Environment

Preparatory work for new dioxin measurement requirements for the European metal industry

Final Report

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Disclaimer

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1 Executive Summary

In its Communication "*On the Road to Sustainable Production: Progress in implementing Council Directive 96/61/EC concerning Integrated Pollution Prevention and Control*", the Commission briefly addressed the issue of mandatory dioxin requirements (June 2003) as follows:

"For dioxin emissions, where the production and processing of metals remains a major emission source, mandatory monitoring requirements for this sector, without any Commission emission limit values in the first stage, might be one option. This could be an effective regulatory tool since the lack of data on emissions is currently a serious impediment to appropriate measures to be taken.

This consideration can further be broken down into two major goals, which could each be reached by implementing mandatory dioxin monitoring:

1. To reduce the uncertainty on current dioxin emission data, in particular those relating to total metal industry and its respective subsectors.
2. To ensure a proper awareness by competent authorities in order to ensure appropriate monitoring of dioxin emissions at the national, regional and local level.

With these two goals in mind the present study was launched in order to evaluate these possibilities, i.e. considering the implementation of dioxin monitoring requirements with respect to IPPC installations.

However, with respect to the scope of the study it should be noted that it

- does not address the possible permit conditions which would be deemed necessary by the competent authorities to ensure that the installations operate in full compliance with the IPPC Directive. Possible actions to reduce dioxins emissions are therefore not addressed in this report.
- takes into account the information present in the BREFs but does not aim at reviewing these documents.
- does not aim at assessing the potential need to set up Community requirements on emission limit values on dioxins emissions.

On the other hand the study is also related to the EU policy on persistent organic pollutants (POPs) [1]. In particular the requirement presented in article 6 of this regulation to draw up release inventories might be substantially supported by dioxin monitoring requirements, even though such inventories may be entirely build on calculations

Thereby, the study followed an approach which comprised the comprehensive collection of information on relevant processes, including the corresponding numbers of relevant installations, their overall dioxin emission levels and their relative relevance and importance. Moreover, available methods of emission measurement and potential limitations imposed by either measurement cost or lack of available laboratory capacity, had to be considered.

To ensure an up-to-date and comprehensive collection of data and to establish a forum for discussion, a network of experts (NoE) was composed, which included all major stakeholder groups, i.e. the iron & steel and the nonferrous metal industry as well as selected experts from measurement laboratories, science, and industry, and the authorities. Two workshops were held with these NoE members, in order to establish not only a direct exchange of important information but also a critical discussion of findings progressively, derived through out this study. It was also attempted to initiate a vivid discussion via an internet forum, putting forward different statements and questions for discussion. However, this mode of group discussion was not embraced enthusiastically by the aforementioned stakeholders. Rather, more progress was achieved off-the-record by technical and scientific discussions which occurred spontaneously and engaged at the level of individual experts.

Further data were retrieved by means of the answers given to simple, yet specialised questionnaires as well as studying the available literature. The latter includes both the official Member States IPPC reports and the relevant BREF documents, but also a host of industrial reports and scientific papers.

The major results of the data collection and its analysis are:

- There are several metallurgical processes that have potential for dioxin formation. Some of these processes are applied in many different installations in Europe and have also been identified as major dioxin emitters, e.g. the iron ore sintering plant, the electric arc furnace (EAF) for scrap processing in steel production, and non-ferrous metal scrap processing. Many other processes, particularly those in the non-ferrous sector, are applied in Europe in a smaller numbers of installations, often at a smaller scale and frequently are quite specific, or even unique. Some still remain to be investigated for the very first time.
- The number of IPPC installations in the metal sector, as defined according to Annex I(2) of the IPPC Directive, cannot be identified accurately as yet. This is due to both lack of data from some of the New Member States and the availability of only highly aggregated figures for most of the former EU 15. The total number of relevant IPPC installations in the EU 25 is estimated at 6,000 –8,000. From more detailed data, only obtained for a few countries, a share of approximately 25%, or some 1,500 to 2,000 installations for the whole metal production sector, may be potentially eligible for dioxin emission mandatory monitoring. Further uncertainty is caused by the definition of “installation” given in the IPPC Directive.
- The following figures for the number of the most relevant plants as regards dioxin emissions were obtained from the answers to the project questionnaires and from industrial information and other data sources:
    - ♦ some 50 iron ore sintering plants
    - ♦ some 250 electric arc furnaces for steel production, with ca. 100 of these producing carbon steel, 60 stainless steel and the remaining used or miscellaneous other purposes
    - ♦ 8 Waelz kilns for zinc oxide recovery starting from EAF filter dusts
    - ♦ at least some 300-600 non-ferrous scrap processing units; many of which are not really covered by the IPPC Directive, due to the current

capacity thresholds

- at least some 4,200 ferrous and non-ferrous foundries; the major part of these being small facilities and thus not covered by the IPPC Directive.

From the data available, it may be concluded that the number of installations covered by the IPPC Directive which may be considered as being relevant for dioxin emissions ranges from ~ 600 to ~ 1,500.

- The contribution of the metal sector to the European dioxin emissions was assessed from emission inventories to be approx. 20% of the total emissions and up to 50% of the emissions from all industrial sectors. In the group of known metallurgical sources the iron & steel emissions predominate, exceeding those from non-ferrous metal installations by a factor of ~3. According to inventory reports which refer to the year 2000 following emissions were reported for the main source types [1]:

sinter plants	702 g I-TEQ/year
electric arc furnaces	223 g I-TEQ/year
secondary non-ferrous metal production	206 g I-TEQ/year
non-ferrous metal foundries	62 g I-TEQ/year

- Analysis on the data reported in the European Pollutant Emission Register (EPER) clearly show that the threshold value of 1 g I-TEQ/year set for dioxins and furans is too high in order to achieve a desirable comprehensive consideration of emissions from the metal sector (less than 90% of emissions – as expected under EPER - are covered). It can be estimated that substantial emissions may be released by the group encompassing the large number of installations with unit emissions between 0.1 and 1 g I-TEQ/year. Moreover, given that these emissions of dioxins are always variable and that hence their evolution is uncertain, it is plausible that there are a number of sources being underestimated. From this viewpoint it is desirable to enhance monitoring efforts, especially since in many cases emissions are still being estimated rather than established by actual sampling & analysis.
- It has been possible to draw up a good picture of the current practice of dioxin monitoring of the metal industry in the Member States. However, a complete overview could not be gathered. In most countries with important metal industry the awareness of dioxin emissions from metallurgical installations is high. Nevertheless, large differences were found, with on the one hand some Member States with no regulation at all (neither emission limit values nor any monitoring organised), and on the other hand Member States or Regions thereof practising very strict rules for particular plants, involving emission measurements several

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[1] These figures are best estimates based on emission factors and activity rates and therefore contain significant uncertainties. Hence the values might be over- or underestimated. Compared to 1995 the emissions reported for the year 2000 decreased (at least in the Western European countries, except for EAFs). From this trend it appears plausible that actual emissions are somewhat lower than the figures shown. For more detailed information see [12 – 15]

times a year. Occasional measurement programs, although highly appreciable as a first step, are not sufficient to get a comprehensive view of the emission situation and are not appropriate to detect trends. This might be an obstacle when developing appropriate national strategies for long-term reduction of dioxin emissions. Even in those countries with a national regulation of monitoring requirements, the frequency of measurements is often quite low (e.g. in comparison with two annual measurements required from waste incinerators). This practice must be considered as inadequate particularly in the case of installations with highly unstable operating conditions. Hence, in spite of lacking of some more detailed information about the actual monitoring practice on the individual plant level there is no doubt that significant deficiencies regarding the dioxin emission monitoring exist in several Member States which would justify an European regulation on monitoring requirements

- There are several approaches available to measure dioxins and furans in flue gases; among these the international standard EN 1948 1-3 is predominantly used, mainly because it is the only method accepted by authorities in case of compliance tests. Semi-continuous measurements, although in principle complying to EN1948, have rarely been applied in the metal sector so far.

  On top of the mere determination of PCDD/F emissions advantage may be taken by analysing other POP compounds (PCBs, PAH, PCBz) in the emission samples. Such analyses are available for comparably low extra costs and would provide useful additional information, e.g. with respect to the requirements of the Stockholm POPs Convention. For plant operators such data may give more deep insights in dioxin formation conditions and mechanisms which might lead to the potential application of surrogate compounds replacing conventional dioxin monitoring.

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- Measurement of dioxins and furans in flue gases is generally more expensive than for other pollutants due to the long time needed for sampling and the consequent clean-up and the use of marked isotope standards in the laboratory. By comparison with typical gross margins and taking into account that the IPPC Directive does not apply to very small installations, these costs appear to be generally affordable in case of a reasonable frequency (for instance 1 measurement per year). Measurement costs may however increase significantly in particular situations, e. g. at installations with multiple emission points (stacks) to be monitored. The extent of such situations is not exactly known. However, from general considerations on the technologies in question it is believed that most installations are equipped with one stack only and on the average the number of stacks per installation is not higher than 2 . Regarding the desired reduction in uncertainty of dioxin emission data on the European level, measurement efforts could be optimally distributed if the uncertainty of the emission level and the stability of process conditions are taken into account when deciding on the required frequency of sampling and analysis. Therefore, emission measurements should not be applied to the major emitters exclusively.

Based on these considerations and the resulting discussions, three basic options for further action on the EU level were identified.

In a **“no-policy-change” option** (i.e., without any concerted change in the current legislation) it seems quite improbable that dioxin emissions from metallurgical sources will be monitored and appear under adequate supervision in all Member States. Implementation of IPPC permits to existing installations is considerably delayed in many countries and thus there still is the theoretical possibility that competent authorities would impose monitoring requirements on the major dioxin emissions sources in the metal sector. However, from information provided by the first Member States’ reports on IPPC implementation such a development does not seem very probable.

The dioxin emissions issue could be addressed more appropriately if slight changes to the IPPC Directive were made which provide some supplemental incentives to authorities in their efforts dealing with dioxins. This **“improved instruments” option** would emphasise the particular importance of dioxins and furans in the context of the IPPC Directive, as well as change and enhance the present modes of reporting to the EPER. Such action would include the addition of a recital clause in the IPPC directive emphasising the particular importance of dioxin emissions, a modification of the EPER threshold in the context of the upcoming E-PRTR regulation and the focus on dioxins in the context of the review of the BREFs relevant for this sector. At present, neither the basis of assessment nor the estimated emission value is generally reported to the authorities for all those installations which are known or estimated to have emissions below the threshold emission value. Lowering the EPER threshold value could lead to a significant improvement. It is anticipated that authorities, when obliged to confirm the values related in the EPER declarations, will pay much more attention to those installations with emissions below, but close to the present threshold value and consider an intensified monitoring activity in cases where information appears to be too uncertain.

The third option finally discussed is the **“measurement requirement” option**. It would imply introducing a general obligation to monitor dioxin emissions from the most eligible installations in European metal industry. The scope and selection of installations covered by a future monitoring requirement must be based on a balanced assessment of the expected gains of information versus both economic and organisational constraints. Clearly, only installations covered by the IPPC Directive should be addressed if monitoring requirements are connected to this regulation. Obviously, the IPPC categorisation is not suitable to be used without further specification since the IPPC categories may include activities being relevant and irrelevant for dioxin emissions. From the results of this study, the minimum scope would involve the sintering plants in both the iron & steel and the non-ferrous metal industry (category 2.1), electric arc furnaces for steel production from scraps (belonging to category 2.2) as well as those installations of category 2.5 a which are processing secondary materials. This presumably would represent about from 600 to 1,500 installations at maximum. The total cost for the whole industry for carrying out one measurement per year could be estimated between 1.8 about 4.5 million €/year (one stack, single sampling) and to 7.2 and 18 million €/year (2 stacks/triplicate sampling taking into account that in some cases more than one stack may exist per installation). This cost estimation includes the costs already supported by industry for the on-going monitoring of dioxins. It is however difficult to give a precise estimation of the costs already supported by industry since this depends on the particular regulation (no additional costs for countries already demanding one measurement per year or more, full costs for countries with no requirements, etc.).

Besides bringing forward a general obligation, a number of details also has to be regulated, e.g. the scope, i.e. the selection of eligible installations for monitoring, the frequency, the applicable methods, the quality assurance and the duration of monitoring, as well as more uniform methods of reporting and exchange of information. Preliminary outlines and examples on such rules are presented in this report. Considering that the IPPC Directive is based to a certain extent on the principle of subsidiarity, it is still a matter of debate in how far to insert this level of detailed regulation into the Directive. Instead, these aspects could be exhaustively treated within amended BREFs on monitoring or related to metal industry or may be incorporated into a separate guidance document with an evolutive, yet more binding character.

2 Introduction

In 1996 the European Council adopted the Directive 96/61/EC concerning integrated pollution prevention and control[2] ("the IPPC Directive") and its implementation. This Directive is a key instrument in the environmental policy of the EU setting a framework for the operation of around 50.000 major industrial installations. The Directive lays down requirements relating to the establishment of national or sub-national systems for permitting industrial installations, with the objective of achieving integrated prevention and control of pollution and a high level of protection of the environment as a whole. IPPC installations have to apply for and operate according to integrated permits with emission limit values and other conditions based on "Best Available Techniques" (BAT – described further below). In addition to its permit requirements, the Directive also contains provisions relating to monitoring and enforcement, public participation and exchange of information.

The Directive is complemented by various regulations addressing specific sectors (e.g. the Waste Incineration Directive 2000/76/EC) and has significant interdependencies with thematic strategies like the Clean Air for Europe (CAFÉ) process or the Strategy on Dioxins, Furans and Polychlorinated Biphenyls. The latter, adopted in 2001, provides for measures to reduce dioxin emissions from a number of sources including those in the metal production and processing industry.

According to results of emission inventories made for the European Countries during the last decade abroad range of industrial and non-industrial emission sources exist. Industry and non-industrial sources appear to have approximately equal contributions to the overall emissions. This assessment is however biased by uncertainties regarding the emission estimates of both groups, with larger unknowns regarding the non-industrial sources.

Today, with a strict EU-wide regulation already in force for waste incineration setting an emission limit and imposing monitoring requirements the metal industry appears to be the industrial sector predominating the industrial emissions of dioxins and furans.

Consequently In its Communication "On the Road to Sustainable production: Progress in Implementing Council Directive 96/61/EC concerning Integrated Pollution Prevention and Control", presented in June 2003, the Commission briefly addressed the issue of mandatory dioxin requirements: *"For dioxin emissions, where the production and processing of metals remains a major emission source, mandatory monitoring requirements for this sector, without any Commission emission limit values in the first stage, might be one option. This could be*

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[2] OJ L 257, 10.10.1996, p. 26.

an effective regulatory tool since the lack of data on emissions is currently a serious impediment to appropriate measures to be taken."

This consideration can further be broken down into two major goals, which could each be reached by implementing mandatory dioxin monitoring:

1. To reduce the uncertainty on current dioxin emission data, in particular those relating to total metal industry and its respective subsectors.
2. To ensure an appropriate awareness and monitoring of dioxin emissions by competent authorities at the national, regional and local level.

Within the present study, commissioned by DG Environment, basic information needed for the assessment of the need, scope, technical and economical feasibility was requested and options - including EU-wide monitoring requirements – were to be proposed in order to overcome the apparent lack of data on dioxin emissions from the European metal industry.

3 Objectives and approach

The main objective of the study is to provide recommendations on options to be considered for establishing a mandatory PCDD/F monitoring requirement within a future revised and actualised IPPC directive. To reach this objective the following steps were carried out:

- Evaluation of the most recent data compiled on dioxin emissions to assess the importance of the emissions from the metal industry and its subsectors
- Evaluation of the present situation regarding dioxin monitoring in the individual 25 EU Member States, to confirm or refute the need for Community action
- Analysis of the targeted industrial subsectors for specific particularities that should be taken into account
- Defining a range of options to further define the scope and content of eventual monitoring requirements and which appear both feasible and suitable for achieving all major objectives regarding the targeted industrial sector
- Evaluation of both technical feasibility and the possible socio-economic impact as a result of enforcing more systematic and in all likelihood increasing dioxin monitoring activities according to the range of options defined before.

For these steps the gathering of relevant information from numerous and in some cases disparate sources was a key element of success. In practice this was done by

- drafting and submitting a questionnaire to the Member State authorities (IPPC experts) as well as to the industrial associations on both an EU and national level (Eurofer, Eurometaux, WVM Germany, Agoria Belgium)
- informal direct contact with industrial experts, national authorities, dioxin researchers, and analytical laboratories
- studying former files for matters of procedures, needs and frequencies of sampling/analysis, pitfalls encountered, uncertainties, and rational and payable methods of dealing with these

- the implementation of a Network of Experts (NoE) and a NoE Panel
- two workshops with the NoE Panel held at Brussels
- an internet-based discussion forum for the NoE
- using relevant reports (e.g. BREFs, project reports on dioxin monitoring programs, case studies, inventories) and scientific literature
- distribution of the draft final report to the members of the NoE asking them for comments (overall, 9 written comments of 1 to 8 page size were received).
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4 Background information

4.1 Relevant metallurgical processes

In the European metal industry, a vast array of metallurgical processes can be found. A considerable fraction of these have been identified to have the potential for dioxin formation and emission.

In this chapter the underlying technical information leading to this selection will be summarised, with due reference to the supporting ANNEXES. Furthermore, a critical survey on the iron & steel and the non-ferrous metal sector was made, aiming at the identification of potentially relevant processes that should also be taken into account. Particular emphasis will be put on the information provided by the relevant BREF documents, with more details being available in the annexes.

4.1.1 General considerations

Various studies have demonstrated that the metallurgical processes, in particular those in the iron & steel industry, are major dioxin sources. These substantial emissions arise in a wide variety of pyro-metallurgical operations from both the ferrous and the non-ferrous sector, especially those involving scrap and/or filter dust. Still, emissions from sintering plant, the major sources, were only discovered long (ca. 1992) after dioxins were first identified in incineration effluents (1977).

4.1.2 Classification of Metallurgical Industry

Metallurgy is the art and science of extracting metals from their ores and – especially in an ore-poor Europe –from secondary sources also. It also concerns the properties and structures of metals and alloys.

Often, distinction is made between the **iron & steel** and **non-ferrous sector** which includes stainless steel and alloys [3]. Another subdivision comprises hydrometallurgical methods, using both the aqueous phase and solvents in separation processes, and pyro-metallurgical methods, proceeding at medium to elevated temperature. The latter group is a source of dioxin although at high temperature the treatment also serves in decontaminating dioxin-laden feed streams.

Metallurgy may be further subdivided into **primary** operations, i.e. those dealing primarily with ores, and **secondary** production, which largely involves scrap. In the E.U. industry moves more and more from primary towards secondary production. Even in primary industry and in any kind of reprocessing involving melting of metal, internal recycling of byproducts or secondary raw materialss generally applied. Hence, and in line with the BREF for non-ferrous industry, no distinction will further be made between the two types of operations.

Classification of Metallurgical Industry used in this work is that proposed in the last version of the BREF documents. Another Classification appears in the Annexes of the Directive, but is less suitable for handling dioxin emission monitoring or abatement.

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[3] Ferrous alloys are treated in the nonferrous BREF.

In contrast to repeated statements in the first BREF the mere **melting of metal**, as required in metal foundries, metal alloying, and production of mother alloys, has stronger than expected dioxin emitting capabilities. Often, suitable primary and/or secondary measures need to be taken to reduce emissions.

For this reason the scope should not be too restricted regarding both BREF and BAT: just almost any thermal operation involving metals may be expected to generate dioxins to some extent, as long as the contrary has not been proved!

Finally, from metallurgical operations are explicitly excluded some other, specific high temperature processes, involving metal oxides, chlorides, and other salts. Such processes may still exhibit dioxin formation. Examples are:

- The production of titanium oxide by the chloride route.
- Similar processes applying to other elements, including cobalt, nickel, zirconium, etc.

In what follows, in the context of the monitoring of **dioxin emissions**, there is an obvious emphasis on pyro-metallurgical processes and techniques. This does not infer by any means, however, that other treatment techniques would *a priori* be incapable of generating and emitting dioxins[4].

4.1.3 Main factors influencing dioxin formation

Major factors influencing upon dioxin formation are:

- The process feed (raw materials).

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[4] Indeed, these special forms of dioxin generation or appearance can proceed by several routes:

1. **Cold processes**

Dioxins are also formed by so-called 'cold processes', involving the condensation of chlorophenols (the Seveso reaction), a process proceeding not only by thermal or catalytic processes, but even enzymatically, e.g. in the human or animal digestive tract.

Other examples are

- the (now obsolete) chlorine bleaching of pulp, or to a much lower extent, chlorine dioxide bleaching,
- chlorination of potable water, containing organic substances, e.g. humic and fulvic matter.

2. **Chemical treatment**

A chemical treatment involving compounds such as elementary chlorine, hydrogen chloride + oxidants, or other chlorinating chemicals. Such treatment is often capable of cold converting (albeit very partially) various organics into dioxins. Probably, chlorination can also be enhanced by ionisation (as in electrostatic precipitators), radiation, or the presence of flames (cf. the research work of Dr. Brian Gullett at the EPA laboratories).

3. **Diffuse sources**

Dioxins may appear in rainfall, run-off (in both cases firstly in industrial plant surroundings), or be re-mobilised from sinks, such as soil (spread by the wind or floods), sediments, sludge, filter dust, etc.

In case dioxins are already present in filter dust that is treated by, e.g., hydrometallurgical recycling processes, such processes are also likely to become confronted with dioxin problems. Dioxins in that case will probably report to the residual sludge, rather than to the aqueous leachate liquors. Conversely, the application of organic extraction will make dioxins leave these residues and report to the organic fraction.

- The type of metallurgical process.
- The process operating conditions, in particular combustion quality.
- The off-gas cooling conditions, in particular the presence of a boiler or other heat exchangers.
- The type of off-gas treatment systems.
- Memory effects.

In the past, the argument was frequently heard was that the process under scrutiny would not be capable of generating dioxin, for its raw materials do not contain chlorides or organics to any appreciable extent. On this basis many metallurgical processes would readily, and also erroneously, be discarded from further scrutiny Indeed, such essential building stones for dioxin as carbon and chlorine are simply ubiquitous. Ores and even pure metal contains some chloride, even if the level is only 30 – 300 ppm (typical for ores), or a few ppm (metals).

It is an important consideration in monitoring that both PCDD and PCDF never occur alone, but are always accompanied by a host of other compounds surviving combustion, e.g. benzene, alkylbenzenes, naphthalene, phenantrene, anthracene, furan, benzofuran, dibenzofuran, and many other aliphatic and cyclic compounds. Their sheer number is a complicating factor in analytical procedures. In this study, only limited attention is devoted to these compounds, but their potential role as surrogates and precursors is highlighted. It has adequately been shown that the dibenzo-p-dioxin (DD) structure is easily synthesized from two molecules of phenol. The same holds for their chlorinated congeners. Similarly, the polychlorinated dibenzofuran (DF) structure is easily created by a mild oxidation of PCB. Thus, both chlorophenols and PCB are potential precursors.

Some of these compounds are relevant as POPs in their own right, e.g.:

- Hexachlorobenzene.
- PCB.
- Polychlorinated naphthalenes.

Both the marker PCB and the WHO-PCB, PAH, and polychlorobenzenes PCBz (P = 2 to 6) are easily sampled at no extra cost together with dioxins, so that the only extra expense arising from their monitoring is that of the supplemental analyses to be conducted, typically some 100 – 150 € for each of the above classes of compounds, i.e. in total + 400 – 600 €. Their monitoring used to be practised routinely in some countries, e.g. Sweden and Japan and availability of laboratory facilities and of suitable calibration standards is entirely unproblematic. Still, it is in a less general use than that of dioxins, and not further considered in this work. Nevertheless, the use of such supplemental analyses is to be recommended warmly, as the extra cost factor is some 12 to 20 % (only) of the total of sampling & analysis and it results in markedly better documenting dioxin formation conditions and mechanisms, it serves as an internal control of the data, and automatically it paves the way towards a possible use of cheaper surrogates, should this become necessary.

When establishing dioxin balances for plants, equipped with dioxin abatement systems, it is rather likely that the dioxin flows circulating within the plant are even larger than those corresponding to actual emissions, sometimes by one or two order of magnitudes. Establishing comprehensive balances is an important point to be considered in such cases.

Some enterprise converts electronic scrap or treats Automobile Shredder Residues.

Their effluents may then contain brominated and brominated/chlorinated dioxin congeners especially. Because of their huge number (> 1000) and failing availability of adequate standards such analysis and monitoring is not state of the art as yet.

4.1.4 Compartments

4.1.4.1 Survey

Dioxins, or indeed almost any pollutant, may either occur as:

- emissions to air, water, and soil,

or arise as

- waste streams to be eliminated or recycled.

Emissions of dioxins from metallurgical industry may assume different forms, e.g.:

- Off-gases, occurring in guided stack emissions.
- Off-gases, occurring as diffuse emissions.
- Wastewater and sludge.
- Residues.
- Commercial products.

These different compartments will now be discussed.

4.1.4.2 Off-gases

Off-gases, evolving as **guided stack emissions**, are always prime candidates for **monitoring**.

They constitute the bulk of current efforts in monitoring the emission of dioxins.

4.1.4.3 Diffuse emissions

Diffuse emissions are at times evolving from historical sinks, e.g. dioxin contaminated soils or dumps, or raw materials and product flows, such as metal containing dust, residues and scrap. In some cases, they may form substantial sources of diffuse emissions.

Diffuse emissions may also occur:

- in the vicinity of furnaces, especially close to the charging and tapping areas.

These flows are less important, due to the limited concentrations and volumetric flows engaged. However, they form a real or a potential occupational problem. The non-ferrous industry practices extensive personal monitoring, including individual testing of blood for lead levels. In non-ferrous industry, there is much interest for such occupational problems, especially those involving lead, cadmium, mercury, thallium, beryllium, etc. Dioxin monitoring in blood is sometimes practised, but not routinely, in workers from MSWI. In this occupational context, it is referred to the German TRGS 557 (Technische Regeln für Gefahrstoffe, Dioxine).

- Around sources, such as contaminated soil, open air storage of raw materials, dust collection points, etc.

In some cases, either the raw materials or the fate of filter dust has required special attention.

4.1.4.4 Wastewater and sludge

Dioxins occur in rainwater run-off from factories, in wastewater, and in the sludge resulting from wastewater treatment.

Dioxins are almost totally insoluble. Hence, they are always associated with particles in suspension, oily emulsions, associated with humic or fulvic substances, colloid particles, etc.

4.1.4.5 Residues

Pyro-metallurgical production processes routinely generate metal, slag, waste refractory, filter dust, as flows of solid.

For high-melting metals, such as iron, steel, or copper metal and slag are tapped at too high a temperature for active dioxin formation. Data is scarce, but the dioxin values are supposed to remain below Detection Limits and are of no real concern. Nevertheless, the tapping hole may be closed using plugs incorporating bituminous or tarry materials, the effects of which have not been analysed. Low melting metals may be covered by a protective salt layer that under circumstances may lead to dioxin formation, whether in the salt layer, on filter dust, or in the space between bath and filter plant.

Waste refractory, when derived from a hot furnace, is unlikely to support strong contamination. Some of this is recovered and reused, while most of it is landfilled.

Waste refractory, when derived from flues, is generally covered by dust deposits. These are likely to show substantial contamination with heavy metals and dioxin.

The major dioxin carrier is filter dust. A recent study by ENEA [22] showed that the dioxin flow in filter dust is at least of similar size as the filtered flow of gas emitted to the atmosphere. An earlier Aminabel[5] study proved the same in a wide range of metallurgical enterprise.

Off-gas treatment yields some filter dust that is locally or externally recycled for its content in valuable metals in most cases. This filter dust is mildly to heavily charged with dioxins. Thermal processes treating such dust do destroy dioxins often to some large extent, but the destruction and removal efficiency (DRE) must be verified.

The amount of particulates in **raw** gas is widely variable. Fluidised bed processes may yield as much 10 – 100 g/Nm^3. Quiet processes, such as the melting of metal using gas oil or

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[5] the management division of the Flemish Environmental Authority Aminal

natural gas, yields only 1 – 10 mg/Nm^3. A majority of processes is situated in between, at 0.1 – 1 g/Nm^3 (in **raw** gas).

The dioxin load in dust typically attains:

- A very low load: 1 – 10 ng I-TEQ/kg
- A low load: 10 – 100 ng I-TEQ/kg
- A medium low load: 100 – 1000 ng I-TEQ/kg
- A medium high load 1 – 10 µg I-TEQ/kg
- A high load: > 10 µg I-TEQ/kg

Filter dust arises in each process. Filtering requirements are actually considered less important in ferrous than in nonferrous metallurgy, because of the higher toxicity and value of most metals in this group. Iron ore sintering generally features electrostatic precipitators as dust separator with up to 3 or 4 individual fields [6]. Nevertheless, salts and some heavy metal containing aerosols still escape. In nonferrous metallurgy, baghouse filtration is standard. Steady maintenance and inspection will limit particulates emissions to 1-5 mg/Nm^3.[7]

The processing of dust is likely to involve dioxins in the feed, as well as de novo formation during the cooling of the flue gases. Such processes deserve close scrutiny of emissions for dioxin.

Residues from thermal processes, especially those from incineration and metallurgy, are important dioxin streams, comparable in magnitude or larger than emissions to air. The problem has been studied for a large number of metallurgic processes in a report commissioned by Aminabel (see footmark No. 5).

4.1.4.6 Establishing Dioxin Balances

Inputs.

From the Minidip project [2] it follows that the samples of raw ores, entering metallurgical plant, are often slightly charged with dioxins. The origins of such dioxin loads are entirely unclear. One could consider dust deposition, or adsorption from the atmosphere, or even natural genesis (as in Arkansas ball clay) but both the load and fingerprint are variable and more study is needed to assess the problem. Indeed, in processes featuring a counter-current flow of raw materials and off-gas (most shaft furnaces), or a cross-current flow, dioxins may simply evaporate and report to the off-gas, without ever attaining and crossing a combustion zone.

Another input is via recycled streams, mainly filter dust, or materials that are loaded with dioxin, such as zinc dross from hot dip galvanising. Monitoring the whereabouts and processing of such streams seems essential as a precaution.

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[6] In addition several plants have installed abatement systems such as fabric filter and high pressure wet scrubbing. Using these techniques dust emission concentrations < 50 mg/Nm^3 are achieved in normal operation. In case of application of a fabric filter, emissions of 10-20 mg/Nm3 are achieved.

[7] In some processes inadequate attention is given to dust filtration. During the charging of steel converters with scrap the suction hood may become inactive, due to the tilting of the converter. The loading of scrap gives rise to important emissions that presumably have not been taken into account during measurement programmes.

The input from fuel, coke, or air is small and mostly negligible. Values of dioxin load for metallurgical coke only in rare cases have been established. A special case is blast furnace gas, which was documented in the study of German experts. Its dioxin load remains well below 0.1 ng I-TEQ/Nm^3, yet it probably represents a dioxin flow of between 1 – 120 mg I-TEQ/annum. Since blast furnace gas is fired in almost all cases, the eventual residual emission should remain quite low.

Formation.

One of the best documented processes is the sintering process. According to the BREF dioxins in sintering derive from the raw materials load present on the sintering belt. Dioxins are formed in the zone close below to the hot seam and permeate downwards with the off-gas stream until they emerge at the end of the baking process. According to a different theory, they derive from dust deposits on the sintering belt chain, in the plenum chambers below the belt, and in the ducts leading to dust collectors.

Other processes, such as the EAF or scrap melting are still largely unknown with respect to the precise processes leading to dioxin formation.

Outputs.

As stated higher, the main outputs are associated with the off-gases. One reason is that the dioxin is often formed in this off-gas.

When studying a process, it is essential to try and develop a balance with respect to the flows of dioxin, chlorine, carbon, oxygen, and selected catalytic transition metals, e.g. Cu, Pb, Fe.

4.1.4.7 Commercial products

A number of commercial products (e.g. titanium oxide, ferric oxide, cobalt oxide and flocculants based on ferrous or ferric chloride) are produced using processes possibly involving chlorine or chlorides. Such commercial products should also be tested for their dioxin contents.

4.1.5 Conclusion for scope of monitoring requirements

The metallurgical processes considered in the context of harmonised monitoring procedures belong to:

- Ferrous and nonferrous operations.
- Primary and Secondary production, including the treatment of home and acquired scrap, residues, reverts, etc.
- Production and conversion, in case the latter involves melting of the metal.

Emphasis is on **guided sources** (stacks) emitting to air.

However, cases are known in which diffuse sources, e.g. raw materials storage, were relevant in a local context.

Emissions to **watercourses** or to **groundwater** are rarely important.

Their relevance is normally strictly associated with the presence of suspended particles (run-off, scrubbing liquors off-gases), or of organic compounds (oil, oily emulsions, humic substances).

Soil pollution with dioxin and heavy metals may be quite substantial locally, and associated either with the (often historical) spreading of (filter) dust around the filter, dust conveyers, etc. or with dust deposition.

Evaluating aerial deposition from the atmosphere may be a relevant method of monitoring of sources in a geographical area, but there is extensive time lag of aerial deposition when compared to actual emissions. In other words, it will take many months or even a few years before the effects of halting emissions becomes apparent by way of reduced deposition. Re-entrainment is therefore important.

Cold sources, mechanical processes, scrap preparation, shredding, compacting, baling, etc. are *not* considered, as they are highly specific and poorly defined dioxin sources. The same holds for welding, soldering, and cutting.

In principle, processes involving **metal salts** or their solutions (e.g. pickling liquors) are not explicitly considered, although they can form sizeable sources which may require monitoring.

From the information presented before it is obvious that the classification of processes offered in the Annexe I of the IPPC Directive is fairly unsuitable with respect to dioxin emissions. Based on today’s knowledge, the following differentiation of well-known and well-documented metallurgical sources can be made

- **Main sources:**
  - Iron ore sintering plant
  - Electric Arc Furnaces, smelting iron & steel scrap, and (less so) those used for producing stainless steel, or reclaiming metals from filter dust.
  - Waelz process plant, for the recovery of zinc oxide from dust arising in the iron & steel sector.
  - Smelting secondary copper, aluminium, and lead (“dirty” input materials, no adequate operation conditions or gas cleaning).
  - Melting and alloying metals, in particular in the presence of copper.
- **Minor sources:**
  - Iron foundries, in particular those using cupola or rotary kiln furnaces.
  - Non-ferrous foundries.
  - Smelting secondary copper, aluminium, lead (“clean” input materials, optimised operation and /or flue gas cleaning)
  - Hot dip galvanising of steel.
- **Sources not so well known:**
  - Coking Plant. Its emissions are basically unknown. Application of the only estimative data available, combined with typical plant capacity, leads to the classification as a 'large emitter'. However, in this particular case most emissions are fugitive, and PAH, benzene, and aromatics are probably more

  relevant than dioxins. For this reasons it is recommended that more attention is paid to this source, even though conventional monitoring is unlikely to succeed.
  - Steel converters. Converting pig iron into steel is normally not regarded as a major source. However, there are no available data on emissions occurring during scrap charging. Hence, more data is needed.
  - Electric Arc Furnaces applied for smelting various residues.
  - Aluminothermy and silicothermy processes.
  - Other sintering processes, as applied at a relatively modest scale to nonferrous ores
- **Sources that are probably negligible:**
  - Roasting of sulphide ores.
  - Other processes, fitted with well-designed, well-operated thermal or catalytic post-combustion or DeNOx catalysis, and without subsequent heat recovery.

A word of caution: emissions depend on numerous factors and it is hazardous to generalise. For example, the chlorinating roasting of lean copper ores, during World War II was indeed a source of dioxins.

Note that not only the type of process, but also the raw materials, process conditions, off-gas history and cleaning are all cardinal factors that should be taken into account case by case when the potential for dioxin emissions is assessed (c.f. Annex E for more details on these issues).

4.2 Structure of the European metal industry

In the previous section a brief survey on the processes applied in the European metal industry and an assessment on the importance of different pathways for dioxin emissions has been presented. Based on this information, the processes generating major and minor emissions have been compiled. In this chapter data will be presented on the numbers of installations applying these processes, with particular emphasis put on the major emission sources. The information is basically derived from information that was gathered from the IPPC reports of the Member States, BREF documents and project questionnaire replies. This basic data was then enhanced using a wide range of information sources. The aim is to assess the total number of installations that might be covered by new monitoring requirements and their geographical distribution. Additional information on the structure of the European metal industry can also be found in the different BREFS.

4.2.1 IPPC facilities in the metal industry of the EU 15 Member States

Starting from the basic framework and scope of the project the installations primarily targeted are the metal industry 'installations' covered by Annex I(2) of the IPPC directive (seeTable 1).

Table 1 Installations listed in Annex I(2) of the IPPC Directive

2. Production and processing of metals
2.1. Metal ore (including sulphide ore) roasting or sintering installations
2.2. Installations for the production of pig iron or steel (primary or secondary fusion) including continuous casting, with a capacity exceeding 2,5 tonnes per hour
2.3. Installations for the processing of ferrous metals: (a) hot-rolling mills with a capacity exceeding 20 tonnes of crude steel per hour (b) smitheries with hammers the energy of which exceeds 50 kilojoule per hammer, where the calorific power used exceeds 20 MW (c) application of protective fused metal coats with an input exceeding 2 tonnes of crude steel per hour
2.4. Ferrous metal foundries with a production capacity exceeding 20 tonnes per day
2.5. Installations (a) for the production of non-ferrous crude metals from ore, concentrates or secondary raw materials by metallurgical, chemical or electrolytic processes (b) for the smelting, including the alloyage, of non-ferrous metals, including recovered products, (refining, foundry casting, etc.) with a melting capacity exceeding 4 tonnes per day for lead and cadmium or 20 tonnes per day for all other metals
2.6. Installations for surface treatment of metals and plastic materials using an electrolytic or chemical process where the volume of the treatment vats exceeds 30 m³

As required by the IPPC directive the EU member States (EU 15) reported on the numbers of installations that already exist or are in planning. For those mentioned in Annex 1 (2) of the directive, a total of about 6.500 installations can be found (c. f. Table 2). The figure contains some uncertainty due to the fact that Germany and Greece reported the numbers of IPPC “activities” rather than the numbers of installations. For these countries the figures hence is too high because of multiple counting of installations having more than one IPPC activity[8]. This mismatch obviously is caused by the definition of “installation” given in the IPPC Directive: *'installation` shall mean a stationary technical unit where one or more activities listed in Annex I are carried out, and any other directly associated activities which have a technical connection with the activities carried out on that site and which could have an effect on emissions and pollution.* Accordingly, an installation may comprise several different types of processes, provided these have a technical link. This definition opens possibilities for interpretation – for instance, “installation” could mean an entire integrated iron & steel plant with many different, technically linked activities like blast furnaces and coke ovens, or each of these activities may be treated as a separate installation. Therefore, the numbers of IPPC installations can be considered only as a rough estimate of the number of relevant processes and (with regard to monitoring) of the number of stacks from which samples must be taken.

Table 2 Numbers of all IPPC installations/activities in the European metal industry belonging to Annex 1(2) of the IPPC directive (sorted by decreasing numbers, figures taken from official MS IPPC reports for the years 2000-2003 [5]).

