-TEQ.
17.4.2 Secondary iron and steel industry

Within the MOB framework, emission measurements were taken at a company that produces high-grade steel from scrap. Table 17.4 presents the results.

Table 17.4 Data and measurement results from steel production, measured within the MOB framework

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Installation 17B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of furnace (two)</td>
<td>electric furnaces</td>
</tr>
<tr>
<td></td>
<td>direct arc</td>
</tr>
<tr>
<td>Flue gas cleaning</td>
<td>fabric filter</td>
</tr>
<tr>
<td>Operating hours per year</td>
<td>6,000</td>
</tr>
<tr>
<td>Flue gas flow</td>
<td>([m^3 h^{-1}]^{1)})</td>
</tr>
<tr>
<td>Flue gas Temperature</td>
<td>[°C]</td>
</tr>
<tr>
<td>(O_2)</td>
<td>[vol % dry]</td>
</tr>
<tr>
<td>(CO_2)</td>
<td>[vol % dry]</td>
</tr>
<tr>
<td>(H_2O)</td>
<td>[g m(^{-3})](^{1)})</td>
</tr>
<tr>
<td>PCDD/F (^2)}</td>
<td>[ng I-TEQ m(^{-3})] (^2)</td>
</tr>
<tr>
<td>(Cl^{-})</td>
<td>[mg m(^{-3})] (^2)</td>
</tr>
<tr>
<td>CO</td>
<td>[mg/m(^{-3})] (^2)</td>
</tr>
<tr>
<td>(C_xH_y)</td>
<td>[mg m(^{-3})] (^2)</td>
</tr>
<tr>
<td>Yearly emission of PCDD/F</td>
<td>[g I-TEQ yr(^{-1})]</td>
</tr>
</tbody>
</table>

1) Refers to dry flue gases under standard conditions
2) Refers to dry flue gases under standard conditions; not converted to 11% \(O_2\)
3) Also present is a pan-shaped furnace which allows the steel to receive the correct composition
4) The dust exhaust of the electric furnace, the pan-shaped furnace and the ventilation openings in the roof are connected to this fabric filter.

17.5 Measurement Results Outside the MOB Framework

17.5.1 Secondary iron and steel industry

An investigation was made in 1989 of the dust emissions of the 17B installation (confidential report). It showed that the dust emission via the roof caps was 20.7 kg \(h^{-1}\) and via the stack of the fabric filter 1.4 kg \(h^{-1}\). More than a year later, the dioxin concentration of the dust obtained in the dust measurements at the roof caps was determined at an average 7.8 ng I-TEQ g\(^{-1}\) (confidential report).
During a measurement taken within the MOB framework at installation 17B, a sample of dust was collected from the fabric filter. The dioxin concentration of this sample was determined. The concentration was, on average, 0.146 ng I-TEQ g⁻¹ (confidential report). In the period October 1990 to October 1991, 2,354 tonnes of dust were discharged (collected with fabric filter unit 17B; company information; this quantity agrees well with the quantity determined in the above-mentioned 1989 dust emission investigation, i.e. about 6,000 x 460 kg h⁻¹ = 2,760 tonnes per 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 is not known; Rodenburg et al., 1991). In this foundry, scrap iron was melted in induction furnaces at a temperature of 1500 °C (own scrap iron, clean engine blocks, brake drums and the like, however, no chip).

17.5.2 Secondary non-ferrous industry

From confidential reports concerning emission measurements at an aluminium smelter, two emission factors were calculated for melting "strongly polluted" (see Table 17.1) aluminium scrap. In this company, emission measurements were taken before and after a modification to the flue gas cleaning (in addition to lime, activated carbon is now also injected for the fabric filter). The dioxin concentrations measured in the flue gases, as well as the calculated emission factors, are shown in Table 17.5. The dioxin concentration of the filter ash, as stated in the table, was found at two aluminium smelters. This table also includes emission data (from a confidential report) of the company (see Table 17.1) that produces lead scrap. From this data, a yearly emission of 0.1 g I-TEQ was calculated for this company.

<table>
<thead>
<tr>
<th>Type of scrap</th>
<th>Type of flue gas cleaning</th>
<th>PCDD/F concentration of flue gases [ng I-TEQ m⁻³]¹)</th>
<th>Emission factor [µg I-TEQ per tonne of scrap]</th>
<th>PCDD/F concentration in filter ash [ng I-TEQ g⁻¹]¹)</th>
<th>Emission factor [mg I-TEQ per tonne of scrap]</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;Strongly polluted&quot; aluminium</td>
<td>fabric filter with lime injection</td>
<td>2.9</td>
<td>35</td>
<td>3 - 4</td>
<td>0.15</td>
</tr>
<tr>
<td>&quot;Strongly polluted&quot; aluminium</td>
<td>fabric filter with lime and activated coal injection</td>
<td>0.13</td>
<td>1.7</td>
<td>not known</td>
<td></td>
</tr>
<tr>
<td>Lead</td>
<td>fabric filter with lime injection</td>
<td>1.3</td>
<td>5</td>
<td>7.7 and 17.8</td>
<td>not known²</td>
</tr>
</tbody>
</table>

¹) Refers to dry flue gases under standard conditions
²) No data available concerning the quantity of filter ash
17.6 Evaluation

17.6.1 Base metal industry

Coke production

Emissions into the air
From the measurements on installation 17A (see Table 17.2) it was calculated that the dioxin emission at the quenching of coke is 0.23 μg I-TEQ per tonne of coal. On the basis of the coal consumption, the emission from charging and ejection was estimated for this installation at 0.002 μg I-TEQ per tonne of coal (with wet scrubbers as flue gas cleaning; see Table 17.2). Therefore, the emission factor in total is about 0.23 μg I-TEQ per tonne of coal. It is assumed that for the other two coke plants the same emission factor may be used for the emissions at charging and ejection (flue gas cleaning with fabric filters). On the basis of the total coal consumption of 4.09 million tonnes per year, the total dioxin emission is 0.9 g I-TEQ per year.

Emission to water
The waste water from installation 17A is still treated in a water purification plant. The dioxin emission via the purified water is considered negligible.

Residues
No data is known concerning the quantity of dioxins discharged with sludge coming from the above-mentioned water purification. Neither is it known in what way this sludge is processed. The minimum quantity of dioxins being discharged will be the quantity found in the (unpurified) waste-water stream of installation 17A, i.e. 0.04 g I-TEQ per year (on the basis of the assumption that no dioxins are discharged with the purified water; see previously).

Blast furnaces/oxy-steel process/incineration of blast furnace gas
On the basis of process and production data of the blast furnace and oxy-steel processes, as well as on the basis of confidential results of dioxin measurements, it is assumed that dioxin emission into the air may occur at:
- the incineration of enriched blast furnace gas in the hot blast stoves at the blast furnaces;
- the tapping of iron and slag in the blast furnaces;
- the incineration of enriched blast furnace gas by the UNA;
- the primary and secondary exhausts in the oxy-steel processes.
The total dioxin emission from these sources is probably in the order of 0.5 g I-TEQ per year.

17.6.2 Secondary iron and steel industry

Emission into the air
At installation 17B, the dioxin emission via the stack of the fabric filter is 0.08 g I-TEQ per year. The dust emission after the fabric filter is 8,400 kg yr⁻¹ (1.4 kg h⁻¹ at 6,000 working hours per year), according to the investigation made in 1989. In addition to the above-mentioned emission, there is another emission via the roof caps. The dust emission via these caps was 124 tonnes per year (20.7 kg h⁻¹ and 6,000 h yr⁻¹), according to the 1989 investigation (see section 17.5.1). The dust emitted by these roof caps is actually the dust that is not extracted by the dust arrester. The dioxin concentration of this dust has been determined at 7.8 ng I-TEQ g⁻¹ (see section 17.5.1). This concentration corresponds well with the dioxin concentration of the dust that is emitted via the stack (after the fabric filter), i.e. 9.5 ng I-TEQ g⁻¹. On the basis of the data stated, the dioxin emission via the roof caps is 0.97 g I-TEQ per year. The total dioxin emission into the air by this company is approximately 1 g I-TEQ per year (processing 230 ktonnes of iron scrap per year).
Of the remaining 38 companies, one company did not show any dioxins (< 0.09 ng I-TEQ m⁻³; see section 17.5.1) in the ventilation air (with induction furnaces; temperature 1500 °C). Aal that is known about the raw material use, is that both iron scrap and pig were applied. Concerning the flue gas cleaning systems, it is only known that a fabric filter is used in the rotary drum and in the majority of the electric and cupola furnaces. It is assumed that no dioxin emissions occur in companies that use only clean scrap iron and/or pig. In view of the available data on the secondary iron and steel industry, a worst-case approach is assumed, the assumption being that:
- dioxins are formed at half of the 38 companies involved;
- in total, this half also processes half of the inventoried quantity of scrap iron, i.e. about 65 ktonnes;
- all dioxins formed are emitted into the air.

An emission factor was calculated on the basis of data of the above-mentioned company (installation 17B), where various measurements were taken. The quantity of dioxins formed by this company is a total of 1.35 g I-TEQ per year (into the air 1 g I-TEQ and together with the residues, see later, 0.35 g I-TEQ). At a processing rate of 230 ktonnes of scrap iron per year, this means that a quantity of about 6 μg I-TEQ per tonne of processed scrap iron is formed. On the basis of this emission factor and the above assumptions, the dioxin emission of the other companies totals about 0.4 g I-TEQ per year.

The dioxin emission of the secondary iron and steel industry into the air boils down to a total of 1.4 g I-TEQ per year.

Residues
At installation 17B, 2,354 tonnes of dust (collected with the fabric filter) were removed to the C3 storage basin in 1991. The dioxin concentration of this dust is 0.146 g I-TEQ g⁻¹, so that 0.35 g I-TEQ of dioxins is discharged annually with the dust. Too little data is known on flue gas cleaning techniques possibly applied by other companies in the branch of industry under consideration (see section 17.3.2) to be able to make a sound estimate of the discharge of dioxins together with the residues.

17.6.3 Secondary non-ferrous industry

Emissions into the air
It is assumed that no dioxin emission occurs at smelters that exclusively process clean scrap iron. The emission factors for the processing of "strongly polluted" aluminium scrap are known for the two flue gas cleaning techniques applied (on the basis of measurements outside the MOB framework, see section 17.5.2), i.e.:
- a fabric filter with lime injection: 35 μg I-TEQ per tonne of aluminium scrap;
- a fabric filter with lime and activated carbon injection: 1.7 μg I-TEQ per tonne of aluminium scrap.

No emission data are known on the processing of "slightly polluted" non-ferrous scrap in installations without flue gas cleaning. As the scrap contains only few pollutants (see Table 17.1), it is assumed that the emission factor is lower than the emission factor found in the processing of "strongly polluted" scrap in which a fabric filter with lime injection is present as flue gas cleaning. With the processing of "slightly polluted" scrap without flue gas cleaning, an emission factor of 10 μg I-TEQ per tonne of scrap is assumed. With the processing of "slightly polluted" aluminium scrap with lime injection and a fabric filter, an emission factor of 5 μg I-TEQ per tonne of scrap is assumed.

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Emission data on the company that processes copper/bronze are not known. Considering the fact that here "strongly polluted" scrap is processed and a fabric filter with lime injection is used as flue gas cleaning, an emission factor is assumed for this company which is identical to that of the processing of aluminium scrap, i.e. 35 $\mu$g I-TEQ per tonne of scrap.

No emission data are known on the 45 inventoried foundries that together produce about 18,500 tonnes of non-ferrous metal. Pollutants will hardly occur in the raw materials used because instead of scrap, mostly so-called "pig" is used. No dioxin emissions are expected from these foundries.

The dioxin emission from the secondary non-ferrous industry was calculated on the basis of the above-mentioned data, as well as the data stated in sections 17.3.3 and 17.5.2. The results have been summarized in Table 17.6.

Table 17.6  Data of dioxin emissions from the secondary non-ferrous industry

<table>
<thead>
<tr>
<th>Type of metal</th>
<th>Processed scrap [tonne yr$^{-1}$]</th>
<th>Type of flue gas cleaning</th>
<th>Emission factor [(\mu)g I-TEQ per tonne of scrap]</th>
<th>PCDD/F emission [g I-TEQ yr$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smelters</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>messing (2 companies)</td>
<td>48,000</td>
<td>fabric filter</td>
<td>5</td>
<td>0.24</td>
</tr>
<tr>
<td>slightly polluted</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>copper/bronze (1 company)</td>
<td>1,000</td>
<td>lime injection/fabric filter</td>
<td>35</td>
<td>0.04</td>
</tr>
<tr>
<td>lead (1 company)</td>
<td>20,000</td>
<td>lime injection/fabric filter</td>
<td>5</td>
<td>0.11</td>
</tr>
<tr>
<td>aluminium (2 companies)</td>
<td>46,000</td>
<td>injection of lime and activated carbon fabric filter</td>
<td>1.7</td>
<td>0.08</td>
</tr>
<tr>
<td>strongly polluted</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>aluminium (3 companies)</td>
<td>8,000</td>
<td>lime injection/fabric filter or after burner</td>
<td>35</td>
<td>0.28</td>
</tr>
<tr>
<td>strongly polluted</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>aluminium (1 company)</td>
<td>35,000</td>
<td>lime injection/fabric filter</td>
<td>5</td>
<td>0.18</td>
</tr>
<tr>
<td>slightly polluted</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>aluminium (2 companies)</td>
<td>27,000</td>
<td>none</td>
<td>10</td>
<td>0.27</td>
</tr>
<tr>
<td>slightly polluted</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Various foundries (about 45 companies)</td>
<td>18,500 $^1$)</td>
<td>unknown</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td>1.2</td>
</tr>
</tbody>
</table>

$^1$ Concerns produced product

Residues
From the data at two aluminium smelters (with fabric filters with lime injection), it was calculated that per tonne of scrap about 0.15 mg I-TEQ was discharged with the filter ash. The quantity of dioxins discharged with the filter ash could not be calculated for the lead smelter, because the quantity of filter ash was not known. An estimate of the quantity of dioxins that is discharged with the filter ash can be given only on the basis of the above-mentioned factor of 0.15 mg I-TEQ per tonne of scrap. The quantity of polluted scrap that is processed in secondary non-ferrous companies applying a fabric filter as flue gas cleaning amounts to a total of 154,000 ktonnes per year (see Table 17.6). The quantity of dioxins discharged in filter ash is then calculated at 23.1 g I-TEQ per year.
17.7 Summary

The emissions from the three sectors of the metal industry have been summarized in Table 17.7.

Table 17.7 Data for dioxin emissions from the metal industry

<table>
<thead>
<tr>
<th>Sector of metal industry</th>
<th>PCDD/F emission into the air [g I-TEQ per year]</th>
<th>Residue [g I-TEQ per year]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base metal industry</td>
<td>1.4</td>
<td>0.04</td>
</tr>
<tr>
<td>Secondary iron and steel industry</td>
<td>1.4</td>
<td>&gt; 0.35 (^1)</td>
</tr>
<tr>
<td>Secondary non-ferrous industry</td>
<td>1.2</td>
<td>23.1</td>
</tr>
<tr>
<td>Total</td>
<td>4.0</td>
<td>&gt; 23.5</td>
</tr>
</tbody>
</table>

\(^1\) Data are not known for all installations (companies).

The dioxin emissions from the metal industry to water are regarded as negligible.
18. CHEMICAL PRODUCTION PROCESSES

18.1 General

In production processes in the chemical industry in the Netherlands, 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 majority will end up in solid or liquid waste and/or sludge. Only a small part of the dioxins formed is emitted into the air or to water during these processes. The waste is incinerated as hazardous waste. This has been dealt with in Chapter 4. Sludge from purification plants is usually incinerated in installations for sludge incineration (see Chapter 5) or in installations for hazardous waste incineration.

The quantity of dioxins that remains behind in the end products in Dutch production processes is 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 19.

18.2 Process Description

Chlorophenols, chlorobenzenes and derivatives

These compounds are used in the manufacture of pesticides, medicine and in the production of chemical specialties, which in turn are used again as intermediate products for medicine or pesticides.

The production processes mostly occur at temperatures that are higher than room temperature, during which dioxins can be formed via condensation reactions. Dioxins are especially formed at temperatures above 150 °C in an alkaline environment. The forming of dioxins can be minimized by setting optimum process conditions and monitoring the process control well.

The end products are purified by processes such as filtration, scrubbing or distillation. As far as it is known, the solid and liquid residues of these purification processes are always incinerated as hazardous waste (see Chapter 4). Discharged wash water is purified via a purification installation. The sludge thus generated is usually incinerated in sludge incineration installations (see Chapter 5) or in installations for hazardous waste incineration (Chapter 4). The vent gases and the ventilation gases are usually cleaned with scrubbers or an after burner.

Sometimes chlorobenzenes are used as a solvent in a chemical process. The solvent does not always take part in the chemical process, and must be removed again ultimately, e.g. by distillation. During the process and the purification, 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 usually unsaturated hydrocarbons or alcohols. Formation of chloraromatics from the unsaturated compounds and, consequently, formation of dioxins is possible under the usual process conditions.

Solid and liquid wastes that are released from the manufacturing and purification processes are incinerated as hazardous wastes (see Chapter 4). The vent gases and the ventilation gases are usually purified with scrubbers and/or an after burner, 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. In the regeneration, the carbon deposit formed on the catalyst is burnt off (temperature about 600 °C), after which the chlorine concentration of the catalyst is brought again to the correct level using a chlorinated hydrocarbon (temperature about 500 °C). The flue gases at this regeneration are usually cleaned with a gas scrubber.

Activated carbon is used for cleaning waste water, drinking water and flue gases. In addition to the regeneration of the activated coal, the reactivation of activated carbon also takes place (in some cases, the activated carbon is incinerated; see Chapter 4). In regeneration (usually "on site"), the activated carbon is heated (with steam or hot gases), so that the adsorbed substances are desorbed. The reactivation of activated carbon takes place in cooperation with special companies (mostly the supplier of the activated carbon). In reactivation, the carbon is heated to 800-1000 °C, making the pore structure suitable again for the adsorption process. The gases released in the reactivation are burnt in an after burner at temperatures between 800 and 1000 °C, depending mainly on the presence of chlorine compounds.

18.3   Inventoried Processes
Chlorophenols, chlorobenzenes and derivatives
Three companies in the Netherlands manufacture pesticides in which process chlorobenzenes, and derivatives of chlorobenzene or chlorophenol are used or produced. Besides, these compounds are applied as raw material in less than 20 companies in the chemical industry (Bremmer, 1991). The quantities produced or applied are not known.

Chlorinated aliphates
The production of chlorinated aliphates in the Netherlands is approximately 1.3 million tonnes per year. Applications are specifically found in the production of plastics and of solvents, propellants and foaming agents. Tables 18.1 and 18.2 show some examples.
Table 18.1  Application of several chlorinated aliphates as a raw material or intermediate product in the production of other halogenated hydrocarbons (Verhagen, 1990)

<table>
<thead>
<tr>
<th>Component</th>
<th>Production (1988) [tonne per year]</th>
<th>Production of</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-dichloroethane (DCE)</td>
<td>700,000</td>
<td>vinyl chloride</td>
</tr>
<tr>
<td>Allyl chloride</td>
<td>&gt;70,000</td>
<td>epichlorohydrin (ECH)</td>
</tr>
<tr>
<td>Chloroform</td>
<td>15,000</td>
<td>HCFK 22</td>
</tr>
</tbody>
</table>

Table 18.2  Application of several chlorinated aliphates as a raw material for polymers or non-halogenated compounds (Verhagen, 1990)

<table>
<thead>
<tr>
<th>Component</th>
<th>Production (1988) [tonne per year]</th>
<th>Production of</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinyl chloride</td>
<td>375,000</td>
<td>PVC/VC co-polymers</td>
</tr>
<tr>
<td>1,2-dichloroethane (DCE)</td>
<td>50,000</td>
<td>ethylenediamine</td>
</tr>
<tr>
<td>Epichlorohydrin</td>
<td>&gt;50,000</td>
<td>(mainly) epoxy resins</td>
</tr>
</tbody>
</table>

Approximately 95% of the total quantity of aliphatic chlorinated hydrocarbons are produced by six companies. The remainder is produced by about 10 other companies (Verhagen, 1990).

Various chemical processes
The regeneration of the catalyst that is used in reforming processes takes place in six installations at five companies. In the Netherlands, the reactivation of activated carbon is done by one company.

18.4  Measurements Within the MOB Framework

Chlorophenols, chlorobenzenes and derivatives
Within the MOB framework, dioxin measurements were carried out at a plant for pesticides and a plant for crop protection chemicals. The measurements were purposely carried out at these companies because, in view of the size of these companies, the raw material package and the reaction conditions, the largest dioxin emission could be expected in these chemical processes. Table 18.3 states the results of these measurements.

Chlorinated aliphates
Within the MOB framework, no measurements were carried out during the production or the application of chlorinated aliphates.

Various chemical processes
One dioxin measurement was carried out at an installation for the regeneration of catalyst used in reforming processes. Table 18.3 also states the results of this measurement.
### Table 18.3 Data and measurement results for chemical production processes measured within the MOB framework

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Installations</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>18A</td>
<td>18B</td>
<td>18C</td>
<td></td>
</tr>
<tr>
<td>Type of process</td>
<td>plant for pesticides</td>
<td>plant for crop protection chemicals</td>
<td>regeneration of catalyst</td>
<td></td>
</tr>
<tr>
<td>Type of flue gas</td>
<td>vent gases</td>
<td>vent and ventilation gases</td>
<td>vent gases</td>
<td></td>
</tr>
<tr>
<td>Flue gas cleaning</td>
<td>gas scrubber</td>
<td>gas scrubber</td>
<td>gas scrubber</td>
<td></td>
</tr>
<tr>
<td>Operating hours per year</td>
<td>7,200</td>
<td>8,760</td>
<td>8,000</td>
<td></td>
</tr>
<tr>
<td>Flue gas flow</td>
<td>[m³h⁻¹]¹</td>
<td>260</td>
<td>6,500</td>
<td>260</td>
</tr>
<tr>
<td>Flue gas temperature</td>
<td>[°C]</td>
<td>22</td>
<td>23</td>
<td>46</td>
</tr>
<tr>
<td>O₂ (vol % dry)</td>
<td>1.4</td>
<td>20.7</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>CO₂ (vol % dry)</td>
<td>-</td>
<td>-</td>
<td>21.6</td>
<td></td>
</tr>
<tr>
<td>H₂O₂ (g/m³)</td>
<td>20</td>
<td>-</td>
<td>-</td>
<td>72</td>
</tr>
<tr>
<td>PCDD/F</td>
<td>[ng I-TEQ/m³]²</td>
<td>7.2</td>
<td>0.02 - 0.05</td>
<td>8</td>
</tr>
<tr>
<td>Yearly PCDD/F emission</td>
<td>[g I-TEQ yr⁻¹]</td>
<td>0.013</td>
<td>0.001 - 0.003</td>
<td>0.017</td>
</tr>
</tbody>
</table>

¹) Refers to dry flue gases under standard conditions
²) Refers to dry flue gases under standard conditions, conversion to 11% O₂ is not relevant for this flue gas flows
³) Not measured; calculated with moisture content of ambient air for correction to dry cubic metres
⁴) Company statement

### 18.5 Measurements Outside the MOB Framework

Emissions to water
Data concerning the emissions to water are known for a number of chemical production processes. These data, however, are confidential and will therefore not be stated here individually. On the basis of these data, an estimate of the dioxin emissions to water will be given in the Evaluation.

### 18.6 Data from the Literature

Dioxins are formed in the oxychlorination of ethene (the first reaction step for the production of vinyl chloride monomer (VCM, also called MVC) (Evers, 1989). Copper chloride, used as a catalyst in this process, appears to play a central role in this dioxin formation.

Abroad, dioxins were shown to be present in the sludge of graphite electrodes that are used in the chloroaalkali process (Rappe, 1990). These electrodes have, since the end of the 1970s, no longer been used in the Netherlands (company information).
18.7 Evaluation

18.7.1 Emission into the air

Chlorophenols, chlorobenzenes and derivatives
The dioxin emissions into the air of the two companies that were measured within the MOB framework were 0.013 and 0.001 - 0.003 g I-TEQ per year. The emission of these two together is approximately 0.013 g I-TEQ per year.

The installations at which measurements were carried out have been equipped with a gas scrubbing unit (see Table 18.2). It is assumed that in smaller units the gases are not always cleaned. It is also assumed that the dioxin emission of the other 20 companies (see 18.3) is, per company, of the same order of magnitude as the average emission of the plants measured within the MOB framework, i.e. 0.007 g I-TEQ per year. The total dioxin emission into the air of the processes in question is then approximately 0.2 g I-TEQ per year.

Chlorinated aliphates
Nothing is known of these processes as to their emissions into the air. According to the literature (NATO-CCMS, 1988; Hutzinger, 1989), fewer dioxins are formed in these processes than in the processes that produce chlorophenols, chlorobenzenes and derivatives. The flue gas flows of the larger processes are incinerated in an after burner or cleaned via a gas scrubbing unit, also in the production of chlorinated aliphates. The dioxin concentrations of flue gas flows after gas scrubbers and after burners are small (see Chapter 4). A gas scrubbing unit may sometimes increase the dioxin concentration (in TEQ) (Frede, 1991). However, this only occurs to a limited extent under specific conditions (at low concentrations). Emissions of the small-scale processes occur via ventilation. As the flow rates and the emission concentrations are low here, this also applies to the emissions. On the basis of the above, it is roughly estimated that the emission in the production of chlorinated aliphates will be smaller than in the production of chlorophenols and chlorobenzenes (i.e. smaller than 0.2 g I-TEQ/year). In order to be able to better ascertain this estimate, a more detailed study of the waste flows for the various process types is required, as well as (possibly) measurements.

Various chemical processes
Within the MOB framework, the dioxin emission of one of the six inventoried installations for catalyst regeneration was measured. An emission of 0.017 g I-TEQ per year was determined. Considering the size and the process conditions of the other five installations, it is assumed that the annual emission per installation will be smaller than that of the installation whose emission was determined.

In view of the process conditions and the temperature used in the after burner, it is assumed that, for the only installation for reactivation of activated carbon, the dioxin concentration of the flue gases is of the same order of magnitude as for the thermal after burners mentioned in Chapter 4. The dioxin emission is therefore regarded as being small.

The total dioxin emission of the installations in question is roughly estimated at 0.1 g I-TEQ per year.
18.7.2 Emission to water

In the working document, it was estimated that the emission to water caused by chemical production processes was 2 g I-TEQ per year. This estimate was based on particularly on data supplied by RIZA (Turkstra and Pols, 1986). More recently, dioxin measurements were carried out on the emissions to water from a number of chemical production processes. In a number of companies where the possibility of dioxin emission was not excluded, no dioxin was found in the waste water. Various companies have modified their plant operation, reducing the discharge of dioxins drastically, or even to 0. Some companies have put into operation biological purification installations, discharging the effluent via the purification installation. A considerable portion of the dioxins is discharged with the sludge.

As far as it is known, the sludge is incinerated as hazardous waste, or incinerated in a sludge incinerator. On the basis of the above information and confidential data concerning the dioxin emission to water, it is estimated that the total dioxin emission to water is approximately 0.5 g I-TEQ per year.

18.7.3 Emissions via wastes and sludge

In a number of processes in the chemical industry, considerable quantities of dioxins are formed. The dioxins occur mainly in the waste substances (distillation residue, etc.) and partly in the sludge of the wastewater purification installations of the companies involved. These wastes and sludges are, as far as it is known, incinerated. The dioxin emissions from this incineration have been reported on in Chapters 4 and 5.

18.8 Summary

Table 18.3 summarizes the emissions to air and water in the chemical production processes. The waste substances and sludges being released in these processes are incinerated (see Chapters 4 and 5).

Table 18.3 Dioxin emissions in chemical production processes

<table>
<thead>
<tr>
<th>Type of process</th>
<th>Emissions into air [g I-TEQ per year]</th>
<th>Emissions to water [g I-TEQ per year]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorophenols, chlorobenzenes and derivatives</td>
<td>0.2</td>
<td>-</td>
</tr>
<tr>
<td>Chlorinated aliphates</td>
<td>0.2</td>
<td>-</td>
</tr>
<tr>
<td>Various chemical processes</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>0.5</strong></td>
<td><strong>0.5</strong></td>
</tr>
</tbody>
</table>

1) The dioxin emissions from the incineration of hazardous wastes and sludge have been included in Chapters 4 and 5.
19. USE OF PESTICIDES, specifically WOOD PRESERVATIVES

19.1 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 and are thus spread into the environment only at their application. Despite a ban on the application of some of these products, emissions can still take place through evaporation or washing away 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;
- pentachlorophenol as a preservative in Thomas slag;
- pentachlorophenyllaurate as a fungicide in the textile industry;
- pentachlorophenol as a wood preservative, particularly in the past.

These subjects will be discussed below.

19.2 Agricultural Pesticides and Agents for Veterinary Use

In the working document, it was estimated that in 1989 about 0.6 g I-TEQ was brought into the environment because of the use of agricultural pesticides and agents for veterinary use. This estimate was based on the consumption of chlorinated pesticides and a number of determinations of the dioxin concentration of pesticides (Bremmer, 1991). The production methods for pesticides have been improved in the last few years. It is expected that fewer dioxins will now be formed (internal company information). Recent analysis data is not known. It is assumed that because of meticulous production the quantity of dioxins that is brought into the environment will at least be halved to 0.3 g I-TEQ per year, the majority of which will be spread with the pesticides over agricultural land.

19.3 Pentachlorophenol as a Preservative in Slug Poison

For about the last two years, pentachlorophenol has no longer been used as a preservative in Slug poison (internal company information). Emission of dioxins, also because of their use in the past, does not occur any more.

19.4 Pentachlorophenyllaurate as a Fungicide in the Textile Industry

Since 1 July 1992, pentachlorophenyllaurate is no longer allowed as a fungicide (Statute Book 1992, 455). Before that date, it was particularly applied in products with a medium lifetime, such as tents and sunblinds, and in the production of sponges. In the working document, an estimate for 1989 was given for the emissions of dioxins as a consequence of the use of fungicides containing pentachlorophenyllaurate. Because of the recently issued ban on their application, the emissions will slowly decrease. For the emissions in 1991, the same values are taken as in 1989; Table 19.1 shows these.
Table 19.1  Dioxin emissions from the application of pentachlorophenyllaurate as a fungicide  
(1989 situation)

<table>
<thead>
<tr>
<th>Emission to</th>
<th>PCP emission [tonne per year]</th>
<th>PCDD/F emission [g I-TEQ yr⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>2</td>
<td>0.06</td>
</tr>
<tr>
<td>Water</td>
<td>3</td>
<td>0.09</td>
</tr>
<tr>
<td>Soil</td>
<td>5</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Waste from products treated with pentachlorophenyllaurate will be partly incinerated, during which 
dioxins are largely decomposed. Another part will be dumped. The total quantity of dioxins 
discharged with waste substances of products treated with pentachlorophenyllaurate is estimated at 
6.7 g I-TEQ for 1989 (Slooff et al., 1991). Nothing is known about the leaching behaviour. 
Because of the low solubility in water, leaching is deemed improbable.

19.5  Pentachlorophenol as a Wood Preservative

19.5.1  Introduction

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. 
In order to give an indication of the dioxin emission, the quantities of PCP and dioxins present in 
wood should be known. Section 19.5 successively deals with:
- the quantities of PCP and Na-PCP that have been applied as wood preservative in the past 
years;
- the quantity of dioxin that has been emitted in relation to the PCP emission.

19.5.2  Quantities of PCP and Na-PCP used

As from 1 January 1989, there has been a ban in the Netherlands on the use of PCP and salts of 
PCP for wood preservation and fungistasis. PCP was used since 1955, particularly in exterior wall 
carpentry. It was never allowed for use on wood in dwellings. Yet an investigation made in 1988 
detected the presence of PCP in 22% of the samples of imported parquet wood (Mensink et al., 1988).

Na-PCP was applied as a fungicide in recently sawn wood. It protects against blue moulds (wood 
discolouring) for some weeks. Na-PCP was used in the cultivation of mushrooms as a disinfectant 
of wooden floors and side shelves. As from 1 January 1990, this application has also been 
prohibited.

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 (internal company 
information). The import of wood treated with PCP has considerably decreased in the last few 
years. Imported wood that has been treated with Na-PCP is mainly used in the packaging industry. 
The trade association for the packaging industry (EPV, 1992) estimates that in 1991 a maximum of 
5% of wood imported for the packaging industry was treated with Na-PCP. This concerned 
mainly wood from Chile and Portugal. In 1987, an investigation made by the National Food
Inspection Department for the district of Drenthe (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.