Country	Number	Comment
DE	1908	(IPPC activities)
FR	1303	
IT	1227	
UK	1190	
ES	475	
SE	135	
PT	87	
DK	83	
FI	69	
AT	63	
BE	60	
NL	54	
EL	42	(IPPC activities)
IE	39	
LU	16	completed by industry information
Total	**6751**	

From the figures listed in Table 2 it becomes clear that the first six countries dominate the metal industry in the former EU 15, together making up 93% of the total number. The relative shares are shown in Figure 1. More detailed data regarding the subsectors of Annex 1(2) installations are available for Germany [3], Spain, Italy, Hungary, Portugal and Slovenia [4], as shown in

Table 3. Except for Germany, these figures were obtained in the framework of the present project. Apparently, the numbers of installations considerably differ from those shown in table 2. The exact causes for these discrepancies are not known. They might be due to changes in the interpretation of the term “installation” as well as to updates of the lists carried out in the meantime.

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[8] For Germany, a total (all categories) of 9759 IPPC activities and 7705 installations were reported. Thus, on the average the number of installation in the metal industry might be overestimated by 27%.

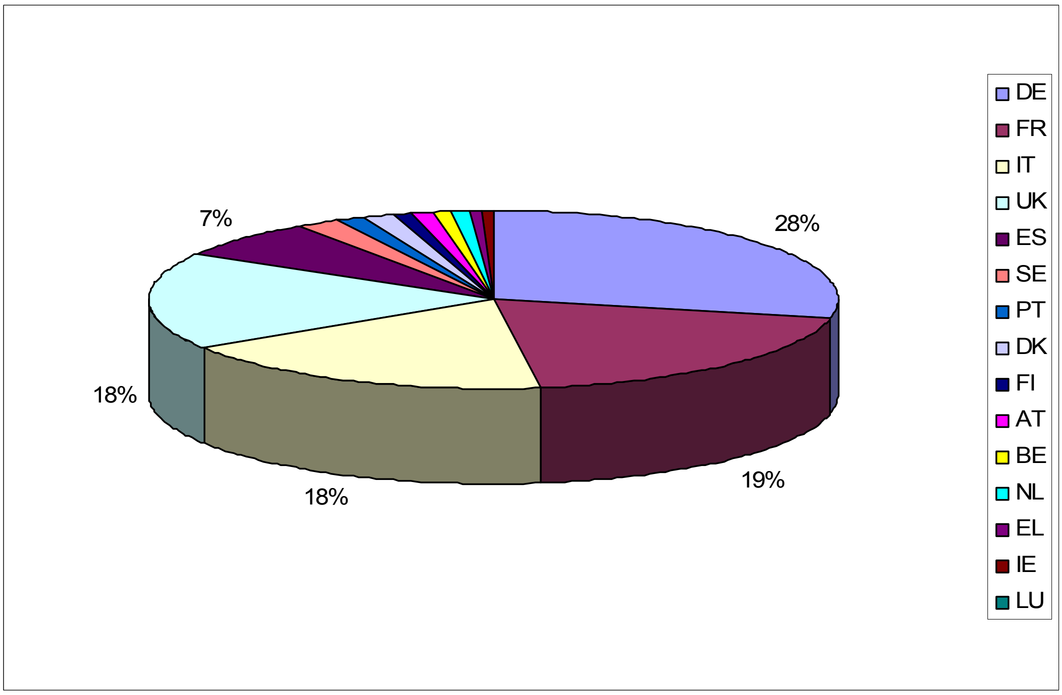

Figure 1 Shares on the number of IPPC installations in the European metal industry (Annex1(2) of IPPC directive);
Germany, Greece: IPPC activities reported

Table 3 Numbers of installations (ES, IT, HU, PT, SI) and IPPC activities (DE) for the IPPC metal sector

IPPC directive Annex 2 no.	**Activity**	**Country**					
		DE	ES	IT	HU	PT	SI
2,1	Metal ore (including sulphide ore) roasting or sintering installations	*12*	*1*	*1*	*2*	*0*	*0*
2,2	Installations for the production of pig iron or steel (primary or secondary fusion) including continuous casting	*235*	*20*	*45*	*2*	*2*	*3*
2,3	Installations for the processing of ferrous metals:	*219*	*44*	*43*	*43*	*5*	*1*
2.3a	*hot-rolling mills*	61	10		3	0	0
2.3b	*smitheries*	23	1		1	0	0
2.3c	*application of protective fused metal coats*	135	33		2	5	1
2,4	Ferrous metal foundries	*277*	*38*	*34*	*4*	*12*	*10*
2,5	Installations	*601*	*74*	*85*	*12*	*15*	*9*
2.5a	*for the production of non-ferrous crude metals from ore, concentrates or secondary raw materials*	74	17		3	0	3
2.5b	*for the smelting, including the alloyage, of non-ferrous metals*	527	57		9	15	6
2.6	Installations for surface treatment of metals	*564*	*231*	*259*	*50*	*72*	*16*
Total		**1908**	**408**	**467**	**113**	**106**	**39**
Dioxin relevant (2.1/2.2/2.4/2.5)	Total number	1125	133	165	20	29	22
	share of all IPPC installations	59%	33%	35%	18%	27%	56%

In the last two rows of

Table 3 the number of those installations that in principle are relevant with respect to dioxin emissions, (categories 2.1/2.2/2.4 and 2.5), are summed up. Categories 2.3 and 2.6 predominantly cover non-thermal processes or processes (in the case of e.g. hot-rolling mills) with quite negligible potential for dioxin formation. It should be noted, however, that the actual number of installations with significant dioxin emissions might be even lower than indicated in

Table 3.

4.2.2 IPPC facilities in the metal industry of the New Member States

Comparable information could unfortunately not be obtained for any of the New Member States. For the Czech Republic, some 190 IPPC installations in the metal sector (of a total of ca. 1.300) were mentioned in a report available on the internet [5]. Among these, non-ferrous metal foundries (category 2.5b, 57 installations) and surface treatment installations (category 2.6, 53 installation) predominate. Dioxin relevant installations could approximately amount to 50 installations if similar proportions as presented in

Table 3 are assumed.

4.2.3 Dioxin-relevant installations in the European metal industry

As shown before, information taken from the official reports of the Member States on implementation of the IPPC Directive, as regards the metal industry installations, is of limited value and does not allow for systematic extraction of the number of facilities which are relevant for the tasks of this project. Therefore, a specific questionnaire was sent to the authorities and industry asking for data on a pre-selected highly relevant group of processes, namely:

- Iron ore sintering plants
- Electric arc furnaces
- Waelz furnaces for zinc recovery (from EAF filter dust)
- Non-ferrous metal scrap processing (sec. production of e.g. Cu/Al/Zn/Pb)
- Foundries
- Other relevant metal producing/processing plants

The selection of these processes was based on the relevance of these sources for dioxin emissions to air, as indicated earlier (c.f. chapter 4.1) and on the expertise of the project team. Furthermore, other sources of information were sought to either complete or confirm the responses obtained with the questionnaire replies.

Table 4 shows the data provided by these replies to the questionnaire. It is obvious that the response was quite incomplete. Not all 25 EU Member States replied to the questionnaire. Reasons for not having answered might be different. In several cases, such as Ireland, Malta, Latvia and Estonia, the local metal industry is irrelevant, or almost so. Unfortunately the authorities of some countries with intensive metal industry (Poland, Germany) have also have not provided answers to the questionnaires as yet. In the case of Germany quite comprehensive data was obtained from the Iron and Steel industry for this sector, which was confirmed by the Federal Environment Agency. Therefore Table 4 has been completed by information provided by industry replies and IPPC report [6] data.

Table 4 Data on dioxin-relevant installations provided by questionnaire replies;
meaning of the colours: yellow: no reply; blue: no reply by authority, data completed by industry replies; green: data provided according to IPPC Annex 1 structure and included as far as assignable;

Country	iron ore sintering	EAF	Waelz kilns	Non-ferrous scrap proc.	Foundries total	Foundries (iron)	Foundries non-ferrous	Foundries ferrous/ non-ferrous	other relevant/comments
Austria	2	3	0	5	53	16	29	8	
Belgium	4	5		3	7				6 shredders in Flemish region
Cyprus	0	0	0	1	2		2		
Czech Republic	5	20		30	80				
Denmark									
Estonia									
Finland									
France	4	8	0	2					2 : recycling of lead-acid battery (not listed in EPER) 1 : recycling of waste coming from metal industry (not listed in EPER)
Germany	6	20			804	277	527		figures in green fields are activities rather than installations data provided by German Steel industry were confimed by Federal Environment Agency; no further information appears to be available at Federal Level.
Greece		5		18	48	30	18		30 ferrous/18 on-ferrous casting installations as part of larger plants; all small plants with less than 10 employees
Hungary	2	2		4	4				Primer aluminium production(Várpalota-Inota) and Pig Iron production (Duanaújváros)
Ireland									
Italy	??	35	3	65	1100	300	800		
Latvia									
Lithuania	0	0	0	0	1				
Luxembourg	0	3	0	1	0				Direct reduction of filter dust
Malta									
Netherlands	1	2			17				
Poland									no official data were submitted by Polish authorities.
Portugal	0	2	0		27				
Slovakia	7	9	0	5	25				
Slovenia		2			0				
Spain	1	20		74	95	38	57		
Sweden	4	8		2					
United Kingdom	3	9		92					There are 32 installations listed in the Environment Agency's Pollution Inventory regarding ferrous metals, and 94 non-ferrous metals. The EPER report indicates some 262 UK metals facilities in 2003, reflecting additional installations regulated in Scotland by SEPA and in England and Wales by Local Authorities (all small dioxin emitters compared to the three Environment Agency regulated integrated steel works)
TOTAL	**39**	**154**	**3**	**303**	**2278**	**661**	**1433**	**8**	
	2777								

In view of these data limitations other sources of information were successfully sought to achieve a more complete picture on the industrial structure (see next sections and Annex A). Quite comprehensive data were obtained from DG Enterprise 7 for the iron & steel sector concerning sintering plants and EAFs. Further data on sintering plants were taken from a report related to heavy metals [8]. An additional, but to some degree incomplete overview on sintering plants and EAFs with distinguishing Carbon steel and stainless steel EAFs was provided by Eurofer.

From the web-site of the European Foundry Association (CAEF) statistics on ferrous and non-ferrous metal foundries were available (9 ANNEX B). Finally, the BREFs also contain information on plant numbers or production sites at least for most of the considered processes.

4.2.3.1 Iron ore sintering plants

In spite of the various sources of information it proved, however, to be quite difficult to get a reliable picture even for a sector like iron ore sintering with a comparably small number of installations. The main problem appears to be that single sinter strands (belts) and installations covering one or more belts are counted but without a clear indication what is meant.

From DG Enterprise information [7] for iron ore sintering, there exists a total capacity of 127.7 M tons, spread over 47 sintering plants in the enlarged E.U. A number of 53 “installations” (presumably single strands are meant) are reported by another Commission report[9] [8] for the same geographic scope. In the iron & steel BREF, 47 installations are reported to be operated in the EU 12. Presuming this figure is related to sinter strands, 11 further installations may be assigned to the other 13 countries. However, even in the 10 New Member States more than these 11 sinter strands exist; so there is some inconsistency in the available data, which maybe in part due to the closure of some plants in Western Europe. Most of the sintering plants were erected in the seventies or sixties. Combining the available information, a geographical distribution of sintering capacities can be given as shown in Table 5. Obviously, there is a mismatch for the Czech Republic which could be due to increased activity in the recent years or just erroneous counting. In the case of Sweden pelletising installations have most probably been reported by the industry in the replies to the questionnaire, which are not included in the other information sources.

Summarising, the available data are relatively reliable, with the biggest discrepancy being related to the closure of plants in some MS, e.g. those in Luxemburg, as well as to the distinction between installations and lines.

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[9] Note, that the total value of 58 installations given in the table of ANNEX A apparently has been calculated incorrectly.

Table 5 Sinter strands or plants and the share of iron ore sintering capacity in EU Member States

Country	“plants”[8] (presumably sinter strands)	“plants“ (from replies to the questionnaire)	“plants” (from Eurofer)	share of production capacity (from [7])	cumulative share
Germany	12	6	8	23 %	23 %
France	6	4	7	17 %	40 %
Belgium	5	2	3	12 %	52 %
The U.K[10]	5	3	4	11 %	63 %
Italy	7	no data.	2	9 %	72 %
Poland	4	2	no data	7 %	79 %
Czech Republic	1	5	no data	5 %	84 %
Spain	2	1	1	4 %	88 %
The Netherlands	3	1	1	3 %	91 %
Slovakia	n.d.	7	no data	3 %	94 %
Austria	2	2	2	3 %	97 %
Finland	3	no data	1	2 %	99 %
Hungary	2	2	no data	1 %.	100 %
Sweden	n.d.	4	0	n.d.	
Portugal	1	0	1	n.d.	
TOTAL:	53[11]	37	30	100 %	

4.2.3.2 Electric arc furnaces

Also regarding EAFs there is some inconsistency between the different sources of information. A total number of more than 200 units for the “EU 12” are mentioned in the ISP BREF document (c.f. Table 6). From another graph in the same document ca. 250 installations in EU 15 are indicated. Similar figures are provided by DG Enterprise ([7], c. f. Annex A; 208 AC operated EAFs and 47 DC operated plants). According to this data more than 90 % of the EAF capacity in the EU 25 is concentrated in 9 countries: Spain, Italy, Germany, France, United Kingdom, Belgium, Poland, Luxemburg, Greece.

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[10] data in [8] comprise a plant meanwhile closed; according to industry there are 4 sinter strands in operation, with 2 of them connected to the same stack, thus leading to 3 emission points.

[11] The figure for total given in the reference document [8] apparently is a miscalculation

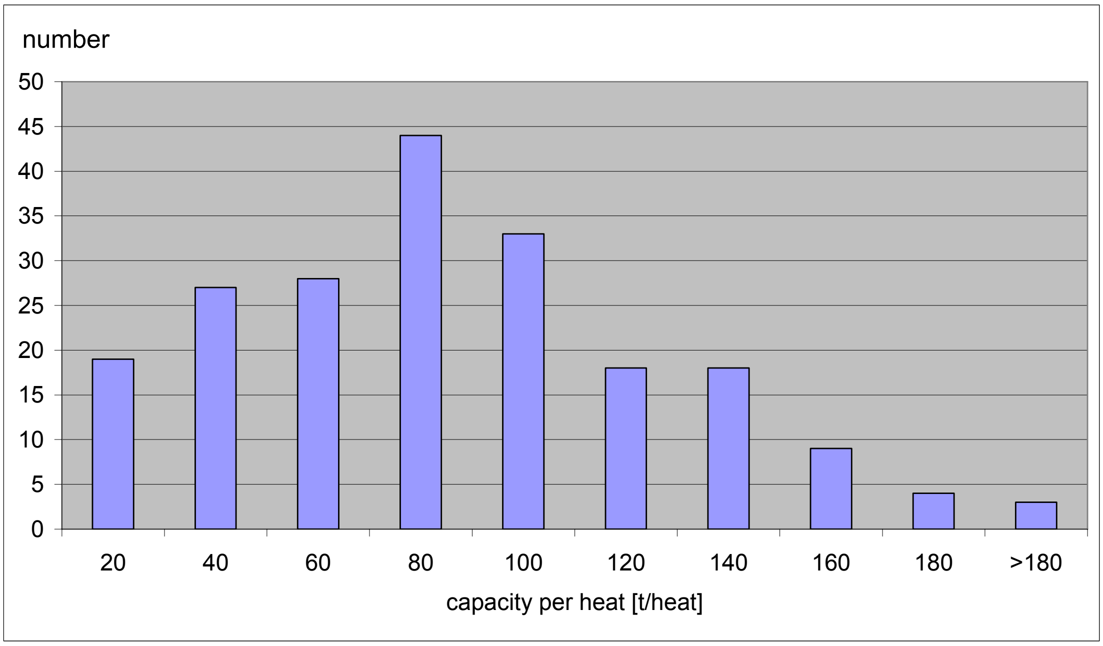

Figure 2 Distribution of AC EAFs to classes of melting capacities (for EU 12, I&S BREF)

However, in the questionnaire replies only 148 installations were reported. This figure fits quite well with the number of so-called “supplementary units” in the DG Enterprise data and with ca 170 EAFs listed by Eurofer (c.f.Table 6). Moreover, with respect to dioxin emissions it may be relevant if the EAF is used for carbon steel production or for stainless steel production. According to information provided by Eurofer in the latter case negligible dioxin emissions occur. Thus only ca. 105 of 170 EAFs should be considered as dioxin relevant according to the information from Eurofer. It was not reported whether this assessment is based on sound and thorough surveys or derived from a few measurement results. This affirmation indeed has been verified in some plant, but it would be reckless to extrapolate results from one single plant to all plant.

Table 6 Numbers of Data on Electric Arc Furnace installations

	Eurofer data		DG Enterprise data
Country	Carbon Steel	Stainless Steel	"supplemental units"
Austria	1	2	2
Belgium	3	3	2
Cyprus			0
Czech Republic	3	5	22
Denmark			0
Estonia			0
Finland	1	1	1
France	12	9	11
Germany	13	16	26
Greece	5		6
Hungary	2		
Ireland			0
Italy	27	10	15
Latvia			0
Lithuania			0
Luxembourg	3		
Malta			0
Netherlands	1		2
Poland	4	4	18
Portugal	2		
Slovakia			
Slovenia			2
Spain	20	6	13
Sweden	4	4	3
United Kingdom	5	4	18
Total	**105**	**65**	**141**

4.2.3.3 Waelz furnaces

Waelz furnaces are installations mainly used to recover non-ferrous metals, particularly zinc, lead, and copper from EAF, dust and sludge of various origins, etc. Hence, this sector is affiliated to the non-ferrous metal industry, but they are also closely related to steel production because they mainly process by-products from this sector.

Waelz units operate at a limited number of locations. The Waelz process has been found to be a major PCDD/F source, unless suitable measures are taken to reduce emissions. The installations located in DE and FR have been upgraded with dioxin abatement systems; however, there are also some installations in the EU for which no dioxin emission results have been published. According to the replies to the questionnaire 3 installations are operating in Italy. There is additional information that one plant each exists in Spain and Poland [10]. Thus overall there appear to be 8 installations in The EU 25 (DE: 2, FR:1, ES:1, IT: 3, PO:1).

4.2.3.4 Non-ferrous scrap processing

A further class of installations covered in the questionnaires concern the secondary production of non-ferrous metals, particularly copper, aluminium, lead and zinc, from scrap. According to the information gathered, ca. 300 installations appear to be in operation with the major fraction located in UK, DE, IT and CZ. A considerable number is also expected for Poland, for which however no complete data could be obtained[12].

In the relevant BREF, the data on production sites is presented. This information is summarised in Table 7. Since, in many cases, production sites may involve more than one installation, the actual number of installations cannot be assessed without uncertainty from this data. Another reason for uncertainty could be an sector overlap, because semi production may involve metal casting in non-ferrous metal foundries and thus might be counted twice. Moreover, it is not clear in every case if the New Member States have been considered or not.

Table 7 Data on production sites given in the non-ferrous metal BREF

Metal	Primary/secondary	secondary	semi products
Copper	5	8	53 ^{1}
Aluminium	30	200 ^{2}	
Zinc	15	8 ^{3}	
Lead	7	30	
TOTAL	**57**	**246**	**53**

^{1} including wirerod; ^{2} capacity > 1000t/year; ^{3} Waelz kilns

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[12] According to informal communication the number of non-ferrous scrap processing installations in Poland might range to up to 300; however, among this figure may include many small installations which are not covered by the IPPC directive.

4.2.3.5 Foundries

Iron and non-ferrous metal foundries are the last class of installations treated in the questionnaires. These facilities have limited capacity and related flue gas flows, as well as dioxin gas loads. Hence, they have the lowest potential for dioxin releases among the selected processes. Still, they might be important for the European dioxin emissions, due to the large number of installations. Another specific factor for concern is the large variability in this sector when it comes to unit capacity (ranging from the micro-scale at a jeweller's shop to relatively large units), raw materials, technology used and abatement of emissions.

Beside the replies to the questionnaire statistical information on this industrial sector could also be found on the website of the European Foundry Association ([9], c.f. Annex B). According to this information, ca. 1,600 foundries for iron and iron alloy casting and ca. 2,600 installations for non-ferrous metal casting were in operation in 2003. The overall number reported by the replies to the questionnaire (ca. 2.200 installations) apparently only cover a part of these, which is not surprising, given the differences in scale, the fact that smaller enterprises are often not affiliated to the relevant federation and the dramatic changes the sector went through during the last ten years. Our data on Belgium are relatively recent and complete, and show numerous enterprises either closed or converted from an industrial to a purely commercial activity. Given the disparate size and character of the operations, the focus should be on larger plant, which use technology that is more proficient in generating dioxins. These are mainly ferrous foundries operating a certain type of furnace (cold blast cupola furnace, sometimes two in tandem mode) which was shown in measurement programs to have elevated dioxin emissions compared to other techniques, or electric arc furnaces. The overall number of these two furnace types in the EU is estimated by the foundry association to be ca. 600.

Of course, not necessarily all installations listed in the compilation are covered by the IPPC directive due to the capacity thresholds.

4.2.3.6 Other potentially relevant installations

By and large, the thermal processes involving filter dust from various origins, laudable as they may be from a viewpoint of recycling, merit increased attention with respect to dioxins. As with the processes using aluminothermic and silicothermic heating, they are poorly documented.

Some unusual, small capacity sintering belts, used for processing miscellaneous minerals, remain completely undocumented.

Generally speaking, the treatment of ferrous metal by operations, such as hot and cold rolling, welding, or machining, are not regarded to be essential sources fitting into the frame of a study of this nature.

The same holds for coking plant, the blast furnace, and basic oxygen converters. Still, relevant industry has not really produced much evidence to disregard the latter series of processes. According to Swedish surveys and the Dutch inventory they are tangible, but minor sources. The factors of influence are entirely unknown.

Hot dipping of ferrous metal in zinc has been considered in both German and Spanish research as a notable source of dioxin. The emissions to air are rather limited as long as the off-gas stream is filtered, but the dross and filter dust are relatively highly charged. Recently, a Spanish study offered a comprehensive survey of the state of the art [11].

Some processes involve chlorine gas or hydrogen chloride. Most of these processes are highly specific and not necessarily applied in the E.U.

Examples are:

- the chloride route for titanium oxide pigment production. Several plants are active in the E.U, e. g. in Germany and Belgium.
- the treatment of iron chloride (steel pickling liquors), cobalt chloride (pigment production), nickel chloride (step in refining), zirconium chloride (nuclear industry). Some processes are active in the E.U.

In the replies to the questionnaire some remarks were made on additional processes and installations that are seen by the authorities as potentially relevant to PCDD/F emissions. Among these, shredder installations are out of scope of the IPPC directive, but a proven source of PCDD/Fs and even more so of PCBs.

Of the other processes pig iron tapping could be of concern. However, in the inventories, considerable emissions from this source type have been reported only by very few countries.

4.2.4 Summary and conclusions

An evaluation of available information on the numbers of installations in the European metal industry covered by the IPPC directive was made. Information sources comprised

- the official IPPC reports of member States to DG Environment
- replies by authorities and industry to project related questionnaires
- information from DG Enterprise
- open data taken from the internet

From the information collected it was not possible to get a clear and unequivocal picture of the structure of the European metal industry. This is to a large part due to different categorisation of installations and different terminology used in the various sources of information. Nevertheless, for the most relevant emission sources with respect to dioxin emissions approximate numbers of installations and their distribution in the 25 Member States could be obtained. From this data, the picture emanates that the numbers approximate to

- ~50 iron ore sintering plants (IPPC category 2.1)
- ~250 electric arc steel plants (IPPCcategory 2.2)
- ~300 - 600 non-ferrous metal scrap processing installations (IPPC category 2.5 a)
- ~1,500 ferrous metal foundries (IPPC category 2.4)
- ~2,600 non-ferrous metal foundries (IPPC category 2.5b)

Taking into account that most of the foundries might be too small to be covered by the IPPC directive and that cupola and electric arc furnaces are the most relevant processes regarding dioxin emissions an overall maximal number of ca. 1,500 installations can be expected to be in principle under the regime of new monitoring requirements.

Combining the available information on plant numbers or capacities, a ranking list can be established showing which countries are most important regarding these parameters and thus would also be affected predominantly by additional monitoring requirements. In Table 8 the relative shares of country installations of the European total is shown; the ranking was made by sorting according to the sums of the given percentages. It should be noted that this is not necessarily equivalent with the relative importance of the countries regarding their overall dioxin emissions from metal industry (for this question, see next chapter), nor that there must be a strong correlation with production figures.

Overall, in spite of the information gaps identified, sufficient data on the numbers of existing installations in the EU being the most relevant with respect to dioxin emissions could be gathered.

Table 8 Ranking list of EU Member States according to relative shares of installations (sinter plants, foundries) or nominal capacities (EAFs);
sum of given percentages were used as sorting criterion

	Sinter	**EAFs**	**foundries**
Italy	10%	19%	26%
Germany	18%	15%	15%
France	9%	11%	12%
Spain	3%	20%	5%
United Kingdom	7%	7%	12%
Poland	6%	5%	10%
Belgium	7%	6%	1%
Czech Republic	7%	1%	5%
Sweden	6%	2%	3%
Slovakia	10%	0%	0%
Hungary	3%	1%	4%
Finland	4%	2%	1%
Austria	3%	1%	2%
Portugal	1%	1%	3%
Netherlands	4%	0%	1%
Luxembourg		4%	0%
Greece		4%	0%
Slovenia		1%	0%
Lithuania		0%	0%
Denmark		0%	0%
Cyprus		0%	0%
Estonia		0%	0%
Ireland		0%	0%
Latvia		0%	0%
Malta			0%

4.3 Relevance of metal industry dioxin emissions

In the previous parts of the study the most important processes in the metal industry being relevant for dioxin emissions have been extracted qualitatively and the approximate numbers of installations assignable to these processes have been evaluated.

In this chapter the available information on national and EU-wide dioxin emissions from these sources will be described to identify the most relevant subsectors and the countries with highest emissions.

The option to establish harmonized PCDD/F monitoring requirements within a future revised IPPC directive has to be seen against the background of already available information and data files (both national and E.U.) on PCDD/F emissions to air, water, soil and other compartments, as well as the relative importance of the targeted sectors, and the possible health hazards involved. Such information has been compiled quite comprehensively in recent years in the European Dioxin Inventory [12], in the report on "Dioxin Emissions in Candidate Countries" [13], and also within the IPPC framework by the release of the first European Pollutant Emission Register (EPER). Moreover, additional information on air emissions is also provided by the study on POPs in waste compartments [14].

These various studies were carefully assessed to evaluate the relevance, when compared to all presently known sources, of the metal industry as a sector, and to define its share relative to the total of all known industrial emissions. Furthermore, the individual contributions of particular subsectors or of specific conversion processes important in the total emissions from metal industry were also assessed.

4.3.1 European Emission Inventory/Dioxin emissions in Candidate Countries

Two emission inventories have been set-up for covering the geographic area of the European Union. The first one, the so-called "European Dioxin Inventory", considered the 15 EU Member States and additionally also Norway and Switzerland. Emission estimates were based on national inventory reports and other available data from the international literature. for the present study, data related to the former EU 15 countries are taken from the Stage II report of that inventory. [15].

More recently, this inventory for Western Europe was completed by preparing a compilation of air emissions for the 13 Candidate Countries with which negotiations had already started for their accession to the EU [13]. Meanwhile 10 of these countries have effectively become Member States, so only Bulgaria, Romania and Turkey remain in their former Status of Candidate Accession Countries. Hence, these countries will not be considered here. This new inventory (called hereafter "CC-Inventory") followed the approach provided by the UNEP Chemicals Division, using the "Toolkit for emission inventories" [16]. The CC inventory therefore had a slightly different source structure and also the emission factors applied were not always comparable with those applied in the EU Dioxin Inventory. In several cases the Toolkit emission factors were replaced by specific data submitted by Candidate Countries; further missing factors were completed by figures taken from the literature (incl. the EU Dioxin Inventory data). The reference year for both inventories was the year 2000; so it may be assumed that meanwhile, by further improvement of processes, some changes have occurred, which most probably would lead to a decrease of the industrial emissions as indicated by the 2nd column of Table 9. Due to the different approach, the absolute figures obtained for EU 15 and the New Member States are not entirely comparable. However, the general picture can basically be regarded as reflecting the general trends and status correctly.

Table 9 Annual PCDD/F emissions in the EU 25 as estimated by the inventory studies [12, 13, 15] [13]

Source	**emission [g I-TEQ/year]**	
studies quoted	**[12, 13]**	**[15]**
Sinter plants	**702**	**503**
Electric furnace steel plant	**223**	**177**
Ferrous metal foundries	**n.d.**	**21**
Secondary zinc production	**27**	**3**
Secondary copper production	**88**	**84**
Secondary aluminium production	**91**	**58**
Metal reclamation from cables	**40**	**n.d.**
Non ferrous metal foundries	**62**	**n.d.**

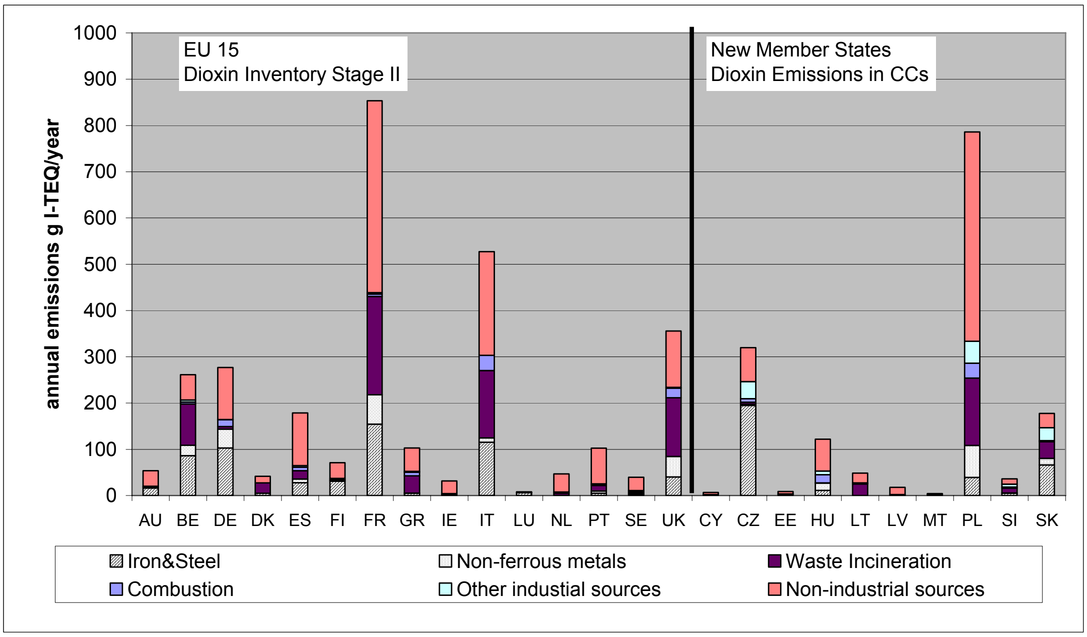

Figure 3 Estimates of annual PCDD/F emissions in the EU 25, reference year 2000 [13, 15]

Figure 3 displays the annual PCDD/F mass flows, as reported for four categories of industrial sources and also for the total of non-industrial sources[14]. Obviously, there are some "major

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[13] ferrous foundries accidentally had not been considered on EU level in the European dioxin Inventory; country specific emissions were reported for the year 1995 showing comparably low overall emissions.

players" active with respect to emissions from the metal industry, having emissions of the order of 100 g I-TEQ/year: these countries are BE, DE, FR, IT, UK CZ, PL, SK. Metal industry emissions from these countries make up nearly 90% of EU wide emissions reported for this industrial sector.

Figure 4 displays the same data, represented this time as shares of total emissions arising in the country considered. The shares assigned to the "major players" mentioned before range from 14% (PL) to ca 60% (CZ); still higher shares can be found for some countries such as LU with, however, low absolute emission values.

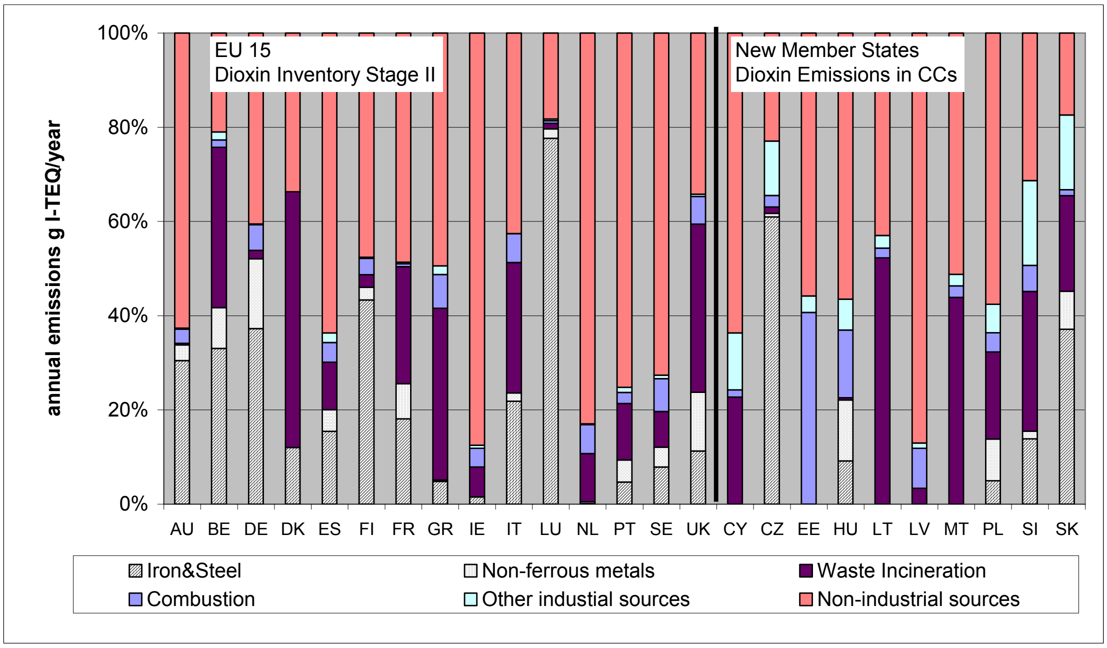

Figure 4 Share of total emissions in the EU 25 according to , reference year 2000 [13, 15]

Besides metal industry, waste incineration (not comprising open burning, barrel burning, or other domestic burning of waste) is the second important industrial source of dioxins in the majority of countries. Very often non-industrial sources are of equal importance as all industrial sectors together, or even higher.

Looking closer at metal industry, the relative contributions from iron & steel industry and from non-ferrous metallurgical enterprises (as far as they are all considered in the inventories) can also be assessed tentatively. From the figures it follows that the iron and steel sector (which emits 925 g I-TEQ/year), and in particular iron ore sintering (702 g I-TEQ/year) appear to be predominant. Non-ferrous metal industry contributes about 300 g I-TEQ/year, with secondary aluminium and metal foundries being the two major contributors.

Thus, according to these inventories the emission from iron & steel sector is about 3 times more important than the entire non-ferrous metal industry.

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[14] it should be noted that the overall emissions presented in this study are not necessarily the same as those evaluated in national inventories. As example, in case of Poland the official total emission for the years 2001, 2002 and 2003 were 447.5, 433.4 and 482.3 g I-TEQ/year, respectively.

4.3.2 Study for POPs regulation

The data shown in the previous section should be compared to the more recent emission estimates given in the report on POPs releases to waste streams [14]. The air emissions given therein are largely based on information taken from the IPPC BREF documents and thus reflect the situation after implementation of Best Available Technologies (BAT). In some cases, particularly for data regarding the New Member States, emission factors were adopted arising from the aforementioned inventory for Candidate Countries.

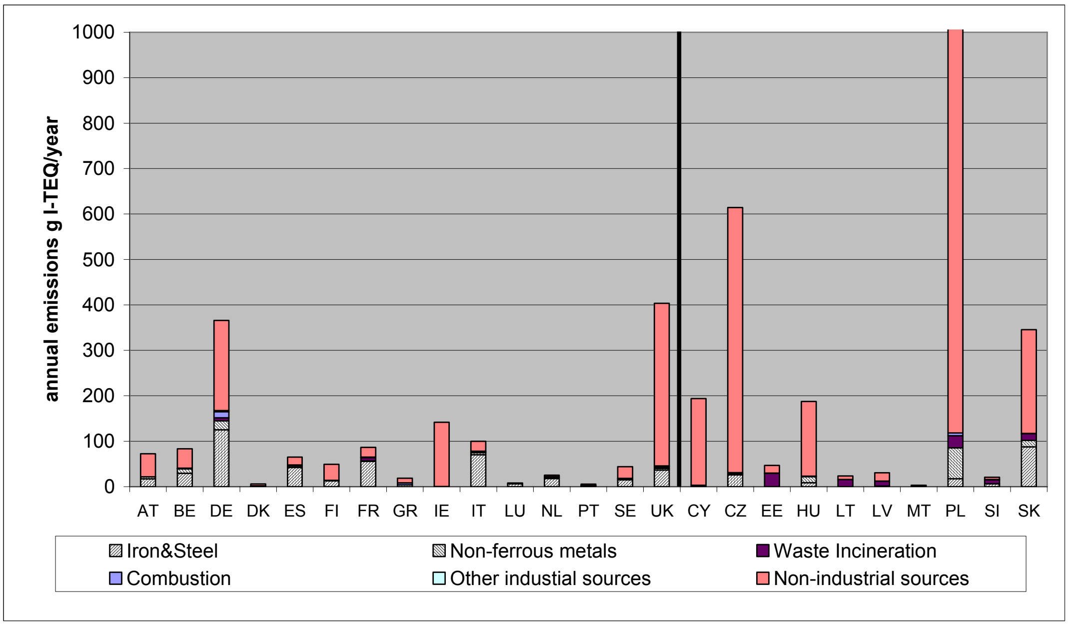

Figure 5 Annual PCDD/F emissions in the EU 25 as reported in the POPs study [14]

Comparing Figure 3 with Figure 5 there is an obvious decrease of emissions in the EU15 countries, with the most pronounced decrease in regarding waste incineration that was assumed to be complying with the emission standards required in the E.U. Waste Incineration Directive. Considerable differences can be seen also for the New Member States for which industrial emissions are assumed to be lower than described by the CC inventory, while, on the contrary, the non-industrial emissions frequently have higher values.

The above differences clearly illustrate the uncertainties that are inherent to all emission inventories. Therefore, absolute emission figures must be used with care. Hence, it appears prudent to compare only the qualitative characteristics and the relative relations of these inventories.

Within this framework it is important to note that all inventories assign higher emissions to the iron & steel than to the non-ferrous metal sector. The estimates in the POPs study reveal a ratio of 4:1, in comparison to ratios of about 3:1 indicated by the earlier emission inventories.

4.3.3 European Pollutant Emission Register

As part of the IPPC Directive the EU Member States were required to communicate emission values to the Commission for those industrial facilities, which have annual emissions above pre-defined thresholds. These facilities are put into a register that first became open to the public in 2003. Data given therein relate to the situation of 2000-2002. So far, only the EU 15 Member States are included.