With respect to the use of PCP and Na-PCP in the Netherlands, a number of consumption data from 1980 on are known (Bremmer, 1991). Additional data concerning the period before 1980 was obtained through information from the corporate sector and public institutions. Table 19.2 presents the estimates of the consumption of PCP and Na-PCP in the Netherlands and of the quantities imported via treated wood. These quantities are presented because this data is necessary to estimate the dioxin emissions (see section 15.5).

Table 19.2  Estimates of the PCP and Na-PCP consumption in the Netherlands, and of the import of PCP and Na-PCP in wood (in tonnes)

<table>
<thead>
<tr>
<th>Year</th>
<th>PCP consumption</th>
<th>PCP import</th>
<th>PCP total</th>
<th>Na-PCP consumption</th>
<th>Na-PCP import</th>
</tr>
</thead>
<tbody>
<tr>
<td>1955 - 1960</td>
<td>175</td>
<td>25</td>
<td>200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1961 - 1965</td>
<td>225</td>
<td>50</td>
<td>275</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1966 - 1975</td>
<td>225</td>
<td>50</td>
<td>275</td>
<td>25</td>
<td>75</td>
</tr>
<tr>
<td>1976 - 1979</td>
<td>200</td>
<td>50</td>
<td>250</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1980</td>
<td>35</td>
<td>10</td>
<td>45</td>
<td>20</td>
<td>60</td>
</tr>
<tr>
<td>1981</td>
<td>30</td>
<td>10</td>
<td>40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1982</td>
<td>25</td>
<td>10</td>
<td>35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1983</td>
<td>20</td>
<td>8</td>
<td>28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1984</td>
<td>10</td>
<td>5</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1985</td>
<td>4</td>
<td>2</td>
<td>6</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>1986</td>
<td>3</td>
<td>1</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1987</td>
<td>2</td>
<td>2</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1988</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1989</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1990</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1991</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>Total</td>
<td>955</td>
<td>221</td>
<td>1,176</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
</tbody>
</table>
19.5.3 Emission of dioxins in relation to the PCP emission

From literature data that has also been used for the working document (Bremmer, 1991) the conclusion is drawn that, on average, PCP was polluted with 3 mg I-TEQ kg$^{-1}$ and Na-PCP with 0.3 mg I-TEQ kg$^{-1}$. A (possible) reduction in the dioxin concentration in PCP as a result of process improvements that were carried out in the early 1980s is of less importance to the Dutch situation because the PCP consumption (Table 19.2) was already decreasing at the time. A starting-point for an index-linked dioxin emission will therefore be the above-mentioned data in the working document.

Dioxin emission as a result of the use of Na-PCP
The use of Na-PCP is limited to small quantities of imported wood that is applied especially in products with a short lifetime. Dioxin emissions into the air are currently no longer expected because of the low consumption and the low dioxin concentration in Na-PCP.

During the treatment of wood against blue moulds, Na-PCP is dissolved in water and applied superficially. The first type of work in the wood industry is quite often planing, milling or something similar. This means that Na-PCP disappears with the sawdust. The sawdust is incinerated or dumped. Nothing is known about the behaviour of dioxins bound to wood once dumped. Dioxins are insoluble in water and, under damp conditions, will be washed away less easily than the water-soluble Na-PCP. Emission to water will hardly occur.

Dioxin emissions as a result of PCP use
From Table 19.2 it was calculated that 1,176 tonnes of PCP have been processed in wood or have been imported with preserved wood since 1955. The most important field of application is the building industry. The dioxin concentration in PCP is 3 mg I-TEQ kg$^{-1}$. From that, it follows that since 1955 a total quantity of 3,525 g I-TEQ has been processed in wood.

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 10 times slower from wood than PCP. Therefore, half the quantity of dioxin present in wood will be evaporated only after 150 years. This means a percentage of 0.45% per year, calculated over the quantity that remains behind in wood.

Apart from evaporation, the level of dioxin emission will also be reduced because of wood being replaced. Wood that has been preserved with PCP is mainly used in exterior wall carpentry. It is assumed that per year 1, 2, 3 and 4% of the wood used for this application will be replaced after a period of 10-20, 20-30, 30-40 years and after 40 years, respectively. Further, of the quantity of dioxins that remain behind in the wood, an annual evaporation percentage of 0.45% is assumed. By combining these assumptions with the quantities used (Table 19.2), the dioxin emission from wood can be calculated. Figure 19.1 shows the result of this calculation. On the basis of the above-mentioned assumptions, it was calculated 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*10$^{-6}$. In 1991, the evaporation from wood in the Netherlands was estimated at 25 tonnes PCP (a decrease of 4.5% per year). On the basis of this data, this would mean an emission of 125 g I-TEQ.
It is emphatically pointed out that both methods of calculation indicate one order of magnitude. Päpke did not find a direct connection between the emission of dioxins and PCP. The ratio found in the indoor air would mean that the evaporation rate of dioxins is almost identical to that of PCP. Considering the vapour pressures and the molecular weights, this is very improbable. Therefore, the most value is attached to the first method of approach. Even if the evaporation rate is somewhat larger than in the calculation example, the dioxin emission is not expected to exceed 25 g l-TEQ per year. This value is taken as an indication for the maximum emission.

Under practical conditions it is not quite possible to measure the dioxin emission from wood preserved with PCP. Simulation tests on a laboratory scale have been described in the literature. Additional simulation tests probably do not lead to a more accurate estimate of the above-mentioned dioxin emission. Further investigation is therefore not recommended.

Figure 19.1 Dioxin emission into the air from PCP-preserved wood (1955-2010)
19.6 Summary

Table 19.3 presents a summary of the dioxin emissions due to the use of pesticides (specifically wood preservatives).

Table 19.3 Data of dioxin emissions due to the use of pesticides (1991)

<table>
<thead>
<tr>
<th>Field of application</th>
<th>PCDD/F emission to</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Air [g I-TEQ per year]</td>
</tr>
<tr>
<td>Agricultural pesticides and agents for veterinary use</td>
<td>-</td>
</tr>
<tr>
<td>Pentachlorophenol as a preservative in Slug poison</td>
<td>-</td>
</tr>
<tr>
<td>Pentachlorophenyllaurate as a fungicide in the textile industry</td>
<td>0.06</td>
</tr>
<tr>
<td>Use of pentachlorophenol as a wood preservative</td>
<td>max. 25</td>
</tr>
<tr>
<td>Total</td>
<td>max. 25</td>
</tr>
</tbody>
</table>

1) An estimate cannot be given of the emission of dioxins to soil and water as a result of the use of PCP as a wood preservative.

19.7 Future

The future emission can also be read from Figure 19.1. In the year 2000, the emission will be about 12 g I-TEQ according to the calculation. On the basis of the reasoning in section 19.5.3 for the 1991 situation, a maximum emission of 20 g I-TEQ is assumed for the year 2000.

The slow evaporation of dioxins from treated wood cannot be influenced. Further, the source intensity will decrease by itself. It is hardly (or not at all) possible to make an investigation to diminish the uncertainties in the emission estimate. Further investigation into this matter is, for these reasons, not advisable.
20. DISCUSSION

20.1 Introduction

In 1990, measurements were carried out in all MSW incinerators in the Netherlands into the emission of chlorinated dioxins and dibenzofurans (further to be called "dioxins"). In addition, emission measurements were conducted at several other sources. Within the framework of the "Measurement of Other Sources" (MOB) programme, in the period 1991-1992, additional measurements were carried out at dioxin sources that had not yet been measured before. In combination with measurement results obtained earlier and, if required, supplemented with data from the literature, a rather complete picture of the total dioxin emission in the Netherlands became available. Table 20.1 gives a summary of this picture.

20.2 Measurement Plan

In setting up the project, it has been assumed that the emissions of process categories with the greatest anticipated contribution to the Dutch dioxin emission should be determined most accurately. As the sources are smaller and the number of sources not too large, the effect of inaccuracy in the emission determination on the correctness of the final estimate of the total emission is usually smaller. On the basis of this assumption, measurements were taken more often at those process categories where the most significant contribution to the national emission was expected, than at the smaller types of sources. Per process category, always one or more plants or installations serving as the best possible model for the process category considered were selected.

20.3 Accuracy

On the basis of the method described in 20.2, an indication of the accuracy of the emissions mentioned has been given in the table. The process categories of which the emissions were determined on the basis of more measurements (in particular the incineration of municipal solid waste and hazardous wastes, and sintering processes) belong to category A. With the MSW incinerators, a number of measurements were conducted at all installations. The results showed that the measurement results over the three days, in general, differed less than a factor of two. In the incineration of hazardous waste and the sintering processes, measurements were conducted at more than half the installations. The extrapolation of the measurement result to the annual emission of the installation (and consequently the estimated annual emissions for the process category) is reasonably accurate for these process categories.

Category B includes those process categories whose annual emissions were estimated on the basis of just one or several measurements. These estimates are therefore less accurate. The annual emissions of most of these process categories are low (i.e. traffic 1.5% and the rest < 1%), compared with the estimated total emission. The effect of the accuracy of the process categories belonging to category B on the accuracy of the total emission estimated for the Netherlands is limited, because of their being small.

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5) The number of non-industrial, diffuse sources can be so large that a small deviation actually has a great effect on the final result.
For a number of other process categories, i.e. cable burning, domestic wood combustion and the use of pesticides (wood preservation), the estimate of the annual emission is indicative because of the lack of sufficient data (category C). The uncertainty in the stated emissions is therefore great. As the index-linked annual emissions for wood combustion and pesticides are relatively high, the deviation in it will affect the accuracy with which the total emission was determined. However, if the mistake in estimating the emissions of these sources was 100%, then the deviation caused by it in the final result would not be more than 10%.

From data from the literature it appears that dioxins are released from fires (forest fires, fires in buildings), but also from the burning of (garden) waste. The data on this is too limited even to be able to give an indication of the annual emission (category D).

The selection criteria for inventorying processes that could be sources of dioxin emission were: the temperature and the presence of chlorine and organic material. In all measurements carried out, dioxins were actually found, even with a number of processes of which this was not expected at first. It is quite possible that there are still a few processes that release dioxins in small concentrations (order of magnitude 0.1 ng I-TEQ m\(^{-3}\)). Only in the case of large discharges could the annual emission for those processes affect the estimate of the total Dutch emission.

In view of the depth and the size of the inventory carried out, can it be assumed that all process categories releasing dioxins and occurring in the Netherlands were inventoried. The contribution of non-inventoried sources will be only a small percentage of the total at the most.

On the basis of the above, it can be concluded that the emission picture illustrated in Table 20.1 is a reasonable rendering of the real emission in the Netherlands.
Table 20.1 Sources of dioxins in the Netherlands (situation end 1991)

<table>
<thead>
<tr>
<th>Process category</th>
<th>Indication of accuracy</th>
<th>Emissions to air $^2$</th>
<th>Emissions to water $^2$</th>
<th>Bound to residue $^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Incineration of domestic waste</td>
<td>a</td>
<td>382</td>
<td>-</td>
<td>1,030</td>
</tr>
<tr>
<td>Incineration of hazardous waste</td>
<td>a</td>
<td>16</td>
<td>0.8</td>
<td>unknown</td>
</tr>
<tr>
<td>Incineration of landfill gas, biogas and sludge</td>
<td>b</td>
<td>0.3</td>
<td>-</td>
<td>unknown</td>
</tr>
<tr>
<td>Burning of cables, electromotors, etc.</td>
<td>c</td>
<td>1.5</td>
<td>-</td>
<td>unknown</td>
</tr>
<tr>
<td>Waste incineration at hospitals</td>
<td>b</td>
<td>2.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Asphalt-mixing installations $^4$</td>
<td>b</td>
<td>0.3</td>
<td>-</td>
<td>unknown</td>
</tr>
<tr>
<td>Oil combustion</td>
<td>b</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Coal and lignite combustion</td>
<td>b</td>
<td>3.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Wood combustion</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>* Industrial</td>
<td>b</td>
<td>0.8</td>
<td>-</td>
<td>unknown</td>
</tr>
<tr>
<td>* Domestic $^5$</td>
<td>c</td>
<td>11.2</td>
<td>-</td>
<td>unknown</td>
</tr>
<tr>
<td>Crematoria</td>
<td>b</td>
<td>0.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fires</td>
<td>d</td>
<td>unknown</td>
<td>unknown</td>
<td>unknown</td>
</tr>
<tr>
<td>Various high-temperature processes</td>
<td>b</td>
<td>2.7</td>
<td>-</td>
<td>unknown</td>
</tr>
<tr>
<td>Traffic</td>
<td>b</td>
<td>7.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sintering processes</td>
<td>a</td>
<td>26</td>
<td>1.5</td>
<td>-</td>
</tr>
<tr>
<td>Metal industry $^6$</td>
<td>b</td>
<td>4.0</td>
<td>-</td>
<td>&gt;24</td>
</tr>
<tr>
<td>Chemical production processes $^4$</td>
<td>b</td>
<td>0.5</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>Use of pesticides (specifically wood preservation)</td>
<td>c</td>
<td>25</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Total (excluding fires) 484 3 1055

1) a: based on more measurements taken at a major part of the plants;
   b: based on one or several measurements;
   c: indication; d: no indication possible.
2) * The indication "-" means: no emission or emission < 0.1 g I-TEQ per year.
   * Values <10 have been rounded down or up to tenths; the number of figures included is no indication for accuracy.
   * Residues containing dioxins at pg I-TEQ g$^{-1}$ level have not been included.
3) Approximately 0.6 g I-TEQ per year of the ESP ash residue is being emitted again as a result of wear and tear of
   the asphalt in which this ESP ash is processed.
4) The emission as a result of the heat generation has been included with the relative energy carrier.
5) Large uncertainties in the emission factors; see text in section 11.7.2.
6) Excluding sintering processes
20.4 Emission Into the Air

The estimated emissions (Table 20.1) relate to the situation at the end of 1991. Installations that were involved in the investigation, but closed down before end 1991, have not been included in the estimates of the annual emissions.

Dioxins were actually found in all processes that were inventoried and where measurements were carried out. The measured dioxin concentrations (excluding MSW incinerators) varied from about 0.001 to 19.5 ng I-TEQ m\(^{-3}\). The emitted quantities per process varied from 0.02 mg to about 24 g I-TEQ per year. The quantity of dioxin being emitted by a source per unit of time is determined not only by the dioxin concentration in the flue gases; this quantity also depends on the flue gas flow (the volume of gas discharged per unit of time).

Initially, a negligible emission was expected from asphalt-mixing installations, crematoria and from the combustion of coal. MOB measurements at two crematoria and an asphalt-mixing plant, however, showed the dioxin concentrations in the emission of these plants to be in the order of 0.45 - 1.3 ng I-TEQ m\(^{-3}\). Although the concentrations were thus relatively high, the calculated emission (0.002 - 0.007 g I-TEQ per year) is in the end low, as a result of the limited flue gas flow of those installations. Consequently, the annual emission estimated for the process category in question contributes only a little to the total emission in the Netherlands. At a coal-fired power station, however, a low dioxin concentration of 0.02 ng I-TEQ m\(^{-3}\) was measured, but this installation has a large flow rate still resulting in the annual emission being 0.46 g I-TEQ. From the estimate of the annual emission for all coal-fired power plants of 2.7 g I-TEQ per year, it appears that the dioxin emission at coal-firing is not negligible in relation to the national emission.

In 1991, another 16 g I-TEQ was emitted through the incineration of hazardous waste. Meanwhile one of the furnaces (by far the largest) for incinerating hazardous waste was modernized, resulting in the total emission of this process category decreasing to about 6 g I-TEQ per year. A similar modernization is anticipated in the other installations.

All but one cable burning plant have been closed, also as a result of this investigation. An uncertain factor in estimating the emission of the process category is the illegal burning of cables. Considering the index-linked high dioxin concentrations in the combustion gases, great priority should be given to taking measures in the field of enforcement.

In the course of 1991, a number of plants for incinerating hospital waste at hospitals were closed following measurements in which annual emissions were found that are comparable with those of MSW incinerators with a low emission (see Table 3.1). Among the closed plants were the two largest plants of the Netherlands. Because of their closure, the emission at hospitals from an incinerator decreased more than 50% to 2.1 ng I-TEQ per year, calculated per December 1991.

For domestic wood combustion, only an indication can be given of the annual emission. Insufficient data is available on the quantities of wood that are being combusted, particularly polluted and pentachlorophenol (PCP)-containing wood. The number of measurements from which emission factors can be derived is still insufficient to obtain an accurate picture. Considering the index-linked order of magnitude of emissions caused by domestic wood combustion, further investigation is desired.