In Figure 6 the distribution of emissions reported to EPER is shown, after assigning these emissions to different sectors. Apparently, the European metal industry is the leading source followed by the sectors combustion, waste incineration and cement production. However, from the description of facilities given in the EPER database, it is doubtful that the assignment to different sectors is correct in some cases. For instance, the major single source listed belongs to the chemicals production sector. However, from additional information on this plant, it appears that probably an incinerator for industrial waste operated by the chemical plant is responsible for the PCDD/F emissions.

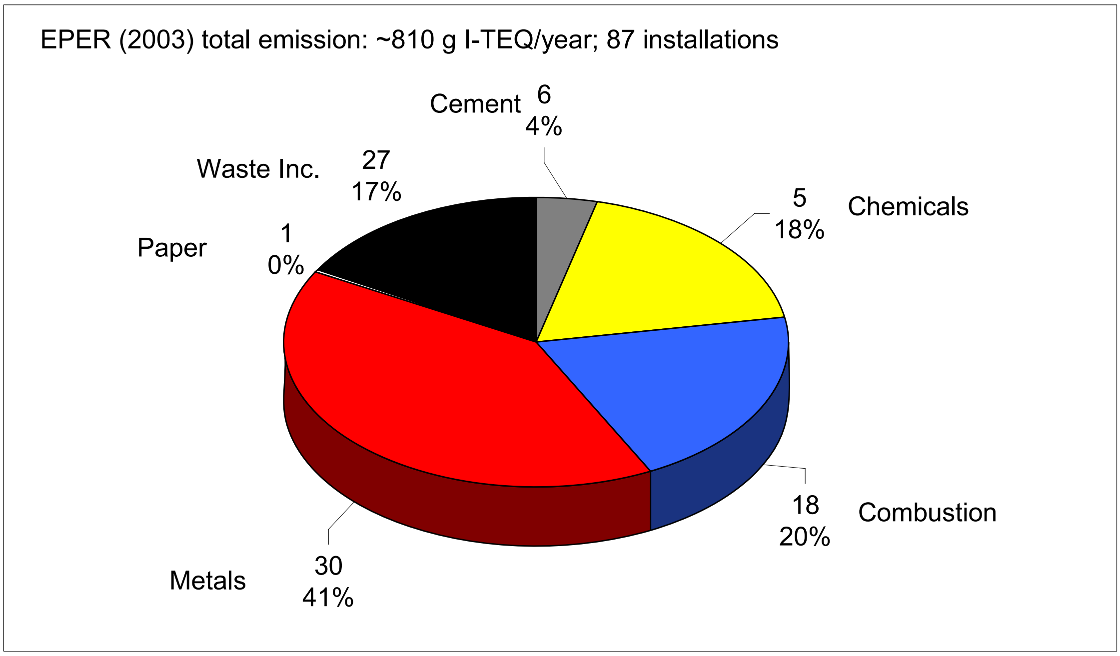

Figure 6 Numbers of installations and share of different industrial sectors to PCDD/F air emissions registered in the EPER

Moreover, a considerable fraction of the reported emission values has been assessed by calculations (using emission factors) or even by pure estimation, rather than being based on actual emission measurement results. The fractions of emissions assignable to these different methods of assessment are shown in Table 10. Overall, only 40% of the reported emissions are actually based on emission measurements. For the metal industry, this fraction of measured values is higher but still only about one third of the emissions has been assessed by estimation.

Table 10 Shares of different assessment methods used for PCDD/F emissions reported to EPER (C = Calculation; E = Estimation; M= Measurement)

Method	C	E	M
Cement	40%	13%	46%
chemicals production	10%	79%	10%
Combustion	93%	4%	2%
Metals	1%	36%	62%
Paper	0%	0%	100%
Waste incineration	2%	30%	69%
All sectors	23%	35%	41%

The threshold values for inclusion in the EPER data bank in general were established to cover all facilities, which together represent about 90% of the emissions of a given pollutant [17]. Regarding PCDD/Fs, a threshold of 1 g I –TEQ/year was set. Comparing emissions calculated for the EU 15 in the EU inventory and in the POPs report with EPER figures it can be checked whether this 90% criterion is reached. This comparison is shown in

Table 11 both for the overall emissions and also for comparable sectors in particular.

Table 11 Comparison of PCDD/F emissions reported to EPER with Inventory data.

Sector	EPER	EU Inventory	% in EPER	POPs report	% in EPER
All sectors	809.2	2446.4	33%	911.4	89%
Combustion	165.0	173.8	95%	39.5	418%
Waste Inc.	135.0	907.5	15%	134.8	100%
Metals	326.7	915.4	36%	585.4	56%

Apparently, no consistent picture is obtained. Compared with the EU Inventory data, much less than 90% of emissions are actually reflected by the EPER, except for the combustion sector. With regard to the POPs study, the overall emissions and those for waste incineration appear to be well covered by EPER, while for metal industry little more than 50% is included really. The strange value of 418 % obtained for combustion indicates either that EPER emissions are overestimated or that the emission factors used in the POPs study are too low.

It is striking that the number of installations listed in the EPER (only 30 for the metal sector) is so low compared with ca. 4,500 installations with potential relevance for dioxin emissions. Hence either a considerable number of installations has erroneously been assessed to have emissions below the threshold or a major part of the emissions is released by installations with annual freights below1 g I-TEQ/year. In the latter case, the EPER clearly has missed its goal of covering 90% of the EU-wide emissions.

This conclusion can be further supported by analysis and discussion of the distribution of both emissions and installation numbers, plotted as a function of the unit emission level. Such an analysis reveals that the number of installations with increasing emission levels is decreasing. Conversely, the total emission in each class is increasing, reaching a peak in the class of installations with annual emissions between 32 and 64 g I-TEQ/year.

Figure 7 represents these two parameters, i.e.:

- emissions in EPER inventories, and
- installation numbers

as a function of an exponentially increasing series of unit emissions per year, i.e. < 2, < 4, < 8 … g I-TEQ.

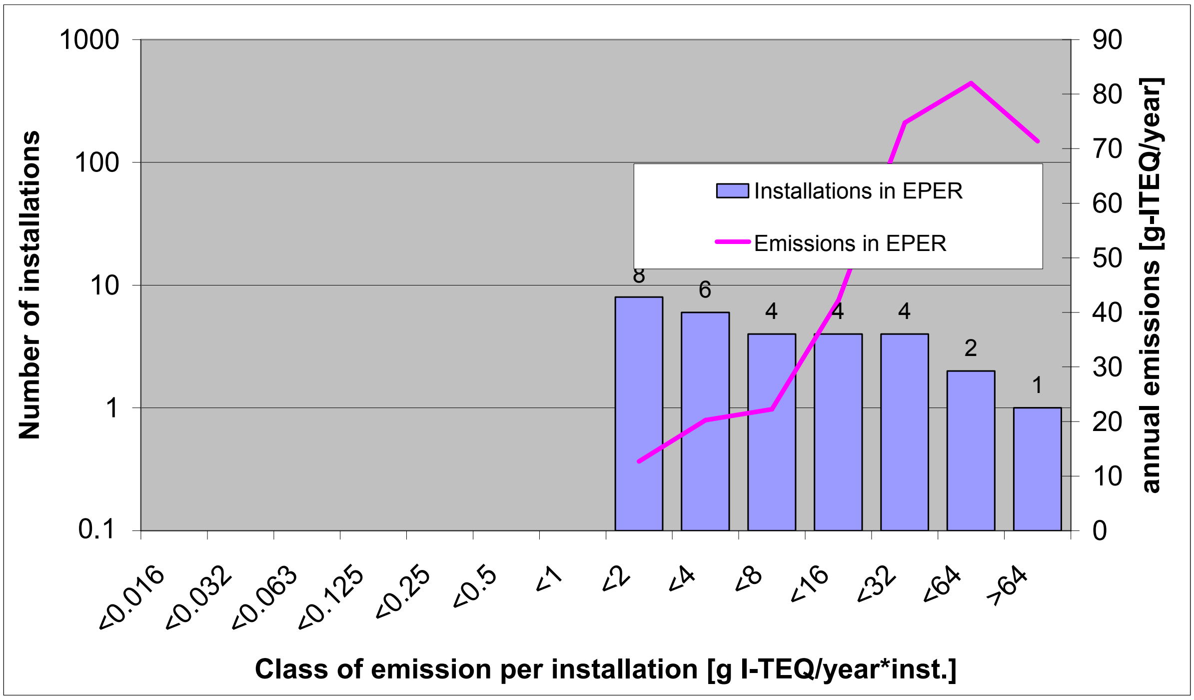

Figure 7 Distribution of installation numbers and total emissions to classes of annual emission levels according to EPER data for the metal sector

An interesting question is how these curves would look like in the range below the present EPER threshold value of 1 g I-TEQ/year. From the function shown in Figure 7, one could assume that the emissions may steadily continue to decrease, as shown in Figure 8. Based on this assumed curve of total emissions the number of installations corresponding to these values can be constructed by dividing the emissions by the average emission per installation (= mean value of each class).

This has been done for classes of specific emission levels exceeding 8 mg I-TEQ/year*inst[15]., which can reasonably be assumed to be reached or exceeded by most of the ca. 4,500 metallurgical installations mentioned in section 4.1.1. The result of this calculation is shown in Figure 8. Not surprisingly the number of installations continues to increase with declining emission values. However, the total number of installations needed to generate the assumed total emission curve is quite low and amounts to only ca. 435 installations, just covering only 10% of the expected number.

Moreover, taking into account the knowledge available on the typical flue gas dioxin concentrations for installations like EAFs and secondary non-ferrous metal smelters, most of these installations are to be expected to have annual emissions between 0.1 and 1 g I-TEQ/year each [16]. According to the information presented in section 4.1, the number of such installations in Europe is at least 550, whereas only ca. 150 installations are required to generate the assumed emission function shown in Figure 9 as the total for this range of unit emissions.

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[15] this annual emission value is reached e.g. by an installation with PCDD/F flue gas concentration of 0.1 ng I-TEQ/m³, 10,000 m³/hour and 8,000 hours annual operation time.

[16] From the EU Inventory, total annual emissions for EAFs were reported to be ca. 120-153 g I-TEQ/year. With ca. 250 EAFs, the average unit emission is 0.48-0.62 g I-TEQ/year

Hence, the assumed extrapolation of the emission function to lower installation specific emissions shown in does not fit well to the structure of metal industry and to the current knowledge on emission levels from metallurgical processes.

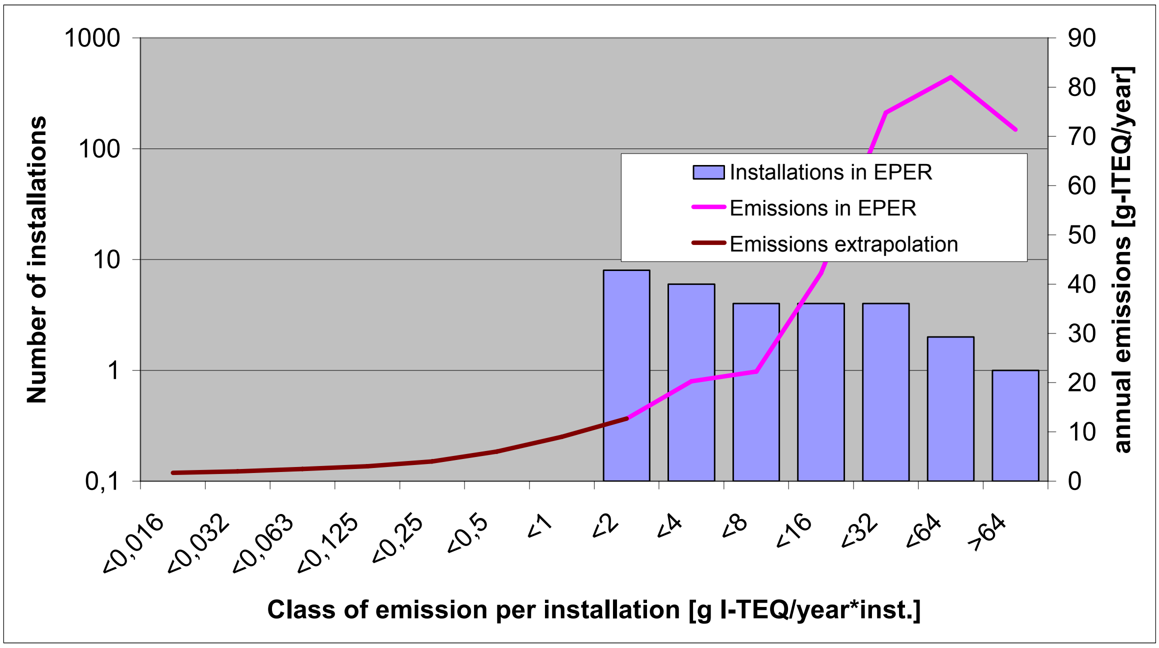

Figure 8 Extrapolation of the EPER distribution function to lower emission levels – total emissions approach

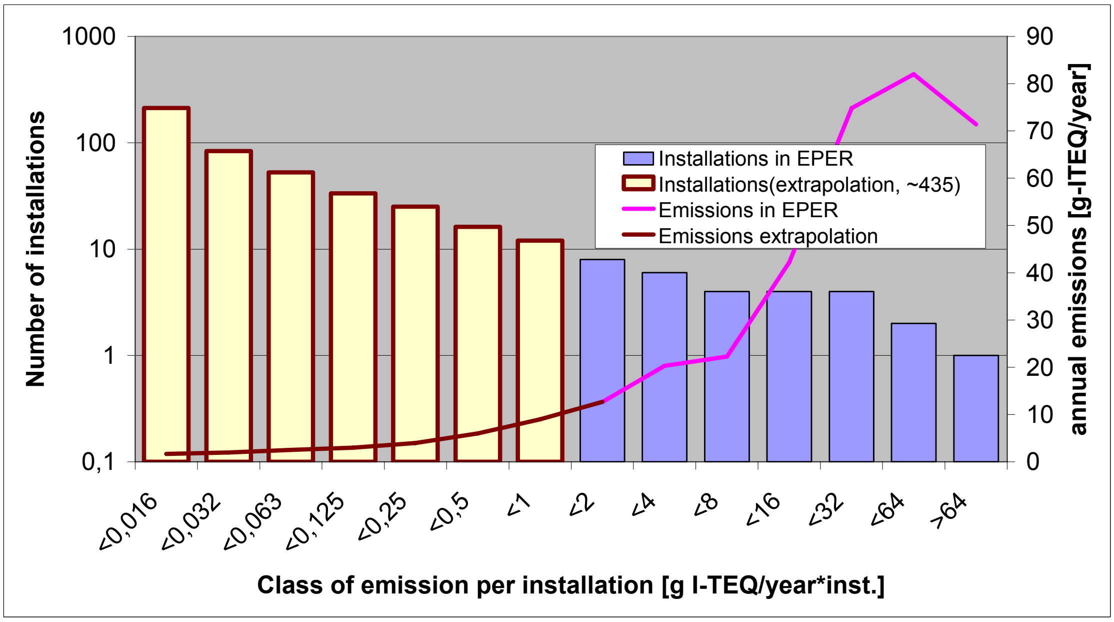

Figure 9 Extrapolation of the EPER distribution function to lower emission levels – total emissions and installation numbers

An emission curve which might be more plausible can be obtained if the probable distribution of installation number is defined firstly and the emission distribution is calculated afterwards. Boundary conditions for this experiment may be approximately set as follows:

- The overall number of installations covered by the given classes shall be at least 70% of the total number of 4,500 revealed from the analysis made in section 4.1.1
- the classes between ca. 0.1 an 1 g I-TEQ/year*inst. should cover a number of ca. 480 installations (=sum of EAFs and non-ferrous scrap proceeding installations, as well as some sinter plants)
- of the ca 300 installations in Iron & steelindustry (Sinter plants and EAFs) ca. 50% may be assumed to have specific emissions of more than 0.25 g I-TEQ/year (see footnote 16).

A distribution of installation numbers that fit to these boundary conditions and the curve of total emissions calculated from these is shown in Figure 10. Based on this distribution of installations, a bimodal distribution for the emissions is obtained with a second peak around specific emissions of 0.2 g I-TEQ/year*inst. The total number of installations in all classes amounts to ca. 3100 thus covering nearly 70% of the 4.500 installations. The large majority of these installations still would not be required to report their emissions under EPER. For the emissions, the total figure including those reported to EPER amount to ca. 530 g I-TEQ/year, which reflects the emission estimate given in the POPs study and by ca. a factor of two lower than the total emissions for the metal sector reported in the European emission inventories (c.f. Table 9). Also from this point of view this distribution therefore appears plausible and is clearly not overestimated.

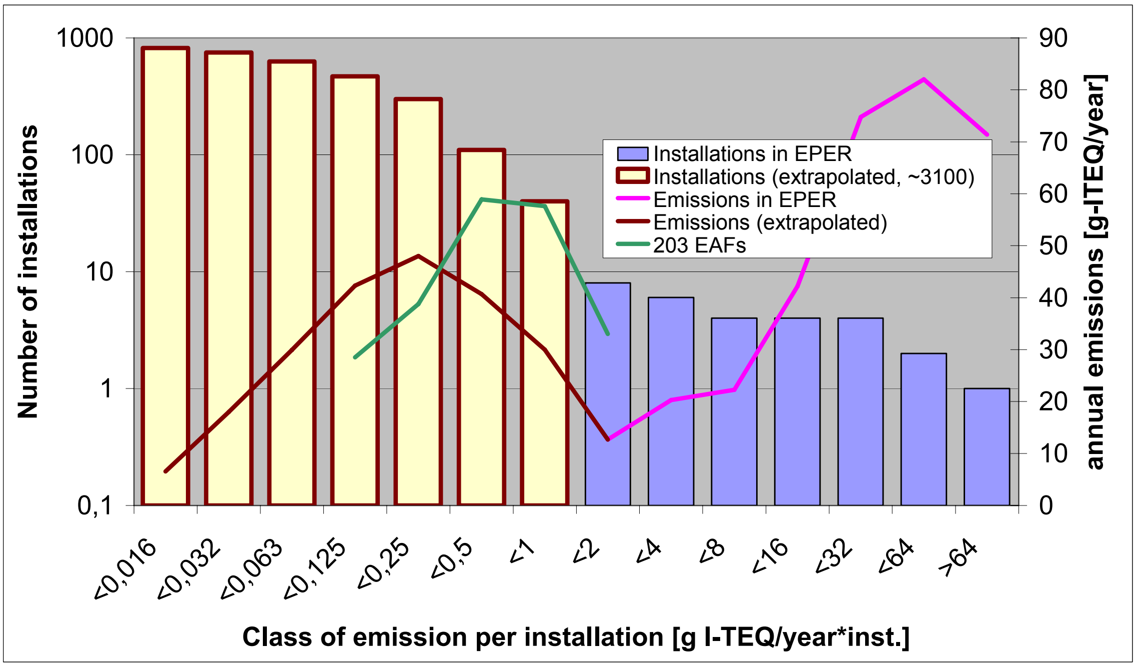

Figure 10 Extrapolation of the EPER distribution function to lower emission levels –installation number approach

An additional plausibility control was made using data provided by the iron & steel BREF for electric arc furnaces. The BREF provides the distribution of installation numbers per classes of capacity, expressed as “tons per heat”. Using this data and assuming 6 heats per day on 300 days/year the annual unit capacity in tonnes per year can be calculated (c. f. Table 12). From this, unit dioxin emissions are available by multiplication with appropriate emission factors, and total emissions by multiplication with the numbers of installations given in the second column of Table 12.

For EAFs, a wide range of emission factors is reported in the BREF covering 2 orders of magnitude (0.07 to 9 µg I-TEQ/ton). This is based on results from various studies:

- Swedish study (1992, 8 installations) 0.2 to 9, average 4 µg I-TEQ/t
- German study (1995, 4 installations): 0.07 to 1.8 µg I-TEQ/t
- EU Inventory (1997): 0.3-5.7 µg I-TEQ/t
- Danish study (1997, 1 installation) : 1.8 µg I-TEQ/t average value.

A quite recent study carried out in Italy [22] revealed emission factors ranging from 0.92 up to 8 µg I-TEQ/ton, with an average of 4.5 µg I-TEQ/t.

As a conservative approach the geometric mean of this range (2.7 µg I-TEQ/t) was taken for the calculations made here.

Table 12 Calculation of annual dioxin emissions from EAFs using installation data provided by the I&S BREF

Basic assumptions: 6 heats/day, 300 days/year, emission factor 2.7 µg I-TEQ/t [17]

t/heat	**number**	**unit capacity**	**unit emissions**	**total emissions**
		t/year	g I-TEQ/year*inst.	g I-TEQ/year
20	19	36 000	0.097	1.8
40	27	72 000	0.194	5.2
60	28	108 000	0.292	8.2
80	44	144 000	0.389	17.1
100	33	180 000	0.486	16.0
120	18	216 000	0.583	10.5
140	18	252 000	0.680	12.2
160	9	288 000	0.778	7.0
180	4	324 000	0.875	3.5
200	3	360 000	0.972	2.9
total	**203**	0	0.000	**84.6**

From the data presented in Table 12 the distribution of annual emissions related to the classes of unit emissions can be constructed. The resulting distribution is also shown in Figure 10. A similar curve to that already constructed from the previous considerations on installation numbers is obtained, revealing a maximum of emissions in the area just below the EPER threshold.

Hence, the overall impression derived from these comparisons is that the EPER threshold limit of 1 g I –TEQ/year for dioxins and furans has been set at too high a value to reach the desired 90% coverage of emissions. This aim might only be reached in the future when most facilities will be upgraded to BAT and only a few particular plants will cause the majority of emissions. The emission data from metallurgical plants in the German State of North Rhine-

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[17] According to expert opinion the given assumptions may be considered as conservative, because in modern EAFs tap-to-tap cycles are usually below 60 minutes. Therefore more than the approximated average of 6 heats/day are likely to occur. Consequently, also the capacity distribution would shift to higher values leading to higher emission estimates.

Westphalia may be seen as an example for such a situation (c.f. Table 13, EPER registered installations marked by yellow colour).

Table 13 Dioxin emissions from metal industry installations located in North-Rhine Westphalia, Germany
Data from [18]

Enterprise	Installation	Emission g I-TEQ/year	Share (Cumulative)
Total		**56.519**	
Thyssen Krupp Stahl AGWerk Schwelgern	Sinteranlage0176	42.000	74.3%
HKM Hüttenwerke Krupp Mannesmann GmbH	Sinteranl.(Möllerv.)0000	9.000	90.2%
DK Recycling und Roheisen GmbH	Sinteranlage0120	2.000	93.8%
Hüttenwerke Kayser AG	Kupfersekundärhütte0001	0.681	95.0%
HKM Hüttenwerke Krupp Mannesmann GmbH	Stahlwerk0050	0.507	95.9%
Krupp Thyssen Nirosta GmbHWerksteil Höntrop	Stahlwerk0230	0.396	96.6%
Thyssen Krupp Stahl AGWerk Beeckerwerth	Stahlerzeugung0280	0.375	97.2%
B.U.S Metall GmbH	Wälzanlage0012	0.331	97.8%
Thyssen Krupp Stahl AGWerk Bruckhausen	Stahlerzeugung0270	0.295	98.3%
ISPAT Stahlwerk Ruhrort GmbHWerk Ruhrort	Oxygenstahlwerk1060	0.148	98.6%
Bender,Metallwerke GmbH	Schmelzwerk Leicht-u.Buntmetall0100	0.142	98.9%
Metallwerke Bender GmbH	Aluminium-Umschmelzwerk0010	0.137	99.1%
VAW-IMCO Guß und Recycling GmbH	Umschmelzbetrieb I 0003	0.112	99.3%
Krupp Thyssen Nirosta GmbHKTN	Stahlwerk0265	0.105	99.5%
Thyssen Krupp Stahl AGWerk Phoenix	Oxygenstahlwerk0420	0.087	99.6%
Edelstahl Witten-Krefeld GmbH	Elektrostahlwerk Witten0267	0.082	99.8%
Metallhüttengesellschaft SchumacherGmbH & Co	Anlage zur Gewinnung von NE-Metallen0001	0.025	99.8%
M.I.M. Hüttenwerke Duisburg GmbH	Heißbriketieranlage0013	0.018	99.9%
Metall-Rückgewinnungsgesellschaft	Aluminium-Schmelzanlage0010	0.016	99.9%
DK Recycling und Roheisen GmbH	Hochofenbetrieb0140	0.013	99.9%
Metallwerk Dinslaken GmbH&Co.KG	Schmelzanlage f.Zink o.Zinklegierungen0010	0.008	99.9%
HKM Hüttenwerke Krupp Mannesmann GmbH	Hochofenbetrieb0020	0.007	99.9%
Metallhüttenwerke Bruch GmbH	Umschmelzanlage für NE-Metall 0010	0.006	100.0%
HKM Hüttenwerke Krupp Mannesmann GmbH	Hochofenbetrieb0030	0.005	100.0%
Aluminiumwerk Unna	Schmelzanlage f. Aluminium0001	0.005	100.0%
VAW Aluminium AGWerk Grevenbroich	Zweikammer Herdschmelzofen I0010	0.003	100.0%
Heinrich Schneider NE-Metallverarbeitung GmbH	NE-Schmelze0001	0.003	100.0%
M.I.M. Hüttenwerke Duisburg GmbH	Sinteranlage0020	0.002	100.0%
Deutsche Giessdraht GmbH	Schmelzanlage NE-Metall0001	0.002	100.0%
Thyssen Krupp Stahl AGWerk Schwelgern	Hochofen0212	0.002	100.0%
VAW-IMCO Guß und Recycling GmbH	Umschmelzbetrieb II0005	0.002	100.0%
Thyssen Krupp Stahl AGWerk Westfalenhütte	Hochofenwerk0320	0.002	100.0%
Thyssen Krupp Stahl AGWerk Schwelgern	Hochofen0211	0.002	100.0%
Eisenwerk Brühl GmbH	Gießerei0001	<0.001	100.0%
Thyssen Krupp Stahl AG	Hochofen0209	<0.001	100.0%
Thyssen Krupp Stahl AG	Hochofen0204	<0.001	100.0%
Schmitz Metallbearbeitung GmbH	Pyrolyseofen0001	<0.001	100.0%

4.3.4 Summary and Conclusion

The relevance of PCDD/F emissions from metal industry was evaluated by analysing the data, as reported in the dioxin emission inventories for Western European countries and the New Member States, as well as more recent data provided by a study on POPs release to waste streams, and the first EPER data, as already published on the EPER website. The contributions from the iron & steel and the non-ferrous metal industry are summarized in Table 14, both for the total and for all industrial emissions.

Accordingly, metal industry is responsible for about one quarter of total PCDD/F emissions to air and these represent at least 50% of industrial emissions. Emissions from the iron & steel sector clearly dominate these emissions, since they are probably a factor 3 to 4 higher than the releases from non-ferrous metal industry. This statement assumes an equal quality of data gathering from the two sectors. Indeed, in any inventory it is difficult to assess the completeness, as well as the representative character of the data and the emission factors used, etc.

From an analysis of EPER data it may further be concluded that a large part of the PCDD/F emissions from metal industry is not yet covered by this register. This indicates that on the one hand quite a large number of facilities have annual emissions below the EPER threshold, which on the other, all together, could still sum up to ca. 50-70 % of the emissions from the entire metal sector. This situation seems even more pronounced for non-ferrous metal industry than for the iron & steel sector, for the latter comprises the larger individual sources.

These comparisons show that the EPER data bank is still in a preliminary state of development, bringing along considerable uncertainty on the completeness and representative character of the data and making it unsuitable at present as an instrument for decision making. The geographical distribution of emissions from the metal sector reveals that almost 90% of the EU 25 emissions from metal industry (and of each subsector) are attributable to 8 countries, of which 3 belong to the New Member States. These countries are BE, DE, FR, IT, UK CZ, PL and SK. The remaining emissions are predominately generated in ES, FI, GR, PT and HU.

Table 14 Overview on the metal industry's relevance regarding annual dioxin emissions to air in the 25 EU Member States

	Metal Industry	Iron & steel	Non ferrous metals
EU Dioxin Inventory (EU 15)			
share of total	27%	20%	7%
share of industry	49%	37%	12%
Dioxin emissions in CCS (EU 10)			
share of total	28%	21%	7%
share of industry	50%	38%	12%
Pops study (EU25)			
share of total	28%	26%	2%
share of industry	62%	53%	9%

4.4 Current state of dioxin monitoring in the EU Member States

In the previous sections of this study it was shown that there is a large number of installations in the metal industry with potential relevance for dioxin emissions. The number of installations with significant emissions may amount to several hundred, but only for 30 of these have reports to the EPER been required so far. Furthermore, emissions of 10 EPER registered installations were not assessed by measurements but by calculation or estimation procedures.

However, it would be grossly negligent to draw conclusions from these results on the dioxin emission monitoring in the Member States. It is therefore crucial, with respect to the need for additional monitoring requirements, to assess the coverage of metal industry installations by Member States' monitoring approaches in more detail.

4.4.1 Qualitative overview

To obtain an overview on the current state of the member States' monitoring activities fairly simple questionnaires were prepared and sent to the national authorities and industry associations. Beside the replies to these project-related questionnaires also the official national IPPC reports and some other sources of information [19] were also used.

As is the case with the data on the numbers of installations, the information on monitoring is incomplete. Available data vary from one country to another. For instance in the case of Germany most information needed could be obtained from other available sources of information (industry replies/previous IPPC reports). In the case of Poland the only information on monitoring activities available was compiled from recently finished research projects and a single personal contact. Table 15 presents a survey summarizing the information gathered on:

- existing limit values regarding dioxin emissions from metallurgical facilities
- whether actual dioxin emission monitoring takes place and if it is done occasionally or more systematically

More systematic, or better regular monitoring is normally specified by local codes or operating permits. Many countries or regions have provisions for characterising all relevant emission, e.g. on a yearly basis.

It should be conceded that both in theory and in practice an enterprise can escape from regular monitoring should its potential for dioxin emission not have been recognised as yet.

With regard to PCDD/F emission limit values (ELVs) it is concluded that general ELVs applying to metal industry have been introduced only in a few countries, e.g. AU, BE, CZ, DE, SE. For Italy information could be obtained by contact to a member of the NoE. Accordingly, a general emission limit for dioxins has been in force since 1990 which all industrial installations must comply with. That ELV refers to total dioxin concentration instead of TEQ. The value is quite high even if a conversion factor of 100 is taken into account and thus will hardly be exceeded by any plant.

Some countries, including AT, BE (Flanders especially), FR, LU, NL, SI, UK sometimes implement limit values on a case-by-case basis as introduced into new operating permits. No limits at all are set in 11 countries and for Poland no information could be obtained yet.

However, in many cases general PCDD/F emission limits apply only to new plants or to installations subject to substantial changes. Existing plants may have particular limits in their operation permits, but only limited information is available on the extent of this practice. Another possible difference concerns the time period, for which the plant considered can seek compliance.

In theory, the existence, implementation and enforcement of regulations stipulating limit values for PCDD/F emissions implies that there must be some “systematic”, or better “regular” monitoring concept active, since the IPPC directive contains related requirements. From the answers to the questionnaires this was confirmed for some countries (A, BE, DE, LU), whereas in other cases the information was not sufficiently clear.

Regular monitoring means that industry has a duty to monitor dioxin emissions on a periodic basis. This may vary from 3 times a year (Vlarem, Flanders) to once every 3 years (general approach of TA Luft 2000 DE and frequently referred to in AT). As regards particular installations or types of installations, significantly higher monitoring frequencies are reported, with the maximum being 1 sample per month for sinter plants located in the Flemish region of Belgium. However, **regular monitoring does not necessarily mean that all important or potentially relevant installations are subjected to emission measurements**. Such requirement may be limited to a selected group of installations.

Regular monitoring was generally declared in the questionnaire replies by all countries handling general emission limits and by most of the countries practising case by case ELVs. However, for several countries neither the frequency of monitoring nor the coverage of installation types has been reported.

In case of France, some additional information was provided on occasion of the 2nd project workshop (see Annex D). According to this data and related information from the website of the French Ministry of the Environment [20], 17 metallurgic facilities are obliged to regularly carry out measurements and report the results. They predominantly belong to the iron and steel sector (4 sintering plants and 8 EAFs), with the remaining 5 installations being ferrous and non-ferrous smelters/foundries and a Waelz kiln for zinc recovery. These 17 installations were shown in 1998 to have emissions above 1 g I-TEQ/year and in that year together comprised more than 90% of the total emissions registered for the metal sector. In 2003, the emissions from these installations made up ca 36 g I-TEQ/year out of a total of 50 g I-TEQ/year and so still comprised 72% of the emissions monitored . The list of emissions is updated on an annual basis, so at least one measurement per year may be assumed. No information is provided how the balance is made to calculate the total emissions. Presumably, calculation based on emission factors and activity rates is used rather than emission measurements.

“Occasional” monitoring is defined here as monitoring conducted at a given point in time and triggered by initiative of either plant operators (or their hierarchical ladder, e. g. their corporate environmental division) or environmental authorities, whether those at the local or national level. “Occasional” monitoring therefore is a less systematic and generally unregulated type of emission gathering.

It is applied in seven further countries with variable intensity. Such monitoring can be termed reactive, e.g. as a reaction to complaints from the neighbourhood or to local pollution problems such as elevated dioxin values in the dairy sector. Also, special designed research programs addressing exemplary installations selected for emission measurements are covered by this term. Examples for such approaches are the DANCEE study [21]carried out in Poland and the measurement program in the Italian metal industry [22]. Obviously, in case of “occasional” monitoring most installations are measured only once without obligation to repeat the emission test regularly[18].

Only a few countries explicitely state that no monitoring at all takes place, and for some no information is available at all.

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[18] In this context it is useful to have a look at the factor “uncertainty”. For the sake of example a real case is considered. An enterprise had its dioxins emission checked for the first time in 1996. The value reported was not alarming, at some 0.5 ng I-TEQ/Nm^3 and has hence been checked yearly. Since, the productivity of the unit has steadily been increased and – due to tight market conditions – it becomes impossible to be quite strict regarding the quality of raw materials. Probably this has caused dioxin values to rise steadily to a range of 1 - 2 ng I-TEQ/Nm^3. A more recent value was 10 ng I-TEQ/Nm^3. The original annual emission was 0.3 g I-TEQ/year, but today this would represent more than 5 g I-TEQ/year should the last value be confirmed. Such a development is not unrealistic and with occasional monitoring it is unlikely that the gradual increase of this source would be recognised using occasional monitoring.

Table 15 Evaluation of information on emission limit values and assessment of monitoring activities

meaning of the colours: yellow: no reply; blue: no reply by authority, data completed by industry replies; green: data provided according to IPPC structure and included as far as assignable;
1): replies to project questionnaires by MS authorities; 2) replies to project questionnaires by industry; 3) data from official IPPC report [3] 4) information from recent research projects [21, 22]

Country	**limit values; all concentrations (bold figures) in ng I-TEQ/m^3**	**mode of dioxin monitoring**	**monitoring frequency**	**installations monitored**
Austria	1): National ELV: New sinter plants **0.4**; EAF (new/major changes): **0.4** other iron&steel (new/major changes): **0.4** decreasing to **0.1** until 2006; case-by-case: existing sinter plants: 0.4/none; sec. Al. **0.1, 0.4**; Sec. Cu: **0.9**	1): regular; occasional	1/year to 1/3-6years; occasional for EAF and other iron & steel	sinter plant sec. aluminium (several furnaces) sec. copper (shaft furnace)
Belgium	1): metals production & transformation, ng TEQ/Nm^3: existing plants: limit: **1** (sinter: **2,5**), **0,4** guide, new: **0,5** limit, **0,1** guide sinter pl.: 2.5 ; proposition **0.5** 2): **1/0.5** national for metals; case specific **0.4**/**0.1** for existing/new inst.	1): regular; occasional	3/year acc. to law; 1/month (sinter plants); 6/year for EAF;	sinter, foundry copper smelters zinc: sec. melters lead: sec. melters
Cyprus		1): none	-	
Czech Republic	1): National ELV **0,1** as the general ELV. It has not been applied in the metal industry yet. IPPC permits give some possibilities	1): regular	1/3years	no information
Denmark	3): none			
Estonia				
Finland	3): none			
France	1): case-by-case limits for all the potential metallurgic dioxin sources	1): regular	1/year at least	17 installations (sinter pl., EAFs, sec. non-ferrous smelters)
Germany	2): TA-Luft 2002 *) (all facilities needing permit): General ELV **0.1** or 0.25 µg/h; particular ELVs **0.4** (sinter plants, non-ferrous metals except Al and ferro alloys, cooper shaft furnaces), target Value **0.1** 3): Existing Inst.: Target Value **0,1** ; minimisation obligation for prim. aluminium New/Changed Inst: **0.1** or 0,25 µg/h ; sinter plants LV **0.4** , **0.1** Target Value	2): regular	1/year to 1/3years	iron & steel industry: sinter plants, EAFs
Greece	1): none	1): occasional	1) no info	no information
Hungary	1): presumably none, questionnaire reply comment by authority: "keeping of emission level"	1): occasional	initiating of the inspectorate by public complaint	no information
Ireland	1): no relevant metallurgical installations		-	
Italy	3): 0.01 mg/m^3; mass flow >= 0.02 g/h (refers to total PCDD/F, not TEQ, see also section 4.4.1)	1): occasional (research) 4) EAFs, various n-f installations	1) no info	2001-2002: 5 EAFs, 1 shredder ,10 non-ferrous metal installations

Country	limit values; all concentrations (bold figures) in ng I-TEQ/m³	mode of dioxin monitoring	monitoring frequency	installations monitored
Latvia				
Lithuania	1): none	1): none	-	
Luxembourg	1): EAF **0.1** . Al production from scrap **0.1** ; Target Value **0.1** 2): Electric Arc Furnaces and EAF dust processing : **0.1**	1): regular	1-2/year +1-2 additional	EAF, Al furnace, zinc: direct reduxtion of filter dust
Malta				
Netherlands	1): yes, **0.1-0.4** case-by case	1): regular	1) no info criterion: > 2g dioxins/year in raw gas	no information
Poland		4): ocasional (research), I&S, n-f installations		2002-2004: ca. 25 installations, both sinter plants, EAF, prim. and sec. non-ferrous smelters
Portugal	1): none	1): occasional	set case by case during IPPC permit procedures	some measurements performed within the EU Dioxin Inventory (EAF, sec. Aluminium)
Slovakia	1): none	1): none	-	no information
Slovenia	1): will be included in case of IPPC permits 2): BREF values **0,07** - **9**	1): occasional	1) no info 2) 1/year	info by iron & steel industry: primary installations
Spain	1): none	1): occasional/ none substantial voluntary mode, e.g. galvanising sector		no information
Sweden	3): 2.1.1/2.1.2: 0.5 g/year 2.2/2.3/2.4/2.5a1: none 2.5a2: **0.1**	4) occasional	2) only declaration 1/year	info by industry: copper or lead prod. (Boliden)
United Kingdom	ELVs typically set are **2** for sinter plant, **0.3** for EAF	1) regular; 1) Occasional	1) no info; 1) Special one-off reviews usually specified in permits in the form of sector co-ordinated improvement conditions	1) prim. steel installations (sinter plants, EAFs) no information

4.4.2 Quantitative evaluation

The above qualitative description can now be complemented with more quantitative considerations, e.g. by making use of the annual emissions reported by existing emissions inventories (c.f. 4.2). The main point here is to decide which fraction of reported annual emissions is already covered by either “regular” or “occasional” monitoring activities, and which fraction still requires additional efforts to obtain appropriate levels of information. It is quite difficult to assess the fraction of the national emissions being covered by only occasional monitoring activities. Countries belonging to this group with most relevant emissions from the metal industry are Italy, Spain and Poland.