It is known from data from the literature that dioxins are formed from fires. However, there is insufficient measurement data available to estimate the emission. In order to obtain an insight into the significance of this source, an investigation in a test set-up is recommended.
Estimates of the emission by traffic are based on two different methods of approach, the results of which differ by a factor of 3.5. The table states the highest value.

In the sintering processes, one process is decisive for the total emission of the process category.

In the past, pesticides polluted with dioxins were applied on a large scale, specifically for wood preservation. The dioxins slowly evaporate from the wood that is highly diffusely applied (in construction and as packaging material). The estimate of the emission from this diffuse source was based on limited data and is therefore uncertain. The estimated size of this source, however, is such that it must be regarded as one of the larger ones in the Netherlands.

20.5 Comparison With the Data From the Working Document

Before the measurements within the frame of this investigation started, an estimate of the dioxin emissions in the Netherlands (on the basis of the then known data from literature) was made in 1989. The selection of the sources to be measured within the frame of this investigation took place particularly on the basis of the data from that "working document" (Bremmer, 1991). The inventory now conducted makes the picture that was then available more complete and more reliable. The differences are discussed below.

In the working document, a total emission of 960 g I-TEQ per year was estimated for the Netherlands for the year 1989. The dioxin emission of about 484 g I-TEQ, as estimated for 1991 on the basis of this investigation, is considerably lower.

The difference can mainly be explained by the shut-down of three MSW incinerators and the modernization of several others, thus reducing the emission of MSW incinerators with more than 400 g I-TEQ from 790 g I-TEQ in 1989 to 382 g I-TEQ in 1991. Further, additional data is available about the use of PCP-containing wood preservatives. This resulted in the now estimated dioxin emission from pesticides (wood preservation) of 25 g I-TEQ being only half of what was originally stated in the working document.

In 1989, an emission of 45 g I-TEQ was estimated for the metal industry, with inclusion of a sintering process. Meanwhile, emission-reducing measures have been introduced with a number of secondary metallurgical processes. Further, the emission for the base metal industry turned out to be too high an estimate, so the emission for sintering processes and the metal industry together is now put at 30 g I-TEQ. The closure of incinerators at hospitals and of cable burning plants gives a reduction of several grammes of I-TEQ per year, in an absolute sense. The section "Emissions into the air" has dealt with the differences in the emission estimates for crematoria, coal combustion and asphalt-mixing plants. Incidentally, these differences have a limited effect on the total difference, just like the other process categories that have not yet been mentioned here.

Although the investigation now conducted gives quite a complete picture of the dioxin emissions in the Netherlands, some gaps in knowledge still remain. This concerns mainly diffuse sources, i.e. the emissions by wood combustion, traffic and by evaporation of dioxins from the former use of pesticides (wood preservation). Also, no accurate estimate is possible for the (illegal) burning of cables, etc. and for the dioxin emissions as a result of fires. It is advisable to determine the emissions of wood combustion more accurately, and to take up subsequent research to this end. The same holds for the emissions caused by fires. The emission by traffic will decrease automatically (see 20.9); the evaporation from the already applied pesticides (for wood preservation) will also decrease by itself. It is recommended preventing the illegal burning of
cables by stricter enforcement. An investigation to determine the emissions of these process categories is therefore less relevant.

20.6 Emission to Water

On the basis of the information in Table 20.1, it can be concluded that, as far as it is known, the dioxin emissions from the inventoried sources to the surface water are small. An annual total of about 3 g I-TEQ is emitted to water.

20.7 Residues

The emission into the air is the most important route for dispersing dioxins into the environment. This aspect will therefore always receive the most attention. In incineration processes, particularly where the flue gases are purified, usually more dioxin, bound, however, to residues (slag, filter ash, soot) is discharged than the quantity that is emitted into the air. From recent measurements of residue at MSW incinerators, it was estimated that more than three times as much dioxin is bound to residues than is emitted into the air. The total quantity of dioxins bound to residues is estimated to be 1,050 g I-TEQ per year.

A third part of the ESP ash that is being released at MSW incinerators is applied in asphalt. Through wear and tear of the road surface, dioxins bound to dust can then be released. The estimated quantity is 0.6 g I-TEQ per year. This quantity may double in the years to come because of its increased use and the replacement of asphalt that does not yet contain fly ash. Furthermore, Table 20.1 shows that there is still little known about the occurrence of dioxins in solid residues of the different process categories.

20.8 Spreading of Dioxins via the Air and Risks for Public Health

In addition to the quantity of dioxin released at the various processes, the way in which dioxins are dispersed into the environment is of great significance, also for the local environmental impact. This spreading depends on a number of source characteristics and on the weather conditions (Appendix 6).

In the Netherlands, the calculated deposition of dioxin from the air on the soil in 1990 was on average 8 ng I-TEQ m^{-2} (background deposition). The foreign contribution to it is about 50%. In the surroundings of a source, the deposition is higher as a result of the direct influence of that source. This direct influence of a source is noticeable over a distance of several kilometres (depending on source characteristics). About 70% of the dioxins emitted in the Netherlands is "exported". Degradation of dioxins in the environment takes place on a limited scale only.

The impact on the population can take place via several routes. The direct routes of inhalation and intake via skin and mouth are negligible compared with the indirect impact via food. Exposure takes place for a substantial part by consumption of milk, milk products and products with fish oil. From measurements at different places in the Netherlands (outside the direct sphere of influence of large sources), a national background concentration in cow's milk was determined at 0.8-2.5 pg I-TEQ g^{-1} milk fat. Because of the presence of a dioxin source, the concentration in milk may locally be higher than the background level.
For the Netherlands, the Commodities Act sets a standard of 6 pg I-TEQ g\(^{-1}\) milk fat. Milk with a higher dioxin concentration may not be put on the market. Using a distribution model, a quantitative relation can be made between dioxin emission and dioxin concentrations in milk. With this model it was calculated that the emissions of the individual sources on which measurements were conducted do not show exceeding of the standard (Appendix 6). This model was validated by monitoring cow’s milk in the surroundings of several MSW incinerators. Considering the selection of processes at which measurements were conducted, it may be assumed that the standard for cow’s milk will not be exceeded either by the emissions of processes at which no measurements were conducted. Apart from possibly fires, no processes relevant in this connection were withheld from the investigation.

20.9 Future Developments

In addition to the standard for cow’s milk, an emission standard of 0.1 ng I-TEQ m\(^{-3}\) (ind. at 11% O\(_2\)) was included in the 1989 Combustion Directive (RV '89) in order to decrease the environmental impact and thus human exposure as much as possible. This standard has not been based on the Tolerable Daily Intake (TDI) (see also Appendix 6), but on the principle of the best available techniques for flue gas cleaning. The standard for cow’s milk is related to the TDI. There is no relation between the emission standard and the standard for cow’s milk.

On 21 February 1993, the "Incineration Decree" became effective (Statute Book 1993, no. 36). The decree concerns institutions for the incineration of domestic waste or of industrial waste that is incinerated together with domestic waste (the so-called MSW incinerators). As of 21 February 1993, new plants (to which a permit was granted on or after 1 April 1990) must meet the emission standards stated in the Decree. Existing plants (permit granted before 1 April 1990) must meet these standards as from 1 January 1995. For plants other than the MSW incinerators, emission standards are stated in Chapter 3 "Special Rules" of the Dutch Emission Guidelines (NER); these standards are based on the RV '89 and take into account the specific nature of the plants.

Once the conditions set by the government are met, the emissions of MSW incinerators will drop to several grammes per year. (Depending on the quantity of waste to be incinerated, all MSW incinerators together will then emit 2.5-4 g I-TEQ yr\(^{-1}\). Once also the furnaces for the incineration of hazardous waste have been modernized, the annual emission for incinerating hazardous waste will drop from 16 g I-TEQ in 1991 to about 1.7 g I-TEQ in 2000 (based on the present incineration capacity).

Incineration of waste at hospitals, the emission of which had already been reduced to about 1 g I-TEQ in 1993, will no longer occur in 2000, so the emission in Table 20.1 has been put at 0.

The emission at sintering processes was estimated at 26 g I-TEQ yr\(^{-1}\), 24 g of which comes from one process. Both the authorities involved and the company strive for the introduction of emission-reducing measures in accordance with the directives. Thus the emission of sintering processes will be reduced to about 3 g I-TEQ yr\(^{-1}\).

Sources such as domestic combustion of wood occur widespread across the country. The annual emission of the individual installations is low and it will not be easy to modify the process conditions of those small sources. If the use of polluted wood were to completely disappear as a result of good information and education, this would mean that an emission of maximally about 9 g I-TEQ yr\(^{-1}\) will remain (at constant use).
Compared to the present emission, the emission of traffic will drop because of the further introduction of unleaded petrol and the use of catalytic converters.

It is expected that in the year 2000 the dioxin emission will have dropped from about 484 g I-TEQ yr\(^{-1}\) to about 58 g I-TEQ yr\(^{-1}\). An estimate of the distribution over the process categories is given in Table 20.2. This table only includes the effects resulting from the developments that have already been started. In estimating the emissions for 2000, no account was taken of any growth in, or shift between, certain categories, apart from the MSW incinerators.

Table 20.2 Sources of dioxins in the Netherlands. Expectations for the year 2000 (for comparison sake also the 1991 sources are given)
Emissions into the air, after introducing the measures resulting from the developments already started.

<table>
<thead>
<tr>
<th>Process category</th>
<th>Emissions into the air (g I-TEQ yr(^{-1})) (^1)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1991</td>
</tr>
<tr>
<td>Incineration of domestic waste</td>
<td>382</td>
</tr>
<tr>
<td>Incineration of hazardous waste</td>
<td>16</td>
</tr>
<tr>
<td>Incineration of landfill gas, biogas and sludge</td>
<td>0.3</td>
</tr>
<tr>
<td>Burning of cables, electromotors and such like</td>
<td>1.5</td>
</tr>
<tr>
<td>Waste incineration at hospitals</td>
<td>2.1</td>
</tr>
<tr>
<td>Asphalt-mixing installations (^2)</td>
<td>0.3</td>
</tr>
<tr>
<td>Oil combustion</td>
<td>1.0</td>
</tr>
<tr>
<td>Coal and lignite combustion</td>
<td>3.7</td>
</tr>
<tr>
<td>Wood combustion (^4)</td>
<td>12</td>
</tr>
<tr>
<td>Crematoria</td>
<td>0.2</td>
</tr>
<tr>
<td>Fires</td>
<td>unknown</td>
</tr>
<tr>
<td>Various high-temperature processes</td>
<td>2.7</td>
</tr>
<tr>
<td>Traffic</td>
<td>7.0</td>
</tr>
<tr>
<td>Sintering processes</td>
<td>26</td>
</tr>
<tr>
<td>Metal industry</td>
<td>4.0</td>
</tr>
<tr>
<td>Chemical production processes (^2)</td>
<td>0.5</td>
</tr>
<tr>
<td>Use of pesticides (wood preservation)</td>
<td>25</td>
</tr>
</tbody>
</table>

\(^1\) The number of figures included is no indication for accuracy; values < 10 for 1991 have been rounded off up or down to the nearest tenth.

\(^2\) The emission as a result of heat generation has been included with the relative energy carrier(s).

\(^3\) In estimating the emissions for 2000, no account was taken of any growth in, or shift between, certain categories, apart from the MSW incinerators.

\(^4\) Great uncertainties; see section 11.7.2.
From the table it follows that, after introducing the now anticipated emission-limiting measures, the former use of agents for wood preservation will be the largest source. The emission is mainly caused by the application of dioxin-containing wood preservatives in the past. In the Netherlands, as well as in many other countries, the use of chlorophenols as wood preservatives has been banned. Thus the dioxin emission from this source will slowly decrease in the course of time.

Considering the possible large amount of emission from wood combustion in fireplaces and wood-burning stoves, further investigation into this emission is desired. If the present estimate is confirmed by that investigation, wood combustion would appear to be the second largest future source. The larger part of this emission is then presumably caused by the burning in fireplaces. Once again, however, the great uncertainties are pointed out, specifically in the emissions established for fireplaces.

The prognosis for the year 2000 has been based on:
- Carrying out measures, as these were initially set in the RV’89 and have now been copied in the Incineration Decree (Statute Book 1993, 36) and the Dutch Emission Directives (NER);
- The implementation of the EC legislation that is being prepared concerning the incineration of "hazardous" waste;
- The policy that has already been started by the competent authorities within the frame of permit granting concerning several sources mentioned in this report.

When the emission of dioxins in the Netherlands has been decreased to about 58 g I-TEQ yr\(^{-1}\), the background deposition will have decreased (at a constant contribution of foreign sources) from an average 8 ng I-TEQ m\(^{-2}\) yr\(^{-1}\) in 1991 to about 4 ng I-TEQ m\(^{-2}\) yr\(^{-1}\) in the year 2000. By that time, the background deposition in the Netherlands will be mainly determined by the dioxin emission abroad.

Because of the decrease in the background deposition, the background concentration in cow’s milk will also further drop. Apart from the (small) contribution from the soil, the background concentration in milk in the year 2000 will be mainly determined by the contribution of foreign sources. A further decrease will therefore mainly be determined by the extent to which measures are taken abroad to reduce the dioxin emissions. This emphasizes the importance of an international approach to abatement.

Locally, in the vicinity of a source, the deposition will be increased compared to the background. According to the model calculations (see 20.8), nowhere in the direct surroundings of sources in the Netherlands (apart from the Lickebaert area) is the standard for dioxin in milk exceeded, according to the emissions of 1991. As the standard for dioxin in cow’s milk is currently not exceeded, this will certainly not be the case once all measures now anticipated have been taken. For the Lickebaert area it is expected that measurements this year (1993) will show that, there too, the dioxin concentrations in cow’s milk are below the standard.

Dioxin emissions can be restricted by modifying process conditions and/or improving the cleaning system for the gases being released during the process. By installing advanced techniques to clean the discharged gases, the emissions may be restricted, but one problem remains, i.e. the dioxins in the solid waste substances of the process. Therefore there is a strong preference for a process-integrated approach. It is of importance that investigation into process conditions, during which so few dioxins as possible are formed, is continued and that better possibilities are sought to upgrade the residues of the process.
20.10 Congener Patterns

In the measurement of dioxins and dibenzofurans, a total of 17 (out of the 210) different congeners (see Appendix 1) are determined. A survey is given in Appendix 7 of all the processes discussed in this report on the basis of the analysis results. This survey gives the interrelationships of these 17 different congeners in the samples collected.

From a superficial point of view, there seem to be quite a few similarities between these congener patterns, particularly within one process category. The number of variables that plays a role in this is, however, very large. Within the framework of this project, insufficient opportunity was available to seek the causes and on that basis give an explanation of the similarities and differences occurring. However, the material needed to do this is available.

Investigation into this may, however, be important. It is expected to bring about information that contributes to the knowledge of the formation and origin of dioxins. This knowledge is useful in developing measures to reduce dioxin formation in various processes. On the other hand, it may be possible on the basis of the congener patterns to roughly establish the origin of the dioxins and dibenzofurans found in the environment (fingerprinting).

It is recommended that further investigation be carried out into the congener patterns; such investigation should centre around the above goals.
21. CONCLUSIONS AND RECOMMENDATIONS

21.1 Conclusions

General

1. Estimates of the annual dioxin emissions of the process categories that were expected to give the highest emissions (specifically sintering processes and the incineration of domestic and hazardous wastes) are reasonably reliable. Although for several other process categories only an indication can be given of the annual emission, the reliability of the established annual emission of dioxins and dibenzofurans has markedly increased, compared with earlier estimates. The survey presented in this report can therefore be regarded as a reasonably good presentation of the total dioxin emission in the Netherlands - with the exception of the emissions by fires.

2. The results of this investigation show that the measures already taken have affected the total dioxin emission. The extent to which further measures are necessary can be determined, also on the basis of the results now at hand.

Emissions

3. The dioxin concentrations in the flue gases of the investigated processes (MSW incinerators excluded) varied from about 0.001 to 19.5 ng I-TEQ m⁻³, with strongly different flow rates. The emissions of the investigated sources vary from 0.02 mg to about 24 g I-TEQ per year. Only two sources emit more than 10 g I-TEQ per year. For all other sources, emissions of less than 1 g I-TEQ per year were estimated, two thirds of which were less than 0.1 g per year.

4. Using the data from the emission measurements, in a number of cases supplemented with literature data, it was estimated that the dioxin emission in the Netherlands (end 1991, exclusive of fires) was about 484 g I-TEQ per year. Installations that were closed before December 1991 were not included in this calculation. No estimate can be made of the emission resulting from fires.