In Italy, a first PCDD/F emission measurement project [22] has been carried out covering electric arc furnaces and various non-ferrous metal smelters (secondary aluminium, bronze/brass and secondary lead). Of these, secondary aluminium production was revealed to be the most relevant source. Emissions from sources of integrated steel plants, particularly from sinter plants, have not yet become published.

In Spain, some integrated steelworks also exist, as well as numerous non-ferrous metal plants. Apparently, almost no information can be obtained on the PCDD/F emissions from these installations. Still, an excellent study on the hot dip galvanising of steel was identified [11].

Regarding Poland the situation again is different. At least two larger emission measurement projects have been carried out during recent years, which covered installations in the metal industry: on the one hand the measurement program of the “Dioxin emissions in Candidate Countries” project and on the other hand a project directly targeting dioxin emissions from metallurgical facilities and funded by the Danish “DANCEE” project [21].

Put together, 25 installations were investigated by these projects with a few being tested by both projects (e.g. iron ore sinter plants). Besides the sintering plants electric arc furnaces, iron foundries, and various installations from the non-ferrous metal sector (copper, aluminium, zinc) were also covered. Since participation by industry was voluntary the selection of installations is not necessarily identical with the most relevant emission sources in Polish metal industry. Nevertheless, the results give a first picture of the situation and serves as a starting point for further work.

The results obtained in the Dancee project showed comparatively low emissions from the iron ore sintering plant and an emission factor slightly above 1 µg I-TEQ/Mg product was reported. The highest emission factors were found for an aluminium scrap smelter and a hot air cupola foundry. In the CC dioxin project some small installations with high PCDD/F flue gas concentrations were found which however have low annual emissions due to intermittent operation and low throughput. In general, no unexpectedly high emission was found and in most cases the emission levels corresponded well to typical levels found in Western Europe.

Obviously, there are only two countries having relevant emissions in the metal sector which have none or unknown monitoring activity, i.e. Slovakia and Finland. For Finland, there appears to be considerable uncertainty on the emission level since the estimates provided by the EU Dioxin Inventory and the POPs report differ by more than a factor of 2 (30.8 vs. 12.9 g I-TEQ/year). Moreover, in a publication from the Finnish Environment Institute [23] much lower PCDD/F emissions (0.003 g TEQ/year) are reported mainly based on emission factor calculations using factors which originate from UNEP, the Swedish EPA and the Danish Ministry of Environment.

Table 16 shows a compilation of the EU 25 countries, sorted according to their monitoring approaches (column 2) and showing the annual emissions as reported respectively in the project “EU Dioxin Inventory” or “Dioxin Emissions in Candidate Countries” (columns 3, 5 and 7 for iron and steel, non-ferrous metals and total metal sector respectively.). The shares of each MS emission to total emissions has been calculated (not shown) and summed up to yield cumulative shares of the total emissions (columns 4, 6, and 8). For example, in column 3 the share of 9% obtained for Belgium together with the 2 % share of Austria adds to a cumulative share of 11 %, and so on.

This analysis shows that those countries declaring a “regular” approach contribute to about 60% of the EU-wide emissions from the metal industry. For the countries with regular or “occasional” monitoring, ca. 90% of the emissions are assignable. Doing the same analysis with the emission data provided in the POPs report [14] the figures change to 49% (“regular” monitoring) and 82% (regular or occasional monitoring), respectively.

The conclusion to draw from this analysis is that some awareness of the dioxin emissions from metal industry is prevalent in those Member States which are major contributors to the overall emissions. It cannot be assessed, however, how much of the emissions actually is under monitoring since the monitoring activity may vary considerably from country to country and also with respect to the different sectors within metal industry. Taking into account that

- “occasional” monitoring mostly means a single screening measurement at selected installations
- “regular” approaches in many countries probably does not cover all relevant installations

the fraction of emissions actually covered by monitoring might be substantially less than indicated by the figures in Table 16.

Table 16 Quantitative evaluation of the PCDD/F emissions from metal industry covered by regular and/or occasional monitoring activities in the EU member States
Emission data taken from inventory projects [13, 15] for ref. year 2000 19.

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[19] According to industry comments the emissions have been decreasing significantly in some countries since the given reference year, due to plant closures or installation of abatement systems. However, such trends appear to be more prominent in countries with regular monitoring and therefore would lead to increasing shares of total emissions by countries with occasional or no monitoring activities.

		Iron&Steel g I-TEQ/year	share (cumulative) %	Non-Ferrous g I-TEQ/year	share (cumulative) %	Metal Ind. g I-TEQ/year	share (cumulative) %
Total		915,4		298,6		1214,0	
AU	1): regular; occasional	16,4	2%	1,8	1%	18,2	1%
BE	1): regular; occasional	86,4	11%	22,6	8%	109,0	10%
CZ	1): regular	195,0	33%	2,4	9%	197,4	27%
DE	2): regular	103,0	44%	41,0	23%	144,0	39%
FR	1): regular	154,5	61%	63,8	44%	218,3	57%
LU	1): regular	6,5	61%	0,2	44%	6,7	57%
NL	1): regular	0,1	61%	0,2	44%	0,2	57%
UK	2): regular	40,1	**66%**	44,3	**59%**	84,4	**64%**
ES	1): occasional/none substantial	27,7	69%	8,2	62%	35,8	67%
GR	1): occasional	5,0	69%	0,3	62%	5,3	67%
HU	1): occasional	11,2	71%	15,8	67%	27,0	70%
IT	1): occasional	115,3	83%	9,2	70%	124,5	80%
PO	4): occasional	39,0	87%	69,5	94%	108,5	89%
PT	1): occasional	4,8	88%	0,9	94%	5,7	89%
SI	1): occasional	5,0	**88%**	0,6	**94%**	5,6	**90%**
CY	1): none	0,0	88%	0,0	94%	0,0	90%
LT	1): none	0,0	88%	0,0	94%	0,0	90%
SK	1): none	66,0	96%	14,3	99%	80,3	96%
DK		5,0	96%	0,0	99%	5,0	97%
EE		0,0	96%	0,0	99%	0,0	97%
FI		30,8	100%	1,9	99%	32,7	100%
IE		0,5	100%	0,0	99%	0,5	100%
LV		0,0	100%	0,0	99%	0,0	100%
MT		0,0	100%	0,0	99%	0,0	100%
SE		3,1	100%	1,7	100%	4,8	100%

4.4.3 Summary and conclusions

An evaluation of the current situation of PCDD/F monitoring in the EU 25 Member States is made based on the existing inventories, the replies to the project-related questionnaires and other sources of information, e.g. official IPPC reports submitted to the Commission and research reports dealing with dioxin measurement programs. Results on the state of implementation and usage of emission limit values in metal industry of the various Member States are presented and these Member States are subsequently grouped into “regular ”, “occasional”, or no substantial dioxin monitoring activity at all.

In 11 out of the 25 EU Member States there are already either general emission limit values or case by case limit values (present or in a near future). In case such emission limits are or will be inserted in the operating permits for metallurgical plants one may expect some emission monitoring for these installations. However, it is likely that not every installation belonging to those with potential dioxin emission relevance will be targeted. Hence, even if a “regular” monitoring approach is reported this does not mean for sure that all relevant emissions sources are covered by monitoring approaches.

In the other countries – that is 14 out of the 25 EU Member States - no limit values exist. Some of these countries do not have large or numerous dioxin-relevant activities in the metallurgical sector. However, some relevant countries, such as Poland, Slovakia, Spain and Finland, do belong to the group of Member States, which did not report the existence of emission limits for dioxins in permit conditions. For these countries, some “occasional” emission monitoring has been indicated for Spain and Poland with respect to monitoring activities.

The countries declaring to carry out “regular” monitoring to certain extent contribute about 50-60% of the dioxin emission from the metal industry. However, it seems unlikely that these emissions are covered entirely by regular monitoring and thus there is a large uncertainty on the fraction of emissions actually being monitored.

For those countries with at least "occasional" monitoring, a value of 20-30% of the total emissions from metal industry can be assigned. Due to the wide range of approaches covered by "occasional" monitoring, the fraction of measured emissions must clearly be much lower than the maximum estimate.

Therefore, it is concluded that approximately 50% (or even more) of the PCDD/F emissions in the EU metal industry might not sufficiently be covered by the present monitoring programmes. Using the approximate share of emissions from the metal industry (as presented in section 4.3) this figure converts to 25% of all industrial emissions and about 13% of total PCDD/F emissions including non-industrial sources.

4.5 Technical and economic feasibility, and model for cost/precision analysis of dioxin monitoring

In this section basic information is provided on the current situation as regards laboratory and sampling team capacity in the EU in order to assess whether additional monitoring requirements could lead to significant constraints. Furthermore, the costs for PCDD/F emission measurements are compared with relevant economic indicators in order to get direction as to which types of installations/sectors additional monitoring requirements might be unaffordable for. Finally, with respect to the aim of decreasing the overall uncertainty of the emission inventories a cost/precision analysis is presented. The goal of this model is to draw some general factors influencing the number of emission measurements to be carried out in order to reach the desired state of uncertainty.

4.5.1 Analysis of the technical feasibility

To assess the feasibility of introducing mandatory monitoring requirements, contacts have been made with several laboratories. This first occurred at the NoE in March 2005 and was strengthened by private visits. The purpose was to learn whether it is technically and practically possible to perform a greater number of samplings and analyses among all EU MS in the case of new requirements.

4.5.1.1 Dioxin Sampling

In the UK, sampling can only be performed by accredited personnel operating in accredited organisations. The same holds for Germany and many other EU Member States. Concerning sampling activities, it seems that teams can be trained to perform such sampling according to EU norms in as little as two or three weeks. Then they need to get accreditation. Obviously, this training should be preceded by a careful selection of personnel involved, ensuring that the teams to be trained on the one hand are sufficiently motivated to operate under harsh climatic and working conditions and on the other hand are capable of operating consistently according to strictly normalized procedures [20].

It appears from interviews of 3 major sampling and analysis teams that:

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[20] Regulations in many countries require several years proven experience from the responsible project/team leader who is in charge of reporting. This requirement could lead to constraints in case such experienced technicians are not available locally.

- EU-wide, the existing dioxin sampling teams can perform more work than is required at present.
- Lack of sampling capacity, if any lack appears, will never be an issue in the EU15 but only in the new MS.
- Existing sampling teams can be educated to work according to EU norms (EN 1948) in two or three weeks [20].
- For people with no specific prior knowledge in sampling, a 2 to 3 months period is necessary to train them in the art of sampling

Therefore, according to the opinion of the professional sector, there is enough sampling capacity available at present. Still, should a problem arise in the short term, then this is likely to occur in the new MS. A pre-existing sampling team (trained for other pollutants and pollution sources) could be educated in a couple of weeks to work according to the relevant EU standards. If there is a long-term problem, new sampling teams could be created from scratch in only a few months.

Dioxin sampling is only one part of the problem, since the same team should also be able to perform the numerous other measurements on the stack in the course of a dioxin sampling campaign, all using a variety of instruments, equipment and tools. The associated data collection involves the measurement of gas flow, velocity and temperature, pressures, oxygen concentration, carbon dioxide and monoxide concentrations, nitrogen oxides, TOC, and dust load.

4.5.1.2 Dioxin Analysis

From interviews of laboratories it seems that approximately 30,000 to 40,000 (max 50,000) analyses (all activities merged) are yearly performed in the EU.

Among these analyses, 30% to 40% concerns dioxins present in food, 30% to 40% refers to dioxins in soil and only the balance, i.e. somewhat more than 20% are emission analyses derived from stack sampling and mainly concerning waste incineration. As a result, the analysis of dioxin emissions from metal industry accounts for only some 5 to 10% of the total number of dioxin analyses (25-50% of the total of emission analyses).

It should be seen that locally and for limited periods there may be a short term increase in the number of analyses required following a number of metallurgical enterprises or incineration plants encountering emission problems and commissioning frequent measurement campaigns. Another example is the Belgian dioxin crisis, during which all analytical capacity available was required for analysing a host of food samples.

Nowadays, there is a strong tendency towards concentration of dioxin analyses within a small number of dedicated highly automated laboratories. This happened as a result of a take-over moves, as well as from fierce competition between the remaining laboratories. This shows that there is no intrinsic lack of analytical capacity. As a result of this fierce competition, sample analysis that used to cost from € 1,000 to € 1,500 just a few years ago, now costs only between € 400 and € 450. As another result, the impact of academic and research laboratories in this analytical activity has lowered continuously with non-commercial laboratories being incapable of providing the necessary equipment for affordable automatic handling of sample extraction and purification for a large numerous of samples.

Moreover, if there were to appear any lack of analytical capacity, it is possible to carry out more analyses with the current methods and materials. Sampling preparation capacity can be increased by employing more staff and analysis capacity is easily increased by acquiring supplemental GC-MS[21] units

4.5.1.3 Conclusion

Therefore, **a new dioxin measurement requirement for the European metal industry appears to be technically feasible**.

4.5.2 Economic feasibility

Considering the relatively high cost of the complete dioxin measurement, i.e. including sampling and analysis, the financial consequences must be assessed for those companies which could be concerned by new dioxin monitoring requirements.

The analysis is based on a calculation of the relative importance of the measurement cost in comparison to the gross margin of the most sensitive (i.e. the smallest) installations and those who are considered by IPPC operating on the smallest added value margins.

4.5.2.1 Measurement cost[22]

The measurement of dioxin emissions sampled from stack gas and performed in accordance to the European standard EN 1948, costs approximately € 3,000 (for one day sampling at one stack), of which approximately 70% for sampling (~ € 2,100) and 30% for analysis (~ € 900).

Taking 3 samples on consecutive days will increase the costs to about € 6,000.

The prices mentioned refer to routine measurements as usually done for the repeated control of emissions, which is the relevant subject for this study. It should be noted, however, that a measurement campaign targeting at a plant description and a report on its actual operation, thus incorporating a wider set of emission variables, may be several times more expensive.

If scale effects exist, they are relatively weak, because sampling needs constant care and attention for 6 hours (inferring that a team cannot simultaneous sample several stacks all at once). In that case, the cost of each next measurement at the same site reaches € 2,500 to € 3,000.

These costs vary, depending on local competition factors, but are similar within the EU.

Regarding competition, there is some link between operators and sampling teams and continuity is regarded as an asset. Nevertheless, operators periodically require quotations from the team they use to work with.

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[21] Gas chromatograph – Mass spectrometer

[22] In this chapter (4.5.2), yearly emissions, capacities (cf. Table 17), number of measurements and cost are given per stack.

In addition to the external measurement costs, there are also some internal cost (personnel, administration etc.). This cost can be estimated as follow : 4 days * 250 €/day = 1000 €/measurement (this value is lower for several measurements). In view of its low level, these internal costs have not been included in the following analysis since it is part of the general operating costs of an installations but inclusion would not affect the main conclusions.

A further factor to be considered is the number of sampling points (stacks) per installation. Most of the facilities in question will have only one main flue gas duct where the sampling will be done. However, at some sinter plants with multiple strands there are separate stacks for each strand which discharge the primary emissions. (the opposite does also exist, thus reducing the number of stack/installation). Secondary dedusting from the hot crushing of sintered material may exist but may only be taken into account if primary emissions are significantly elevated (e.g. > 10 ng I-TEQ/Nm^3)

Also, EAFs usually have a primary and secondary flue gas collection system which not in all cases is unified to be treated by the same abatement system, thus generating the need for separate sampling. In particular and presumably rare cases, especially to be expected in the non-ferrous metal industry, one “installation” might consist of a battery of similar process units with separate emission points. In such cases it would be wise to check the similarity of emissions initially and, if this can be proven, to monitor only one of the emission points on a regular base with random checks of the other.

Exact data on the stack number per installation is not available. From the considerations presented before and the numbers of installations in question it is estimated that on the average the number of stacks per installation will not be higher than 2. Hence, using the cost estimates presented above (3,000 to 6,000 €/stack) and the numbers of IPPC installations that may be targeted by a mandatory monitoring requirement (from 600 to 1,500) the overall costs for the European metal industry could range from 1.8 to 18 million €/year [23].

This has no consequence for the analyses presented in the following parts since these are merely based on the specific cost per stack. Nevertheless, with regard to the overall costs expected for the whole industry the factor should be taken into account.

4.5.2.2 The relative importance of the measurement cost

The relative importance of the measurement cost in comparison to the gross margin[24] of installations can be calculated in several ways so that the financial burden on enterprise may be evaluated. In this sector, it is customary to consider production as a sequence of events within set margins, e.g. a copper refining margin.

Since this is customary in metallurgy, further evaluation is made using the following ratio:

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[23] It should be noted that the waste directive requires 2 measurements per year without defining the number of samplings. This may be interpreted as 2 samplings, as being done e.g. in Germany. German law actually requires 3 samplings which however may be combined in one measurement campaign carried out on consecutive days. On basis of this interpretation only one sampling per year would be required from the metal industry with therefore decreased maximum costs of 9 million €.

[24] The gross margin is only relevant for installations for which it can be calculated. In some cases (typically a sintering unit), the unit is a part of a production chain and no gross margin can be associated to this operation. The production cost is then more relevant and has been used.

$$\frac{\text{Cost of measurements (€/year)}}{\text{Gross margin (€/year)}}$$

$$= \frac{\text{Cost of 1 measure (€) * Measurement frequency (year}^{-1}\text{)}}{\text{Gross margin (€/t) * Production (t/year)}}$$

The lower this ratio, the less affected will be the economic viability of the metal industry, e.g., by monitoring requirements.

Hence, the ratio was calculated for different types of installation:

Table 17 Relative importance of measurement cost of the most sensitive installations

measurement cost = € 3 000					
Type of installation		minimum capacity per stack (ton/year)	gross margin (or production cost for sintering plants) (€/ton)	(€/year)	relative importance of measurement (%)
Iron ore sintering plants	Fe-ox	300 000	10	3 000 000	0.100%
Electric arc furnace	steel	15 000	88	1 320 000	0.227%
Waelz furnace for zinc recovery	ZnO	50 000	150	7 500 000	0.040%
Foundries	Fe	11 200	100	1 120 000	0.268%
				Maximum value of ratio	**0.268%**

The gross margin values are low estimates made by the team, based on his specific experience (partly supplemented by confidential operator's information).

Note : Minimum capacity is given per stack

We see from the table above that measurement cost is in most cases entirely negligible (i.e., less than 0.1%) compared to the gross margin of metallurgical plants but it can become more significant for very small facilities (max 0.268% for a facility with a € 150,000 gross margin) e.g. those in the foundry sector. It should be noted that administrative and management costs for the measurements are not included.

4.5.2.3 Conclusions

Based on the above elements, measurement cost is estimated to remain several orders of magnitude lower than the gross margin or production costs of enterprise. The metallurgical industry, generally speaking, can afford the cost of any reasonable measurement requirement.

4.5.3 Model for cost/precision analysis

4.5.3.1 Goal

When a measurement is performed it contributes to the reduction of the uncertainty about the dioxin emissions. The level of this reduction depends on :

- The plant flue gas flow (Nm^3/year)
- The dioxin concentration in the gas flow (ng TEQ/Nm^3)
- The number of measurements already performed
- The type of plant (degree of stability of the process and the emissions)

The first aim of this assessment is to **determine the reduction of the uncertainty** obtained by performing an additional dioxin measurement as a function of these four parameters.

The second aim is to determine **the optimized distribution of measurement efforts** (cost) among metallurgical plants. It is stated that this distribution will be optimized when measurements are performed where they will most contribute to the reduction of the absolute uncertainty. As this study does not analyse the benefits of measurements and the possible subsequent actions, the optimized absolute number of measurements cannot be determined. Therefore, this study only intends to optimize the distribution of measurement efforts for different hypothetical levels of acceptable uncertainty.

4.5.3.2 Approach – modelling assumptions

Calculation of the reduction in the uncertainty

A major assumption is that measured emission values are distributed around the average value according to a Normal distribution[25]. Therefore :

— the absolute uncertainty (AU) of a specific source (Probability =95%) =

$$\boxed{AU = (+/-)\ 1.96\ \sigma_{abs} / \sqrt{n}}$$

with

σ_{abs} : the absolute standard deviation

n : number of measurements per stack

1.96 : factor corresponding to a 95% chance that the average value is included within the uncertainty margin. As the same factor is

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[25] The assumption of a Normal distribution would hold in continuously operated installations which always have to deliver a similar product within small range of characteristics.

For discontinuous installations, operation conditions vary significantly in practice, and this variation is not by chance but by purpose (depending on the raw materials and product to be delivered). In this case, the uncertainty due to the variation of the emission value is larger than the uncertainty due to the precision of measurement and therefore such measurement cannot have a normal distribution.

It is indeed a well known characteristic in natural and also technical processes that the statistical distribution of measurement values often is not symmetrical, but is skewed to the side of lower values.
The same is observed for emission measurements, which usually have more "high" than "low" outliers which result in a asymmetric shape of the distribution function. This is particularly pronounced when the **mean** value is approaching zero, because low outliers then would mean to have negative values that do not exist. Therefore a log-normal distribution could be more appropriate.

However the error propagation model applied in our report needs normal distribution as a mathematical precondition. If a log-normal distribution would be used, the geometric mean would be used instead of the arithmetic mean and the error propagation would have to be changed accordingly. But to some degree, a log-normal distribution would still be erroneous.

Therefore and considering that the model only serves to give an impression about how an emission measurement strategy could be optimised with regard to an ensemble of different installations having a large range of emission levels, the inherent limitation of validity due to a normal distribution has been considered as acceptable applied to all calculations, it does not influence the calculation of the optimized distribution

This formula is not applicable for n=0 as this would mean that the uncertainty is infinite. In practice, it is not infinite as historical data from similar plants provide a relevant reference to determine the maximum emission level.
For the calculations to find the optimized distribution of measurement efforts, we assume that the uncertainty without any measurement is 100 times higher than with a single measurement (as this is the range of variations between similar plants).

The reduction in absolute uncertainty (RAU) due to an additional measurement is the difference between the uncertainty with and without this additional measurement.

— the reduction in absolute uncertainty (RAU) of a specific source =

$$RAU = 1.96\ \sigma_{abs} / \sqrt{(n+1)} - 1.96\ \sigma_{abs} / \sqrt{n}$$
$$RAU = 1.96\ \sigma_{abs} * (1/\sqrt{(n+1)} - 1/\sqrt{n})$$

as : σ_{abs} = average emission * σ_{rel}
with $\boldsymbol{\sigma_{rel}}$: the relative standard deviation

➔ $RAU = 1.96$ (average emission * σ_{rel}) * $(1/\sqrt{(n+1)} - 1/\sqrt{n})$

as : **average emission** =
flue gas flow (Nm^3/year) * dioxin concentration in the gas flow (ng TEQ/Nm^3)

➔ RAU (n+1) = 1.96 (flue gas flow * dioxin concentration * σ_{rel}) * $(1/\sqrt{(n+1)} - 1/\sqrt{n})$

This formula provides the reduction of absolute uncertainty as a function of the four above mentioned parameters, where the degree of stability of the process and the emissions is represented by the relative standard deviation of the process.

For n=0, we assume that

RAU (1) = 1.96 (flue gas flow * dioxin concentration * σ_{rel}) * 100

Calculation of the optimized distribution of measurement efforts

The RAU is calculated for :

- Different values of average emission
- Different values of n (number of measurements)
- Two types of process stability : stable and unstable (see further)

An optimal distribution of the measurement efforts is reached when the RAU is the same for all plants.

If measurement efforts are optimally distributed over the entire metallurgical sector, this will mean that the diminution of the absolute uncertainty on emission values affected by the last measurement is the same for all plants.

4.5.3.3 Input data for the model

Average emission

Yearly emission = flue gas flow rate (m³/year) * dioxin concentration (ngTEQ/Nm³).

The calculated tables consider a range of yearly emission from 1 µg TEQ/year to 100 g TEQ/year.

Relative standard deviation of dioxin emissions

The relative standard deviation is an aggregated value for two types of uncertainties:

- The variation of emissions with time, due to process instability
- The uncertainty about the measured value

1° Process instability

This is an important consideration linked to the appropriate value for the dioxin emission value. Past experience shows that there are many factors to consider :

1. The type of process. Some processes tend to generate high emissions while others have rather low values.
2. Raw materials, e.g. some are richer in chlorine or carbon than others.
3. Stochastic variations in operating conditions. Such factors can only be identified after extensive study.
4. The composition of the gas cooling train. Longer residence times, more deposits, higher frequency of critical temperatures enhance the generation of dioxins.
5. Memory effects. Heat exchangers store extensive deposits, enhancing emissions and also the evolution of dioxin with time.
6. Time effects. Gradual fouling of a boiler or cracks developing in filter sleeves both enhance emissions.
7. Accidental effects, such as leaks developing in filter sleeves or in valves in short-circuiting ducts over filter units, etc.

Consequently, individual dioxin emission values must not be regarded as being wholly representative of actual emissions. In a recent trial programme, earmarked to assess the effect of variables, dioxin emission values could be varied in a range 1:100 on industrial plant!

For the calculations, two extreme cases were used in the model:

— One is exemplified by means of a large, continuous plant, with rather limited time periods of inactivity and a steady influence of memory effects. Such emissions evolve fairly slowly and are termed '**stable'**. Even modified operating conditions or feed quality has only a limited influence upon dioxin emission.

— At the other extreme, one finds a plant, operating in a batch or in a cyclic mode. The emissions here being strongly related to each individual charge. There is no boiler or long flue lines equalising emissions by means of memory effects. Such are the conditions for obtaining '**unstable**' emissions.

2° Precision of measurement

Most uncertainty comes from sampling (due to non-reproducible emission values, mainly related to erratic variations in raw materials and process conditions). The sampling team does not control operating conditions.

For the calculations, the following parameters data are used (consultant's assumptions, regarded as realistic by 3 measurements labs):

- σ for stable processes (continuous processes using ores) = **60**%
- σ for unstable processes (batch processes or continuous processes using metal scrap) = **200**%

Those values include both types of uncertainties (process and measurement).

Number of measurements per stack

The number of measurements corresponds to a reference period during which there has been no significant change in the process that could influence the dioxin emission. A maximum duration for this period should be considered, e.g. 3 or 5 years.

4.5.3.4 Results

The two first tables presented in Annex H give the **absolute uncertainty** for a specific plant as a function of 3 parameters:

- Different values of average emission (from 1 µg to 100 g TEQ/year)
- Different values of n (number of measurements)
- Two types of process stability : stable and unstable (see above)

In the 3rd and 4th tables of Annex H, the ***reduction* of the absolute uncertainty** is shown as a function of the same 3 main parameters.
The values are the difference between two consecutive columns from the tables above. For example, for n = 5, the value is the difference between column 'n=5" and "n=4" from the tables above.

For example, to increase the number of measurements from 4 to 5 in a stable plant (σ =60%) that emits about 100 mg per year will reduce the uncertainty about the emission by $6.21*10^{-3}$ g/year.

Indeed, by making the development for this example:

RAU (n+1) = AU (n+1) – AU (n)

RAU (n+1) = 1,96 (average emission * σ_{rel}) * (1/√(n+1) – 1/√n)

➔ RAU (5) = 1.96 (0.1 gTEQ/year * 60%) * (1/√(5) – 1/√4) = 0.00621 gTEQ/year

In order to impose coherent requirements to the different plants, the reduction in absolute uncertainty due to the last measurement should be the same for all plants. The absolute level of uncertainty depends on the cost that is considered acceptable to reduce this uncertainty.

This cost reflects what public authorities consider as acceptable cost to decrease uncertainty. The values for acceptable cost used in the following tables correspond to the reduction in uncertainty by 1gTEQ/year per plant. Of course, the lower the acceptable cost, the less the number of measurement required.

E.g. if Public Authorities consider it is acceptable to spend 1000 € to reduce the uncertainty by 1gTEQ/year per plant, then it is worth to perform a measurement if the uncertainty decreases by more than 3gTEQ/year (3000€ / 3 g = 1000€/g) and measurement should not be performed if the uncertainty decreases by less than 3 g.

The following table summarizes all results as it gives the optimal number of measurements per stack for different (see also the full tables in annex I)

- Yearly emissions
- Process stabilities
    - σ for stable processes = 60%
    - σ for unstable processes = 200%
- Values of acceptable cost to reduce the uncertainty.
    - 1,000 €/ (gTEQ/year)
    - 10,000 €/ (gTEQ/year)
    - 100,000 €/ (gTEQ/year)
    - 1,000,000 €/ (gTEQ/year)

Table 18 Optimal number of measurements per stack for different parameters

Optimal number of measurements

Measurement cost : 3000€ Probability coefficient : 1.96			Parameters							
		σ_{rel}	60%				200%			
		AC [€/(gTEQ/year)]	1 000	10 000	100 000	1 000 000	1 000	10 000	100 000	1 000 000
		MC/(AC*1.96*σ_{rel})	2.5510	0.2551	0.0255	0.0026	0.7653	0.0765	0.0077	0.00077
Yearly emission	3	µg TEQ/year	-	-	-	-	-	-	-	-
	5		-	-	-	-	-	-	-	-
	8		-	-	-	-	-	-	-	1
	10		-	-	-	-	-	-	-	1
	20		-	-	-	-	-	-	-	1
	30		-	-	-	1	-	-	-	1
	50		-	-	-	1	-	-	-	1
	80		-	-	-	1	-	-	1	1
	100		-	-	-	1	-	-	1	1
	200		-	-	-	1	-	-	1	1
	300		-	-	1	1	-	-	1	1
	500		-	-	1	1	-	-	1	1
	800		-	-	1	1	-	1	1	1
	3	mg TEQ/year	-	1	1	1	-	1	1	2
	5		-	1	1	1	-	1	1	2
	8		-	1	1	1	1	1	1	3
	10		-	1	1	2	1	1	1	4
	20		-	1	1	3	1	1	1	6
	30		1	1	1	3	1	1	2	7
	50		1	2	3	4	5	6	7	8
	80		1	1	1	6	1	1	3	14
	100		1	1	2	7	1	1	4	16
	200		1	1	3	12	1	1	6	26
	300		1	1	3	15	1	2	7	34
	500		1	1	5	21	1	2	10	47
	800		1	1	6	29	1	3	14	65
	3	g TEQ/year	1	3	15	70	2	7	34	157
	5		1	5	21	99	2	10	47	220
	8		1	6	29	135	3	14	65	249
	10		2	7	34	157	4	16	75	249
	20		3	12	54	249	6	26	120	>250
	30		3	15	70	249	7	34	157	>250
	50		5	21	99	>250	10	47	220	>250
	80		6	29	135	>250	14	65	249	>250
	100		7	34	157	>250	16	75	249	>250
minimum emission to require measurement (mg TEQ/year)			30	3	0.3	0.03	8	0.8	0.08	0.008

Let’s consider the case where the acceptable cost is € 1,000/(gTEQ/year).
The table indicates that, according to the model developed, a plant would have to perform a number of measurements that depends on its yearly emission (for a stable process) :

- If yearly emission < 30 mg/y, then n=0
- If 30 mg/y ≤ yearly emission ≤ 8 g/y, then n=1
- If yearly emission = 10 g/y, then n=**2**

- If yearly emission = 50 g/y, then n=5
- …

Comparing a stable and an unstable process, this table shows that :

- the higher the process stability, the less will be the optimal number of measurements according to the acceptable cost.
  (see also charts presented in Annex I)
- to guaranty that the reduction in absolute uncertainty due to the last measurement will be the same for all plants, the lowest yearly emission for which the model require a first measurement must be between 3 and 4 times lower for a unstable process in comparison to a stable process (see last row of table above).

Graphical presentation of the results

The following figure presents the absolute uncertainty versus the number of measurements performed at a stable installation emitting 10 g TEQ/year.

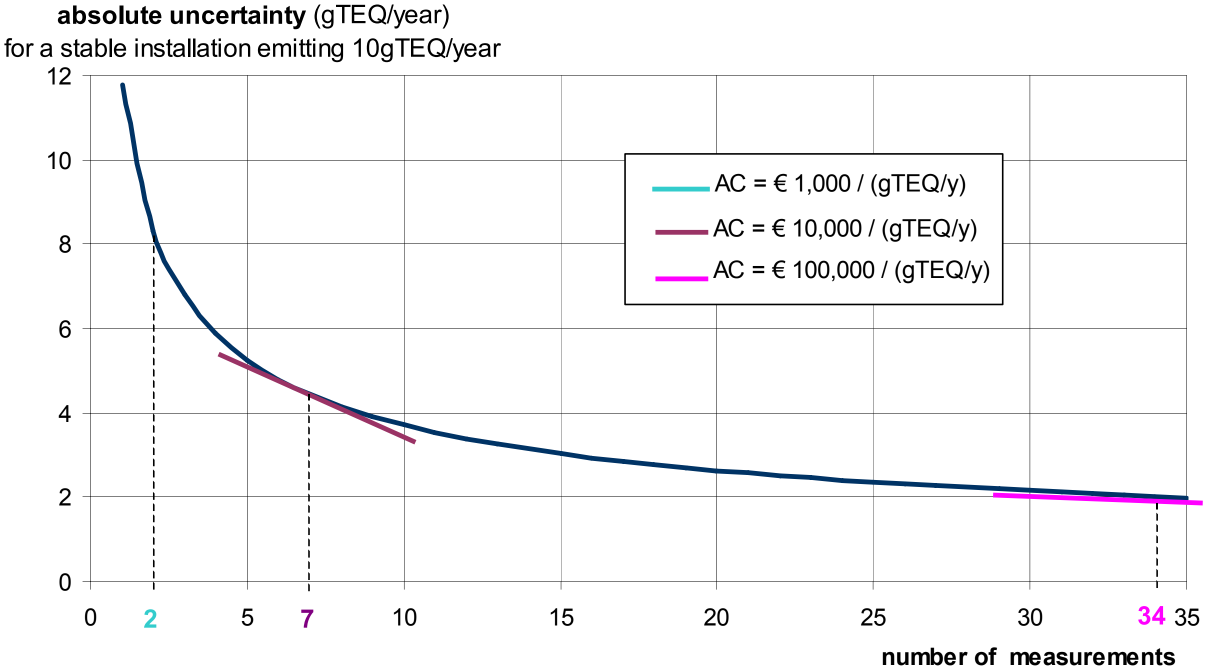

Figure 11 Absolute uncertainty versus the number of measurements performed at a stable installation emitting 10 gTEQ/year

As the measurement cost is fixed, the X-axis of this curve also represents the cost of measurements. The derivate (tangent angle) of the curve is thus the marginal cost of reducing uncertainty. Therefore, the optimal numbers of measurements corresponds to the point of the curve where the tangent angle is equal to the acceptable cost.

In the case of this installation, if the acceptable cost is € 10,000/(g TEQ/year), the tangent angle for this value corresponds to **7** measurements. This is thus the optimal number of measurements.

Approach by formula

The following tables represent how is select the optimal number of measurements to perform by application of the formula described above.

In the case of this installation, if the acceptable cost € 10,000/ (g TEQ/year), the optimal number of measurements corresponds to the lowest reduction value greater than 1.

Table 19 Optimal number of measurements to perform at a stable installation emitting 10 gTEQ/year for increasing acceptable costs

	n	**Reduction in Absolute Uncertainty (gTEQ/year) per € 1,000** = 1.96 (average emission * σ_{rel}) * (1/√(n+1) – 1/√n) * € 1,000/€ 3,000
➡	**2**	**1.15**
	3	0.51

	n	**Reduction in Absolute Uncertainty (gTEQ/year) per € 10,000** = 1.96 (average emission * σ_{rel}) * (1/√(n+1) – 1/√n) * € 10,000/€ 3,000
	5	2.07
	6	1.53
➡	**7**	**1.19**
	8	0.96

	n	**Reduction in Absolute Uncertainty (gTEQ/year) per € 100,000** = 1.96 (average emission * σ_{rel}) * (1/√(n+1) – 1/√n) * € 100,000/€ 3,000
	33	1.06
➡	**34**	**1.01**
	35	0.97
	36	0.93

Obviously, the higher the acceptable cost, the higher the optimal number of measurements and the lower the reduction of uncertainty per additional measurement.

In the case of this installation and according to the model developed, the table below presents the reduction in absolute uncertainty per additional measurement for different acceptable cost values.

Table 20 Reduction in absolute uncertainty per additional measurements to reach the optimal number of measurements to perform at a stable installation emitting 10 gTEQ/year

σ_{rel}	60%		
AC [€/(gTEQ/year)]	1,000	10,000	100,000
optimal number of measurements	**2**	**7**	**34**
reduction in absolute uncertainty (gTEQ/additional measurement)	3.44	0.36	0.029

Of course, This is only a **theoretical example**. It aims to show that, if a measurement is required at a stable installation emitting 0.3 mg TEQ/year, 34 measurements must be required at a stable installation emitting 10 g TEQ/year <u>to guaranty that the reduction in absolute uncertainty due to the last measurement will be the same for all plants</u>

The following figure presents the optimal number of measurements for a stable installation as a function of the yearly emission and the acceptable cost.

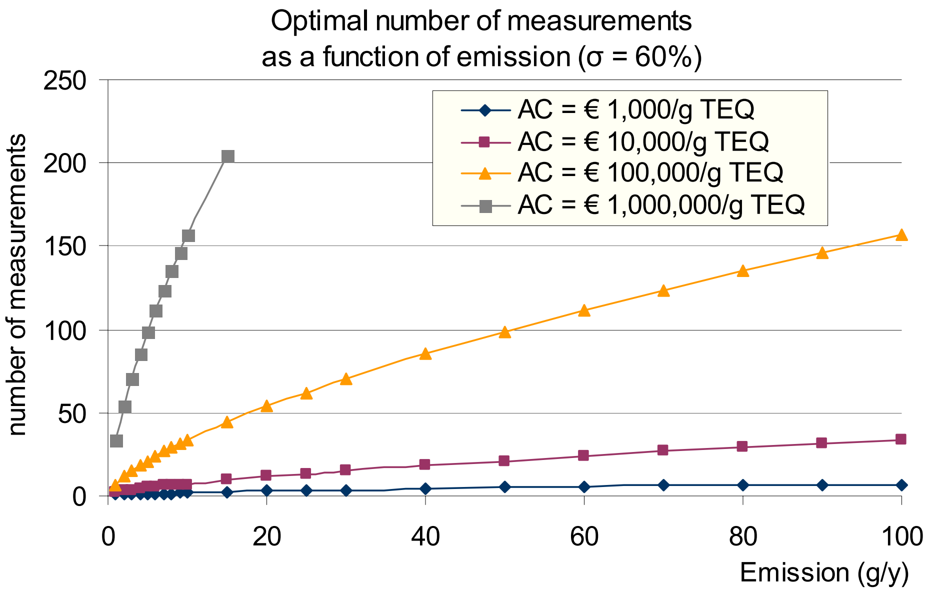

Figure 12 Optimal number of measurements per stack as a function of a stable plant emission for different acceptable cost

As shown in the tables and figures presented in Annex I the number of measurements will obviously be greater for an unstable plant.

4.5.3.5 Conclusions

This model has been developed to estimate the uncertainty about the dioxin emission and to calculate the optimal number of measurements per stack as a function of 5 parameters:

- The plant flue gas flow (Nm^3/year)
- The dioxin concentration in the gas flow (ng TEQ/Nm^3)
- The number of measurements already performed
- The type of plant (degree of stability of the process and the emissions)
- The acceptable cost to reduce the uncertainty about the emissions.

It appears that :

- Measurement efforts should be focused on large emitters
- Measurement frequency should be 3 to 4 times higher for unstable processes
- For small emitters measurement is not relevant with respect to the reduction of the overall uncertainty in dioxin emissions from metal industry

5 Discussion of background data

In the previous chapters, the available information has been compiled regarding:

- the processes in metallurgy with relevant dioxin formation potential

- the number of installations in the metal industries covered by the IPPC Directive and of potential relevance for dioxin emissions
- the relevance of dioxin emissions from metal industry sectors compared to other industrial and non-industrial emission sources
- the data provided by the EPER and any apparent data gaps within this inventory
- the current regulations – emission limit values and monitoring requirements – being applied to metal industry in the EU Member States.

In addition, the capacities of laboratory and sampling teams in the EU Member States has been assessed. Furthermore, an analysis of the affordability of measurement costs as well as a study on the number of measurements required to decrease the uncertainty in emission inventories to an acceptable level have been presented.

From this background information, the following conclusions can be drawn:

1. In the European metallurgical industry, a large variety of thermal production processes are in use, with some occurring quite frequently and others being almost unique. With respect to dioxin formation it is difficult to both exclude processes and predict emission values from process parameters. Some general rules exist to assess the dioxin formation potential but measurement is the only way of knowing for sure. However, from experience gained by measurement programs carried out during the last decade, major and minor emission sources can be distinguished. However, there is still a risk that processes not investigated so far might reveal to be significant sources.
2. The number of installations which may be considered under the IPPC Directive covers most of the known major emission sources and some emission sources of medium and minor relevance.
   The processes to be considered as major sources include
      iron ore sintering plants (IPPC Annex I, 2.1)
      Electric arc furnaces for steel production from scraps (IPPC Annex I, 2.2)
      the Waelz process plants, for the recovery of zinc oxide from dust arising in the iron & steel sector (IPPC Annex I, 2.5a)
      Installations for smelting secondary non-ferrous metals (IPPC Annex I, 2.5a), in particular from scraps.
      Installations for melting and alloying metals, in particular in the presence of copper (IPPC Annex I, 2.5b).

   In addition, ferrous metal foundries (IPPC Annex I, 2.4) do belong to the installations which are of concern. However, due to the capacity limit threshold set by the IPPC Directive, only a small fraction of the existing installations can be targeted.
   The categories 2.3 and 2.6 of the IPPC Annex I comprise installations which are not suspected to be dioxin emission sources.

3. It appears difficult to get exact figures on the numbers of dioxin relevant installations. From various sources of information an overall number of ca. 5,000 installations, including about 4,200 foundries, could be estimated for the EU 25. As already mentioned only a part of these are covered by the IPPC Directive, presuming up to 1,500. They comprise
   ca. 50 iron ore sintering plants
   ca. 250 electric arc steel plants
   8 Waelz kilns for zinc oxides recovery processing EAF filter dust
   ca. 300-600 secondary non-ferrous metal smelters
   up to 400 ferrous and non-ferrous foundries (out of ca. 4,200 being operated in the EU)

4. Dioxin inventories compiled at the national or EU level in the recent years have shown that the metal industry is a sector that significantly contributes to the overall dioxin emissions. The metal industry's share of total emissions is estimated to be about 20% and up to 50% of all industrial sources. Clearly the emissions are dominated by sources in the iron and steel sector whose emissions are is higher by a factor of 3 to 4 than those of the non-ferrous metal sector.

5. From comparison of the emission data provided by the European Pollutant Emission Register (EPER) with the number of relevant installations found in this study, it appears highly probable that significant emissions are caused by those installations which are not registered. In the case of the metal sector, the EPER system failed to achieve the goal set by the EPER decision to include 90% of the emissions.

6. The high relevance of metal industry sources compared to other industrial processes for monitoring activities, though known, is not yet mirrored by appropriate regulations in the Member States. As yet, there is a number of countries with no regulation at all despite the presence of significant metallurgic industry. Some MS have performed some screening measurements at metal industry installations but without requirements for repeated monitoring. A considerable number of other MS others have already implemented general or process specific emission limit values. The monitoring requirements – as set by the national regulations or in case by case - in the metal industry are however largely variable, ranging from several measurements per year down to one measurement in 3 years or even less. In some countries, e.g. in the Flemish part of Belgium much more intense monitoring requirements have been set for some installations on a case by case basis within the operational permits.

7. The costs of dioxin emission measurements are considerably higher than those for other compounds. For a single-day measurement (including laboratory analysis) costs of about € 3,000 are typical. A 3-day campaign may take some € 5,000. Assuming one measurement per year, these costs are low compared to typical gross margins. However, hidden costs spent on administrative efforts and operator's support of the measurement team, must be taken into account as well as the fact that some installations may have more than one stack where samples must be taken. Therefore, although the costs for dioxin emission measurements appear to be affordable, at least for larger installations, in certain cases they might become substantial, in particular when very high emission is reported and regular

monitoring is necessary. It is assumed however that such cases are rare due to the fact that the IPPC Directive particularly concerns installations with a minimum capacity.

8. The existing laboratory capacity in the EU 15 member States is assessed to be sufficient even in the case of increasing monitoring requirements. A lack of sampling teams might exist in the new Member States which could be overcome on the short term by subsidiary action from old MS or foundation of new local teams in the medium/long term.
9. With respect to the aim of reducing the uncertainty in the emission estimates at national or EU level, it appears favourable to direct more intense monitoring requirements to installations with higher emissions. However, depending on the actual distribution of emissions a mixed monitoring approach, also addressing low and medium emissive installations, could make optimal use of available financial resources.

Putting these conclusions into a general picture it appears obvious that **the metal industry is a factor to take into account when it comes to the evaluation of industrial dioxin emissions** and that this has already been recognised by many Member States. However, **there is still considerable uncertainty** on the actual situation and on the past and future development of these emissions since much of the information is derived indirectly and not based on emission measurements. **Occasional measurement programs, although highly appreciable as a first step, do not seem to be sufficient to get a comprehensive view of the emission situation and are not appropriate to detect trends.** This might be an obstacle when developing appropriate national strategies for long-term reduction of dioxin emissions. Even in those countries with a national regulation of monitoring requirements, **the frequency of measurements is often quite low** (e.g. in comparison with two annual measurements required from waste incinerators). **This practice must be considered as inadequate** particularly in the case of installations with highly unstable operating conditions.

6 Options for EU-wide dioxin monitoring requirements

In the previous chapters, the information has been compiled and analysed in order to assess the current situation with respect to

1. the uncertainty of current assessments of the general dioxin emissions from the metal industry
2. the current dioxin emission monitoring at installation level.

It was concluded that the situation does not appears to be satisfactory since both the overall knowledge on the dioxin emissions is considerably uncertain and the monitoring practice in the EU Member States is highly variable, with many countries not applying systematic approaches undertaking of comprehensive and repeated surveys for the main sources.

The question to ask is whether this undesirable situation is caused

- by incomplete or delayed implementation of the IPPC Directive
- by inappropriate requirements set within the existing legislation, or

- by a lack of appropriate and harmonised measures (monitoring requirements) in the European Union.

In the first case it would more or less be a matter of time until the situation improved. In that case, no additional measures would be needed. This option is called the “no policy change” option, which will be briefly discussed in the next section.

In the second case, an option for achieving the desired state could be to make slight changes to the existing regulations, setting incentives for more appropriate treatment of dioxin emissions and closing loopholes. This option may be called the “improved instruments” option and is discussed in section 6.2

Finally, evidence or strong indications may be found that additional regulations, e.g. EU-wide monitoring requirements, are needed to reach the desired results. In this case, called the “measurement requirement” option, numerous technical and organisational issues must be considered and are described in section 6.3.

6.1 „No Policy Change“ option

Whether or not emission limits and monitoring requirements would be set in a specific permit depends on the assessment of the issue by competent authorities. According to the integrated approach of the IPPC Directive a trade-off of diverging requirements may be done to ensure an overall optimised operation based on BAT. Such trade-off processes could lead to an inappropriate treatment of potential dioxin emissions, particularly if no measurement results have become available previously. Thus, for all installations passing the permit procedure without such permit conditions, there will be no apparent reason to carry out measurements.

The question to ask with respect to the no policy change option is whether there is evidence that competent authorities usually hesitate to set emission limit values and monitoring requirements where dioxin formation is probable. Such evidence can only be derived from information from already executed IPPC permit procedures.

The IPPC Directive was adopted in 1996 and meanwhile has been transposed in all Member States. The full implementation must be accomplished by October 2007 through the granting of permits to all existing installations covered by the Directive.

From an analysis of the first official Member States reports on the implementation issued in June 2004 [3], the conclusion was drawn that there was substantial variation between the Member States regarding the degree of implementation. Concern was raised that in several Member States a disproportionate number of permit applications will be filed immediately prior to the deadline. This could lead to an increased load on the competent authorities and thus to delays in the permitting procedures.

In the metal industry sector (Annex I, 2 of IPPC Directive), the fraction of granted IPPC permits compared number of the existing installations was significantly higher than the above mentioned average. Unfortunately no data is available for the sub-categories, so many of the permits could have been granted to installations which are not relevant for dioxin emissions.

However, additional information is provided in the same report about whether dioxin emission limit values existed or have been set, respectively, during the 1st 3-year reporting period for existing and new installations (Table 21). From that data it is obvious that only few countries in the former EU already apply emission limit values to metal industry installations. It should be noted in addition that the ELV for existing installations in Italy is the general ELV for industrial installations and was already issued by 1990, being set to 0.01 mg total dioxins/Nm³. Depending on the profile of emitted dioxin congeners, it can be estimated that this ELV converts to a range of 100-500 ng I-TEQ/Nm³ which is orders of magnitude higher than all other currently applied ELVs.

Table 21 Overview on information about PCDD/F emission limit values applied to existing or set for new installations during the reporting period 2000-2003;
data taken from [6]; „+“: ELV set; „-“: no ELV; „0“: no installation; blank field: no information [26]

PCDD/F limit values set for existing installations (either national or case by case)

Cat	sub-cat.		AT	BE	DK	FI	FR	DE	EL	IE	IT	LU	NL	PT	ES	SE	UK
2.1	2.11	Copper ore roasting or sintering	0	**+**	0	-	0	+	0	0	+	**0**	0	0	-	+	
	2.12	Zinc ore roasting or sintering	0		0	-	-	+	0	0	+	**0**	-	0	-		
	2.13	Iron ore roasting or sintering	+		0	-	-	+	0	0	+	**0**	+	0	-	-	-
2.2		Pig iron/steel production	+		-	-	-	+	-	0	+	**+**	-		-	-	-
2.3		hot-rolling mills	+		-	-	-	+	-	0	+	**-**	-	0	-	-	+
2.4		Ferrous foundries	-		-	-	-	+	-	0	+	**0**	+		-	-	-
2.5	2.5a1	aluminium prod. from ores	0		0	0	-	+	-	0	+	**0**	-	0	-	-	-
	2.5.a2	aluminium prod. from sec. raw materials	+		-	-	-	+	-	-	+	**+**	+	0	-	+	-
	2.5.a3	zinc prod. from ores	0		0	-	-	+	-	0	+	**0**	-	0	-	-	

PCDD/F limit values set for new installations in 1st IPPC reporting period (2000-2003)

Cat	sub-cat.		AT	BE	DK	FI	FR	DE	EL	IE	IT	LU	NL	PT	ES	SE	UK
2.1	2.11	Copper ore roasting or sintering	0		0	0	0	0	0	0	0		0	0	0	0	
	2.12	Zinc ore roasting or sintering	0		0	0	-	0	0	0	0		0	0	0	0	
	2.13	Iron ore roasting or sintering	0		0	0	0	+	0	0	0		0	0	0	-	
2.2		Pig iron/steel production	PCDD/F not mentioned in the report														
2.3		hot-rolling mills	+		0	-	-	+	0	0	0		0		-	-	
2.4		Ferrous foundries	0		0	-	0	+	0	0	0		+		0	0	
2.5	2.5a1	aluminium prod. from ores	PCDD/F not mentioned in the report														
	2.5.a2	aluminium prod. from sec. raw materials	0		-	0	0	+	0	0	0		+	0	-	0	
	2.5.a3	zinc prod. from ores	0		0	0	0	+	0	0	0		0	0	0	0	

Putting this information together it appears obvious that in most countries the inclusion of PCDD/F emission limits was not a frequent practice in the IPPC permit procedures carried out so far. Based on the information available, it is not possible to finally decide if this is because the permits were largely granted to installations without dioxin emission potential or if it indicates inappropriate awareness to a considerable degree of the dioxin problem.

In the latter case there must be concern that even after full implementation of IPPC permits based on BAT, the fraction of installations with dioxin monitoring requirements will be less than desirable.

Moreover, in case of the EPER there is no requirement to report emissions on the basis of measurements. Therefore, calculated and estimated emission values must be accepted. Most, but not all, of the metal industry facilities registered in EPER reported measurement results as the basis for their annual emissions. These few installations are only the “tip of the

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[26] Notes:
DE (existing inst.): : Target value of 0.1 ng I-TEQ/m³
PT: case by case analysis generally applied in IPPC permit procedure
bold symbols: information obtained by industry comments

iceberg“, comprising maybe 10 % or less of the potentially relevant installations in the EU (c. f. section 4 of this study). According to current plans on the advancement of the EPER to an EPRTR, neither this situation nor the EPER threshold limit will change. Hence, it appears probable that the state of information about the major dioxin emission sources in the EU metal industry will continue to be afflicted with significant uncertainties.

The previous considerations lead to the conclusion that a “no policy change” option would not be favourable to achieve the two goals of decreasing uncertainties in the European dioxin emissions and assuring appropriate treatment of the issue by the Member States at the installation level.

6.2 “Improved instruments” option

As outlined in the introduction to this section, improvements with respect to the overall uncertainty on dioxin emissions could be achieved by sharpening the existing instruments. In the framework of the IPPC Directive these instruments are

- the directive itself
- the BREF documents
- the EPER

With regard to the Directive, a more appropriate consideration of PCDD/F emissions could be achieved if the particular importance of this pollutant is stressed in the directive. This could be done by inserting a corresponding paragraph into the preamble of the Directive, e.g. following No. 17 of the Directive. Such an additional clause could be formulated like

> ”whereas with regard to the Community Strategy on Dioxins, Furans and Polychlorinated Biphenyls the emission of these pollutants needs particular consideration“.

In the BREF documents relevant for the metal industry installations, the issue of dioxin formation is taken into account quite comprehensively. However, frequently the impression is induced that dioxin formation could only occur in extreme cases or may be considered as an exception. It might be useful to improving awareness of operators and competent authorities to check the corresponding parts of the BREFs and to reformulate those parts in order to emphasise that dioxin formation cannot be ruled out in the first place and must therefore be taken into account when decisions on the BAT is made.To assure that new insights and developments as well as most recent inventory results are taken into account a regular updating process of the BREF documents would be needed.

Finally, the reporting procedure to EPER could be improved considerably. As yet, in some countries operators, may declare their emissions to be “zero” if the EPER threshold limit is not exceeded. Apparently there is no obligation to justify such an assessment. This practice appears to be highly inefficient, since operators have to make a declaration anyway and in many cases will do some calculations or even measurements to decide on whether they must register their installation with EPER or not. Neither for operators nor for the authorities would there be an unaffordable rise of effort if the actual emission value were reported instead of “zero” values. Such data, once collected by the authorities and checked by them for plausibility, could be very useful to assess the emission situation more comprehensively and accurately and to address policy measures more efficiently. The obligation to report actual emission values (still based on estimates, calculation or measurements) could be addressed particularly to the metal sector, thus leaving other less relevant sectors unaffected.

6.3 "Monitoring requirement" options

The most far reaching option to reach the desired goals is to set minimum EU monitoring requirements for dioxins and furans. As simple as this option seems at first glance, it is as complicated in reality since it opens a wide range of consecutive possibilities and options. Options on monitoring requirements may differ from each other by the scope, the selection and the detailed description of the types of installations covered and by the details of the monitoring procedure being fixed. These issues are discussed in more detail in the following sections.

6.3.1 Scope of covered processes/installations

The most important issue is obviously to define the criteria for inclusion of given plant in future monitoring requirements. Some major possibilities for such a selection are:

I. Option I : Short List of notorious Dioxin Generators.

Limit the requirements to an inclusive list of operations that are sufficiently large scale, widespread, well-identified, and notorious sources of dioxins, thus explicitly excluding all minor or non-identified sources from further scrutiny. Such a list would certainly include the major iron & steel emission sources, i.e. sintering plants, EAF, treatment of filter dust from iron & steelmaking (cf. Waelz process) and also a number of operations involving the treatment of scrap. The latter category in particular includes ferrous scrap, because of the large scale of the related operations, as well as Al, Cu, Pb, Zn … scrap, because of the high emission factors recorded at times during their treatment. It would *not* include all kinds of smaller, unique or less usual operations, or target unidentified and uncertain sources.

II. Option II Define **conditions** potentially **leading to Dioxin Generation**.

No processes are mentioned, but rather those conditions (processes, operating conditions, heat recovery options, and raw materials) likely to lead to dioxin formation and hence eligible for further dioxin emission monitoring. This option leaves more room for individual interpretation on the part of the Authorities of individual Member States. It may adapt the local selection to the historical, economic, and social context prevailing.

Those possibleconditions are treated more fully **in Annex D.**

III. All eligible IPPC Plant

The option with the widest scope would cover all IPPC installations in the European metal industry, whether ferrous or nonferrous, except for those which a priori can be excluded (categories 2.3/2.6).

Each option has specific merits, as well as shortcomings.

Option I has the merit of simplicity and clarity. The important sources are all explicitly identified and must be monitored. Since sources are all large and undisputed, the socioeconomic benefits are obvious and the costs bearable. In addition, since minimum EU requirements would be set this could be combined with a comprehensive, nationwide approach addressing a complete inventory of all sources and tracking all possible sources of dioxins.

Option II paves the way to applying a maximum of subsidiarity, which while opening numerous new possibilities for tracking hitherto unknown sources, still leaves ample and adequate room for adapting the new monitoring requirements to the specific local historical, economic and social factors. However, the application of such option is likely to bring an non-uniform monitoring of dioxins across the EU, even for the largest sources. In addition, this would be technically difficult to check the compliance with such technical conditions.

Option III would be an extreme case because not only sources with proven or expected dioxin emissions but also many irrelevant installations would be targeted. At first glance being logical due to the direct link to the IPPC Directive this option certainly would cause inappropriate and excessive workload and costs to both, industry and operators.

6.3.2 Details of monitoring procedure

With respect to the details of monitoring procedure there are two major options:

- Leaving all details of execution to the established bodies, who will organise the preparation and publication of standards, the accreditation of laboratories, the organisation of round-robin tests, etc. with only a brief reference to these details.
- Fixing minimum requirements, such as those enumerated below:
    a. Acceptance procedures for already existing measurement results.
    b. Number and frequency of required additional emission measurements.
    c. Time period for carrying out the measurements.
    d. Measurement methods to be applied.
    e. Reporting procedures, including a description of the plant, the raw materials used and the operating conditions during testing, the flue gas flow, conditions, and composition, its dust content and composition, etc.

Following these parameters a – e will be discussed briefly.

6.3.2.1 Acceptance of previous measurement data

Regarding the inclusion of inventories and the acceptance of measurement data, which already are available prior to the introduction of monitoring requirements, some decisions should be made on

- the maximum time previous results may date back in order to be still acceptable, i.e. being considered as still representative for the emissions from the plant.
- criteria for the requirement of a new measurement even if the last measurements fits to the allowed period (e.g. if major changes to the plant, to the effluent treatment, or to the raw materials used occurred in the meantime).
- quality of measurement data that will be deemed satisfactory (this is related to the requirements on reporting, see below)

6.3.2.2 Applicable measurement methods

A survey on available methods of emission measurement is presented in ANNEX F and summarised in Table 22. From this survey the following conclusions can be drawn:

- In practice the manual, (discontinuous) standardized and validated measurement methods (e.g. EN 1948) are almost generally used and can hence be recommended. These measurement methods, developed for waste incineration plants, are transferable to the metallurgical industry and are already in use there[27].
- Semi-continuous long term sampling methods essentially apply the EN 1948. In waste incineration and similar industrial sectors this kind of sampling is also often used and in Belgium it is even mandatory. Provided a high frequency of discontinuous measurements is required, these methods may be regarded as competitive to the manual sampling due to a high degree of automisation. In case numerous stacks have to be monitored with different frequencies the usual discontinuous sampling methods are advantageous References from the metallurgy industry are not available as yet, except for a comprehensive application made at Umicore, Belgium (see Annex F).
- Surrogate and indicator compounds are substances which show a close correlation to the PCDD/F concentration. PCBz and PCPh are the compounds which are proposed most frequently as surrogates. The results for different incineration plants and metallurgical processes are often between $r^2 = 0.92\text{-}0.98$. Correlations from surrogate compounds in relation to The I-TEQ of PCDD/Fs are more or less strongly process dependent and cannot be generalized. In each individual case a joint measurement and result validation program has to be carried out to prove the correlation to the I-TEQ of PCDD/F and its sensitivity to changing process conditions.

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[27] Some problems have been identified, though, relating to the reproducibility of measurements taken on stacks that are far larger than is usual in MSW incineration, e.g. in sintering plant.

From the responses to both the project questionnaires and the discussion during the first workshop it became clear that only those methods leading to results which are accepted by authorities should be applied in any future monitoring requirement.

Table 22 Survey on Measurement methods for PCDD/F in flue gases

Methods	PCDD/F emission concentration, Dust loading, other organic compounds (PCB); Validation; References
Discontinuous monitoring	
EN 1948 (European guideline)	PCDD/F ≈ 0.1 ng I-TEQ/m³; dust loading up to 15 mg/m³; dioxin-like PCB inclusive, no limited sampling time, validated for waste incineration plants; metallurgical processes possible
VDI 3499 (German guideline)	Part A: PCDD/F ≈ 0.1 ng I-TEQ/m³; dust loading up to 15 mg/m³, Part B: PCDD/F > 0.1 ng I-TEQ/m³, higher dust loading, tarry particles possible, raw gas possible, Part A and B: sampling time up to 8 hours, PCB and other organic pollutants possible; validated for waste incineration plants; metallurgical processes possible
EPA 23 A (American guideline)	PCDD/F ≈ 0.2 or 0.4 ng I-TEQ/m³; Dust loading = no information (up to 15 mg/m³), PCB and other organic pollutants possible (no information), Validated for waste incineration plants (no information)
Continuous monitoring (Long-term sampling)	
AMESA	PCDD/F ≈ 0.0001 – 10 ng I-TEQ/m³; Dust loading up to 20mg/m³; many references for waste incineration plants
DMS	PCDD/F ≈ 0.0001 – 10 ng I-TEQ/m³; Dust loading up to 150mg/m³; many references for waste incineration plants
Surrogates	Correlations to I-TEQ of PCDD/F process dependent, calibration necessary; some references for metallurgical processes
Future developments	
Short term sampling	PCDD/F < 0.1 to > 1.0 ng I-TEQ/m³; Dust loading up to 1 g/m³; references for waste incineration plants
Bioassays	Sum I-TEQ-substances as results (references for food and feed)
Biosensor	New development from Japan, not available on the market, no references

6.3.2.3 Number/frequency of additional measurements

Within Member States having already regulations for the monitoring of dioxins in the metal industry, the required frequencies vary considerably between a maximum of several times a year down to 1 measurement in 3 years.

Regulation on monitoring requirements also needs to define how many measurements should be carried out and the frequency of measurement repetition. The demanded frequency may be set to a common value for all plants or may rather be determined individually in consideration of operating conditions, emission levels, total emissions, plant capacity, the presence of boilers and heat exchangers, of dust cleaning equipment, or of abatement using adsorptive or catalytic systems. Lower frequencies might be satisfactory in the case of stable, continuous processes, having relatively low emission levels, while increased measurement efforts may be needed to characterise the emissions from a batch-wise operated process with large batch to batch differences in emissions. Recently, during a single testing programme, a ratio of 1:100 was noted between the lowest and the highest emission level.

6.3.2.4 Period for measurement execution

Besides the frequency of measurement, the time period should also be defined for which the new requirements are valid, as well as a deadline for providing the first measurement. The period could be made dependent on the estimated or the actually recorded emission level. It could be dynamically changed (lowered) in case the emissions are decreased by permanent preventive or abatement measures. The deadline for first reporting has also to be set in order to avoid unreasonable delays.

6.3.2.5 Reporting requirements

To ensure the quality of emission measurement reports it is advisable to suggest or even demand a standard format, providing all the information needed to check if the measurements were done appropriately. The European standard EN1948 and those standards referred to therein require a considerable number of pieces of information to be provided with the report. However, no standardised reporting format exists as yet at the European level. Some MS (e.g. Germany) have developed such standard reporting formats on their own which, however, are not dioxin specific. In Annex G, the information which could be provided in connection with a measurement report and the technical/scientific aspects that have to be taken into account are presented in more detail.

Some other aspects to be considered are:

- Data format. While some protocols only mention a total TEQ-value, the large majority gives a figure for the “dirty 17” congeners, and some also state the 5 PCDD and the 5 PCDF isomer groups. As a rule, maximum transparency should be encouraged.
- Fingerprints. Some enterprises supply fingerprints on a routine basis. Here, there are also many possible ways of representation and no effort in standardisation is as yet underway.

7 Conclusions

7.1 Conclusions from background data

From the evaluations presented in this report it can be concluded that

- there are numerous metallurgical processes which have a significant potential to form and emit dioxins and furans. Major sources have been identified in both the iron and steel sector and the non-ferrous sector. Still, there are many more less substantial sources. Due to the almost ubiquitous availability of the basic compounds needed for dioxin formation it is impossible to predict if and to what extent dioxins are formed. Hence, it is probable that also processes not yet investigated might prove to be dioxin emittors .

  the main processes to be considered are
    iron ore sintering plants
    electric arc furnaces for steel production
    non-ferrous secondary smelters producing aluminium, copper, zinc from scraps and/or filter dusts
    ferrous and non-ferrous foundries

- The number of IPPC installations in the metal sector, as defined according to Annex I(2) of the IPPC Directive, cannot be identified accurately as yet. This is due to both lack of data from some of the the New Member States and the availability of only highly aggregated figures for most of the former EU 15. The total number of relevant IPPC installations in the EU 25 is estimated to 6,000 – 8,000. From more detailed data, only obtained for a few countries, a share of approximately 25%, or some1,500 to 2,000 installations can be assumed to be potentially eligible for dioxin emission mandatory monitoring. Further uncertainty is caused by the definition of “installation” given in the IPPC Directive. Of these, up to 1,500 installations may be regarded as relevant dioxin emission sources to be targeted by a regulation on dioxin monitoring.

- Inventories of dioxin emissions indicate the predominant role of processes from the iron & steel sector which contribute ca. 75% of the emissions from the metal industry. The metal sector makes up ca. 50% of the total industrial PCDD/F emissions and approx. 20% of the estimated overall emissions including non-industrial sources.
  Concerning the EPER, it can be expected that significant emissions by installations with specific emissions below the current EPER threshold of 1 g I – TEQ/year. In case of the metal industry these emissions could equal those already covered by the EPER.

- The MS activities regarding monitoring of dioxin emission sources in the metal sector are highly variable. While monitoring in some countries is negligible, in others monitoring varies by different approaches and the extent of occasional measurements. Several countries with significant metal industry already have a legal obligation for emission measurements, but again the intensity of supervision varies considerably with measurement frequencies ranging from one measurement in 3 years up to monthly tests for particular sources. In light of the assessment carried out above and despite the lack of detailed information for certain Member States, significant deficiencies regarding the dioxin emission monitoring are apparent which justify an action at EU-level.

- Analyses of laboratory and sampling team capacities reveal no particular limitations with respect to future expansion of monitoring requirements. Sampling teams are frequently lacking in the New Member States but already are available in those countries with the most relevant metal industry.
  Despite the costs for a dioxin emission measurement being high compared to other emission tests, these cost do not appear unaffordable for most installations, even if there might sometimes be more than one emission point to be investigated at a particular installation.
- With respect to the aim of reducing the uncertainty in emission inventories, it is obvious that measurements should preferably, but not exclusively, be addressed to the major sources.

7.2 Conclusions regarding options to improve the situation

Three main options have been discussed as possible routes to achieve the desired goals of closing the apparent data gaps and assuring appropriate awareness by competent authorities. All of these options have potential to be sufficient for these purposes, but with different risks:

The “no policy change” option, i. e. leaving the IPPC Directive and its implementation unchanged with respect to the consideration of dioxin emissions, might prove to be sufficient if the competent authorities in all Member States use the provisions on emission limit values and corresponding monitoring in the Directive appropriately. An important prerequisite would be that the indications on potential dioxin formation were taken seriously and an adequate assessment on the issue is made in the permit granting process.

However, there is a significant risk that, in some countries, the issue of dioxin emission is underestimated or entirely ignored concerning particular installations since no mandatory obligation to do so is included in the Directive. Therefore this option cannot provide an guarantee that the situation will be substantially better after full implementation of the Directive than how it is at present.

With the “improved instruments” option a pathway is presented which on the one hand would need only slight changes of the current legislation and could be a way to gather more data particularly for the “grey zone” where installations have unit emissions below the current EPER threshold value. Reports on emission data from operators, if at “non-zero” level, might also be an incentive to the competent authorities to consider dioxin emissions more appropriately in the course of permit granting procedure.

On the other hand, still a high uncertainty in reported emission must be taken into account if “estimation” or “calculation“ methods of reporting of were retained. Moreover, it is unlikely that the reporting under EPER or the future E-PRTR would automatically trigger action by competent authorities for the permitting and control of IPPC installation as regards dioxins emissions.

Finally, the option to introduce mandatory monitoring requirements is the most far-reaching one. Certainly, in case such regular monitoring and reporting of measured emissions is installed, both goals will be reached and within a few years the dioxin emission situation of the EU metal industry will become much more transparent and accurate than it is today.

However, it is probably the most expensive of the three options (for both industrty and the authorities). In the case of moderate and appropriate frequency of measurements, the costs will remain affordable in particular since, within this sector, mainly large installations are covered by the IPPC Directive.

The desired level of harmonisation for the most technical issues linked with the measurement of dioxins still need to be further discussed. The development of such an amendment of the Directive could be accompanied by guidance documents for the most technical issues.This could be done as a separate guidance document or in the context of the revision of the BREFs related to this sector.

Of course, such guidelines for the monitoring requirements will need a concerted development process involving all stakeholder groups. From the analyses made in this study and from information obtained from consultations with stakeholders some **initial key boundary conditions** can be identified:

The scope and selection of installations covered by a possible future monitoring requirement must be based on a balanced assessment of the expected gains of information versus. both economic and organisational constraints. The description of IPPC activities in the Annex I of this Directive does not appear to be suitable for further specification in the context of dioxins monitoring.For example, category 2.2 may include activities in integrated iron and steel plants which are of low or negligible relevance regarding dioxin emissions (e.g. coke ovens, blast furnace). From the results of this study, **the minimum scope therefore would involve the sintering plants in both the iron & steel and the non-ferrous metal industry (category 2.1), electric arc furnaces for steel production from scraps (belonging to category 2.2) as well as those installations of category 2.5a which are processing secondary materials.**

The dioxin measurement method proposed as a guideline for dioxin monitoring must be acceptable to all authorities. Thus **the standard method according to EN 1948 is largely preferred**. Other methods, such as the use of surrogates or continuous sampling, may be considered in particular cases. Surrogate methods have significant advantages in studies on the mechanisms of dioxin formation and in the development of prevention and abatement measures, while continuous sampling could be justifiable in case of unexpected high environmental contamination which cannot be linked to the emissions measured by spot tests. Such considerations should however be left entirely to case by case discussions between operators and authorities.

The frequency of measurements to be performed and other monitoring requirements should not necessarily be identical for all eligible installations. Important factors to be considered are the emission level the variability of emissions and their stability with time. Authorities must be given the possibility to lower or to raise the frequency, depending on the monitoring results and local conditions. To determine a reference value for the desirable frequency, the actual range of dioxin monitoring requirements practised in the Member States (every 3 years or as often as monthly) as well as the requirements set for waste incineration plants may provide direction. Waste incinerators are imposed with 2 measurements a year at emission levels of typically less than 50 mg I-TEQ/year. Taking this into account, a frequency of **one measurement per year in case of significant emissions** does not appear to be excessive.[28]

It is recommended to industry in general that more attention is paid to those factors enhancing or suppressing dioxin emissions. Preventive measures, i.e. those affecting emissions by optimising feed factors or operating conditions, are expected to be much cheaper. Sectors in which most individual emission values are well below current or future emission thresholds are advised to monitoring one or more plants intensively and in such a way as to derive general views on the factors influencing emissions. It was concluded that the mechanisms of dioxins formation are rather ill-documented and that their further scrutiny may well, in the long term, assist in reducing monitoring requirements.

Measurement results already obtained due to obligations set by other regulations – national or regional – **should also be taken into account** when determining the need for an additional measurement or the frequency of monitoring. Still, it must be ascertained that these measurements are representative for standard operating conditions and that worst case conditions are identified and avoided in day-to-day operation.

Establishing a standardised reporting format would be highly desirable for dioxin emission measurements. This would ensure a standard quality of reporting in all EU Member States and facilitate improved data collection and management at the EU level. Introducing such a format could be carried out under possible new EU legislation.

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[28] With respect to the approach proposed here involving a dynamically changing measurement frequency depending on the significance of emission it would be necessary to set criteria for determining the appropriate monitoring frequency. Such criterion could be the emission mass flow (hourly or annually), but it is envisaged that a combination of mass flow and flue gas concentration might be advantageous to avoid installations being imposed to measurements just because their virtual PCDD/F mass flow – calculated from flue gas flow rate multiplied by the PCDD/F detection limit – exceeds the mass flow limit set as criterion. To give an example how such regulation could look like: the lower boundary (no monitoring requirement) could be set for instance at annual emissions below 40 mg TEQ/year or concentration below 0.1 ng TEQ/m³. These values reflect the typical situation of a (large) municipal waste incinerator complying to the waste directive. There might be installations in the non-ferrous sector (e.g. processing clean scrap) for which this situation could apply. Standard monitoring frequency of 1 measurement/year may then be imposed above 200 mg TEQ/year or > 1 ng TEQ/m³. This would be envisaged for most of the electric arc furnaces used for carbon steel production, most non-ferrous metal installations and also for a number of sintering plants. Enhanced measurement frequency would be demanded for values above 1 g TEQ/year or 10 ng TEQ/m³, which could be expected for some sinter plants and large EAFs with insufficient abatement technology. .

8 ANNEX A Data on Installations in the European iron & steel industry

8.1 Electric Arc Furnaces –Information provided by Eurofer

The table below is an estimation based on information available at Eurofer but it has to be noted that it is neither complete nor up-to-date. However, it might give an idea of the number of installations in the steel industry covered by the IPPC directive and relevant for this study. The blank spaces represent lack of information.

Table 23 Number of Sinter plants and EAFs (Information at Eurofer)

Country	Number of Sinter plants	Number of EAFs	
		Carbon Steel	Stainless Steel
Germany	8	13	16
Belgium	3	3	3
France	7	12	9
Italy	2	27	10
Netherlands	1	1	-
UK	3	5	4
Spain	1	20	6
Poland		4	4
Austria	2	1	2
Finland	1	1	1
Hungary		2	1
Greece		5	-
Luxembourg		3	-
Portugal	1	2	-
Sweden	-	4	4
Czech Republic		3	5
Total	30	105	65

8.2 Information derived based on data provided by DG Enterprise

8.2.1 Sintering plant

In the enlarged E.U. there are an estimated 58 belts with a total capacity of 127.7 M tons, spread over 47 sintering plants, with a total surface of aspiration of 11,751 m^2. Most of this plant was erected in the seventies or sixties [7].