The discharge while bound to residue is 1,050 g I-TEQ per year. The emission to water is about 3 grammes annually.

5. The waste incinerators for domestic waste and waste that can be compared with it together emit over 380 g I-TEQ per year, that is almost 80% of the totally estimated emission (situation end 1991).

6. The remaining part of the estimated annual emission (about 105 g I-TEQ) is divided over 16 process categories, the most important categories being sintering processes (5.4% of the total emission), the (former) use of wood preservatives (5.2%), hazardous waste incineration (3.3%) and wood combustion (2.5%).

7. According to the current information, the emissions at the combustion of wood are largely determined by the combustion in fireplaces and wood-burning stoves. Available information, however, is incomplete and based on only a few measurements. Further investigation into the
dioxin emission of this source category is necessary. It is desirable in anticipation of this to intensify the information about the negative effect of the combustion of polluted wood in wood-burning stoves and fireplaces.

8. The estimate of the emission by traffic is still quite uncertain. Considering the source intensity and its decrease because of the further implementation of catalytic converters and the use of unleaded petrol, it does not appear advisable at this moment to take away this uncertainty by way of further investigation.

9. The emission of dioxin through evaporation from (PCP containing) wood preservatives used in the past is not accurately known. It is estimated to be a large source (25 g I-TEQ per year). It is not probable that the source intensity can be determined more accurately by further research. Also, the decreasing source intensity does not require this.

Comparison with the working document

10. In the working document, a total dioxin emission of 960 g I-TEQ per year was estimated for 1989. The emission now estimated for 1991 on the basis of this investigation is 484 g I-TEQ per year. The most important cause of this difference is the closure of three MSW incinerators, of the majority of cable burning plants, and of a number of incinerators at hospitals. Meanwhile, several MSW incinerators and processes in the metal industry have also been modernized. The other differences in the estimated emission are attributed to the fact that because of the conducted investigation more (and more reliable) information has become available on the emissions of dioxin.

Dispersion and risks

11. From calculations with a chain model with which there is a connection between the dioxin emission and the dioxin concentrations in cow's milk, it appears that it is not expected that the dioxin limits in milk will be exceeded in the direct surroundings of the industrial sources considered in this investigation. Such an exceedance does still occur in the Lickebaet polder. It is expected that in 1993 it will be established that the standard is no longer exceeded there as well.

Future developments

12. It is expected that, if process size remains constant, the total dioxin emission in the Netherlands (excluding fires) will maximally be about 58 g I-TEQ per year, as a result of the developments that have already been started. The contribution of MSW incinerators to this will be a maximum of 4 g I-TEQ.

13. It is expected that in the year 2000 the emission through evaporation of wood preservatives used in the past will be the most significant dioxin source, possibly followed by the combustion of wood.

14. Once the emission of dioxins in the Netherlands has been pushed back to about 58 g I-TEQ per year, the background deposition will have dropped from an average 8 ng I-TEQ m^-2 yr^-1 to about 4 ng I-TEQ m^-2 yr^-1, at a constant contribution of foreign
sources. Because of this decline, the background concentration in cow's milk will also decrease further. Apart from the (small) contribution from the soil, the background concentration in the milk will then be mainly determined by the contribution of foreign sources. A further decrease is then mostly determined by the extent to which measures are taken abroad to reduce the emission. It may be expected that also this contribution will decrease in the future. In this respect, it should be stated that locally, in the vicinity of a source, the deposition will be increased, compared with the background.

Concluding remarks

15. Because of the measures that have already been taken (also influenced by this investigation), the dioxin emission in the Netherlands decreased from about 960 g I-TEQ per year in 1989 to 484 g I-TEQ per year established for 1991. Once all measures that are now anticipated have been carried out (including RV'89), the dioxin emission in the Netherlands will be (maximally) 58 I-TEQ per year in 2000. One third of this cannot be influenced, as this concerns the evaporation of wood preservatives used in the past.

16. According to the model calculations, the standard for dioxin in milk is exceeded nowhere in the Netherlands (with the exception of the Licebaert area) as calculated for the 1991 emissions. For the Licebaert area it is expected that 1993 measurements will confirm that dioxin concentrations in cow's milk are also below the standard.

21.2 Recommendations

1. In order to obtain a better estimate of the emissions through the domestic combustion of wood, an investigation is required into the representativeness of the dioxin emissions measured so far and the quantities of clean and polluted wood (with and without PCP) that are burned. Investigation into the possibilities of reducing the dioxin emission from wood combustion is also desired, as well as investigation into the dioxin concentration of ash residues. An inventory of the smokehouses occurring in the Netherlands and the emissions taking place at these installations is also desired.

2. In order to check how, and to what extent, dioxins are formed from fires, emission measurements are required for open fires, with different fuel compositions. The composition of the residues should also be part of such an investigation.

3. Considering the indicated dioxin concentrations in the combustion gases of particularly the illegal burning of cables, great priority should be given to measures in the field of enforcement. Considering the dioxin concentrations found in the soil material at sites where illegal cable burning took place, it is recommended to pay attention to this within the framework of soil cleanup.

4. The lagging emission because of the use of wood preservatives in the past and the uncertainties in the emission estimate of traffic need not be investigated further, in particular because only a limited result is expected from such investigation when compared with the costs.
5. In the case of measures to reduce dioxin emissions, process integrated solutions are preferred to so-called "end-of-pipe" techniques, this to prevent the shift of the dioxin impact from air emission to emission via residues. It is recommended to investigate the cleaning of residues and the usability of process-integrated techniques versus end-of-pipe techniques.

6. Considering the size of the estimated emission to water from one of the sintering processes, it is advisable also to determine the dioxin emission to water with the other sintering processes.

7. It is recommended to investigate the relations in which the individual congeners occur in the emissions, with the goals of investigating the possibilities of source recognition, and of finding points of departure for preventing or combatting dioxin formation in the processes distinguished.
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Chemosphere 19: 1881 - 1895
### 23. OVERVIEW OF SYMBOLS, ABBREVIATIONS AND CONCEPTS USED

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACT</td>
<td>Toxicology Consultancy (RIVM)</td>
</tr>
<tr>
<td>additional flue gas cleaning</td>
<td>cleaning technique for flue gases applied along with conventional cleaning</td>
</tr>
<tr>
<td>AOO</td>
<td>Consultative Body for Waste</td>
</tr>
<tr>
<td>ARN</td>
<td>Nijmegen Regional Waste Processing Plant</td>
</tr>
<tr>
<td>AVI</td>
<td>Municipal Solid Waste Incinerator (consisting of one or more incineration lines)</td>
</tr>
<tr>
<td>AVIRA</td>
<td>Arnhem Regional Waste Processing Plant</td>
</tr>
<tr>
<td>AVR</td>
<td>Rijnmond Waste Processing Plant</td>
</tr>
<tr>
<td>BACA</td>
<td>Indication Decree on Hazardous Wastes</td>
</tr>
<tr>
<td>BGA</td>
<td>German Health Ministry (Bundes Gesundheits Amt)</td>
</tr>
<tr>
<td>bioavailability</td>
<td>the proportion of substances entering the body that is actually absorbed by the blood</td>
</tr>
<tr>
<td>BMRO</td>
<td>Environment and Physical Planning Agency of the Council of the Dutch Employers Organizations VNO and NCW</td>
</tr>
<tr>
<td>CBS</td>
<td>Central Bureau of Statistics</td>
</tr>
<tr>
<td>CCRX</td>
<td>Co-ordination Committee for Radioactivity and Xenobiotics</td>
</tr>
<tr>
<td>CEN</td>
<td>Comité Européen de Normalisation</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>methane</td>
</tr>
<tr>
<td>chain model</td>
<td>model system consisting of three models to predict the concentration of dioxin in cow’s milk on the basis of dioxin emission</td>
</tr>
<tr>
<td>cleaning residue</td>
<td>solid residue that remains behind after flue gas cleaning</td>
</tr>
<tr>
<td>CML</td>
<td>Centre for Environmental Research, Leiden University, The Netherlands</td>
</tr>
<tr>
<td>CO</td>
<td>carbon monoxide</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>carbon dioxide</td>
</tr>
<tr>
<td>congener</td>
<td>one of the compounds belonging to the group of PCDDs and PCDFs</td>
</tr>
<tr>
<td>CVN</td>
<td>Netherlands Crematorium Association</td>
</tr>
<tr>
<td>C$<em>4$H$</em>{10}$</td>
<td>gaseous organic compounds (hydrocarbons)</td>
</tr>
<tr>
<td>DGM</td>
<td>Directorate-General for Environment</td>
</tr>
<tr>
<td>dioxins</td>
<td>polychlorodibenzo-p-dioxins (PCDDs) and polychlorodibenzofurans (PCDFs); also referred to as PCDD/F</td>
</tr>
<tr>
<td>domestic waste</td>
<td>the waste that is processed in the plants discussed in this report. Apart from waste from households, the term includes industrial waste comparable to domestic and bulk waste</td>
</tr>
<tr>
<td>DRSH</td>
<td>Sludge incineration plant at Dordrecht</td>
</tr>
<tr>
<td>d.m.</td>
<td>dry matter concentration (e.g. of sludge)</td>
</tr>
<tr>
<td>DTO</td>
<td>Rotary kiln</td>
</tr>
<tr>
<td>effluent</td>
<td>emission of cleaned waste water</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency (USA)</td>
</tr>
<tr>
<td>EPV</td>
<td>Association for the Packaging and Pallets Industry</td>
</tr>
<tr>
<td>ESP</td>
<td>ElectroStatic Precipitator for removing particulates</td>
</tr>
<tr>
<td>FME</td>
<td>Federation of Enterprises in the metal, electronics and electrotechnical industries, and related processes</td>
</tr>
<tr>
<td>GEVUUDO</td>
<td>Dordrecht and District Municipal Solid Waste Processing Plant</td>
</tr>
<tr>
<td>half-life</td>
<td>period during which a quantity or concentration is halved</td>
</tr>
<tr>
<td>halogens</td>
<td>collective name for chlorine, fluorine and bromine</td>
</tr>
</tbody>
</table>
HCl - hydrogen chloride
HIMH - Chief Inspectorate of Public Health for Environmental Protection
ICD - Interdepartmental Co-ordination Committee on Dioxins
ICM - Isolating, Controlling and Monitoring (waste substances)
IMET-TNO - TNO Institute of Environmental and Energy Technology
imission - concentration in the air at the level of the (natural) environment

incineration line - combination of furnace, boiler, flue gas scrubbing and stack
ind. - in normal state dry (referring to the state of flue gases; 101.3 kPa, 273 K)
inv. - in normal state moist (referring to the state of flue gases; 101.3 kPa, 273 K)
IPO - Inter Provincial Consultation
LAE - Laboratory for Waste Material and Emissions (RIVM)
LNV - Ministry of Agriculture, Nature Management and Fisheries
mg - milligramme; 10^{-3} gramme
μg - microgramme; 10^{-6} gramme
MJ - mega joule; 10^6 Joule
MOB - Measurements at Other Sources
NATO/CCMS - North Atlantic Treaty Organization / Committee on the Challenges of Modern Society
ng - nanogramme; 10^{-9} gramme
NOx - nitric oxides (NO and NO_2)
OPS model - Operational atmospheric transport model for Priority Substances
PCBs - polychlorobiphenyls; group of 209 chemical compounds with a varying degree of chlorination (1-10 chlorine atoms)
PCDD - polychlorodibenz-p-dioxins; group of 75 chemical compounds with a varying degree of chlorination (1-8 chlorine atoms)
PCDF - polychlorodibenzofurans; group of 135 chemical compounds with a varying degree of chlorination (1-8 chlorine atoms)
PCP - Pentachlorophenol
pg - picogramme; 10^{-12} gramme
PJ - peta joule; 10^{15} Joule
Planary PCBs - three of the 209 PCBs, i.e. 3,3',4,4'-tetraCB (PCB-77), 3,3',4,4',5-pentaCB (PCB-126), and 3,3',4,4',5,5'-hexaCB (PCB-169); these three PCBs have a toxicity comparable to that of dioxins
PVC - Poly Vinyl Chloride (a plastic)
quenching - rapid cooling of flue gases by water injection
RDF - Refused Derived Fuel (fuel of fraction remaining after waste separation)
RIMH - Regional Inspectorate of Public Health for Environmental Protection
RIVM - National Institute of Public Health and Environmental Protection, Bilthoven, the Netherlands
RIZA - National Institute for Inland Water Management and Waste-water Treatment
ROTEB - Rotterdam Municipal Service for Cleaning and Disinfecting, Transport and Industrial Sites, Rotterdam, the Netherlands
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>RV’89</td>
<td>1989 incineration</td>
</tr>
<tr>
<td>SEP</td>
<td>Association of Electricity Generating Companies</td>
</tr>
<tr>
<td>slag</td>
<td>solid residue that remains after combustion and is discharged from the oven</td>
</tr>
<tr>
<td>SO₂</td>
<td>sulphur dioxide</td>
</tr>
<tr>
<td>Substitution level</td>
<td>the number of Cl atoms in the dioxin molecule (or: the number of H atoms of the benzene ring that has been replaced with a chlorine atom)</td>
</tr>
<tr>
<td>TAUW</td>
<td>TAUW Infra Consult B.V.</td>
</tr>
<tr>
<td>2,3,7,8-TCDD</td>
<td>2,3,7,8-tetrachlorodibenzo-p-dioxin, the most well-known and most toxic congener of the dioxins</td>
</tr>
<tr>
<td>TDI</td>
<td>Tolerable Daily Intake</td>
</tr>
<tr>
<td>I-TEF</td>
<td>Toxicity Equivalence Factor relating to 2,3,7,8-TCDD as proposed by the TEF working party (Van Zorge et al., 1989); see also Appendix 1</td>
</tr>
<tr>
<td>I-TEQ</td>
<td>2,3,7,8-TCDD toxicity equivalence, calculated on the basis of the TEFs</td>
</tr>
<tr>
<td>TNO</td>
<td>Netherlands Organization for Applied Scientific Research</td>
</tr>
<tr>
<td>UNA</td>
<td>Power plant for Utrecht, North Holland and Amsterdam</td>
</tr>
<tr>
<td>VBW Asfalt</td>
<td>Association to Promote Working in Asphalt</td>
</tr>
<tr>
<td>VCP</td>
<td>Food Consumption Monitoring</td>
</tr>
<tr>
<td>VDI</td>
<td>Verein Deutsche Ingenieure</td>
</tr>
<tr>
<td>VEABRIN</td>
<td>Association of Operators of Solid Waste Incinerators in the Netherlands</td>
</tr>
<tr>
<td>VEEEN</td>
<td>Association of Operators of Power Stations in the Netherlands</td>
</tr>
<tr>
<td>VHR</td>
<td>Association for Fireplaces and Stacks</td>
</tr>
<tr>
<td>VNCI</td>
<td>Association for the Dutch Chemical Industry</td>
</tr>
<tr>
<td>VROM</td>
<td>Ministry of Housing, Physical Planning and Environment</td>
</tr>
<tr>
<td>VVAV</td>
<td>Association of Refuse Processing Plants</td>
</tr>
<tr>
<td>WHO</td>
<td>World Health Organization</td>
</tr>
<tr>
<td>WVC</td>
<td>Ministry of Welfare, Health and Cultural Affairs</td>
</tr>
<tr>
<td>ZAVIN</td>
<td>Hospital Waste Incinerator, Dordrecht</td>
</tr>
</tbody>
</table>
APPENDIX 1  Information on Dioxins

General

Dioxins is the collective name of polychlorodibenzop-p-dioxins and polychloro-dibenzo furans, also shortened to PCDD/PCDF (or PCDD/F). The structure of the basic skeletons of a dibenzo-p-dioxin and dibenzofuran 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 replaced (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".

![PCDD and PCDF structures](image)

The most toxic congener is 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD); however, the various congeners show great differences in toxicity amongst themselves. It appears that only the 17 congeners that have been substituted with a chlorine atom on the 2nd, 3rd, 7th and 8th place have a significant toxicity. These 17 congeners (the "dirty seventeen") have all obtained a so-called "toxicity equivalence factor" (TEF) stating the congener's toxicity in relation to 2,3,7,8-TCDD.

Various TEFs are made out for one and the same congener because of differences in interpretation of experimental animal data. In an international joint venture, chaired by the NATO/CCMS, in which the Netherlands participated, consensus was reached in 1988 about one TEF scheme. For this reason the Netherlands uses this international scheme for TEFs, called the "I-TEFs" (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 B.1.1).