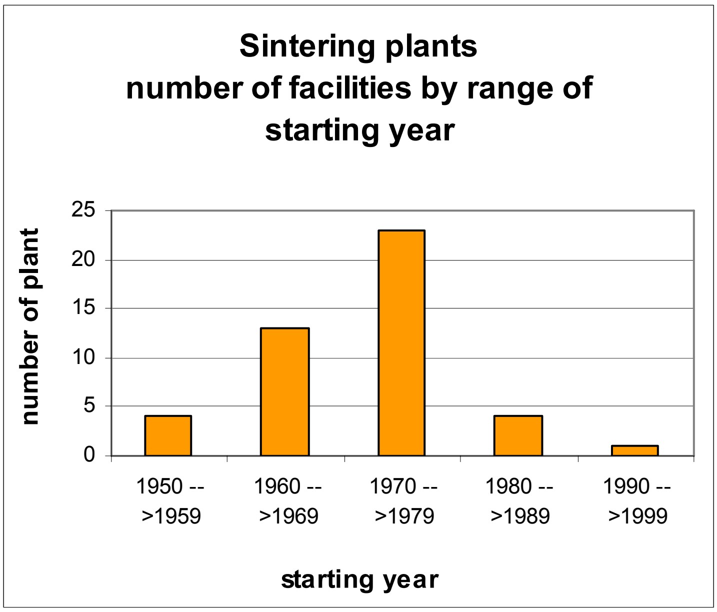


Figure 13 Age Distribution of the sintering plants

Unit capacity kept rising from a minimum of 300,000 to a maximum size of 7.3 M tons:

Table 24 Capacity of different sinter plants

	Year of Construction	capacity 1000 t / y
min	1952	300
middle	1971	2717
median	1972	2200
max	1999	7300

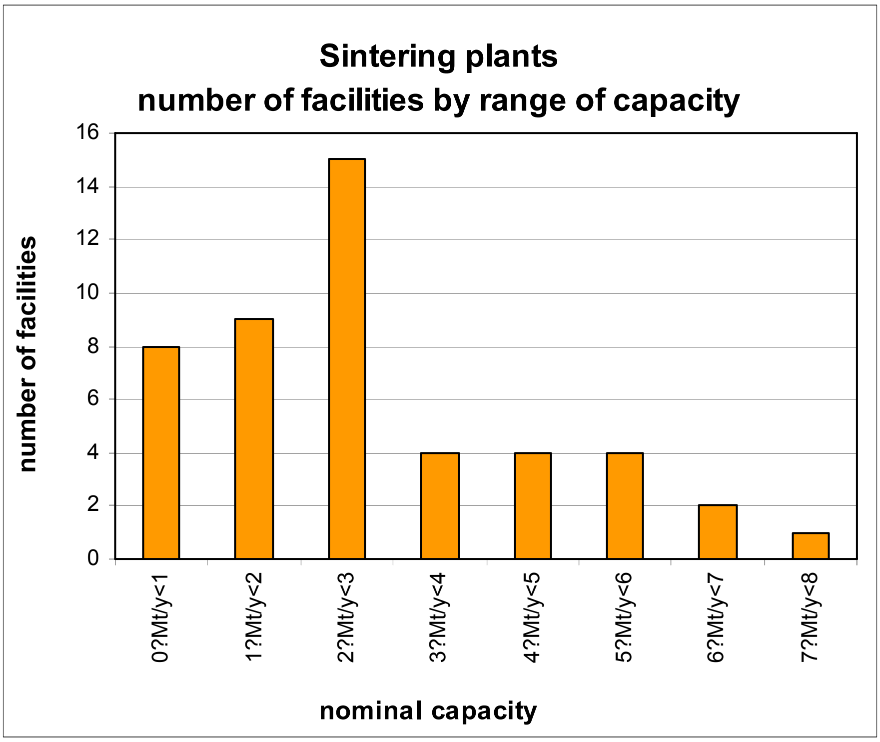
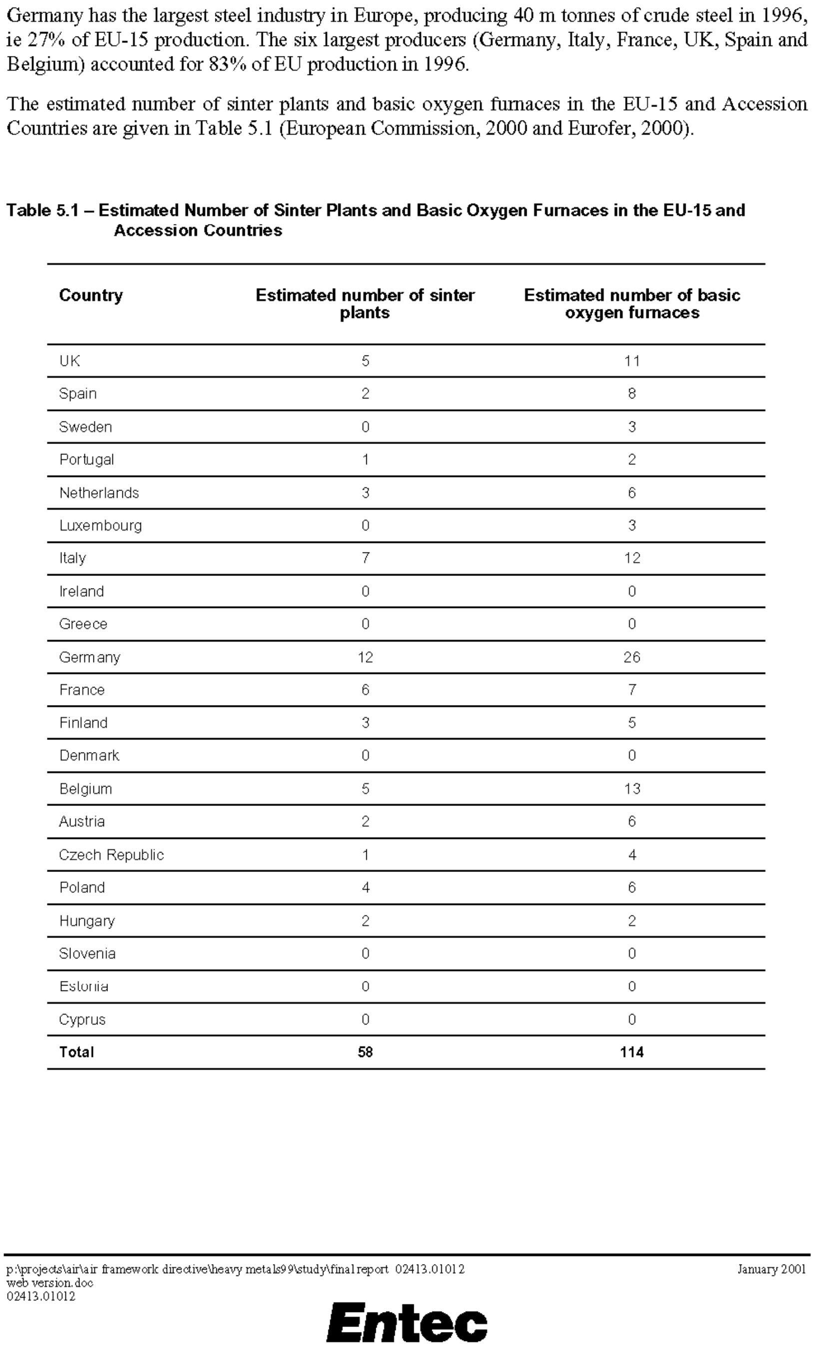


Figure 14 Distribution of the sintering plants (> 1 M tons) according to capacity

Table 25 Geographical Distribution

Country	Strand surface		Nominal Capacity	
	m²	% of total	1000 t/year	% of total
Austria	310	3%	3500	3%
Belgium	1405	12%	15300	12%
Cyprus				
Czech Republic	735	6%	6330	5%
Denmark				
Estonia				
Finland	225	2%	2700	2%
France	2008	17%	21550	17%
Germany	2282	19%	29400	23%
Greece				
Hungary	100	1%	900	1%
Ireland				
Italy	962	8%	11500	9%
Latvia				
Lithuania				
Luxembourg				
Malta				
Netherlands	354	3%	4400	3%
Poland	1161	10%	9000	7%
Portugal				
Slovakia	400	3%	4000	3%
Slovenia				
Spain	481	4%	5400	4%
Sweden				
United Kingdom	1328	11%	13700	11%
Total	**11751**	**100%**	**127680**	**100%**

Table 26 Geographical Distribution of installations (taken from [8]) [29]:



Germany has the largest steel industry in Europe, producing 40 m tonnes of crude steel in 1996, ie 27% of EU-15 production. The six largest producers (Germany, Italy, France, UK, Spain and Belgium) accounted for 83% of EU production in 1996.

The estimated number of sinter plants and basic oxygen furnaces in the EU-15 and Accession Countries are given in Table 5.1 (European Commission, 2000 and Eurofer, 2000).

Table 5.1 – Estimated Number of Sinter Plants and Basic Oxygen Furnaces in the EU-15 and Accession Countries

Country	Estimated number of sinter plants	Estimated number of basic oxygen furnaces
UK	5	11
Spain	2	8
Sweden	0	3
Portugal	1	2
Netherlands	3	6
Luxembourg	0	3
Italy	7	12
Ireland	0	0
Greece	0	0
Germany	12	26
France	6	7
Finland	3	5
Denmark	0	0
Belgium	5	13
Austria	2	6
Czech Republic	1	4
Poland	4	6
Hungary	2	2
Slovenia	0	0
Estonia	0	0
Cyprus	0	0
Total	**58**	**114**

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[29] According to information from industry there have been significant changes since the quoted report was published. In particular there is no BOF in Luxemburg and the number of sinter plants in the UK has been reduced to 3.

8.2.2 Electric Arc Furnaces – Alternating Current AC

There are in total 208 AC EAFs in the E.U., with 141 supplemental units and a total capacity of 75.75 M tons, or 8240 MW [7]. Most of this plant was erected in the seventies and also the nineties. The most significant producers are: Italy (21 %), Spain (20 %), Germany (14 %), France (10 %), the U.K. (8 %), Poland (6 %), Belgium (5 %), Greece (4 %), and Sweden (3 %).

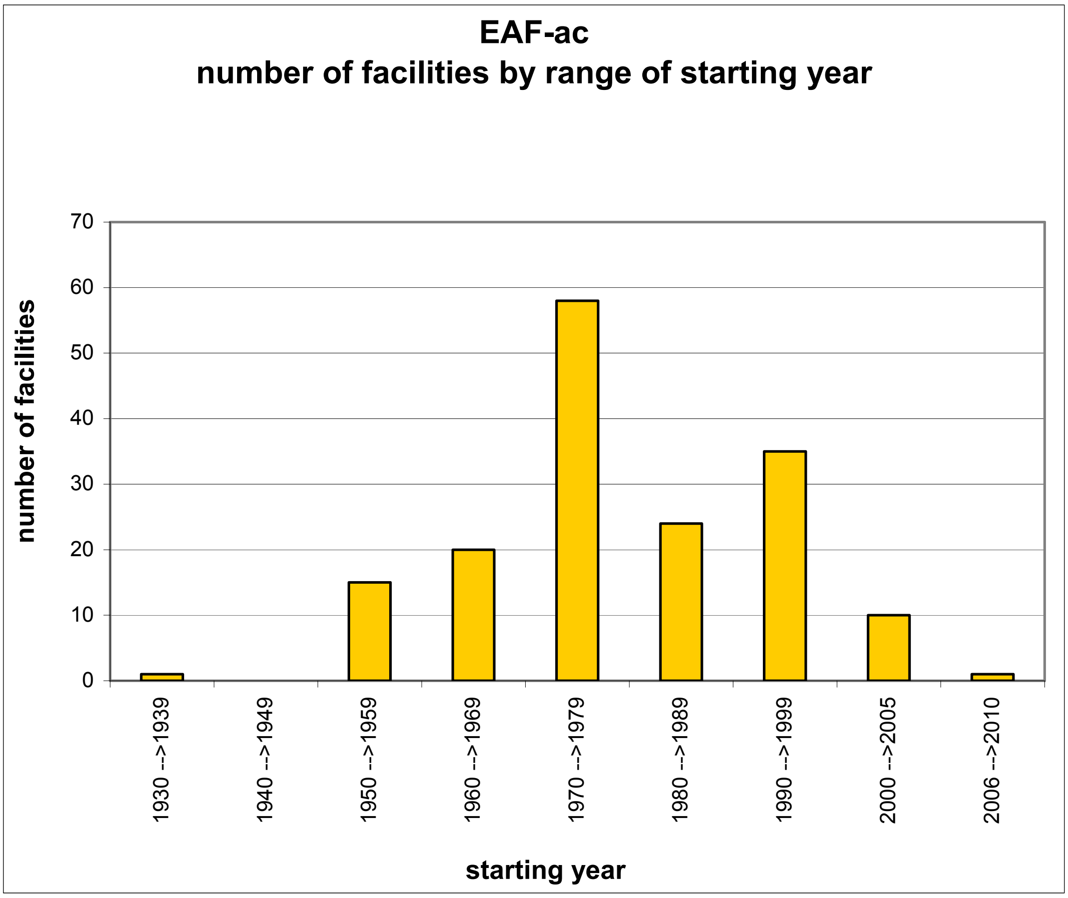

Figure 15 Distribution of EAFs by year of construction

Capacity kept rising from a minimum cast of 3 tons to a maximum one of 200 tons. Annual plant capacity varies from a minimum cast of 3 ktons to a maximum of 1300 ktons and the installed power from 3 to 160 MW.

Table 27 Plant capacity of AC EAFs

	Year of Construction	Other Electric Furnaces Units	Average weight of a single Cast, tons	Installed Power, MW	Nominal Capacity, ktons
min	1939	-	3	3	3
middle	1979	1.24	74	61	399
median	1977	1.00	75	61	400
max	2006	3.00	200	160	1300
TOTAL		**141**		**8412,5**	**75748**

The distribution is bimodal: there is a relatively large number of rather small plants, and additionally a quasi-Gaussian distribution, peaking around a capacity of roughly 500 ktons per year.

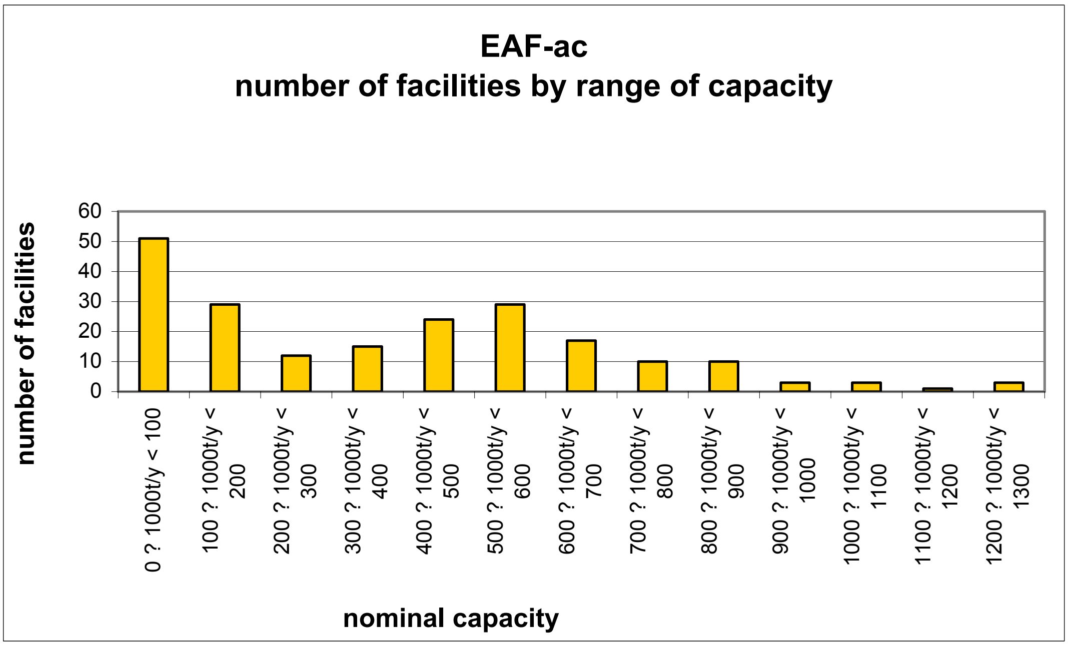

Figure 16 Number of AC EAFs by range of capacities

Geographical Distribution –Distribution in Physical Units and %

Table 28 Geographical Distribution of AC EAFs in physical units

	Electric Arc Furnaces ac			
Country	Number of supplemental steel furnaces	Average weight of a single Cast [t]	Installed Power [MW]	Nominal Capacity [kt/year]
Austria	2	117	84	520
Belgium	2	685	361	3850
Cyprus	0	0	0	0
Czech Republic	22	416	95	735
Denmark	0	0	0	0
Estonia	0	0	0	0
Finland	1	305	275	1560
France	11	1781	1129.7	7538
Germany	26	2269	1654.1	10784
Greece	6	508	50	2700
Hungary		140	42	940
Ireland	0	0	0	0
Italy	15	2775	1281.5	15878
Latvia	0	0	0	0
Lithuania	0	0	0	0
Luxembourg		95	105	1300
Malta	0	0	0	0
Netherlands	2	70	30	260
Poland	18	1130	502	4325
Portugal		190	42	1100
Slovakia		60	60	350
Slovenia	2	175	136	645
Spain	13	2610	1405.2	14935
Sweden	3	630	381	2155
United Kingdom	18	1315	779	6173
Total	141	15271	8412.5	75748

Table 29 Geographical Distribution of AC EAFs as a % of the Total

Country	Number of supplemental steel furnaces [%]	Average weight of a single Cast [%]	Installed Power [%]	Nominal Capacity [%]
Austria	1.42	0.77	1.00	0.69
Belgium	1.42	4.49	4.29	5.08
Cyprus	0.00	0.00	0.00	0.00
Czech Republic	15.60	2.72	1.13	0.97
Denmark	0.00	0.00	0.00	0.00
Estonia	0.00	0.00	0.00	0.00
Finland	0.71	2.00	3.27	2.06
France	7.80	11.66	13.43	9.95
Germany	18.44	14.86	19.66	14.24
Greece	4.26	3.33	0.59	3.56
Hungary	0.00	0.92	0.50	1.24
Ireland	0.00	0.00	0.00	0.00
Italy	10.64	18.17	15.23	20.96
Latvia	0.00	0.00	0.00	0.00
Lithuania	0.00	0.00	0.00	0.00
Luxembourg	0.00	0.62	1.25	1.72
Malta	0.00	0.00	0.00	0.00
Netherlands	1.42	0.46	0.36	0.34
Poland	12.77	7.40	5.97	5.71
Portugal	0.00	1.24	0.50	1.45
Slovakia	0.00	0.39	0.71	0.46
Slovenia	1.42	1.15	1.62	0.85
Spain	9.22	17.09	16.70	19.72
Sweden	2.13	4.13	4.53	2.84
United Kingdom	12.77	8.61	9.26	8.15
	100	**100**	**100**	**100**

8.2.3 Electric Arc Furnaces – Direct Current

A more recent technology is the DC Electric Arc Furnace. There are 14 units with a total capacity of 12.2 M tons, spread over 13 sites, with a total installed capacity of 1995 tons and a total installed power of 1,592 MW [7]. Most of this plant is relatively new (one from 1985, the others 1993 or after). One furnace load represents 80 – 155 tons.

Important countries: Germany and Spain (each 21 %), Luxemburg (19 %), France (17 %), Belgium (12 %) and Italy (5 %). However, the total production capacity is much smaller than for AC Electric Arc Furnaces.

Table 30 Plant capacity of DC EAFs

	Year of Construction	Average weight of a single Cast [tons]	Content of the Furnace [tons]	Installed Power, [MW]	Nominal Capacity [ktons/year]
Min	1985	80	100	65	600
Middle	1995	117	143	114	873
Median	1995	125	148	125	800
Max	2002	160	190	150	1400
TOTAL			1995	1592	12225

Table 31 Geographical Distribution of DC EAFs –Distribution in Physical Units

	Electric Arc Furnaces dc			
Country	Average weight of a single Cast [t]	Content of the furnace, [t]	Installed Power, [MW]	Nominal Capacity, [kt/year]
Austria	0	0	0	0
Belgium	220	275	209	1500
Cyprus	0	0	0	0
Czech Republic	0	0	0	0
Denmark	0	0	0	0
Estonia	0	0	0	0
Finland	0	0	0	0
France	240	290	222	2025
Germany	350	420	390	2600
Greece	80	130	65	600
Hungary	0	0	0	0
Ireland	0	0	0	0
Italy	90	100	96	600
Latvia	0	0	0	0
Lithuania	0	0	0	0
Luxembourg [30]	310	380	280	2300
Malta				
Netherlands	0	0	0	0
Poland	0	0	0	0
Portugal	0	0	0	0
Slovakia	0	0	0	0
Slovenia	0	0	0	0
Spain	350	400	330	2600
Sweden	0	0	0	0
United Kingdom	0	0	0	0
Total		1995	1592	12225

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[30] According to industry actual values for LU are 155 tons/single cast and 180 t furnace content.

Table 32 Geographical Distribution of DC EAFs –Distribution as a % of the Total

Country	Average weight of a single Cast [%]	Content of the furnace [%]	Installed Power [%]	Nominal Capacity [%]
Austria		0.00	0.00	0.00
Belgium		13.78	13.13	12.27
Cyprus		0.00	0.00	0.00
Czech Republic		0.00	0.00	0.00
Denmark		0.00	0.00	0.00
Estonia		0.00	0.00	0.00
Finland		0.00	0.00	0.00
France		14.54	13.94	16.56
Germany		21.05	24.50	21.27
Greece		6.52	4.08	4.91
Hungary		0.00	0.00	0.00
Ireland		0.00	0.00	0.00
Italy		5.01	6.03	4.91
Latvia		0.00	0.00	0.00
Lithuania		0.00	0.00	0.00
Luxembourg		19.05	17.59	18.81
Malta		0.00	0.00	0.00
Netherlands		0.00	0.00	0.00
Poland		0.00	0.00	0.00
Portugal		0.00	0.00	0.00
Slovakia		0.00	0.00	0.00
Slovenia		0.00	0.00	0.00
Spain		20.05	20.73	21.27
Sweden		0.00	0.00	0.00
United Kingdom		0.00	0.00	0.00
		100	100	100

9 ANNEX B Data on foundries

The following information has been retrieved from the CAEF website [9]

I. Number of installations

Number of foundries (Production units) - Iron, Steel and Malleable iron castings

Country	1999	2000	2001	2002	2003	2002 : 2001	2003 : 2002
						+/- %	
Austria	26	25	24	41	37	70,8	-9,8
Belgium	25	24	21	21	21	0,0	0,0
Czech Rep.			140	143	144	2,1	0,7
Denmark		12	12	12	12	0,0	0,0
Finland	23	20	19	19	19	0,0	0,0
France	187	187	183	179	165	-2,2	-7,8
Germany	310	299	288	273	267	-5,2	-2,2
Great Britain	214 b)	198 b)	188 b)	179 b)	294	-4,8	64,2
Hungary	34	32	33		47		
Italy	307	293	291	281	259	-3,4	-7,8
Lithuania	11	9	8	7	9	-12,5	28,6
Netherlands			28		28		
Norway	12	12	11	11	11	0,0	0,0
Poland	230	230	220	190	185	-13,6	-2,6
Portugal	61	61	61	61	61	0,0	0,0
Spain	221		102 a)	98 a)		-3,9	
Sweden	49	49	49	50	48	2,0	-4,0
Switzerland	23	23	22	20	20	-9,1	0,0
Total	1.733	1.474	1.700	1.585	1.627		

a) only members

b) without steel castings

Number of foundries (Production units) - Non-ferrous metal castings

Country	Total		thereof:					
			Pressure die casting		Other Light casting		Other Heavy metal alloy casting	
	2002	2003	2002	2003	2002	2003	2002	2003
Austria	61	59	21	20	25	25	15	14
Belgium	10 a)	8	3	2	5	4	2	2
Czech Rep.	63	69	40 b)	19		37	23	13
Denmark	8							
Finland	25	26	6	8	12	12	7	6
France	283	367						
Germany	400	384						
Great Britain		230						
Hungary		110		23		60		27
Italy		880						
Lithuania		5		2		3		
Netherlands								
Norway	13	12	3	3	6 c)	6	4	3
Poland	260	245						
Portugal	54	54	32	32	9	9	13	13
Spain	57 a)							
Sweden	84	84						
Switzerland	48	47	14	14	23	23	11	10
Total	1.491	2.580	119	123	80	179	75	88

a) only members

b) incl. all light casting

c) incl. Other Heavy metal alloy casting

II. Production Figures

Total production in 1000 t - Iron, Steel and Malleable iron castings

Country	1999	2000	2001	2002	2003	2002 : 2001	2003 : 2002
						+/- %	
Austria	181,7	191,4	192,4	181,2	175,9	-5,8	-3,0
Belgium	149,3	149,8	149,5	151,8	143,6	1,6	-5,4
Czech Rep.	379,1	390,3	413,8	381,6	468,3	-7,8	22,7
Denmark	86,0	96,4	85,7	87,3		1,8	
Finland	109,0	117,6	119,5	112,5	109,6	-5,8	-2,6
France	2.133,9	2.271,5	2.135,4	2.128,6	2.126,8	-0,3	-0,1
Germany	3.555,2	3.758,2	3.801,4	3.749,7	3.858,3	-1,4	2,9
Great Britain	949,2	968,2	906,3	886,3	994,5	-2,2	12,2
Hungary	68,7	74,8	62,8	67,9	84,1	8,1	23,8
Italy	1.492,6	1.516,4	1.433,3	1.460,9	1.441,9	1,9	-1,3
Lithuania	23,8	25,2	25,7	17,6	18,1	-31,5	2,8
Netherlands	121,0	136,0	130,9	123,7	126,1	-5,5	2,0
Norway	67,7	70,1	73,4	67,3	56,7	-8,2	-15,7
Poland	610,2	671,2	673,0	596,5	578,4	-11,4	-3,0
Portugal	97,7	102,3	100,0	96,7	102,8	-3,4	6,3
Spain	759,3	950,5	955,7	992,9	995,1	3,9	0,2
Sweden	253,2	266,7	244,7	234,6	235,9	-4,1	0,6
Switzerland	122,0 a)	119,9 a)	105,5 a)	81,8 a)	73,3 a)	-22,5	-10,4
Total CAEF	11.159,6	11.876,5	11.609,0	11.418,9	11.589,3		
Croatia	33,1	32,4	39,1	40,6		4,1	
Romania	331,9		335,8	400,0 *)		19,1	
Russia		5.600,0		5.700,0 *)			
Slovenia	81,9	86,8	96,3	109,8		14,0	
Slovakia				100,0 *)			
Turkey	837,4	925,0	861,8	876,6	897,0	1,7	2,3
Ukraine	815,0	907,3	1.296,2	942,7		-27,3	

a) without steel and malleable iron castings
*) estimated

Total production in 1000 t - Non-ferrous metal castings

Country	1999	2000	2001	2002	2003	2002 : 2001	2003 : 2002
						+/- %	
Austria	92,4	105,9	113,3	116,2	123,4	2,5	6,1
Belgium	23,8	27,2	26,3	27,6	28,1	5,1	1,7
Czech Rep.	48,0	57,7	58,1	59,6	78,7	2,7	32,0
Denmark	4,0	4,0	4,8	4,6		-3,3	
Finland	10,0	10,0	10,0	9,7	11,0	-3,2	13,7
France	357,3	388,6	394,7	390,3	390,0	-1,1	-0,1
Germany	777,0	842,1	849,6	846,3	864,3	-0,4	2,1
Great Britain					227,0		
Hungary	35,0	44,8	58,4	68,3	71,4	16,9	4,6
Italy	832,1	959,1	960,0	979,7	999,3	2,1	2,0
Lithuania					0,087		
Netherlands							
Norway	25,2	26,4	30,9	26,7	24,6	-13,5	-8,1
Poland	84,0	84,0	72,2	118,5	151,0	64,1	27,4
Portugal	21,2	22,6	25,4	25,6	26,8	0,6	4,7
Spain	153,6	121,1	142,1	149,9	154,7	5,5	3,2
Sweden	55,7	58,5	53,3	52,9	55,7	-0,8	5,3
Switzerland	22,9	25,1	24,1	21,1	19,9	-12,3	-5,7
Total CAEF	2.542,2	2.777,0	2.823,2	2.897,1	3.225,9		
Croatia	12,5	12,3	10,6	12,4		17,5	
Romania	28,2		29,6				
Russia		600,0					
Slovenia	12,9		27,6	34,0		23,2	
Slovakia							
Turkey	36,7	40,0	44,0	45,0	58,0	2,3	28,9
Ukraine	26,0	40,0	73,0	31,5		-56,8	

a) without Zinc
b) only Aluminium

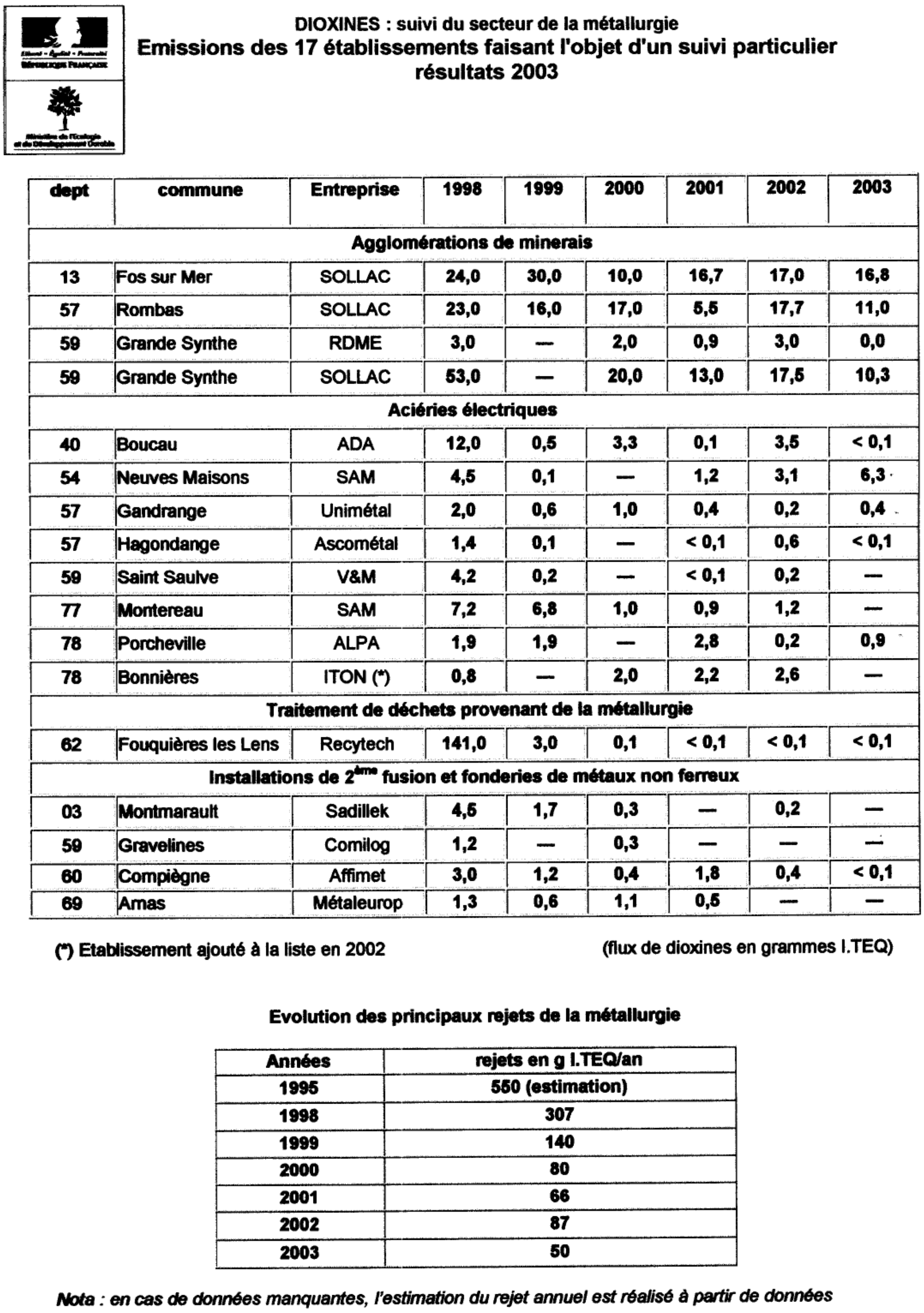
10 ANNEX C Availability of dioxin information in the BREFs

BREF	Process	PCDD/F formation	typ levels		BAT levels		comments
			conc. [ng I-TEQ/m³	emission factor [µg I-TEQ/t]	conc. [ng I-TEQ/m³]	emission factor [µg I-TEQ/t]	
Iron&Steel	sinter plants	yes	0,5-5	1-10 (sinter) 0,5-6,5 (Liquid steel)	0,5-1,5 (UK) 2-3 (DE) 5-6 (other)		Process optimisation
				2		0,6	EOS
			5-10		0,2-1		fabric filter/coke powder
			8		0,4	1,0	fine wet scrubber
					<0,1		coke injection/catalyst (experomentally tested only)
	Pellet plants	yes		0,0057 (pellets)	no figures		
	Coke oven	no		no figures	no figures		
	Blast furnace	yes		<0,001-0,004 (liqiud steel)	no figures		
	Basic Oxygen Furnace	yes		< 0.001-0.06 (LS)	no figures	< 0.001-0.06 (LS)	suppressed combustion
	EAF	yes		0,2-9 (SE) 0,07-1,8 (DE, LS) 0,3-5,7 (EU) 1,7 (DK)	<0,5		post combustion/rapid cooling
					<0,1 -<0,5		coke powder injection
Ferrous_metals	Hot rolling mills	no					
	Cold rolling mills	no					
	Wire plants	no					
	hot dipping galvanizing	yes					dust contamination raised, no figures given

BREF	Process	Indication to PCDD/F formation	typical emission levels		levels expected with BAT		comments
			conc. [ng I-TEQ/m³]	emission factor [µg I-TEQ/t]	conc. [ng I-TEQ/m³]	emission factor [µg I-TEQ/t]	
non-ferrous metals	copper&alloys	yes					
	aluminium	yes					
	zinc	yes			<0,1 -< 0,5		dioxin formation not explicitely stated as environmental issue in chapter 1 of the BREF; chapter 5 contains indications to dioxin emissions and abatement measures
	lead	yes					
	ferro-alloys	yes					
	alkali alkaline earth metals	yes					particularly relevant to Mg
	nickel	yes					
	incineration/pyrolysis for metal recovery	yes					
	shaft furnace	yes			<0,1 -< 0,5		applying abatement systems like afterburners, coke-injection, catalytic fabric filters
	sulphuric acid plant	yes			0,001-0,01		
	Sec. Cu: Scrap treatment	yes					
	Sec. Cu:smelting	yes					
	Sec. Cu: Converting	yes					
	Sec. Cu: Refining	yes					
	Cu, semis fabrication, electric furnace		< 5				
	Cu, semis fabrication, rotary furnace		<10				
	Cu, semis fabrication, shaft furnace		<10				
	oxygen injection blast furnace				<0,5		
	Post combustion/coke-lime inj/fabric filter				<0,1		
	Prim. aluminium casting	yes					if chlorine present (degassing)
	Sec. aluminium	yes			<0,1 -< 0,5		HE dust removal, afterburner/quencher etc.
	sec. aAl, swarf drying		<0,1-1				
	sec Al, induction furnace (abated)		<0,1-1				
	sec Al, rotary furnace (abated)		<0,1-1				
	l, reverbaratory/side-well furnace (abated)		<0,1-1				
	sec Al, sloping hearth furnace (abated)		<0,1-1				
	Lead, Zinc Cadmium	yes					
	sec. lead						
	sec zinc (Waelz kiln)						
	sec. cadmium (batteries)						
	roasting sintering smelting						

BREF	**Process**	**PCDD/F formation**	**typ levels**		**BAT levels**		**comments**
			conc. [ng I-TEQ/m^3	emission factor [µg I-TEQ/t]	conc. [ng I-TEQ/m^3]	emission factor [µg I-TEQ/t]	
non-ferrous metals	Precious metal production	yes			<0,1 - 0,5		HE dust removal, afterburner/quencher etc.
	incineration or smelting	yes					
	incineration (small process)		<0,1				
	pyro-metallurgical processes		<0,1				
	Production of ferro alloys	yes					
	FeCr, sinter plant						0.2 g/year up to 4 g/year (in one plant)
	FeSi			5			
	Si-metal			3			
	Primary magnesium	yes					chlorination step of electrolytic production; also emissions to water and residues
	chlorination off-gas tretment		0,8	12			
	chlorination (vent. gas)		0,8	28			
	electrolysis/chlorination			13			
	reuction, refining melting		0,08	3			
	MgCl2 brine dehydration					<10	BAT for new plants
	Nickel and Cobalt production	no			<0,1-0,5		only BAT related conc. given
	carbon/graphite production	no			<0,1		regenrative afterburner
smitheries&foundries	foundry process	yes					
	ferous metal melting				<0,1		BAT associated emission level
	shaft furnace	?					mentioning afterburners for dioxin destruction
	cupola furnace (clld blast)	yes	0,001-5,1				
	cupola furnace (hot blast		0,001-4,1				
	EAF	no					clean input materials
	Coreles induction furnace	no					
	Rotary furnace	yes	0,004-0,61				
	AOD Converter	no					
	VODC	no					
	aluminium melting	no					
	Magnesium/Mg-alloys melting	no					
	Copper/Cu-alloy melting	no					
	zunc/zinc-alloy meletinmg	no					
	lead melting	yes					

11 ANNEX D Data from Dioxin Survey in French metal industry



DIOXINES : suivi du secteur de la métallurgie
Emissions des 17 établissements faisant l'objet d'un suivi particulier
résultats 2003

dept	commune	Entreprise	1998	1999	2000	2001	2002	2003
Agglomérations de minerais								
13	Fos sur Mer	SOLLAC	24,0	30,0	10,0	16,7	17,0	16,8
57	Rombas	SOLLAC	23,0	16,0	17,0	5,5	17,7	11,0
59	Grande Synthe	RDME	3,0	—	2,0	0,9	3,0	0,0
59	Grande Synthe	SOLLAC	53,0	—	20,0	13,0	17,5	10,3
Aciéries électriques								
40	Boucau	ADA	12,0	0,5	3,3	0,1	3,5	< 0,1
54	Neuves Maisons	SAM	4,5	0,1	—	1,2	3,1	6,3
57	Gandrange	Unimétal	2,0	0,6	1,0	0,4	0,2	0,4
57	Hagondange	Ascométal	1,4	0,1	—	< 0,1	0,6	< 0,1
59	Saint Saulve	V&M	4,2	0,2	—	< 0,1	0,2	—
77	Montereau	SAM	7,2	6,8	1,0	0,9	1,2	—
78	Porcheville	ALPA	1,9	1,9	—	2,8	0,2	0,9
78	Bonnières	ITON (*)	0,8	—	2,0	2,2	2,6	—
Traitement de déchets provenant de la métallurgie								
62	Fouquières les Lens	Recytech	141,0	3,0	0,1	< 0,1	< 0,1	< 0,1
Installations de 2ème fusion et fonderies de métaux non ferreux								
03	Montmarault	Sadillek	4,5	1,7	0,3	—	0,2	—
59	Gravelines	Comilog	1,2	—	0,3	—	—	—
60	Compiègne	Affimet	3,0	1,2	0,4	1,8	0,4	< 0,1
69	Arnas	Métaleurop	1,3	0,6	1,1	0,5	—	—

(*) Etablissement ajouté à la liste en 2002 (flux de dioxines en grammes I.TEQ)

Evolution des principaux rejets de la métallurgie

Années	rejets en g I.TEQ/an
1995	550 (estimation)
1998	307
1999	140
2000	80
2001	66
2002	87
2003	50

***Nota** : en cas de données manquantes, l'estimation du rejet annuel est réalisé à partir de données*

12 ANNEX E Factors influencing potential dioxin release

The generation of dioxins during thermal processes depends on the availability of carbon or of organic precursors, of chlorine or chlorides, of oxygen, and a suitable catalytic system. The latter is created accidentally and in situ, by spontaneous processes that are neither clarified nor controllable. The most important influencing upon dioxin generation are:

- Raw materials.
- Process operating conditions.
- Cooling conditions in the off-gases, and finally
- Cleaning the off-gas before their release into the atmosphere.

12.1 Raw Materials

Raw materials are a source of metals, as well as of potential contaminants. Dioxin emissions may unexpectedly occur, despite the fact that ores or pure metals are the only raw materials used. The apparent absence of recognisable sources of chlorine, carbon or organics is an insufficient condition for waiving any kind of monitoring. Yet, the probability of substantial dioxin generation is much larger when **secondary raw materials** are at least a part of the feed. Avoiding visible pollution by attached organics, oil, or plastics will tend to reduce all emissions, including those of carbon monoxide, Total Organic Compounds, PAH, PCB, and dioxins. Conversely, the obvious absence of any organic contaminants is *insufficient a guarantee* that dioxin emissions will remain negligible.

Some processes deserve particular attention, since chlorine or chlorides are ostentatiously used in the process, e.g.

- Chloride metallurgy, cf. a conference in Montreal, 2002[31].
- Electrolysis of metal chlorides.
- Chlorination involving salts.
- Degassing of molten aluminium using chlorine gas or chlorinated hydrocarbons.
- Electronic scrap. Here bromine largely substitutes chlorine as the origin of potential problems.

Scrap processing deserves special attention, as well as supplemental efforts in monitoring.

Operating modes – Reducing Conditions

Metallurgical processes differ in their operating principles, conditions and modes, in the forms, shapes and composition of the raw materials, and in the fate of the off-gases. Most favourable from a dioxin viewpoint is the absence of internal combustion, with a most complete combustion as second best. The composition of off-gases (oxygen, water vapour,

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[31] visit: www.metsoc.org and click on Chloride 2002

dust and chloride content …) is a second important parameter. A third factor is related to the critical window for dioxin formation, roughly 500 to 200 °C. in this window are generally situated:

- ❑ Heat recovery by means of a waste heat boiler, air pre-heaters, etc.
- ❑ Heat recovery by means of a heat exchange between the incoming feed and the out flowing gas.
- ❑ Filtration of particulates from the off-gases.

A counter-current or cross-current flow is often used, e.g. with the purpose of heating the incoming feed with hot off-gases. Heat exchange and recovery, however, markedly increases the off-gas load with respect to dust, carbon monoxide, and other Products of Incomplete Combustion, in particular Total Organic Compounds, PAH, PCB, and dioxins. Examples are:

- counter-current heat exchange: the blast furnace, the Asarco furnace.
- cross-current heat exchange: the sintering belt.

It is better avoiding such conditions that lead to higher emissions altogether, as in the Top Blown Rotary Converter, or else, using an adequate post-combustion of flue gases (as done for example in Japan).

Some other processes require a reducing atmosphere to avoid the formation of metal oxides, e.g. when treating copper. A reducing atmosphere automatically leads to emission of carbon monoxide and Products of Incomplete Combustion, causing atmospheric pollution.

Reducing conditions *in se* reduce, rather than promote *de novo* formation of dioxins. A better method is avoiding such conditions altogether, as is the case in the Top Blown Rotary Converter, or else, using adequate post-combustion of flue gases

12.2 Heat exchange – Active Temperature Window

As explained above, a gradual decrease in temperature in a boiler or heat exchanger of dust laden gases and of gases brought in contact with earlier deposits in flues will lead to higher dioxin values. Also, high temperature filtration is quite counterproductive, especially when conducted in electro-filters.

Dioxins appear in a temperature window starting at 450 °C (at higher temperature destruction is faster than formation) and slowing down considerably below 250 °C. Hence, formation typically takes place in a waste heat boiler, in flues, and in filters, should these operate in the critical temperature window. Potential dioxin formation during filtration becomes entirely unproblematic below 160 °C.

Heat exchange also leads to memory effects, related to the presence of earlier deposits, and eventual dioxin evolution there from. For that reason, there are several time scales involved in forming and monitoring dioxins. Reactions in the gas phase or related to suspended particulates proceed in a matter of seconds. Dust deposited in flues, filters, or on collecting electrodes may have much longer residence times, and remain available for reaction and dioxin formation over periods of hours or longer. A set-up in operating conditions may still reflect in emissions many hours or even days afterwards. It follows that test programmes, designed to study the link between dioxins and various feed-stocks and/or operating conditions, are likely to fail. Also unsteady conditions, during start-up, shut-down, charging, or tapping may lead to deviations and sometimes to important emissions. It is one of the principal arguments of suppliers of semi-continuous sampling systems that their equipment ensures a comprehensive monitoring, no longer linked to steady-state conditions. It also explains why much process study has been conducted under laboratory conditions.

12.3 Particulates – Oxygen

Particulates play an essential role in dioxin formation. They carry catalyst, carbon, and chloride and are hence at the heart of the dioxin problem. Testing methods have been developed to analyse the potential of particulates to form dioxins.

Oxygen is necessary for forming dioxins and furans in thermal processes. Oxygen free precursors or surrogates, such as PCB and chlorobenzenes are still formed in the absence of oxygen, but to a more limited extent.

Abatement

Both primary and secondary measures are appropriate routes for reducing dioxin emissions, as is illustrated by e.g. the following list of possibilities:

Primary measures are designed to reduce dioxin formation, e.g. by

- Improving combustion conditions. This may involve the use of enriched air or pure oxygen, enhanced or improved mixing of oxygen with combustibles, rising the combustion temperature or the residence time at high temperature …
- Selecting and/or sorting raw materials with as aims:
    - Reducing the organics content (e.g. machining oil, coatings, paints, paper, plastics) of the feed.
    - Reducing the chlorine content of the feed.

Quality control of raw materials should be adapted to the type of process and off-gas treatment used.

- Reducing the oxygen levels in the off-gas within the relevant temperature window.
- Avoiding catalytic activity of transition metals (almost unfeasible in metallurgical processes!) or inhibiting the catalyst, using nitrogen, such as amines or urea, or sulphur compounds. The latter are rarely acceptable in metallurgical processes
- Reducing the acidity of the process conditions (slag, particulates).
- Quality control of scrap inputs depending on the process used. The use of the correct feed material for the particular furnace or process. Selection and sorting to prevent the addition of material that is contaminated with organic matter or precursors can reduce the potential of dioxin formation.

Secondary measures

- High temperature dust removal (a tentative measure, since attempts were not really successful)
- Thermal post-combustion, followed by a rapid quench of the hot gases.
- Catalytic destruction using honeycomb or packed bed types of catalysts.
- Adsorption on activated carbon or lignite coke.

- The use of correctly designed afterburners and rapid quenching of the hot gases <250°C.
- High efficiency de-dusting and post-combustion followed by a rapid quenching

13 ANNEX F Survey on measurement methods

13.1 Introduction

For the determination of dioxin and dioxin-like PCB loads in flue gas different methods exist. The sampling conditions and the analysis method to be used depend on the existing process and flue gas parameters. Substantial parameters are:

- Dioxin concentration range
- Dust load of the flue gas
- Temperature range
- Amount of carbon particles in the flue gas
- Changing process conditions, e.g. continuous or batch process; unsteady operation etc..
- Potential of memory effects

The process conditions determine whether a manual (discontinuous) or a (semi)-continuous measurement procedure is suitable for the problem. Moreover, to prepare for the sampling procedure statements on the expected dioxin concentration, the dust load, as well as the temperature range of the flue gas are indispensable information which affect the spike quantity of the ^{13}C labelled PCDD/F standard compounds and the application of additional dust collectors. Dioxins occur in the flue gas both as particle bound and molecules in the gas phase depending on the flue gas temperature. To differentiate between these phases, the sampling train, particularly the sampling unit, is make up of a filtering and an adsorption stage.

For manual sampling EN 1948 is the European standard guideline. The guideline describes the determination of the mass concentration of dioxins and dioxin-like PCBs from stationary sources. This guideline is developed and validated for waste incineration plants to check the compliance to the emission limit value of 0.1 ng I-TEQ/m³. In many European countries, EN 1948 is the basis for national standard guidelines for the determination of the dioxin emissions (e.g. CSN EN 1948; DIN EN 1948 and VDI of 3499 etc.)

VDI 3499 sheets 1 to 3 are the German standard guideline for the determination of dioxin emissions from stationary sources. This guideline describes two measurement procedures: Part A is an example for application of DIN EN 1948 for PCDD/F-emissions at levels of about 0.1 ng I-TEQ/m³ and in Part B the measurement method is modified for PCDD/F concentrations in excess of 0.1 ng I-TE/m³ . Both measuring procedures are suitable for waste incineration plants and for non-ferrous (NF) and iron metal industries etc. Only the determination of PCDD/F content of flue gases is validated. The determination of other organic pollutants (e.g. PCB) is possible as well, but is not yet validated.

EPA 23 A is the manual sampling method valid in the USA, which is likewise developed for the determination of the dioxin emissions from stationary sources of waste incineration plants.

The long-term, semi-continuous sampling methods, like AMESA and DMS, are established for the analysis of flue gas in waste incineration. Both sampling methods can be used for the determination of mean concentrations over the sampling period of PCDD/F, PCB and/or heavy metals in the flue gas.

An indirect method is the calculation of the dioxin content from so-called dioxin surrogate compounds and/or dioxin indicator substances. These are strongly process dependent and therefore not established in all ranges. However, the determination of certain surrogate compounds can take place continuously and may thus be used for process control.

13.2 Discontinuous monitoring

13.2.1 EN 1948, 1-4

EN 1948 [**24**] describes the requirements of the sampling and analysis for the determination of the mass concentrations of dioxins and dioxin-like PCB in emissions from stationary sources. This guideline is developed and validated for the measurement of PCDD/F emissions in the **range of 0.1 ng I-TEQ/m^3** with **dust loading up to 15 mg/m^3.** PCB concentrations should be in the range of **0.01 ng WHO TEQ PCB/m^3.** This specification is taken from part 4 of the guideline. Part 4 still has the status of draft.

Sampling (EN 1948-1:1996/ prEN 1948-1:2003)
It can be differentiated into three methods. For all methods, the sample gas is taken in isokinetic conditions in accordance with EN 13284-1:2001, whereby a maximum sampling time is given as 8 h. This temporal restriction is no longer mentioned in the draft of the revised EN 1948 (prEN 1948-1:2003). In the following pages the three sampling methods are schematically described. They are suitable both for the separation of the PCDD/F and the dioxin-like PCB.

<u>Filter/Condenser Method</u>

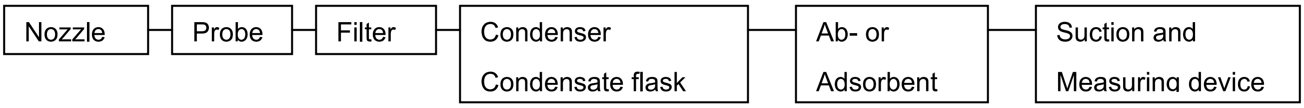

Figure 17 Filter/Condenser Method

The sample gas passes through a particle filter. Depending on the dust content of the flue gas, the particle filter can be composed of a plane filter or a combination of a particle filter and packed glass wool filter or a particle filter and cyclone. The temperature in the particle filter shall not exceed 125°C and shall not fall below the dew point of water. Behind the filter the sample gas is cooled down to below 20°C. The gaseous PCDD/F compounds are collected either in absorption solutions (impinger) or on a solid adsorbent. All surfaces which are in contact with the sample gas must be manufactured from glass. The total PCDD/F content is determined as the sum of the contents in the following compartments:

- Glass tube of the probe (if used)
- Particle filter (and packed glass wool filter or cyclone)
- Condensate

- Impinger solution and/or solid adsorbent
- Rinsing solution (used for cleaning of all glass surfaces)

Dilution Method

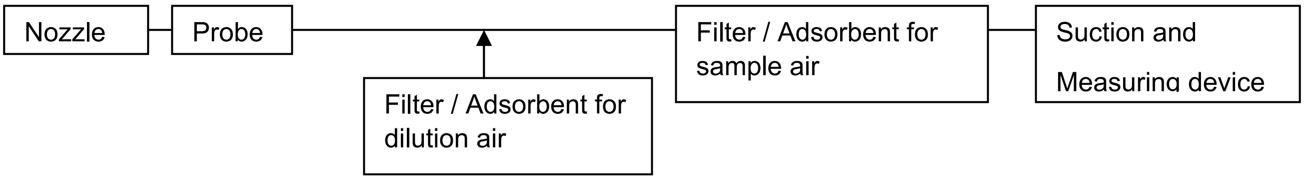

Figure 18 Dilution Method

The sample gas is collected in isokinetic condition via a heated probe and cooled down very rapidly to below 40°C in a mixing channel by diluting the gas with dried and filtered air. The dilution prevents the temperature from falling below the dew point of water.

A combination of a particle filter and solid adsorbent is used to separate and accumulate the PCDD/F contained in the sample gas. All surfaces which are in contact with the sample gas must be manufactured from glass.

Compartments for the analysis are

- Particle filter
- Solid adsorbent
- Rinsing solution.

A control adsorption unit (filter and solid adsorbent) must be inserted for the dilution air, which is changed with each measurement. If the limit value in the flue gas is exceeded, this control adsorption unit has to be analysed too in order to check for possible contamination of the sample by the dilution air.

Cooled probe method

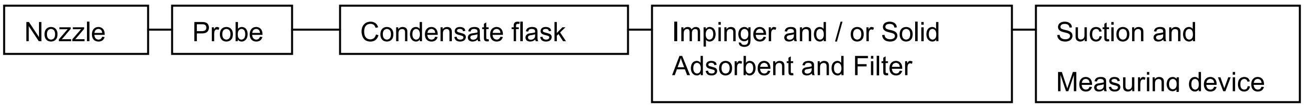

Figure 19 Cooled probe method

The sample gas is collected by a water-cooled probe. The temperature of the sample gas behind the probe should not exceed 20 °C. The formed condensate is collected consequently. Particles mainly collect in the condensate. The gaseous PCDD/Fs from the sample gas accumulate in a sorption step. Solid adsorbents or impingers are used for the sorption step. A particle filter is installed before the final sorption step to collect small particles or aerosols. All surfaces which are in contact with the sample gas must be manufactured from glass.

Compartments for the analysis are:

- Condensate
- Impinger and/or solid adsorbent and filter
- Rinsing solution.

The different configurations for the sample trains of all three methods are described in the appendix of EN 1948.

Requirements of the sampling:

- Before each sampling campaign starts, a field blank value is to be determined (value shall not exceed 10% of the limit value).
- The sampling train is spiked with $^{13}C_{12}$-labelled standard substances (PCDD/Fs and/or PCB). The recovery rate of each standard substance must be greater than 50%, calculated on the basis of the extraction standard.
- The sampling takes place - after a leak test of the equipment – in isokinetic mode at representative points in the flue gas according to EN 13284-1:2001 .

Extraction and clean up (EN 1948-1:1996/prEN 1948-1:2003/prEN 1948-4:200x)

The determination of PCDD/Fs and dioxin-like PCBs is based on quantitative analysis using the isotope dilution technique using a HRGC/HRMS system.

$^{13}C_{12}$-labelled standard substances, which are added to different steps of the overall procedure (sampling, extraction, injection), are used as internal standards for quantification. A cleaning procedure for the raw extract of the sample removes matrix components, which could disturb the further separation process. In addition an enrichment of the PCDD/Fs and/or PCBs is achieved.

As extraction procedures, Soxhlet extraction and liquid-liquid extraction procedures are used. The separation of PCDD/Fs and PCBs takes place with a column chromatography clean-up, e.g. using Florisil or Alumina. In principle each cleaning method (EN 1948 contains several examples) can be used, provided that it is validated.

In each sample the recovery rate of each standard substance of the extraction standards shall be:

- 50 – 130 % for the tetra- to hexa-chlorinated congeners
- 40 - 130 % for the hepta- to octa-chlorinated congeners.

Deviations are permissible if the contributions of the respective congeners do not exceed 10 % to the total I-TEQ (30 - 150% for the tetra- to hexa-chlorinated; 20 - 150% for the hepta- to octa-chlorinated congeners).

The recovery rate for the PCB extraction standard substances shall be 40 - 120 %.

Identification and quantification (EN 1948-3: 1996/prEN 1948-3: 2003/prEN 1948-4: 200x)

The identification and quantification of the PCDD/Fs and dioxin-like PCBs from the extracts of the emission samples is done using a HRGC/HRMS in connection with isotope dilution technology.

For the identification of the congeners

- a HRGC/HRMS with a mass resolution of 10,000 is necessary. A resolution in the range from 5,000 to 10,000 is acceptable if the absence of interferences is well documented.
- At least two ions of the molecular isotope cluster of each chlorination shall be recorded.
- The isotope ratio between the ions must correspond to the theoretical value of 20% (PCDD/F) and 15% (PCB).
- The retention times of the native congeners are within a time window from +3 s to 0 s compared to the signal of the corresponding $^{13}C_{12}$-labelled standard substance.
- The signal-to-noise ratio of the raw data must be at least 3:1 for the signal taken for identification.

Additionally, the identification requirements of the following important points must be fulfilled for quantification:

- The separation of all PCB congeners of interest shall be achieved by using a standard reference mixture.
- It is not possible to separate all 2,3,7,8-chlorinated PCDD/F congeners by using only one chromatography column. Multiple analysis by using different chromatography columns allows for a complete separation. Results of an individual column may be recorded. If the limit value is exceeded, additional confirmation analysis is necessary.

- The recovery rates of the extraction standard substances must correspond to the requirements specified already.
- The measuring range must be linear (at least 5-point-calibration for the determination of the response factors).
- An extraction blank value is to be determined. The concentrations of all congeners should be below the limit of determination and/or factor 10 below the lowest measured concentration.

13.2.2 Other standardised methods

Besides EN 1948 there are further standardised sampling methods [**25**] which are used in the EU. For example VDI 3499, sheet 1-3 and EPA 23 A as stated below.

VDI 3499 is a German standard guideline for the determination of the PCDD/F emissions from stationary sources. The three parts of VDI 3499 describe three different sampling methods, and as specified in EN 1948 are

- sheet 1 - Dilution method,
- sheet 2 - Filter/Condenser method and
- sheet 3 - Cooled probe method.

Each sheet (1, 2 or 3) contains in Part A an example of application of EN 1948 (inclusive sampling and analysis) and in part B a modified measurement procedure of PCDD/F-emissions exceeding *0.1ng I-TEQ/m³ and with possible higher dust load*. This Part B shall be briefly described.

VDI 3499, Part B

The measurement procedure shall be modified in cases of high PCDD/F emission concentrations, emissions with high dust loading, emissions containing tarry particles or for measurements of raw gases.

For high and for low ranges of emission concentrations, separate sampling trains have to be provided to avoid memory effects. A sampling train previously used in a PCDD/F emission concentration range much higher than 0.1 ng I-TEQ/m³ must not be used in the lower concentration range of <0.1 ng I-TEQ/m³. All surfaces which are in contact with sample gas must be manufactured from glass.

In cases of high dust loading an additional particle filter has to be installed for the flue gas, e. g.

- WB 50 filter in case of the dilution method (>100 mg/m³ dust concentration),
- packed quartz wool filter for filter/condenser method (>20mg/m³ dust concentration).

The mass of the $^{13}C_{12}$ labelled standard substances (sampling, extraction and injection standards) is to be adapted to the expected PCDD/F emission concentration.

The sampling time shall be adapted to the measurement task (up to 8 hours).

The extraction and clean up, as well as the identification and quantification are generally done according to the requirements of EN 1948 by using HRGC/HRMS and isotope dilution technology. With the presence of tarry and similar components in the raw extracts of the samples, these can be treated additionally to the normal clean up methods with sulfuric acid. The sulfuric acid effects the decomposition of various organic matrix components. All further requirements correspond to EN 1948.

In addition to the collection of PCDD/Fs the sampling device is also suitable for the determination of further organic compounds (e.g. PCB's, PAH's). However, these measurements are not yet validated.

Table 33 VDI 3499 - Summary

	Section A (EN 1948)	**Section B (modified measurement method**
PCDD/F content	**0.1 ng I-TEQ/m³**	**1 ng I-TEQ/m³ and higher**
Dust loading	**Up to 15 mg/m³**	**Above 20 mg/m³ - filter/condenser method** **Above 100 mg/m³ - dilution method**
Sampling time	**Up to 8 hours**	**Up to 8 hours**

The sampling methods in part B are applied to a wide range of plants, e.g. smelting plants for the recovery of copper and aluminium and for sintering plants.

EPA method 23 A is the American measurement method for the determination of the PCDD/F emissions from stationary sources. Again an isokinetic sampling method (according to EPA method 5) is described. The sample gas is passed and collected by a probe, a glass fibre filter and a solid adsorbent (XAD2). All surfaces which are in contact with the sample gas must be manufactured from glass.

Compared to EN 1948 this sampling method can be called the simplified filter/condenser method. The sampling train is shown in the following figure schematically:

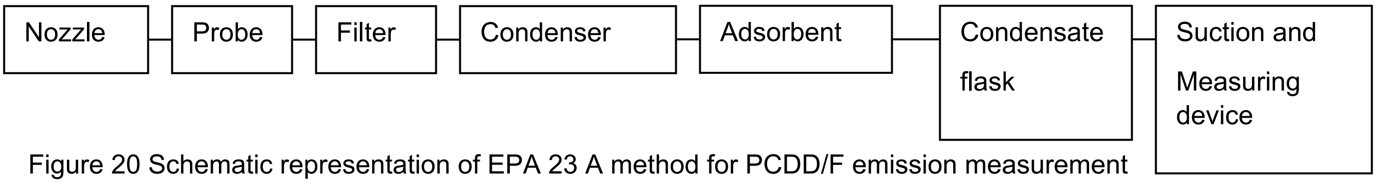

Figure 20 Schematic representation of EPA 23 A method for PCDD/F emission measurement

The sample gas in the probe and filter is brought to a temperature at ≥ 120 °C. Then the sample gas is cooled down in the condenser. The temperature of the sample gas should then not exceed 20°C. The gaseous PCDD/F are collected on a solid adsorbent. The condensate is collected after the adsorption stage exclusively for the determination of the moisture. The relatively complex liquid-liquid extraction of the condensate, as intended in EN 1948 and VDI 3499, is not required.

Compartments for the analysis are

- Particle filter (glass fibre filter)
- Solid adsorbent (XAD2)
- Rinsing solution

The extraction steps, clean up and identification as well as the quantification of the PCDD/F congeners approximately correspond to EN 1948. The configuration of the $^{13}C_{12}$ labelled standard substances differs however somewhat from that in EN 1948. The standard quantity which can be added is also approximately a factor of 2.5 to 5 higher than mentioned in EN 1948.

This guideline is suitable to determine PCDD/F concentrations from **0.2 to 0.4 ng I-TEQ/m³** in the flue gas. These concentrations correspond to the American PCDD/F limit values for hazardous waste combustion.

The standard guideline does not contain any information on the dust load of the flue gas nor other restrictions. Due to the experience with the other standards already presented, the guideline should be suitable for dust loads up to approx. 20 mg/m³ without an additional filtering unit.

With additional filters for particulates, the sampling could be extended to higher dust contents also. With respect to the collection of other organic components, like PCB or PAH, there is no information in EPA guideline. From other standards however it can be derived that adsorption systems consisting of filter and XAD2 can be used for the separation into further components.

13.3 Continuous monitoring

13.3.1 Long-term sampling

With many measurements and evaluations of waste incineration plants in Europe occurring in recent years, it could be shown that the PCDD/F limit values are essentially kept. Occasionally higher PCDD/F emissions may occur and are not detectable as the conventional manual sampling methods cover only a short time (1-3 days) of the operating period. Long-term sampling is a very useful tool to get information on the total emitted mass over the sampling period.

Two systems are on the market (AMESA and DMS, [**26**]), which allow long-term sampling under controlled conditions.

AMESA (Adsorption **ME**thod for **SA**mpling of Dioxins and Furans)

AMESA is similar to the cooled probe sampling method and EPA 23A. The following figure shows the schematic configuration of the system

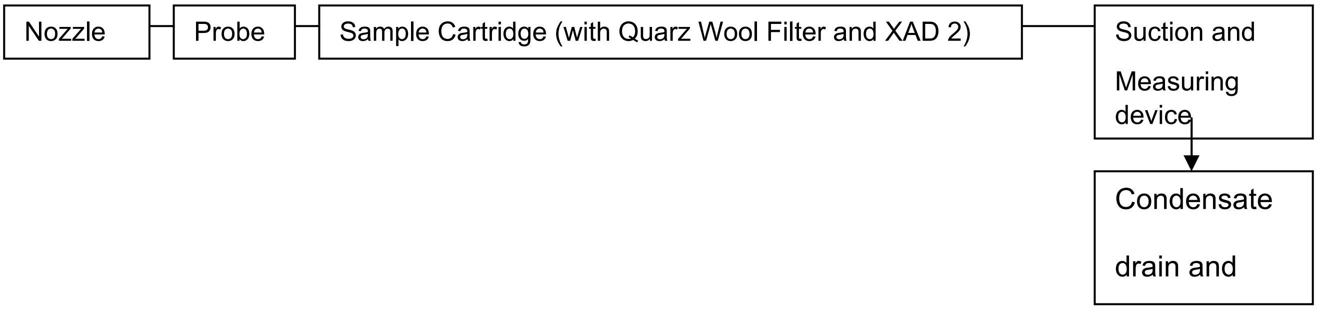

Figure 21 AMESA – System

The sample gas is taken in isokinetic mode from a representative point in the flue gas and cooled down to 70°C within the probe. The sample gas passes an adsorption unit, consisting of a quartz wool filter and solid adsorbent (XAD 2). The PCDD/Fs are collected in the adsorption unit. The condensate is collected (similarly to the EPA 23 A) behind the adsorption unit and is used for the determination of the moisture to normalise the flow rate.

For the determination of the PCDD/Fs content only the adsorption unit is analysed. The PCDD/F content is determined in accordance with EN 1948-2 and EN 1948-3. The collection of the PCB is also possible.

The system allows the determination of the PCDD/F emission content within the range of **0.0001 - 10 ng I-TEQ/m³** with a **dust load of up to 20 mg/m³.** The sampling time can vary between **6 hours and 4 weeks**.

AMESA is installed in more than 70 waste incineration plants in Europe.

Comparative measurements between the Filter/Condenser method, the Cooled probe method and AMESA showed good results. These measurements were accomplished by the GFA in Münster, Germany.

DMS (Dioxin **M**onitoring **S**ystem)

Dioxin monitoring system DMS corresponds to the dilution method of prEN 1948-1:2003. (see Figure 18).

The sample gas is collected in isokinetic mode via a heated probe and cooled down very rapidly below 40°C with dried and filtered air in a mixing channel.

A combination of particle filter (this unit consists of a fine dust filter and a 2 stage foam filter) and solid adsorbent is used to extract and accumulate the PCDD/F from the sample gas.

For the determination of the PCDD/F content, only the adsorption unit is analysed. The PCDD/F content is determined in accordance with EN 1948-2 and EN 1948-3. The determination of the dioxin-like PCBs is also possible and already established in waste incineration plants.

The PCDD/F measurement range lies between **0.0001 and 10 ng I-TEQ/m³** with **dust load up to 150 mg/m³**. The sampling time varies between 6 hours and 4 weeks. DMS is established in various incineration plants. References from the industrial metallurgical sector are not available.

Both systems show comparable results to the manual sampling methods of EN 1948. Compared to this method, the data provided are more suitable for an assessment of the annual emissions or of the long-term compliance to limit values.

Umicore Hoboken in Belgium carried out some initial test attempts with the AMESA system over a period of almost two years. The tests revealed that semi-continuous sampling methods cannot be regarded competitive to manual sampling due to the high investment and maintenance costs. The semi-continuous sampling system can be installed only to one stack and is not suited to move between different stacks. If one plant has a lot of stacks this would mean that more than one system is required. In cases when numerous stacks have to be monitored the usage of discontinuous sampling methods is advantageous.

13.3.2 Indicator and surrogate compound measurements

Due to the relatively high costs and the time needed for the PCDD/F analysis, research was conducted for possibilities of the PCDD/F concentrations in a flue gas being indicated by measurement of other substances which can be detected easier. For this purpose surrogate and/or indicator compounds were used [**27**].

Surrogate compounds are substances which correlate closely to the dioxin concentration. Indicator substances are compounds which indicate the formation of dioxins. The substantially higher concentration of the surrogate or indicator compounds in the flue gas (e.g. factor 1000) not only allows a simple measurement technique, but also offers an additional possibility of process control and monitoring. Most publications on surrogates deal with flue gas from incineration processes. In the flue gas, PCBz (polychlorobenzenes) and PCPh (polychlorophenols) as well as PCDD/Fs were detected. Chlorobenzenes were the first surrogate compounds proposed. Up to now many different compounds have been detected in flue gases that have shown a correlation to the dioxin concentration.

The linear relationship between the different concentration data is characterised quantitatively by a correlation coefficient (r) or a coefficient of determination (r^2).

A number of different approaches for surrogate measurements have been proposed:

1. Feed quality

   It is known that the chlorine input has an influence on PCDD/F formation during thermal processes. However, the dioxin formation is also substantially determined by the process conditions. The dioxin content in the flue gas is also strongly influenced by the existence of abatement measures, too. Therefore, many different factors have an influence on the dioxin concentration in the flue gas.

2. CO content

   CO is a good indicator for the performance of a burning process. Attempts have been made to establish correlations to different organic compounds. Process conditions and the effectiveness of exhaust gas cleaning however are influencing the correlations substantially. For this reason the results presented in the literature for waste incineration are neither consistent nor convincing.

3 Sum parameters

Like CO the content of unburned organic carbon (VOC) is an indicator for the efficiency of a burning process. The correlation determined between the VOC and the TEQ in a combustion plant was however low. A better correlation indicated a summary parameter for halogenated compounds, SNVOX (semi- and non volatile organohalogen compounds) ($r^2 = 0.75-0.83$) in incineration plants.

4 PCBz and PCPh

PCBz and PCPh are the compounds which are used most frequently as surrogates. All correlations determined for combustion plants are very good. The large interest, particularly in chlorobenzenes, is due to the possibility of on-line measurement of these substances (employment of different on-line GC systems).

5 PCDD/F Kongenere

Individual Cl1-Cl3 chlorinated congeners showed good correlations for different thermal processes to the TEQ of the PCDD/F. Also, the correlation of the 2,3,4,7,8-Cl5DF, the most important congener during most thermal processes, to the I-TEQ of the PCDD/F showed very good results.

6 Multiparameter analysis (PLSR – Partial Least Square Regression)

PLSR applied to the correlation of the PCDD/F content with PCBz and PCPh contents. The results for different incineration plants and metallurgical processes are between $r^2 = 0.92-0.98$.

PCBs have a good correlation to the I-TEQ of the PCDD/F for metallurgical processes [32].

All correlations from surrogate compounds to I-TEQ of PCDD/F are strongly process dependent and can not be generalized. Before making use of individual substances as surrogates, which show a close correlation to the I-TEQ of PCDD/F, an extensive measurement program has generally to be carried out first. Surrogate compounds are not only used for the calculation of I-TEQ of PCDD/Fs, but are useful for process control too. The use of surrogate and/or indicator components in the metallurgical industry is documented in some references. [28, 29]

13.4 Future developments

The interest in an economical and simple measurement method for the sampling of the PCDD/Fs is relatively large.

Initial attempts at a simple shorter sampling method were published in the 80's by the GFA in Germany [30]. The published method corresponds closely to the AMESA system (see Figure 21). Both methods were developed and tested together.

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[32] According to industry information other experiments have revealed worse correlations between PCBs and I-TEQ PCDD/F ($R^2 < 0.4$). Since no original data were provided no assessment can be made on this statement.

The sample gas is collected via a cooled probe in a time from 2 to 16 hours depending on the measurement task. The PCDD/F are separated in an adsorption unit, consisting of a quartz wool filter and solid adsorbent (XAD2). The condensate is collected after the adsorption unit and used only for the determination of the moisture. The PCDD/F content is determined from the adsorption unit. Extraction steps, clean up and identification as well as quantification of PCDD/F congeners correspond approximately to EN 1948.

This sampling method was established for PCDD/F contents of 1 ng I-TEQ/m³ with dust loading up to 1 g/m³ and was tested in incineration plants.

However, this method does not contain essential simplifications in comparison to the standardised method (EN 1948) and so no significant time and cost benefit can be expected here.

For the simplification of the analysis step of the PCDD/F determination, bioassays are available on the market [31].

Bioassays, e.g. use a dioxin specific antibody for dioxins and dioxin-similar compounds (PCB, PHAH etc.) to detect and quantify a sample. As a result bioassays directly produce an I-TEQ sum value. The extraction and the clean up are essentially simplified. It takes only 24 hours to get an analysis value. Bioassays are extremely sensitive (fg - range), so that these measurement methods are mostly used for samples with a minor PCDD/F content, e.g. feed and food samples for where this method has been sufficienty established.

In cases where the limit is exceeded, a complete PCDD/F analysis has to be done. References for the metal industry are not available.

The latest developments in this field are coming from Japan. The Kyoto Electronics Manufacturing Co. (KEM) developed a new simplified dioxin method for the analysis of flue gas, fly ash, bottom ash, soil, sediment, air and water. In 2005, as a first step, KEM aims to produce a sample preparation system and a dioxin biosensor for flue gas, flue ash and burnt residues. The sample preparation system contains simple extraction and clean up steps. It is possible to process 3 samples in 150 minutes. The biosensor uses a highly sensitive antibody which recognises 2,3,4,7,8-Cl_5CDF. This dioxin congener shows a close correlation to the I-TEQ of the PCDD/F in most incineration processes. The total I-TEQ is calculated from the results of the 2,3,4,7,8-Cl_5CDF-congener.

This system is not available on the market as yet.

13.5 Costs of the measurement methods

The following table contains an overview of sampling and analysis prices. These prices are to be understood only as a rough estimation. The prices are regionally very different. Generally it can be assumed that more attractive prices can be achieved with larger measurement programs.

Table 34 Cost overview

Method	Costs range (€)
Manuel sampling according to EN 1948 – 1 sample (1 day) inclusive PCDD/F analysis without travel cost	1800 – 3500
Manuel sampling according to EN 1948 – 3 samples (3 days) inclusive PCDD/F analysis without travel cost	4000 – 6500
PCDD/F –analysis (EN 1948)	450 – 800
Dioxin-like PCB – WHO PCB (EN 1948)	110 – 600
Marker PCB	70 – 150
PCBz	65 – 120
PCPh	75 – 120
PAH	65 – 120
Long-term system (acquisition costs)	65,000 – 85,000
Long-term system (installation and starting)	5000 – 8000
Long-term system (yearly attendance and abrasion)	3000/year
Long-term system (12 samples yearly, 5 years)	2500/sample

13.6 Conclusion

In practice the manual (discontinuous) standardized and validated measurement methods (e.g. EN 1948) are used. These measurement methods, developed for waste incineration plants, are transferable to the metallurgical industry and are already in use there.

Semi-continuous long-term sampling methods essentially apply the EN 1948. In the waste incineration and in similar industrial sectors, this kind of sampling is often used. If a high frequency of discontinuous measurements is required in a plant with only one stack, these methods may be regarded as being competitive to the manual sampling. In cases when numerous stacks have to be monitored the usage of discontinuous sampling methods is advantageous, as revealed by a 2-year test carried out at Umicore Hoboken in Belgium.

Surrogate and indicator compounds are substances which show a close correlation to the PCDD/F concentration. PCBz and PCPh are the compounds which are used most frequently as surrogates. The results for different incineration plants and metallurgical processes are between $r^2 = 0.92$-0.98.

All correlations from surrogate compounds to I-TEQ of PCDD/F are strongly process dependent and can not be generalized. For every individual case, a large measurement and validation program has to be carried out to prove the correlation to the I-TEQ of PCDD/F and its sensitivity to changing process conditions.

The following table summarises again all measurement methods.

Table 35 Measurement methods

Methods	PCDD/F emission concentration, Dust loading, other organic compounds (PCB); Validation; References
Discontinuous monitoring	
EN 1948 (European guideline)	PCDD/F ≈ 0.1 ng I-TEQ/m³; Dust loading up to 15 mg/m³; dioxin-like PCB inclusive, no limited sampling time, validated for waste incineration plants; metallurgical processes possible
VDI 3499 (German guideline)	Part A: PCDD/F ≈ 0.1 ng I-TEQ/m³; Dust loading up to 15 mg/m³, Part B: PCDD/F > 0.1 ng I-TEQ/m³, higher Dust loading, tarry particles possible, raw gas possible, Part A and B: sampling time up to 8 hours, PCB and other organic pollutants possible; validated for waste incineration plants; metallurgical processes possible
EPA 23 A (American guideline)	PCDD/F ≈ 0.2 or 0.4 ng I-TEQ/m³; Dust loading = no information (up to 15 mg/m³), PCB and other organic pollutants possible (no information), Validated for waste incineration plants (no information)
Continuous monitoring (Long-term sampling)	
AMESA	PCDD/F ≈ 0.0001 – 10 ng I-TEQ/m³; Dust loading up to 20mg/m³; many references for waste incineration plants
DMS	PCDD/F ≈ 0.0001 – 10 ng I-TEQ/m³; Dust loading up to 150mg/m³; many references for waste incineration plants
Surrogates	Correlations to I-TEQ of PCDD/F process dependent, calibration necessary; some references for metallurgical processes
Future developments	
Short term sampling	PCDD/F < 0.1 to > 1.0 ng I-TEQ/m³; Dust loading up to 1 g/m³; references for waste incineration plants
Bioassays	Sum I-TEQ-substances as results (references for food and feed)
Biosensor	New development from Japan, not available on the market, no references

14 Annex G Information related to the reporting of PCDD/F emission measurements

Scope

In previous Annexes it has been shown that the sampling and analysis of dioxins is both cumbersome and time-consuming and that the resulting emission values depend on numerous different factors, explained in Annex E.

It follows that the type of plant, its operating conditions, the feed materials, as well as operating incidents all influence upon the final result.

In what follows some suggestions are made that may be useful at the moment of preparing for making dioxin measurements.

Format of data presentation

It is proposed defining a standardized E.U.-format for reporting on PCDD/F emission measurements, in order to achieve the following purposes:

- Ensuring ease of reporting to Authorities and the public,
- Enhancing readability of the Report, as well as completeness, comparability of emission data, and focusing further on the most relevant facts.

These relevant facts may be useful, or even necessary, in order to

- make choices for further analyses and evaluate their relevance in monitoring dioxin emission values and
- design trial campaigns for gradually reducing emission values by introducing tentative primary and secondary reduction methods during dedicated trials.

It is recommended limiting reports on individual processing units to a maximum of 2 pages.

Process description

A comprehensive process description is always required, except in cases where a standard and well-established production process is followed. The latter is much more common in the iron & steel sector, since it employs processes that are relatively standard and well documented. Standard processes are those described in this text or in the basic treatises cited (BREF Documents and other reference works) and are either involving **ores**, such as iron ore sintering, the blast furnace, the basic oxygen converter, or else involving **scrap**, such as the Electric Arc Furnace (EAF).

For such well-known processes, it is sufficient to cite some general plant data, which allow visualisation of the plant and assessment of its capacity.

For processes that are less well-known, confidential, or even unique, a **brief description** must be provided, stating essential information, such as:

1. **Title**, stating the **Basic Principle of the Operation**, the **Furnace** Type Used, the Type of **Feed** employed and the **Operating Conditions** used; e.g.

Multipurpose EAF used for processing filter dust and other process fines derived from the production of stainless steel, to recover an alloy of iron, nickel, and chromium under reducing conditions.

A block diagram and/or a cross-section of the process should be included

2. **Feeding system**, e.g.

   gravity feeding, over a system of locks, as in a blast furnace, or else, an EAF, featuring feeding through a hollow electrode.

3. **Feed Flow mode**, i.e.
   a. in counter-current (as in the blast furnace),
   b. cross-current (Dwight Lloyd sintering belt) or in
   c. co-current (ore reduction under entrained bed or pneumatic flow conditions).
4. **State of the charge**, i.e.
   a. stationary,
   b. slowly moving down under gravity,
   c. suspended in a fluidised bed, under either bubbling or circulating conditions,
   d. suspended in a melt,
   e. suspended in a gas flow, …
5. **Typical operating conditions**, including the temperatures attained during operation, the pressure and the way it is maintained, the type of **atmosphere used** (reducing, inert, oxidising) and the method used for constituting this atmosphere, e.g. reducing combustion of natural gas (with an oxygen deficit stated by the carbon monoxide concentration), gasification of coke, provision of argon as an inert gas …
6. **Operating modes**, basically:
   a. Continuous or quasi-continuous operation, the only cyclic event being the actual loading once every few minutes
   b. Cyclic operation, the main event being a periodic operation, constituted by the gradual loading, melting, reaction and conversion by applying oxidation and reduction reactions, and the refining of the charge, eventually followed by a partial casting of slag and metal content
   c. Batch by batch processing

The actual processing mode should be briefly described.

7. Method of **tapping slag and metal** and its cycle time
8. Miscellaneous other data

Brief description of the Feed

Typically the furnace feed is composed of **ores, coke, additives** and **fluxing agents**. The feed may be supplied either as a mixture or it may be charged sequentially, one component after the other. Refining or degassing agents may be supplied later in the cycle.