Multiplying the concentration of a 2,3,7,8-TCDD-related compound with the I-TEQ involved produces the concentration of 2,3,7,8-TCDD Toxic Equivalence (I-TEQ) of that congener. By now adding all I-TEQs of the 17 related 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 B.1.1 Toxicity Equivalence Factors for the 17 dioxins and furans

<table>
<thead>
<tr>
<th>Congener</th>
<th>I-TEF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dioxins</td>
<td></td>
</tr>
<tr>
<td>2378-TCDD</td>
<td>1</td>
</tr>
<tr>
<td>12378-PCDD</td>
<td>0.5</td>
</tr>
<tr>
<td>123478-HxCDD</td>
<td>0.1</td>
</tr>
<tr>
<td>123678-HxCDD</td>
<td>0.1</td>
</tr>
<tr>
<td>123789-HxCDD</td>
<td>0.1</td>
</tr>
<tr>
<td>1234678-HpCDD</td>
<td>0.01</td>
</tr>
<tr>
<td>octa-CDD</td>
<td>0.001</td>
</tr>
<tr>
<td>Furans</td>
<td></td>
</tr>
<tr>
<td>2378-TCDF</td>
<td>0.1</td>
</tr>
<tr>
<td>12378-PCDF</td>
<td>0.05</td>
</tr>
<tr>
<td>23478-PCDF</td>
<td>0.5</td>
</tr>
<tr>
<td>123478-HxCDF</td>
<td>0.1</td>
</tr>
<tr>
<td>123678-HxCDF</td>
<td>0.1</td>
</tr>
<tr>
<td>123789-HxCDF</td>
<td>0.1</td>
</tr>
<tr>
<td>234678-HxCDF</td>
<td>0.1</td>
</tr>
<tr>
<td>1234678-HpCDF</td>
<td>0.01</td>
</tr>
<tr>
<td>1234789-HpCDF</td>
<td>0.01</td>
</tr>
<tr>
<td>octa-CDF</td>
<td>0.001</td>
</tr>
</tbody>
</table>

Dioxins can be formed not only with chlorine, but also with bromine. Brominated dioxins or mixed chlorinated/brominated dioxins could arise in the same way as chlorinated dioxins. Bromine occurs much less commonly 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, as well as for analytical-technical reasons (there are about 5,000 mixed chlorinated/brominated dioxins), the investigation of brominated dioxins did not get high priority. Investigation is currently being done on a limited scale into the way in which these compounds can be analysed.

The "co-planair" PCBs (77, 126 and 169) are closely related to dioxins from a toxicological point of view. Investigation of foodstuffs showed that these PCBs are present in these, as are dioxins. It is not known what the origin of these PCBs is. There may be a connection between the forming of dioxins and the forming of these PCBs. Investigation is currently being done on whether these PCBs occur in the flue gases and the solid residue of the thermal processes that are discussed in this report, and, if so, in what proportion to dioxins they occur.

Sources and emissions of (chlorine) dioxins in the Netherlands

The only known natural sources of dioxins are combustion processes, such as forest fires and the like. The emission from these natural sources is relatively very small. From investigation of sediment from lakes in North America and Switzerland it has appeared that the concentrations of dioxins show the same pattern in the time as the production of chlorine aromatics. Hardly any demonstrable concentrations of dioxins were found in frozen eskimoes hundreds of years old and in the preserved bodies of Chilean Indians. These measurements lead to the conclusion that the contribution from natural sources is small.
Dioxins are not commercially manufactured and have no applications either. Yet they can be formed as undesired byproducts 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 as well) 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 generate), or compounds from which precursors can be formed, are heated to above 150 °C, in the presence of chlorine. This happens for example in production and processing processes or with the use of chlorophenols, chlorobenzenes, HCH, PCBs, but also in 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 in 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 (the emission of dioxins from bleached cellulosic products into the air is highly improbable).

Processes as described under 4) have not been considered in this project; bleaching cellulosic raw materials with activated chlorine does not occur in the Netherlands.

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 the basic material or surroundings).

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 in the selection, these factors (increased temperature, presence of organic matter, oxygen and chlorine) were used as criteria.

Commissioned by the CCRX (the Coordination Committee for Measuring Radioactivity and Xenobiotic Substances), CML (the Centre for Environmental Science, Leiden University) has made a general survey of dioxins (Kleijn and Van der Voet).
APPENDIX 2  Members of the support committee and contacts

Members

H.J. Bremmer  - RIVM
H.W. Holtring  - VROM/DGM, Directorate of Air & Energy
C. Klick  - Province of North Holland/DMW
H.A. Kruyt  - Province of South Holland/DWM
            LVG Department
M. Krijgsman (chairman)  - VROM/DGM, HIMH
L.M. Troost (secretary)  - IMET-TNO, Department of Chemical Engineering

Contacts

J. Derks  - VNCI
A. Hug  - FME
W.M. Zijlstra  - BMRO/VNO-NCW
APPENDIX 3    Information bulletin for companies

Ref.no. 91-014808/112326-23036/MOB

INFORMATION BULLETIN "MEASUREMENTS AT OTHER SOURCES" (MOB)
FOR INSTRUCTION TO COMPANIES
(2nd version, 25 November 1991)

For: Contacts at Provinces and Inspectorates

***************************************************************

Introduction

After the event in the Lickebaert area, in which too many dioxins (polychlorodibenzo-p-dioxins and polychlorodibenzofurans; PCDD/F) were found in cow’s milk, the Ministry of Housing, Physical Planning and Environment (VROM) started an investigative programme. This programme comprised, for example, investigation into dioxin concentrations in cow’s milk, grass and soil at various places in the Netherlands. This investigation, which was conducted by the National Institute of Public Health and Environmental Protection (RIVM), has now been practically completed.

In addition to this investigation, another investigation is currently being conducted into the quantity of dioxins that are "produced" in our country. This investigation that is being conducted by RIVM, TNO, the Environmental Protection Inspectorate and the Provinces, comprises a literature study, an inventory of possible sources, and an inspection measurement programme at Municipal Solid Waste (MSW) incinerators, hospital waste incinerators and other sources.

This bulletin gives some background information concerning the latter investigation, the inspection measurement programme for other sources (MOB), as well as the purpose of this investigation and the course of the project.

Background information

The RIVM conducted the literature study. In collaboration with the provinces and the regional inspectorates, RIVM and TNO made an inventory of processes (other than MSW incinerators) in which dioxins could arise. In this respect, use was made of the following criteria: presence of chlorine and/or chlorine compounds, temperature, and the size of the process.

On the basis of the above-mentioned inventory and the literature study conducted, recommendations were made as to the desirability of taking dioxin measurements in various processes. Companies where these measurements were to be taken were selected to this end by the authorities. In doing this processes were involved in which, from a theoretical point of view, dioxins could be formed. Measurements in practice have to show whether this approach is correct.
Goal of the investigation

The authorities want a clear picture of the dioxin emissions originating in the Netherlands. The data obtained will be used, for example, as a basis for the environmental policy to be followed on the dioxin problems.

General organization

The organization, carrying out and reporting of the investigation will be done by the TNO Institute of Environmental and Energy Technology (IMET-TNO). A support committee has been set up for guidance. This committee consists of representatives from the government, i.e. the Directorate-General for Environment (VROM/DGM), the InterProvincial Consultation (IPO) and the RIVM. The meetings will also be attended by representatives of the corporate sector and by the TNO project manager. The secretarial duties will be carried out by TNO.

Project

Measurement programme

On average, an installation time of half a day will be needed per measurement. Subsequently, the following measurements will be taken on the flue gases of the plant in question in the course of one day:
- flow rate and temperature;
- PCDD/F (one sample during 3-6 hours).
As far as possible and necessary, the following (process) parameters will also be determined:
- the macrocomponents, O_2, CO_2, CO, gaseous organic compounds (continuous recording);
- the gaseous inorganic chlorides (mainly HCl).

In addition to measurements on flue gases/air, determinations on the dioxin concentration of the waste water or sludge (or the like) will also be determined for several processes.

The company will be requested to make the necessary arrangements at the installation so that measurements can be taken. They will also be requested to keep a record of a number of process data to be specified later.

Organization

The measurements will be taken at concerns representative of the various categories of similar concerns. In the first instance, the selected enterprises will be informed by or through the trade association of which they are a member, i.e.
- the chemical companies in the VNCI;
- the metal industry in the FME;
- the other companies in BMRO/VNO-NCW.

\(^6\) VNCI : Association for the Dutch Chemical Industry  
FME : Federation of Enterprises in the metal, electronics and electrotechnical industries, and related processes  
BMRO/VNO-NCW : Environment and Physical Planning Agency of the Association of Dutch Employers Organizations VNO and NCW
Subsequently, the representative of the authorities (Province and/or Inspectorate for Environmental Protection) will make an appointment for a company visit in consultation with TNO. During this visit, the company will be instructed in more detail and arrangements will be made for the measurements to be taken. RIVM will also be present at this company visit, if a further inventory of the process is necessary. If so requested by the company, the representative of the trade association may be present at this visit.

**Reporting**

The results of each measurement will be reported by TNO in the form of a letter (about six weeks after the last measurements of that particular unit have taken place). This report is first only sent to the chairman of the support committee (Mr M. Krijgsman, Chief Inspector of Public Health for Environmental Protection).

Should the report necessitate it (for example, in case of relatively high emissions), the chairman and the trade representative in the support committee will visit the company. If required, new measurements will be taken either at the same company or at another company with an identical process. After agreement of the chairman, the report will be sent to the company. The company will then have 14 days to comment on the report.

After this 14-day period, the report (with any alterations, thus a second draft), as well as any comments of the company and TNO's response to it on behalf of the support committee will be sent to:
- the company;
- the Province;
- the Inspectorate for Environmental Protection;
- the members of the support committee.

The results of the measurements will be discussed by the support committee. RIVM will evaluate the results per process category or cluster of processes. A final report will be drafted at the end of the project.

During the various activities, the required discretion will be shown to prevent the company from being stigmatized and to prevent unnecessary unrest in the surrounding area.

**Further information**

Further information can be obtained from the secretary of the support committee:
L.M. Troost
TNO Institute of Environmental and Energy Technology (IMET-TNO)
P.O.Box 342
NL - 7300 AH Apeldoorn, the Netherlands
Tel. + 31 55 493 146
Facsimile + 31 55 419 837
IMET-TNO Apeldoorn 911125
dbs
APPENDIX 4  Measurement methods

Instruction RV'89

Part of the RV'89 which, at the time of inception, concerned the prescribed measurement methods followed in the MOB measurements, is included below.

Measurement methods

The "Measurement Method" Table below indicates on which basis of standards or directives (as far as they are available) the process parameters and the concentration of the pollutants should be determined. The measurement values must be established as hourly averages. These separate measurements should be performed under "normal" conditions. The representativeness of the process conditions should be proven through plant data.

If it is technically impossible to perform the measurement within a maximum of one hour, the duration of the measurement may be a maximum of eight hours for the individual measurements of dust, heavy metals, PCDDs and PCDFs. The sampling time employed should be in line with the measurement method employed.

If a boiler for energy utilization is available, the CO concentration may be measured directly behind the boiler.

In case of batch processes, the competent authorities will issue adapted instructions on the measurement strategy required.

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7) This part of the RV'89 has been replaced with the "Regulation of Measurement Methods for Air Emissions of Waste Incineration" (Gazette 15 of 22 January 1993). This decree is part of the "Incineration Decree". A number of parts of this decree have been updated.
<table>
<thead>
<tr>
<th>Component</th>
<th>Standard to be employed in determining concentration on the basis of</th>
<th>Continuous measurement</th>
<th>Discontinuous measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Standard</td>
<td>Note</td>
<td>Standard</td>
</tr>
<tr>
<td>Dust</td>
<td>ISO/DIS 10155.2</td>
<td>1</td>
<td>ISO/DIS 9096</td>
</tr>
<tr>
<td>Gaseous inorganic chlorides (as HCl)</td>
<td>general measurement practice</td>
<td>1.2</td>
<td>VDI 3480 Blatt 1</td>
</tr>
<tr>
<td>Gaseous inorganic fluorides (as HF)</td>
<td>not applicable</td>
<td></td>
<td>VDI 2470 Blatt 1</td>
</tr>
<tr>
<td>Gaseous organic compounds (as C)</td>
<td>VDI 3481 Blatt 3</td>
<td>4.5</td>
<td>not applicable</td>
</tr>
<tr>
<td>CO</td>
<td>VDI 2459 Blatt 6</td>
<td>5</td>
<td>not applicable</td>
</tr>
<tr>
<td>SO\textsubscript{x} (as SO\textsubscript{2})</td>
<td>ISO/DIS 7935</td>
<td>6</td>
<td>not applicable</td>
</tr>
<tr>
<td>NO\textsubscript{x} (as NO\textsubscript{2})</td>
<td>ISO/CD 10849</td>
<td></td>
<td>not applicable</td>
</tr>
<tr>
<td>Heavy metals</td>
<td>not applicable</td>
<td></td>
<td>draft NPR 2817</td>
</tr>
<tr>
<td>PCDDs/PCDFs</td>
<td>not applicable</td>
<td></td>
<td>measurement regulation by RIVM/TNO</td>
</tr>
<tr>
<td>Process parameters:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxygen</td>
<td>CAN/CSA-Z223.2-M86</td>
<td>5</td>
<td>CAN/CSA-Z223.2-M86</td>
</tr>
<tr>
<td>Moisture content</td>
<td></td>
<td>8.9</td>
<td>EPA method 4</td>
</tr>
<tr>
<td>Temperature</td>
<td>general measurement practice</td>
<td>10</td>
<td>general measurement practice</td>
</tr>
<tr>
<td>Flue gas flow</td>
<td>not applicable</td>
<td></td>
<td>ISO/DIS 9096</td>
</tr>
</tbody>
</table>
Description of the abbreviations of the standards mentioned:

ISO             International Standardisation Organisation
ISO/DP          ISO Draft Proposal
ISO/DIS         ISO Draft International Standard
ISO/CD          ISO Committee Draft
NEN             Nederlandse Norm (Dutch norm)
NPR             Nederlandse Praktijk Richtlijn (Dutch Practical Guideline)
VDI             Verein Deutscher Ingenieure (Association of German Engineers)
EPA             Environmental Protection Agency (USA)
CAN/CSA         Canadian Standards Association

Notes:
- ISO standards for continuous measurement systems formulate performance characteristics with which these measurement systems must comply. A special kind of device is not prescribed in this respect, although how to verify these requirements is. In this way, the need for a standard or directive to be drawn up for every kind of measuring device is avoided.
- ISO/DIS 9096 is similar to NPR 2788.

**Measurement frequency**

The discontinuous measurements of the components dust, heavy metals, chlorides, and fluorides should be taken four times a year, and the discontinuous measurements for PCDDs and PCDFs twice a year. Each time three measurements must be performed.

The frequency of the discontinuous measurements should be considered a starting value. When the emission picture has been established through several measurements, the continuous measurements can give indications as to the course the emissions will take. Thus permission can be granted after a certain time to adjust the frequency of the prescribed measurements.

**Assessment**

If the concentration of a component is determined on the basis of continuous measurements, the emission limit value is assumed to be met if 97% of the hourly averages of the measurements during a calendar year do not exceed this limit value.

If the concentration is determined on the basis of discontinuous measurements, the emission limit value is met if no single measurement result (of the three measurements minimally required) exceeds this emission limit value. If this is not the case, additional emission measurements should be taken in the short term to obtain a clear picture of the emissions.
Explanation (notes):

1) For the time being, measurement values obtained with these monitors may be considered indicative. Thus enforcement occurs on the basis of discontinuous measurements. As far as it is technically possible, the measurement systems for dust should, however, meet the requirements imposed in the standard. In addition, the recommendations of the manufacturer should be followed.

2) If a monitor which only measures the HCl concentration on a continuous basis is used, this concentration should be multiplied by a certain factor so as to calculate the concentration of gaseous inorganic chlorides (calculated as HCl). This factor should be determined four times a year on the basis of the discontinuous measurements of gaseous inorganic chlorides and HCl.

3) In accordance with NEN 6588, ion chromatography may also be employed for the analysis.

4) Only FIDs that also meet the requirements as stated in Appendix C may be used.

5) Other measurement methods may also be used if they produce measurement results that do not significantly differ from measurement results obtained in measurements per the stated standard, and if at least a similar repeatability is obtained as with measurements per the established standard.

6) Only the concentration of SO₂ is continuously measured. This continuously measured concentration of SO₂ should be multiplied by a certain factor to calculate the concentration of sulphur oxides (SOₓ). This factor should be determined four times a year on the basis of a series of three additional, discontinuous measurements, as per ISO 7934.

7) This NPR is applicable to all metals mentioned in the 1989 Combustion Directive.

8) In the case of the availability of a wet scrubber in the stack gas cleaning system, the moisture content of the stack gases is equal to the saturated water vapour content of air at the flue gas temperature after the scrubber. In the case of continuous measurements, this temperature must also be measured and recorded continuously.

9) If no wet scrubber is used in the stack gas cleaning system, the correction to "dry cubic metres" is performed with the help of a factor. This factor is established four times a year on the basis of the measurement results of a series of three discontinuous measurements.

10) VDE/VDI 3511 and VDE/VDI 3512 Blatt 2 include general recommendations for measuring temperature, inter alia, with respect to the way of performing these measurements and the assembly of the measurement elements.

Note: See Appendix A for the conversion to dry cubic metres and the calculation of the concentration related to 11% O₂.
Practical application

\[ \text{O}_2, \text{CO}_2, \text{CO}, \text{C}_x\text{H}_y, \text{T (measurement car)} \]

The sampled flue gases are led to the measurement car through a temperature-controlled Teflon connection (≥ 180 °C). In the measurement car, the moisture is frozen out, and the dried gases are led to the measuring devices.

The following continuous recording measurement equipment is found in the measurement car:

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td>oxygen</td>
<td>O(_2)</td>
</tr>
<tr>
<td>carbon dioxide</td>
<td>CO(_2)</td>
</tr>
<tr>
<td>carbon monoxide</td>
<td>CO</td>
</tr>
<tr>
<td>hydrocarbons</td>
<td>C(_x)H(_y)</td>
</tr>
<tr>
<td>temperature</td>
<td>°C</td>
</tr>
</tbody>
</table>

Taylor Servomex type 570A 0-100%, paramagnetic (according to CAN/CSA-Z223.2-M86 or equivalent)
Binos model 100 0-20%, infrared (according to CAN/CSA-Z223.2-M86 or equivalent)
Beckman model 880 0-1000 ppm, infrared (according to VDI 2459 page 6 or equivalent)
Beckman model 400 or Ratfisch model RS55 0-10000 ppm, flame ionization, fuel H\(_2\)/He mixture (according to VDI 3481 page 3 or equivalent)
Chromel alumel Thermocouple type K, DIN 73710, IPTS 1986, 0-1200 °C

Before the measurements are started, the flue gas analysis equipment is adjusted on site, using calibration gases with an analysis certificate.

Data acquisition. The measurement signals are collected using an HP 3852 data acquisition/control unit. The data are processed with an HP 1000-A600 computer unit with peripherals.

Cl\(^-\), F\(^-\), Br\(^-\) and H\(_2\)O

The sampling to determine the concentration of inorganic halogenated compounds in the flue gases was performed using midget impingers placed in melting ice.

With random tests, flue gases are led through four impingers (placed in series) via a quartz/glass fibre plane filter. Using a dry gas meter, the sucked flue gas quantities are measured.

The halogenated compounds occurring in the flue gases (forming ions in an alkaline environment) are washed out in the impinger liquid (1 molar caustic soda solution) as Cl\(^-\), F\(^-\), and Br\(^-\). Previously, any sulphur oxides present in the flue gases were oxidized to sulphate in an impinger with hydrogen peroxide in order to prevent a decrease in alkalinity of the caustic solution. After the sampling, the impinger samples thus obtained are analyzed by ion chromatography in the chemical laboratory according to NEN 6588.

The moisture present in the flue gases condenses in the impinger liquids. In the last impinger, the flue gases are dried by the silica gel that is found in this impinger. The vapour concentration of the flue gases can be determined from the difference between the weighing of the liquids and the silica gel before and after the sampling.
Figure B.4.1 Diagram of sampling set to determine the $\text{Cl}^-$, $\text{F}^-$, $\text{Br}^-$ and $\text{H}_2\text{O}$ concentrations.

Flow rate

The flow rate is measured via velocity measurements using a pitot tube according to Prandtl. If this is not possible ("wet" flue gases), use is made of a propellor anemometer.

PCDD/PCDF

Sampling of PCDD/PCDF takes place using the Ströhein dilution device, shown diagrammatically in Fig. B.4.2. The principle is based on the cooling of a substream of flue gases by diluting it with dried and filtered air. Most of the PCDD/F present condense here and are subsequently collected with the dust on an absolute filter. For more volatile components, a fixed adsorption medium is added. The PCDD/F present on the filter and adsorbens are then analyzed.

Using an electrically heated titanium sampling pipe, the flue gases are sucked isokinetically as much as possible, according to NPR 2788. The dilution air is sucked via an air treatment chamber, in which a layer of silica gel is found. The quantity of dilution air is measured with a volume flow meter and can be set with a control valve.

In a special mixing part, the dilution air is turbulently mixed with the sucked flue gases after this air has been led through a hooded filter. The mixing is done in such a way that the temperature of the mixture during the sampling stays below 40°C. At this temperature, the PCDD/F are largely adsorbed to the dust particles. This way of cooling prevents the flue gases from coming under their dew point.

The mixture then passes a similar hooded filter as for cleaning the dilution air, and subsequently the fixed adsorption medium. The quantity of diluted flue gases is measured with a vol-flow meter and can be set with a control valve. Finally, the mixture passes the extractor fan.
1= exhaust opening
2= heated exhaust probe
3= filter for sampled and mixed air
4= air treatment chamber
5= control unit
6= moisture separator

Figure B.4.2 Diagram of Ströhlein dilution unit.

The samples are offered as quickly as possible for analysis, and meanwhile kept in a cool and dark place. The hooded filter is analyzed in the laboratory. To this end, the filter material is taken from the housing, put in an acid solution, and subsequently extracted with toluene in a Soxhlet set-up. The extract is then concentrated by evaporation. The dissolved residue is cleaned and subsequently injected into the separation column of a gas chromatograph. Identification and quantification takes place using a mass spectrometer, in the "selected ion monitoring" (SIM) mode.

The concentration of PCDD/F in the flue gases is calculated from the extracted flue gas volume, referred to standard conditions and the mass of toxic equivalents of the PCDD/F collected on the absolute filter.
APPENDIX 5  Inaccuracy in measurement results of dioxin measurement

For the sake of completeness, it is emphasized here that any inaccuracies in the calculated emissions of a process category are determined by two factors: the inaccuracy of the measurement and the inaccuracy connected with the extrapolation (see section 2.4). Only the inaccuracy in measurement is treated below.

A number of different sampling techniques for sampling dioxins in flue gases have been described in the literature (VDI, 1990; Lützke, 1987). These methods can be divided into the "dilution method" and various "condensation methods". In the Netherlands, the dilution method has been selected for all investigations. Specifically in case of frequent routine measurements, this method is preferred because of its efficiency and the dioxins being concentrated in one place in the sampling system (filter + PUF), which strongly reduces the chance of the sample becoming polluted.

The inaccuracy of the measuring result of a dioxin measurement is determined by the inaccuracies in sampling and in upgrading and analysis.

Inaccuracy in sampling

Comparative investigations in the past have shown that at concentrations above 1 ng I-TEQ/m³ the condensation and dilution methods produce practically the same results (VDI, 1990; Lützke, 1987; VDI, 1986; De Koning and Kleinveld, 1987; Marklund et al., 1992). Recent experience suggests that this is also still the case for lower concentrations. In a current CEN round robin test, different sampling methods are compared with each other at concentrations of about 0.1 ng I-TEQ/m³. The first results of this investigation in which TNO also participated are expected early 1993.

The determination of the extracted flue gas volume is regarded as the largest potential source of error of the dilution method, since the extracted flue gas volume is established from the difference of the volume of mixed air and the volume of diluted flue gases. As two large figures are subtracted here from one another, the inaccuracy of these figures is of crucial importance. Important factors determining this inaccuracy are the reading accuracy, the accuracy of the measuring instruments and the data acquisition, as well as the circumstances under which the measuring instruments are used. Another very important factor is the dilution factor (ratio volume of mixed air/volume of flue gas).

The volumes of mixed air and diluted flue gases are determined by multiplying the results of flow measurements (in m³/s) with the sampling time. The inaccuracy of these volumes is caused by accidental and systematic deviations. By conducting a sufficient number of measurements of the flow rates (several times per second), the accidental deviation in the volume measurements is restricted to a minimum. The systematic deviation can be minimized, for example, by regular measurements.

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8) The inaccuracy (of a measuring method) states the extent to which the measurement value obtained with a certain measuring method approaches the real value (NEN 3114). The 95% confidence interval is taken here as measure for the inaccuracy. The inaccuracy is built up of two components: the accidental deviation and the systematic deviation. The accidental deviation can be caused by influences from the measuring instrument, the observer, the conditions under which the measurements are conducted, etc. At a sufficient number of measurements, the averaged measured value is identical to the real value (when the systematic deviation is zero). In a systematic deviation, factors are at stake that always cause a deviation in a measurement into a certain direction, e.g. by failure, insufficient calibration, etc. This causes a difference between the average measured value and the real value.
calibration and adjustment of the measuring instruments. In addition, the following three checks are essential in determining the extracted flue gas volume: the leak test of the measurement set-up, a comparative measurement with the two flow meters (the "matching" of these meters) and the calibration of the flow meters (with everything being done as much as possible at the measurement site).

In the leak test, the leak-tightness of the measurement set-up is established by bringing the system to a specific underpressure. This underpressure must remain within certain limits during an established time.

In the comparative measurement, the results of the volume measurement of the mixed air are compared with those of the diluted flue gases. In this, no flue gas is extracted (both meters should then give a result that does not differ significantly).

The calibration of the two flow meters is conducted using a (calibrated) gas meter. In doing this check, the systematic deviation of the measured volumes can be restricted to less than 1% (relative).

Figure B.5.1 shows the importance of reducing the inaccuracy of the volumes of mixed air and diluted flue gas to the feasible minimum, by way of the mentioned tests. This figure gives an example of the inaccuracy of the calculated (extracted) flue gas volume as a function of the dilution factor and the inaccuracy of the volume determinations. For example, a 1% inaccuracy in the volume determinations at a dilution factor of 20 produces a maximum possible inaccuracy of 25% in the calculated volume. By correctly conducting the above-mentioned checks and keeping the dilution factor as low as possible, the inaccuracy of the extracted flue gas volume can be reduced to less than 10%.

Figure B.5.1 Inaccuracy of extracted flue gas volume as a function of the dilution factor
\[ A(Q) = \text{inaccuracy of the measured volume of mixed air and diluted flue gas} \]
Other causes of the inaccuracy of the sampling can be the deviation in isokinetic sampling, direction of the probe end with respect to the flow direction, etc. More detailed information about this can be found in the error survey of the Dutch Practice Guideline for determining the dust concentration (NPR 2788). From that survey it can be derived that the sum of these inaccuracies (in as far as it is relevant for the dioxin sampling) is smaller than 10%.

From the above, the conclusion can be drawn that the total inaccuracy as a result of the sampling can be put at maximally 15%.

Inaccuracy as a result of upgrading and analysis

The analytical chemical laboratory of TNO has carried out a number of measurements in order to establish the accidental deviation in upgrading and analyzing flue gas samples. This deviation differs per PCDD/F congener and appeared to be between 2 and 38% relative (95%, n=4) (De Jong et al., 1990). In order to establish the inaccuracy of the total I-TEQ ultimate value, the various absolute deviations are corrected with the I-TEF value of the congener in question and then combined. For a sample with a congener distribution comparable with that of an MSW incinerator, this results in an accidental deviation in the total I-TEQ value of about 6%. The calculated accidental deviation may be different for samples with other congener distributions. The differences occurring because of this are not large. On the basis of the above information, the accidental deviation in the analysis results will be smaller than 10%.

In 1990, a comparison between TNO and RIVM was made of the analysis results of dioxin samples. The dioxin concentrations of the flue gases from which the samples were taken were 10 ng I-TEQ/m³ and higher. The differences between the analysis results of TNO and RIVM were, on average, smaller than 15% for ten independent analyses conducted parallel (De Jong et al., 1990).

In 1992, a round robin test was started in the Netherlands for validating the analysis method for flue gas samples with a dioxin concentration varying from 0.01 to 2 ng I-TEQ/m³. Six laboratories participated in this round robin test. The most important criterion for approval was that 11 of the 12 samples analyzed by each laboratory may deviate no more than 25% from the average of all measuring results. The results of the round robin tests are currently being evaluated. Considering the acceptance criterion, it may be assumed that an inaccuracy of 25% in an analysis result is a reasonable assumption.

Inaccuracy of dioxin measurement

On the basis of the above-mentioned data it can be assumed that the inaccuracy in sampling is maximally 15% and that in upgrading and analysis maximally 25%. The total inaccuracy of the measuring result (in ng I-TEQ/m³) is therefore estimated at about 30%.
APPENDIX 6  Dispersion of dioxins and risks for public health

1.  General

The dioxins emitted by a source disperse into the environment. For the local impact, not only is the emitted quantity of dioxins important, but also the way in which the dispersion takes place. In the last few years, the RIVM dioxin investigation has focused, inter alia, on the dispersion and on the question how and to what extent the population is exposed to dioxins. This investigation has led to the development of a chain model with which, on the basis of the dioxin emission, the concentration of dioxins in milk of cows grazing in the vicinity of a source can be calculated.

Human exposure to dioxins occurs for at least 95% via food (Theelen, 1989). From an extensive investigation of dioxin concentrations in food (Liem et al., 1991) it was established that specifically milk products and products with fish oil substantially contribute to this exposure.

In the Netherlands, the standard for the quantity of dioxins that may be absorbed during one's entire life is 10 pg I-TEQ per kg of body weight (Tolerable Daily Intake, TDI). By combining the results of a food consumption search (VCP, 1988) and the results of the food investigation, less than 1% of the population was found on derivation to be exceeding the TDI, if during an entire life milk products are consumed with a dioxin concentration of 6 pg I-TEQ g⁻¹ of milk fat. On this basis, it was decided in 1991 to maintain the already established, temporary milk standard of 6 pg I-TEQ g⁻¹ of milk fat. (The temporary standard had been established in 1989 on the basis of the data then known).

The chain model consists of three parts: the dispersion through the air, the behaviour on and in grazing land (pasture model) and finally the toxicokinetics in the cow. Chapter 2 of this appendix gives a short description of the chain model. For more information, the reader is referred to the summary report on the incineration of domestic waste (Slob et al., 1992), which also includes a list with original reportings. Chapter 3 presents several sample calculations of concentrations in milk, on the basis of emissions under different circumstances.

2.  The chain model

2.1  Dispersion into the air and deposition

The dioxins emitted by a source are transported through the air and ultimately end up on the soil through deposition. The quantity of deposited dioxins on a certain place depends on a number of source characteristics and on the weather conditions.

Apart from the quantity emitted per time unit, the most significant source characteristics are the stack height, the temperature of the flue gas and the particle size distribution of the dust particles to which the dioxins are mainly bound. The heat content of the flue gas is calculated from the temperature and the wet flue gas flow. A higher stack or a higher heat content result where the largest quantities are being deposited (deposition maximum) to be at a larger distance from the source, while the deposited quantity per surface unit is smaller. The particle size distribution of the dust is important because larger particles are deposited closer to the source than smaller particles.
Important weather factors are the wind direction, the wind velocity and the precipitation. Because the predominant wind direction in the Netherlands is south-west, the deposition maximum over a longer period of time will be north-east of the source.

Average annual weather conditions and the average emission over the same period are usually assumed for model calculations. The accuracy of the predictions is smaller as they are calculated for shorter periods.

In calculating the deposition at a certain place, account should also be taken of a background deposition caused by sources that are at a larger distance, that is, outside the direct sphere of influence of the source. Those sources include foreign sources. The background deposition in the Netherlands is on average 8 ng I-TEQ m$^{-2}$ year$^{-1}$, 50% of which comes from abroad. In the direct vicinity of a source the background deposition may be increased with deposition from other sources in the vicinity. The total deposition with which the soil is burdened by an emission source then consists of that (local) background deposition, increased with the calculated deposition of the source in question.

2.2 Dioxin concentrations in soil

Dioxins are absorbed by cows both via grass and via the soil. The pasture model describes the behaviour of the deposited dust particles and the dioxins bound to them on and in grazing land.

A large part of the precipitated dust particles will end up on the grass. The quantities of dioxins that remain behind on the grass will fluctuate, depending on the weather conditions. In case of rain, the dust particles will be rinsed off the grass and land on the soil. A part of the deposited dioxins will directly end up on the soil. Dioxins in soil are practically non-degradable and are not mobile. This means that the dioxins that have been emitted by a source in the course of the years will accumulate in the top layer of the soil and thus describe the deposition history of the source (if no soil tillage has taken place). Measurements of concentrations in the soil around MSW incinerators are shown to be in good agreement with the concentrations predicted by the model.

2.3 Toxicokinetics in cows

Cows at pasture eat an average 15 kg of grass and 0.225 kg of soil per 24 hours. A part of the dioxins taken up is really taken up by the body during digestion (bioavailable part) and spreads in the cow’s body where it accumulates in fat tissue and milk fat.

Toxicokinetic investigation at RIVM shows that the bioavailability depends on the matrix of the dioxins. Dioxins bound to fly dust have a lower bioavailability than dioxins dissolved in fat. Model calculations assume a bioavailability of 3% for dioxins bound to fly ash.

By measuring dioxin concentrations in cow’s milk after a cow had been exposed to dioxins once, it could be verified that the dioxin concentration in milk is at its maximum 1 to 2 days after the exposure and that the concentration then slowly decreases again. In this investigation, half-lives of 27-56 days were found, depending on the congener. The experimentally found half-lives agreed well with the decrease in the time of the concentration in milk of cows grazing in the vicinity of an MSW incinerator after its closure.
2.4 Measured and predicted dioxin concentrations in milk

Starting from a given dioxin emission, the dioxin concentration in cow's milk at any place and at any time (so dependent on weather conditions) can be calculated with the chain model. The contributions of the routes via grass and soil can be calculated separately. For grass, a division is made between the contribution of a local source and the contribution of the background deposition.

Figure B.6.1 plots the measured dioxin concentrations of 123 milk samples against the calculated concentrations. The milk samples had been taken in the period from 1989 to 1990 in the vicinity of four MSW incinerators. The figure shows good agreement between the real and the calculated values. The model can also be applied well as a policy-supportive tool.

![Comparison of predicted and measured dioxin concentrations in milk.](image)

3. Sample calculations

The highest emissions were measured at MSW incinerators (see Chapter 3). In 1991, 10 MSW incinerators were still operating. Apart from cows in the Lickebaert polder, nowhere was the Food & Commodities Act standard for dioxins in milk exceeded, as had been the case in earlier measurements in the vicinity of other MSW incinerators. It should be noted, however, that in a number of cases the dairy farms are at larger distance from the source than the deposition maximum. North-east of the MSW incinerator of ROTEB in Rotterdam, for example, the nearby pasture lands are 6-9 km from the source. (The deposition maximum is at a distance of about 0.5 km). Dioxin concentrations of 2.6-3.6 pg I-TEQ g⁻¹ of milk fat were found in milk from cattle from those areas.
By measuring dioxin concentrations in milk samples from areas outside the direct sphere of influence of a dioxin source, a national background level of 0.8-2.5 pg I-TEQ g$^{-1}$ of milk fat could be established. The increase in the concentrations of samples from the vicinity of the ROteB with respect to the background concentration is limited. This means that the influence of the source at this distance is small.

From emission measurements outside MOB framework, annual emissions of 1.8, 42 and 24 grammes I-TEQ per year respectively were estimated for three individual sources. This can be compared with the annual emissions of several MSW incinerators (see Table 3.1). The annual emissions calculated from the emission measurements of all other individual sources are below 1 g I-TEQ per year.

In order to get an impression of the contribution of the measured sources to the dioxin concentrations of cows grazing in maximum-deposition areas, a number of sample calculations are given below.

Example 1
The source with an annual emission of 24 g has a stack height of 150 metres and a flue gas temperature of 130-150 °C. A maximum deposition of 6.2 ng I-TEQ m$^{-2}$ year$^{-1}$ caused by the source was calculated. Including the background concentration, the maximum deposition was 14 ng I-TEQ m$^{-2}$ year$^{-1}$. The maximum is at a distance of about 750 m from the source. There are no pasture lands in the direct vicinity of the source.

The maximum deposition of this source (including background deposition) is the same as that of the MSW incinerator of Amsterdam-North. The two sources can therefore be compared with each other. At a short distance from the MSW incinerator, dioxin concentrations of 2-3 pg I-TEQ g$^{-1}$ of milk fat were measured in milk. This means that, if there were pastures in the vicinity of the considered source, the dioxin concentrations in milk at the site would be increased, compared with the background concentration of 0.8-2.4 pg I-TEQ g$^{-1}$ of milk fat. The Food & Commodities Act standard, however, would not be exceeded.

Example 2
The plant with an annual emission of 1.8 g I-TEQ has a stack height of 60 metres and a flue gas temperature of 270 °C. The plant is situated in an area with a calculated local background deposition of 13 ng I-TEQ m$^{-2}$ year$^{-1}$. According to the deposition calculation, the contribution of the source will be 12 ng I-TEQ m$^{-2}$ year$^{-1}$. The deposition maximum is at about 300 metres from the source. From the model calculation it follows that there a dioxin concentration in cow's milk of 1.7 pg I-TEQ g$^{-1}$ of milk fat can be expected.

Example 3
The plants with established annual emissions between 0.1 and 1 g I-TEQ have stack heights of minimally 30 metres and maximally 172 metres. The flue gas temperature is minimally 26 °C and maximally 230 °C. A choice has been made for calculating the two worst situations from this group: a plant with an emission of 1 g I-TEQ yr$^{-1}$ and a stack height of 60 metres, and a plant with an emission of 0.5 g I-TEQ yr$^{-1}$, with a stack height, however, of only 30 metres. In both cases, a low heat content was assumed, as well as a supposedly high (local) background deposition of 15 ng I-TEQ/m$^{-2}$ year$^{-1}$, and a particle size distribution, as determined at MSW incinerators.

The calculated dioxin concentrations in milk fat are 1.8 and 3 pg I-TEQ g$^{-1}$ of milk fat, respectively. For all other plants in this group, it holds that process conditions are more
favourable and that therefore the burden on the cow will be lower than 3 pg I-TEQ g⁻¹ of milk fat.

Example 4
Of all measured plants with an emission lower than 0.1 g I-TEQ yr⁻¹, the plant with an annual emission of 0.02 g I-TEQ yr⁻¹, a flue gas temperature of about 20⁰C and a stack height of 20 metres can be considered to be the worst-case situation. For this situation, a heat content of zero was taken. A dioxin concentration in milk of 1.1 pg I-TEQ g⁻¹ of milk fat was calculated.

Table B.6.1 summarizes the calculations.

Table B.6.1 Calculated dioxin concentrations in cow’s milk for several dioxin sources (worst-case situations) (including a high local background deposition)

<table>
<thead>
<tr>
<th>Example no.</th>
<th>PCDD/F emission [g I-TEQ yr⁻¹]</th>
<th>Background deposition [ng⁻¹ m⁻² yr⁻¹]</th>
<th>Stack height [m]</th>
<th>Heat content of flue gases [MW]</th>
<th>Milk concentration in deposition max. [pg I-TEQ g⁻¹ fat]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>24</td>
<td>5</td>
<td>150</td>
<td>25.2</td>
<td>2.3 ¹)</td>
</tr>
<tr>
<td>2</td>
<td>1.8</td>
<td>13</td>
<td>60</td>
<td>0.82</td>
<td>1.7</td>
</tr>
<tr>
<td>3a</td>
<td>1</td>
<td>15</td>
<td>60</td>
<td>0.067</td>
<td>1.8</td>
</tr>
<tr>
<td>3b</td>
<td>0.5</td>
<td>15</td>
<td>30</td>
<td>0.079</td>
<td>3.0</td>
</tr>
<tr>
<td>4</td>
<td>0.02</td>
<td>15</td>
<td>20</td>
<td>0</td>
<td>1.1</td>
</tr>
</tbody>
</table>

¹) Estimated value on the basis of data of MSW incinerator in Amsterdam-North.

The calculations show that, in relation to the background concentration of dioxins in cow’s milk, an increase in the dioxin concentration in milk can be expected in a number of cases, but that in no case will the standard of 6 pg I-TEQ g⁻¹ of milk fat be exceeded.

Once the emission standards set by the government have been met, the background deposition will then decrease to about 4 ng I-TEQ m⁻² year⁻¹. In this, it is assumed that the contribution of foreign sources will remain unchanged, which is not probable. In that case, the background concentration of dioxins in cow’s milk will also decrease.
APPENDIX 7  Congener patterns

1. Introduction

It was striking in the investigation of the dioxin and dibenzofuran emissions by waste incinerators (Slob et al., 1992) to note that the relations in which the different congeners occurred in the emissions of the various installations were quite similar. This could be retraced to the similarity between the processes considered in this investigation.

It is assumed that within a group of similar processes for other processes it may also hold that the congener patterns are identical. In order to test this, a survey was made of the congener patterns found in the installations involved in the MOB investigation. Also given was an average of the congener patterns of the MSW incinerators. By classifying these congeners per process category and comparing them, one can look for differences and similarities in the patterns. The ultimate goal of this is to see whether it is possible to establish relations between sources and the dioxins found in the vicinity and/or food (fingerprinting).

2. The congeners

The samples taken per installation were analyzed on the (17) 2,3,7,8-chlorine substituted dioxins and dibenzofurans (see Appendix 1) Table B.7.1 shows these congeners, following the numbering using the graphs in this Appendix.

Table B.7.1 Survey of the seventeen congeners

<table>
<thead>
<tr>
<th>Number</th>
<th>Dioxin congener</th>
<th>Number</th>
<th>Dibenzofuran congener</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2378 T4CDD</td>
<td>8</td>
<td>2378 T4CDF</td>
</tr>
<tr>
<td>2</td>
<td>12378 P5CDD</td>
<td>9</td>
<td>12378 P5CDF</td>
</tr>
<tr>
<td>3</td>
<td>123478 H6CDD</td>
<td>10</td>
<td>23478 P5CDF</td>
</tr>
<tr>
<td>4</td>
<td>123678 H6CDD</td>
<td>11</td>
<td>123478 H6CDF</td>
</tr>
<tr>
<td>5</td>
<td>123789 H6CDD</td>
<td>12</td>
<td>123678 H6CDF</td>
</tr>
<tr>
<td>6</td>
<td>1234678 H7CDD</td>
<td>13</td>
<td>123789 H6CDF</td>
</tr>
<tr>
<td>7</td>
<td>12346789 O8CDD</td>
<td>14</td>
<td>234678 H6CDF</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15</td>
<td>1234678 H7CDF</td>
</tr>
<tr>
<td></td>
<td></td>
<td>16</td>
<td>1234789 H7CDF</td>
</tr>
<tr>
<td></td>
<td></td>
<td>17</td>
<td>12346789 O8CDF</td>
</tr>
</tbody>
</table>

3. Method of working

The absolute quantities of dioxins and dibenzofurans found in the samples were taken from the underlying analysis reports. As this involves the relations amongst these substances, there is no sense in multiplying them by the Toxicity Equivalence Factors (I-TEFs). The quantities per congener were then calculated as a percentage of the total of the congeners found. Per process category, the relation in which the 17 congeners occurred in the sample was rendered in small graphs for all sources treated in this report.
The investigated installations were classified as to process category in accordance with the division used in the report. The numbering of the small graphs corresponds to the installation numbering as used in the Chapters 3 to 19. The following process categories are distinguished:

Table B.7.2 Survey of process categories considered

<table>
<thead>
<tr>
<th>Process category</th>
<th>Chapter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Incineration of domestic waste</td>
<td>3</td>
</tr>
<tr>
<td>Incineration of hazardous wastes</td>
<td>4</td>
</tr>
<tr>
<td>Incineration of landfill gas, biogas and sludge</td>
<td>5</td>
</tr>
<tr>
<td>Burning of cables, electromotors, etc.</td>
<td>6</td>
</tr>
<tr>
<td>Waste incineration at hospitals</td>
<td>7</td>
</tr>
<tr>
<td>Asphalt-mixing installations</td>
<td>8</td>
</tr>
<tr>
<td>Oil combustion</td>
<td>9</td>
</tr>
<tr>
<td>Coal combustion</td>
<td>10</td>
</tr>
<tr>
<td>Wood combustion</td>
<td>11</td>
</tr>
<tr>
<td>Crematoria</td>
<td>12</td>
</tr>
<tr>
<td>Fires</td>
<td>13</td>
</tr>
<tr>
<td>Various high-temperature processes</td>
<td>14</td>
</tr>
<tr>
<td>Traffic</td>
<td>15</td>
</tr>
<tr>
<td>Sintering processes</td>
<td>16</td>
</tr>
<tr>
<td>Metal industry</td>
<td>17</td>
</tr>
<tr>
<td>Chemical production processes</td>
<td>18</td>
</tr>
<tr>
<td>Use of pesticides</td>
<td>19</td>
</tr>
</tbody>
</table>

A number of significant process conditions make possible and affect the formation of dioxins:
- temperature between 200 and 800 °C (ideal range between 200 and 400 °C),
- the residence time of the flue gases in this temperature range,
- the presence of chlorine and the quantity of available chlorine,
- the presence of organic (specifically aromatic) matter,
- the presence of oxygen (in basic materials or in the surroundings),
- the presence of fly ash and metals (specifically copper) in the flue gases, which serve as catalysts in dioxin formation.

Wherever these process conditions correspond, similarities in the formation (and thus in the mutual relation in which the congeners occur) can be expected.
4. Results

In considering the graphs in 7.3 to 7.18, similarities here and there, especially within certain process categories, are apparent. The picture is specifically strong in, for example, the incineration of hospital waste and in the sintering processes.

Many other factors, however, should be included in the comparison in order to be able to explain differences and similarities between processes within one category as well as between the process categories themselves, or even to be able to attribute them to certain process conditions.

In addition to the earlier mentioned process variables (B.7.3), moisture, the cleaning technique used (ESP, fabric filter or wet cleaning), etc. also play a role in the formation, and presumably also in the congener patterns arising. All these possible influences should also be included in an intercomparison. The number of variables is therefore so large that much more extensive (statistical) research is needed to obtain some insight into this. Within this framework, it appeared impossible to compare these processes exhaustively. It is expected that such an investigation will produce much knowledge about the way in which the formation of dioxins can be affected. This can be of great importance in preventing dioxin emissions.

5. Conclusions

Within the framework of this report, it was not possible to conduct an exhaustive investigation of the possibilities available on the basis of the congener patterns.

Recommended is an investigation into what extent it is possible, on the basis of these congener patterns, to roughly establish the origin of the dioxins and dibenzofurans found in the environment (fingerprinting).

Further investigation is recommended into what extent useful hints can be found in the proportions in which the different congeners occur in the emissions on the minimization of dioxin formation in the various processes.
3 INCINERATION OF DOMESTIC WASTE

9) This is the average pattern of the MSW incinerators. Large differences may occur mutually, see the reporting of the emission investigation on MSW incinerators conducted in 1990 (Slob et al., 1992).
4 INCINERATION OF HAZARDOUS WASTES
4 continued
5 INCINERATION OF LANDFILL GAS, BIOGAS AND SLUDGE
6 BURNING OF CABLES, ELECTROMOTORS, ETC.
7 INCINERATION OF HOSPITAL WASTE

congenepatroon MOB inst. 7A

congenepatroon MOB inst. 7B

congenepatroon MOB inst. 7C

congenepatroon MOB inst. 7D
8 ASPHALT-MIXING INSTALLATIONS
9 OIL COMBUSTION
10 COAL COMBUSTION
WOOD COMBUSTION
12 CREMATORIA

![Graph 1: Congenerpatroon MOB inst. 12A](image)

![Graph 2: Congenerpatroon MOB inst. 12B](image)
14 VARIOUS HIGH-TEMPERATURE PROCESSES
14 continued \(^{10}\)

\(^{10}\) No individual congeners are known of plant 14H.
15 TRAFFIC

congeneerpatroon MOB inst. 15A

congeneerpatroon MOB inst. 15B

congeneerpatroon MOB inst. 15C

congeneerpatroon MOB inst. 15D
16 SINTERING PROCESSES

congeerpatroon MOB inst. 15A

congeerpatroon MOB inst. 15B

congeerpatroon MOB inst. 15C
17 METAL INDUSTRY

![Graphs showing metal industry data](image)

APPENDIX 7
continued
(emissions to water)
CHEMICAL PRODUCTION PROCESSES