In dioxin studies the characteristic composition of ores, coke, fluxing agents are important factors, in particular the data relative to the **input of chlorine, of salts** and of **volatile metals (Cu, Pb, Zn, Cd, Mo …).** Both volatile salts and metals accumulate in filter dust, which is eventually recycled.

Some other elements **suppress** dioxin formation, e.g. basic compounds can exert such an effect. However, suppression mechanisms are ill-understood. In almost all cases, they reduce the output of chlorinated aromatics, without affecting their fingerprint.

Chlorine Balance

It is important to establish at least tentatively the chlorine balance for a plant.

Important inputs typically are:

- Ores
- Coke, or other reducing agents (e.g. anthracite), or fuels.
- Charges of slag builders, such as silica, limestone, or lime
- Fluxing agents
- Recycling streams, e.g. filter dust, scrap (with drawing or machining oils added), rich slag, and other, miscellaneous process reverts
- Process water

Major outputs are often:

- Metal
- Slag
- Filter Dust
- Flue Gas

Often, the latter two flows are easiest to assess with respect to their chlorine content.

Generally speaking it is quite difficult to analyse chlorine accurately at the levels in which it occurs in ores or coke, slag or metal. Typical values in iron ore are 30 to 300 ppm. Chlorine values in coke are rather variable.

Volatile Salts

Depending on operating conditions chlorine mainly evolves from furnaces as either

- Volatile salts, mainly KCl and NaCl, or as
- Hydrogen Chloride.

Remarkably, hydrogen chloride (HCl) measuring methods mostly determine the chloride ion concentration and erroneously label this concentration as HCl.

Monitoring volatile salts, as well as HCl, in the flue gas is useful while monitoring dioxin generating facilities.

The importance of Volatile Salts is mainly linked to their role in dioxin formation as a transfer agent of chlorine. Heavy metal chlorides generate the catalyst responsible for both this transfer and for oxidising carbonised materials. It is mainly during this process that dioxins are formed.

Volatile Heavy Metals

Copper (chloride) is a premium catalyst in the processes (oxidation, chlorination) responsible for dioxin generation. It becomes volatile at relatively low temperatures (even below 500 °C), in systems containing some chlorine. After evolving from the furnace its vapours condense upon particulates, in situ generating the catalytic system responsible for dioxin generation.

Other easily volatilising elements are lead, zinc, cadmium, mercury, etc .

A single case has been investigated in which copper chloride volatilisation was suppressed by that of lead chloride (cf. earlier VUB studies).

The importance of Volatile Heavy Metals is mainly linked to their role in dioxin formation, which involves at least three distinct types of action:

- Catalytic activity in the chlorination of carbon structures and organic compounds. The mechanism of chlorine transfer is covered in the Ph.D. study of Dr. P. Weber, June 2000[33]
- Catalytic activity in oxidising carbon structures and organic compounds. The mechanism of oxygen transfer is covered in detail in the Ph.D.-study of Jörg Wilhelm[34]
- A source of chlorine, necessary for chlorination.

Volatile Organic Compounds

Volatile Organic Compounds originate from several sources:

- Incomplete combustion of conventional fuels, such as natural gas and gas oil.
- Evolution of Volatile Compounds from coke.
- Evolution of Volatile Compounds from organic and plastic materials adhering to scrap.

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[33] Der Chlortransfer bei der Bildung von polychlorierten organischen Spurenstoffen (PCDD/PCDF) in industriellen thermischen Prozessen (Müllverbrennung), P. Weber, Institut für Technische Chemie, Forschungzentrum Karlsruhe Technik und Umwelt, Wissenschaftliche Berichte, FZKA 6485 Juni 2000

[34] Mechanistische Untersuchungen zum Einfluss intra- und intermolekularer Sauerstoffübertragungsreaktionen sowie zu strukturell bedingten Bildungstendenzen bei der De-Novo-Synthese von PCDD und PCDF, J. Wilhelm, Institut für Technische Chemie, Forschungzentrum Karlsruhe Technik und Umwelt, Wissenschaftliche Berichte, FZKA 6489 Juni 2000

- Evolution of Volatile Compounds from oil adhering to scrap.

There is debate about the role of such compounds in dioxin formation. The statistical correlation with VOC, mostly expressed as Total Organic Carbon (TOC), is weak.

However, this may be linked directly to the large number of parameters, which can influence dioxin formation, rather than to the lack of effect of any of them.

Methods of Studying Dioxin Problems

The following procedure is recommended:

- Completely analyse raw materials for the elements present, with methods such as XRF, AAS, ICP, SEM, or colorimeters.
- Completely analyse several samples of filter dust and compare their composition during different measurement campaigns.
- Collect samples of in-plant deposits and analyse these as well.

In some processes, plant deposits gradually vary from feed end towards the stack. Indeed, the deposition of coarse particles, mechanically entrained by the gases leaving the furnace, is especially important close to the furnace. Further down, deposits are increasingly formed by de-sublimation of vapours formed from volatile salts. Different layers in this deposition are often apparent.

Depending on plant nature, more specific tests may be devised.

In a VUB/TEMCO study programme interesting data was derived by temporarily halting the recycling of filter dust. Remarkably, the composition of filter dust markedly changed in less than an hour, due to a dramatic decrease of a volatile metal e.g. Pb; the reverse of this was obvious when recycling of filter dust was resumed. The test differentiates clearly between volatile elements, and those that are not.

It should be noted that this rapid reaction may last much longer in a larger plant, with an impressive inventory of past deposits.

Past deposits play a material role in dioxin formation. They are responsible for Memory Effects that stabilise dioxin output, which is clearly demonstrated by a series of successive dioxin analysis.

Memory Effects

Memory effects refer to the smoothening effect, exerted on emissions by various phenomena with different causes and - possibly – effects:

- Plant deposits are a source of organic compounds, carbon, chlorides, and catalytic elements. The *de novo* formation of chlorinated organics is a major pathway towards dioxins.
- Such deposits may emit previously adsorbed organics.

- Plastic and rubber materials, present in the cold sections of the plant, may absorb dioxins, releasing these slowly later.

Knowledge on dioxin formation

There has been extensive scientific study of dioxin formation in MSWI. Important results were obtained by a number of pioneers, such as Buser, Hutzinger, Karasek, Louw, Olie, Rappe and several others.

The most important theories are:

1. The Trace Chemistries of Fire
2. The Precursor Theories, and
3. The incomplete, low-temperature (200 – 400 °C) catalytic Carbon Oxidation, also termed de novo theory, developed in quite some detail at ForschungsZentrum Karlsruhe (FZK) by Dr. L. Stieglitz, aided by an impressive series of Ph.D students.

These theories probably all apply.

Trace chemistries lead to the high temperature, gas phase formation of aliphatic and aromatic structures. The latter consist of simple and alkylated aromatics, PAH, dibenzofuran (DF) and dibenzo-p-dioxin (DD) structures.

Dr. E. Wikström suggested that the surviving Products of Incomplete Combustion (PIC) are merely chlorinated to PCDD/F at lower temperatures.

Precursor theories readily explain the Seveso disaster (July 1975). The theory was first launched by Prof. Karasek and many times confirmed by dedicated experiments: two chlorophenol molecules readily combine to form the corresponding PCDD congener. Dr. M. Cieplik, in the framework of MINIDIP, tested cocktails of precursors and successfully generated PCDD/F on iron ore. More detailed investigations were conducted in a Ph.D. study by Jiménez-Leal, using an impressive series of individual precursors, namely:

- n-hexane
- benzene
- toluene, benzaldehyde, chlorophenol
- naphthalene, fluorene

In some experiments, the Fly Ash tested was doped with ^{13}C to discriminate between the precursor route and the de novo, catalytic carbon gasification.

However, although the precursor theory may well be responsible for generating PCDD structures, it fails in generating the corresponding PCDF congeners.

MINIDIP research was capable of extensively simulating dioxin formation, starting from filter dust from, int. al.

- Iron ore sintering,
- manganese ore sintering,
- Waelz processes,

- Copper smelting, as well as melting.

These processes were analysed under laboratory conditions, modelled kinetically, and the process was simulated by complete plant simulations using Computer Fluid Dynamics (CFD).

The right PCDD/F profiles were obtained and the influence of various parameters was studied, int. al.:

- Temperature, from 200 – 450 °C,
- Time, from ½ to 4 hours,
- Oxygen concentration, from 0 to 50 Vol. %,
- Additives, to supply deficient elements (e.g. carbon, copper)
- Suppressing Additives, e.g. ammonia, urea, methylamines (sulphur compounds are good suppressants, but generally undesirable in metallurgical processes).

Kinetic Aspects of Dioxins Formation

The study of de novo dioxins formation leads to the following results:

- Temperature. The rate of formation at a constant time follows a bell-shaped curve, continuously rising from 200 to almost 350 °C, then declining sharply. Formation becomes negligible above 450 °C. In all likelihood, as the temperature increases PCDD/F are decomposed both by oxidation and dechlorination
- Time. The rate of formation at a constant temperature (300 °C) rises continuously with time up to typically 4 hours. At higher temperatures a maximum may be reached. At lower temperatures there may be an initial period of latency.
- Oxygen concentration.

Under inert gas conditions there is only formation of:

- PCDD/F according to the condensation route (mainly chlorophenol) .
- PCB, PCBz, i.e. compounds not containing any oxygen.

Moreover, under inert gas conditions PCDD/F are rapidly (in a few hours) and completely decomposed at temperatures above 300 °C, probably following a stepwise dechlorination, accompanied by destruction of aromatic cycles.

Dioxin formation rises linearly as oxygen concentrations increase from 0 to 10 Vol. %,

- Carbon content

In some smelters the carbon content of the entrained dust is the rate controlling factor.

In synthetic MSWI fly ash dioxin formation rises linearly with carbon concentrations, increasing from 1 to 8 Wt. %,

- Chlorine content

In some smelters with no obvious chlorine in the feed and fuel materials the Chlorine content of the entrained dust is the rate controlling factor.

In (synthetic) MSWI fly ash dioxin formation rises linearly with Chlorine concentrations, increasing from 0.5 to 4 Wt. %,

In many metallurgical systems, e.g. in the iron ore sintering plant, the filter dust is recycled. The dust then contains well in excess of 4 wt. % of Cl.

- Moisture content

The influences of moisture are unclear. Often, dioxin formation increases and the average chlorination level decreases, increasing TEQ-factors.

In most metallurgical systems the moisture content of flue gases is quite low (< 4 vol. %), especially when compared to MSWI.

- Additives, which supply deficient elements (e.g. carbon, copper)

Suppressing Additives, e.g. ammonia, urea, methylamines (sulphur compounds are good suppressants, but generally undesirable in metallurgical processes).

Typical emission data (PCDD/F and PCBs)

It is difficult to cite any typical emission data (PCDD/F and PCBs) for any specific metallurgical process. The major reasons are as follows, when considering a continuous process:

1. The emission values vary with the **raw materials** provided. Some may be much richer in relevant elements (Cl, Cu, etc.) or in volatile organics (scrap, coke) than others!
2. The emission values vary with the **operating conditions**. In some plants some low PCDD/F values have been observed at both high and low flue gas exit temperatures, with the highest values somewhere in the middle range. The operating conditions in the flue gas cooling tract are especially important.
    - Quenching flue gases from 500 to 200 °C will markedly decrease emissions. The measure has successfully been applied in foundries featuring cupola furnaces. The measure is more difficult to apply in iron ore sintering, because of the cross-flow arrangement requiring quenching parallel flows. An alternative, with recycling of hot gases through another part of the sintering strand has been introduced by Lurgi at Corus IJmuiden.
    - It has been demonstrated repeatedly that electrostatic precipitators are responsible for extensive dioxin formation, even though they subtract PCDD/F from the gas stream by collecting PCDD/F-laden dust. Such generation is rising exponentially with temperature up to ca. 350 °C.
    - Filtration in baghouse units is also accompanied by extensive PCDD/F formation, if filtration occurs at high temperature, which is fortunately seldom the case. Most units operate at a safe 90 – 140 °C, sometimes up to 220 – 240 °C (PTFE fibres) but some ceramic filters operate at higher temperatures.

3. The emission values vary with **time**: a new plant has often less PCDD/F generating capacity and its PCDD/F will be less chlorinated than after some deposition has taken place. Boiler fouling and/or deposition in flues sometimes leads to forced plant shutdown. Starting up again a cleaned plant may lead to surprising values, which are in any case unpredictable.
4. The emission values can be lowered by the use of suppressants, generally by some 50 % and in exceptions by 95 %.
5. The emission values vary with numerous other factors that in practice are not always well known and controlled. For further information, relevant literature must be referred to.

15 Annex H Absolute Uncertainty and Reduction in Absolute Uncertainty

σrel = 60% : AU - Absolute Uncertainty (gTEQ/year)

		n ->	0	1	2	3	4	5	10	15	20	30	40	50	75	100
Yearly emission	µg TEQ / year	3	3.53E-04	3.53E-06	2.49E-06	2.04E-06	1.76E-06	1.58E-06	1.12E-06	9.11E-07	7.89E-07	6.44E-07	5.58E-07	4.99E-07	4.07E-07	3.53E-07
		5	5.88E-04	5.88E-06	4.16E-06	3.39E-06	2.94E-06	2.63E-06	1.86E-06	1.52E-06	1.31E-06	1.07E-06	9.30E-07	8.32E-07	6.79E-07	5.88E-07
		8	9.41E-04	9.41E-06	6.65E-06	5.43E-06	4.70E-06	4.21E-06	2.98E-06	2.43E-06	2.10E-06	1.72E-06	1.49E-06	1.33E-06	1.09E-06	9.41E-07
		10	1.18E-03	1.18E-05	8.32E-06	6.79E-06	5.88E-06	5.26E-06	3.72E-06	3.04E-06	2.63E-06	2.15E-06	1.86E-06	1.66E-06	1.36E-06	1.18E-06
		20	2.35E-03	2.35E-05	1.66E-05	1.36E-05	1.18E-05	1.05E-05	7.44E-06	6.07E-06	5.26E-06	4.29E-06	3.72E-06	3.33E-06	2.72E-06	2.35E-06
		30	3.53E-03	3.53E-05	2.49E-05	2.04E-05	1.76E-05	1.58E-05	1.12E-05	9.11E-06	7.89E-06	6.44E-06	5.58E-06	4.99E-06	4.07E-06	3.53E-06
		50	5.88E-03	5.88E-05	4.16E-05	3.39E-05	2.94E-05	2.63E-05	1.86E-05	1.52E-05	1.31E-05	1.07E-05	9.30E-06	8.32E-06	6.79E-06	5.88E-06
		80	9.41E-03	9.41E-05	6.65E-05	5.43E-05	4.70E-05	4.21E-05	2.98E-05	2.43E-05	2.10E-05	1.72E-05	1.49E-05	1.33E-05	1.09E-05	9.41E-06
		100	1.18E-02	1.18E-04	8.32E-05	6.79E-05	5.88E-05	5.26E-05	3.72E-05	3.04E-05	2.63E-05	2.15E-05	1.86E-05	1.66E-05	1.36E-05	1.18E-05
		200	2.35E-02	2.35E-04	1.66E-04	1.36E-04	1.18E-04	1.05E-04	7.44E-05	6.07E-05	5.26E-05	4.29E-05	3.72E-05	3.33E-05	2.72E-05	2.35E-05
		300	3.53E-02	3.53E-04	2.49E-04	2.04E-04	1.76E-04	1.58E-04	1.12E-04	9.11E-05	7.89E-05	6.44E-05	5.58E-05	4.99E-05	4.07E-05	3.53E-05
		500	5.88E-02	5.88E-04	4.16E-04	3.39E-04	2.94E-04	2.63E-04	1.86E-04	1.52E-04	1.31E-04	1.07E-04	9.30E-05	8.32E-05	6.79E-05	5.88E-05
		800	9.41E-02	9.41E-04	6.65E-04	5.43E-04	4.70E-04	4.21E-04	2.98E-04	2.43E-04	2.10E-04	1.72E-04	1.49E-04	1.33E-04	1.09E-04	9.41E-05
	mg TEQ / year	3	3.53E-01	3.53E-03	2.49E-03	2.04E-03	1.76E-03	1.58E-03	1.12E-03	9.11E-04	7.89E-04	6.44E-04	5.58E-04	4.99E-04	4.07E-04	3.53E-04
		5	5.88E-01	5.88E-03	4.16E-03	3.39E-03	2.94E-03	2.63E-03	1.86E-03	1.52E-03	1.31E-03	1.07E-03	9.30E-04	8.32E-04	6.79E-04	5.88E-04
		8	9.41E-01	9.41E-03	6.65E-03	5.43E-03	4.70E-03	4.21E-03	2.98E-03	2.43E-03	2.10E-03	1.72E-03	1.49E-03	1.33E-03	1.09E-03	9.41E-04
		10	1.18E+00	1.18E-02	8.32E-03	6.79E-03	5.88E-03	5.26E-03	3.72E-03	3.04E-03	2.63E-03	2.15E-03	1.86E-03	1.66E-03	1.36E-03	1.18E-03
		20	2.35E+00	2.35E-02	1.66E-02	1.36E-02	1.18E-02	1.05E-02	7.44E-03	6.07E-03	5.26E-03	4.29E-03	3.72E-03	3.33E-03	2.72E-03	2.35E-03
		30	3.53E+00	3.53E-02	2.49E-02	2.04E-02	1.76E-02	1.58E-02	1.12E-02	9.11E-03	7.89E-03	6.44E-03	5.58E-03	4.99E-03	4.07E-03	3.53E-03
		50	5.88E+00	5.88E-02	4.16E-02	3.39E-02	2.94E-02	2.63E-02	1.86E-02	1.52E-02	1.31E-02	1.07E-02	9.30E-03	8.32E-03	6.79E-03	5.88E-03
		80	9.41E+00	9.41E-02	6.65E-02	5.43E-02	4.70E-02	4.21E-02	2.98E-02	2.43E-02	2.10E-02	1.72E-02	1.49E-02	1.33E-02	1.09E-02	9.41E-03
		100	1.18E+01	1.18E-01	8.32E-02	6.79E-02	5.88E-02	5.26E-02	3.72E-02	3.04E-02	2.63E-02	2.15E-02	1.86E-02	1.66E-02	1.36E-02	1.18E-02
		200	2.35E+01	2.35E-01	1.66E-01	1.36E-01	1.18E-01	1.05E-01	7.44E-02	6.07E-02	5.26E-02	4.29E-02	3.72E-02	3.33E-02	2.72E-02	2.35E-02
		300	3.53E+01	3.53E-01	2.49E-01	2.04E-01	1.76E-01	1.58E-01	1.12E-01	9.11E-02	7.89E-02	6.44E-02	5.58E-02	4.99E-02	4.07E-02	3.53E-02
		500	5.88E+01	5.88E-01	4.16E-01	3.39E-01	2.94E-01	2.63E-01	1.86E-01	1.52E-01	1.31E-01	1.07E-01	9.30E-02	8.32E-02	6.79E-02	5.88E-02
		800	9.41E+01	9.41E-01	6.65E-01	5.43E-01	4.70E-01	4.21E-01	2.98E-01	2.43E-01	2.10E-01	1.72E-01	1.49E-01	1.33E-01	1.09E-01	9.41E-02
	g TEQ / year	3	3.53E+02	3.53E+00	2.49E+00	2.04E+00	1.76E+00	1.58E+00	1.12E+00	9.11E-01	7.89E-01	6.44E-01	5.58E-01	4.99E-01	4.07E-01	3.53E-01
		5	5.88E+02	5.88E+00	4.16E+00	3.39E+00	2.94E+00	2.63E+00	1.86E+00	1.52E+00	1.31E+00	1.07E+00	9.30E-01	8.32E-01	6.79E-01	5.88E-01
		8	9.41E+02	9.41E+00	6.65E+00	5.43E+00	4.70E+00	4.21E+00	2.98E+00	2.43E+00	2.10E+00	1.72E+00	1.49E+00	1.33E+00	1.09E+00	9.41E-01
		10	1.18E+03	1.18E+01	8.32E+00	6.79E+00	5.88E+00	5.26E+00	3.72E+00	3.04E+00	2.63E+00	2.15E+00	1.86E+00	1.66E+00	1.36E+00	1.18E+00
		20	2.35E+03	2.35E+01	1.66E+01	1.36E+01	1.18E+01	1.05E+01	7.44E+00	6.07E+00	5.26E+00	4.29E+00	3.72E+00	3.33E+00	2.72E+00	2.35E+00
		30	3.53E+03	3.53E+01	2.49E+01	2.04E+01	1.76E+01	1.58E+01	1.12E+01	9.11E+00	7.89E+00	6.44E+00	5.58E+00	4.99E+00	4.07E+00	3.53E+00
		50	5.88E+03	5.88E+01	4.16E+01	3.39E+01	2.94E+01	2.63E+01	1.86E+01	1.52E+01	1.31E+01	1.07E+01	9.30E+00	8.32E+00	6.79E+00	5.88E+00
		80	9.41E+03	9.41E+01	6.65E+01	5.43E+01	4.70E+01	4.21E+01	2.98E+01	2.43E+01	2.10E+01	1.72E+01	1.49E+01	1.33E+01	1.09E+01	9.41E+00
		100	1.18E+04	1.18E+02	8.32E+01	6.79E+01	5.88E+01	5.26E+01	3.72E+01	3.04E+01	2.63E+01	2.15E+01	1.86E+01	1.66E+01	1.36E+01	1.18E+01

σrel = 200% : AU - Absolute Uncertainty (gTEQ/year)

		n ->	0	1	2	3	4	5	10	15	20	30	40	50	75	100
Yearly emission	µg TEQ / year	3	1.18E-03	1.18E-05	8.32E-06	6.79E-06	5.88E-06	5.26E-06	3.72E-06	3.04E-06	2.63E-06	2.15E-06	1.86E-06	1.66E-06	1.36E-06	1.18E-06
		5	1.96E-03	1.96E-05	1.39E-05	1.13E-05	9.80E-06	8.77E-06	6.20E-06	5.06E-06	4.38E-06	3.58E-06	3.10E-06	2.77E-06	2.26E-06	1.96E-06
		8	3.14E-03	3.14E-05	2.22E-05	1.81E-05	1.57E-05	1.40E-05	9.92E-06	8.10E-06	7.01E-06	5.73E-06	4.96E-06	4.43E-06	3.62E-06	3.14E-06
		10	3.92E-03	3.92E-05	2.77E-05	2.26E-05	1.96E-05	1.75E-05	1.24E-05	1.01E-05	8.77E-06	7.16E-06	6.20E-06	5.54E-06	4.53E-06	3.92E-06
		20	7.84E-03	7.84E-05	5.54E-05	4.53E-05	3.92E-05	3.51E-05	2.48E-05	2.02E-05	1.75E-05	1.43E-05	1.24E-05	1.11E-05	9.05E-06	7.84E-06
		30	1.18E-02	1.18E-04	8.32E-05	6.79E-05	5.88E-05	5.26E-05	3.72E-05	3.04E-05	2.63E-05	2.15E-05	1.86E-05	1.66E-05	1.36E-05	1.18E-05
		50	1.96E-02	1.96E-04	1.39E-04	1.13E-04	9.80E-05	8.77E-05	6.20E-05	5.06E-05	4.38E-05	3.58E-05	3.10E-05	2.77E-05	2.26E-05	1.96E-05
		80	3.14E-02	3.14E-04	2.22E-04	1.81E-04	1.57E-04	1.40E-04	9.92E-05	8.10E-05	7.01E-05	5.73E-05	4.96E-05	4.43E-05	3.62E-05	3.14E-05
		100	3.92E-02	3.92E-04	2.77E-04	2.26E-04	1.96E-04	1.75E-04	1.24E-04	1.01E-04	8.77E-05	7.16E-05	6.20E-05	5.54E-05	4.53E-05	3.92E-05
		200	7.84E-02	7.84E-04	5.54E-04	4.53E-04	3.92E-04	3.51E-04	2.48E-04	2.02E-04	1.75E-04	1.43E-04	1.24E-04	1.11E-04	9.05E-05	7.84E-05
		300	1.18E-01	1.18E-03	8.32E-04	6.79E-04	5.88E-04	5.26E-04	3.72E-04	3.04E-04	2.63E-04	2.15E-04	1.86E-04	1.66E-04	1.36E-04	1.18E-04
		500	1.96E-01	1.96E-03	1.39E-03	1.13E-03	9.80E-04	8.77E-04	6.20E-04	5.06E-04	4.38E-04	3.58E-04	3.10E-04	2.77E-04	2.26E-04	1.96E-04
		800	3.14E-01	3.14E-03	2.22E-03	1.81E-03	1.57E-03	1.40E-03	9.92E-04	8.10E-04	7.01E-04	5.73E-04	4.96E-04	4.43E-04	3.62E-04	3.14E-04
	mg TEQ / year	3	1.18E+00	1.18E-02	8.32E-03	6.79E-03	5.88E-03	5.26E-03	3.72E-03	3.04E-03	2.63E-03	2.15E-03	1.86E-03	1.66E-03	1.36E-03	1.18E-03
		5	1.96E+00	1.96E-02	1.39E-02	1.13E-02	9.80E-03	8.77E-03	6.20E-03	5.06E-03	4.38E-03	3.58E-03	3.10E-03	2.77E-03	2.26E-03	1.96E-03
		8	3.14E+00	3.14E-02	2.22E-02	1.81E-02	1.57E-02	1.40E-02	9.92E-03	8.10E-03	7.01E-03	5.73E-03	4.96E-03	4.43E-03	3.62E-03	3.14E-03
		10	3.92E+00	3.92E-02	2.77E-02	2.26E-02	1.96E-02	1.75E-02	1.24E-02	1.01E-02	8.77E-03	7.16E-03	6.20E-03	5.54E-03	4.53E-03	3.92E-03
		20	7.84E+00	7.84E-02	5.54E-02	4.53E-02	3.92E-02	3.51E-02	2.48E-02	2.02E-02	1.75E-02	1.43E-02	1.24E-02	1.11E-02	9.05E-03	7.84E-03
		30	1.18E+01	1.18E-01	8.32E-02	6.79E-02	5.88E-02	5.26E-02	3.72E-02	3.04E-02	2.63E-02	2.15E-02	1.86E-02	1.66E-02	1.36E-02	1.18E-02
		50	1.96E+01	1.96E-01	1.39E-01	1.13E-01	9.80E-02	8.77E-02	6.20E-02	5.06E-02	4.38E-02	3.58E-02	3.10E-02	2.77E-02	2.26E-02	1.96E-02
		80	3.14E+01	3.14E-01	2.22E-01	1.81E-01	1.57E-01	1.40E-01	9.92E-02	8.10E-02	7.01E-02	5.73E-02	4.96E-02	4.43E-02	3.62E-02	3.14E-02
		100	3.92E+01	3.92E-01	2.77E-01	2.26E-01	1.96E-01	1.75E-01	1.24E-01	1.01E-01	8.77E-02	7.16E-02	6.20E-02	5.54E-02	4.53E-02	3.92E-02
		200	7.84E+01	7.84E-01	5.54E-01	4.53E-01	3.92E-01	3.51E-01	2.48E-01	2.02E-01	1.75E-01	1.43E-01	1.24E-01	1.11E-01	9.05E-02	7.84E-02
		300	1.18E+02	1.18E+00	8.32E-01	6.79E-01	5.88E-01	5.26E-01	3.72E-01	3.04E-01	2.63E-01	2.15E-01	1.86E-01	1.66E-01	1.36E-01	1.18E-01
		500	1.96E+02	1.96E+00	1.39E+00	1.13E+00	9.80E-01	8.77E-01	6.20E-01	5.06E-01	4.38E-01	3.58E-01	3.10E-01	2.77E-01	2.26E-01	1.96E-01
		800	3.14E+02	3.14E+00	2.22E+00	1.81E+00	1.57E+00	1.40E+00	9.92E-01	8.10E-01	7.01E-01	5.73E-01	4.96E-01	4.43E-01	3.62E-01	3.14E-01
	g TEQ / year	3	1.18E+03	1.18E+01	8.32E+00	6.79E+00	5.88E+00	5.26E+00	3.72E+00	3.04E+00	2.63E+00	2.15E+00	1.86E+00	1.66E+00	1.36E+00	1.18E+00
		5	1.96E+03	1.96E+01	1.39E+01	1.13E+01	9.80E+00	8.77E+00	6.20E+00	5.06E+00	4.38E+00	3.58E+00	3.10E+00	2.77E+00	2.26E+00	1.96E+00
		8	3.14E+03	3.14E+01	2.22E+01	1.81E+01	1.57E+01	1.40E+01	9.92E+00	8.10E+00	7.01E+00	5.73E+00	4.96E+00	4.43E+00	3.62E+00	3.14E+00
		10	3.92E+03	3.92E+01	2.77E+01	2.26E+01	1.96E+01	1.75E+01	1.24E+01	1.01E+01	8.77E+00	7.16E+00	6.20E+00	5.54E+00	4.53E+00	3.92E+00
		20	7.84E+03	7.84E+01	5.54E+01	4.53E+01	3.92E+01	3.51E+01	2.48E+01	2.02E+01	1.75E+01	1.43E+01	1.24E+01	1.11E+01	9.05E+00	7.84E+00
		30	1.18E+04	1.18E+02	8.32E+01	6.79E+01	5.88E+01	5.26E+01	3.72E+01	3.04E+01	2.63E+01	2.15E+01	1.86E+01	1.66E+01	1.36E+01	1.18E+01
		50	1.96E+04	1.96E+02	1.39E+02	1.13E+02	9.80E+01	8.77E+01	6.20E+01	5.06E+01	4.38E+01	3.58E+01	3.10E+01	2.77E+01	2.26E+01	1.96E+01
		80	3.14E+04	3.14E+02	2.22E+02	1.81E+02	1.57E+02	1.40E+02	9.92E+01	8.10E+01	7.01E+01	5.73E+01	4.96E+01	4.43E+01	3.62E+01	3.14E+01
		100	3.92E+04	3.92E+02	2.77E+02	2.26E+02	1.96E+02	1.75E+02	1.24E+02	1.01E+02	8.77E+01	7.16E+01	6.20E+01	5.54E+01	4.53E+01	3.92E+01

σrel = 60% : RAU -Reduction in Absolute Uncertainty per additional measurement (gTEQ/year)

		n ->	0	1	2	3	4	5	10	15	20	30	40	50	75	100
Yearly emission	µg TEQ / year	3	legend AC = €/(qTEQ/y)	3.49E-04	1.03E-06	4.58E-07	2.73E-07	1.86E-07	6.03E-08	3.20E-08	2.05E-08	1.10E-08	7.11E-09	5.07E-09	2.74E-09	1.78E-09
		5		5.82E-04	1.72E-06	7.63E-07	4.55E-07	3.10E-07	1.01E-07	5.33E-08	3.42E-08	1.84E-08	1.18E-08	8.44E-09	4.57E-09	2.96E-09
		8		9.31E-04	2.76E-06	1.22E-06	7.28E-07	4.97E-07	1.61E-07	8.53E-08	5.47E-08	2.94E-08	1.90E-08	1.35E-08	7.32E-09	4.74E-09
		10		1.16E-03	3.44E-06	1.53E-06	9.10E-07	6.21E-07	2.01E-07	1.07E-07	6.83E-08	3.67E-08	2.37E-08	1.69E-08	9.14E-09	5.92E-09
		20		2.33E-03	6.89E-06	3.05E-06	1.82E-06	1.24E-06	4.02E-07	2.13E-07	1.37E-07	7.34E-08	4.74E-08	3.38E-08	1.83E-08	1.18E-08
		30	>1 000 000	3.49E-03	1.03E-05	4.58E-06	2.73E-06	1.86E-06	6.03E-07	3.20E-07	2.05E-07	1.10E-07	7.11E-08	5.07E-08	2.74E-08	1.78E-08
		50		5.82E-03	1.72E-05	7.63E-06	4.55E-06	3.10E-06	1.01E-06	5.33E-07	3.42E-07	1.84E-07	1.18E-07	8.44E-08	4.57E-08	2.96E-08
		80		9.31E-03	2.76E-05	1.22E-05	7.28E-06	4.97E-06	1.61E-06	8.53E-07	5.47E-07	2.94E-07	1.90E-07	1.35E-07	7.32E-08	4.74E-08
		100		1.16E-02	3.44E-05	1.53E-05	9.10E-06	6.21E-06	2.01E-06	1.07E-06	6.83E-07	3.67E-07	2.37E-07	1.69E-07	9.14E-08	5.92E-08
		200		2.33E-02	6.89E-05	3.05E-05	1.82E-05	1.24E-05	4.02E-06	2.13E-06	1.37E-06	7.34E-07	4.74E-07	3.38E-07	1.83E-07	1.18E-07
		300		3.49E-02	1.03E-04	4.58E-05	2.73E-05	1.86E-05	6.03E-06	3.20E-06	2.05E-06	1.10E-06	7.11E-07	5.07E-07	2.74E-07	1.78E-07
		500	1 000 000	5.82E-02	1.72E-04	7.63E-05	4.55E-05	3.10E-05	1.01E-05	5.33E-06	3.42E-06	1.84E-06	1.18E-06	8.44E-07	4.57E-07	2.96E-07
		800		9.31E-02	2.76E-04	1.22E-04	7.28E-05	4.97E-05	1.61E-05	8.53E-06	5.47E-06	2.94E-06	1.90E-06	1.35E-06	7.32E-07	4.74E-07
	mg TEQ / year	3		3.49E-01	1.03E-03	4.58E-04	2.73E-04	1.86E-04	6.03E-05	3.20E-05	2.05E-05	1.10E-05	7.11E-06	5.07E-06	2.74E-06	1.78E-06
		5		5.82E-01	1.72E-03	7.63E-04	4.55E-04	3.10E-04	1.01E-04	5.33E-05	3.42E-05	1.84E-05	1.18E-05	8.44E-06	4.57E-06	2.96E-06
		8		9.31E-01	2.76E-03	1.22E-03	7.28E-04	4.97E-04	1.61E-04	8.53E-05	5.47E-05	2.94E-05	1.90E-05	1.35E-05	7.32E-06	4.74E-06
		10		1.16E+00	3.44E-03	1.53E-03	9.10E-04	6.21E-04	2.01E-04	1.07E-04	6.83E-05	3.67E-05	2.37E-05	1.69E-05	9.14E-06	5.92E-06
		15	100 000	2.33E+00	6.89E-03	3.05E-03	1.82E-03	1.24E-03	4.02E-04	2.13E-04	1.37E-04	7.34E-05	4.74E-05	3.38E-05	1.83E-05	1.18E-05
		30		3.49E+00	1.03E-02	4.58E-03	2.73E-03	1.86E-03	6.03E-04	3.20E-04	2.05E-04	1.10E-04	7.11E-05	5.07E-05	2.74E-05	1.78E-05
		50		5.82E+00	1.72E-02	7.63E-03	4.55E-03	3.10E-03	1.01E-03	5.33E-04	3.42E-04	1.84E-04	1.18E-04	8.44E-05	4.57E-05	2.96E-05
		80		9.31E+00	2.76E-02	1.22E-02	7.28E-03	4.97E-03	1.61E-03	8.53E-04	5.47E-04	2.94E-04	1.90E-04	1.35E-04	7.32E-05	4.74E-05
		100		1.16E+01	3.44E-02	1.53E-02	9.10E-03	6.21E-03	2.01E-03	1.07E-03	6.83E-04	3.67E-04	2.37E-04	1.69E-04	9.14E-05	5.92E-05
		200		2.33E+01	6.89E-02	3.05E-02	1.82E-02	1.24E-02	4.02E-03	2.13E-03	1.37E-03	7.34E-04	4.74E-04	3.38E-04	1.83E-04	1.18E-04
		300	10 000	3.49E+01	1.03E-01	4.58E-02	2.73E-02	1.86E-02	6.03E-03	3.20E-03	2.05E-03	1.10E-03	7.11E-04	5.07E-04	2.74E-04	1.78E-04
		500		5.82E+01	1.72E-01	7.63E-02	4.55E-02	3.10E-02	1.01E-02	5.33E-03	3.42E-03	1.84E-03	1.18E-03	8.44E-04	4.57E-04	2.96E-04
		800		9.31E+01	2.76E-01	1.22E-01	7.28E-02	4.97E-02	1.61E-02	8.53E-03	5.47E-03	2.94E-03	1.90E-03	1.35E-03	7.32E-04	4.74E-04
	g TEQ / year	3		3.49E+02	1.03E+00	4.58E-01	2.73E-01	1.86E-01	6.03E-02	3.20E-02	2.05E-02	1.10E-02	7.11E-03	5.07E-03	2.74E-03	1.78E-03
		5		5.82E+02	1.72E+00	7.63E-01	4.55E-01	3.10E-01	1.01E-01	5.33E-02	3.42E-02	1.84E-02	1.18E-02	8.44E-03	4.57E-03	2.96E-03
		8		9.31E+02	2.76E+00	1.22E+00	7.28E-01	4.97E-01	1.61E-01	8.53E-02	5.47E-02	2.94E-02	1.90E-02	1.35E-02	7.32E-03	4.74E-03
		10	1 000	1.16E+03	3.44E+00	1.53E+00	9.10E-01	6.21E-01	2.01E-01	1.07E-01	6.83E-02	3.67E-02	2.37E-02	1.69E-02	9.14E-03	5.92E-03
		15		2.33E+03	6.89E+00	3.05E+00	1.82E+00	1.24E+00	4.02E-01	2.13E-01	1.37E-01	7.34E-02	4.74E-02	3.38E-02	1.83E-02	1.18E-02
		30		3.49E+03	1.03E+01	4.58E+00	2.73E+00	1.86E+00	6.03E-01	3.20E-01	2.05E-01	1.10E-01	7.11E-02	5.07E-02	2.74E-02	1.78E-02
		50		5.82E+03	1.72E+01	7.63E+00	4.55E+00	3.10E+00	1.01E+00	5.33E-01	3.42E-01	1.84E-01	1.18E-01	8.44E-02	4.57E-02	2.96E-02
		80		9.31E+03	2.76E+01	1.22E+01	7.28E+00	4.97E+00	1.61E+00	8.53E-01	5.47E-01	2.94E-01	1.90E-01	1.35E-01	7.32E-02	4.74E-02
		100		1.16E+04	3.44E+01	1.53E+01	9.10E+00	6.21E+00	2.01E+00	1.07E+00	6.83E-01	3.67E-01	2.37E-01	1.69E-01	9.14E-02	5.92E-02

σrel = 200% : RAU -Reduction in Absolute Uncertainty per additional measurement (gTEQ/year)

		n ->	0	1	2	3	4	5	10	15	20	30	40	50	75	100
Yearly emission	µg TEQ / year	3	legend AC = €/(qTEQ/y)	1.16E-03	3.44E-06	1.53E-06	9.10E-07	6.21E-07	2.01E-07	1.07E-07	6.83E-08	3.67E-08	2.37E-08	1.69E-08	9.14E-09	5.92E-09
		5		1.94E-03	5.74E-06	2.54E-06	1.52E-06	1.03E-06	3.35E-07	1.78E-07	1.14E-07	6.12E-08	3.95E-08	2.81E-08	1.52E-08	9.87E-09
		8		3.10E-03	9.19E-06	4.07E-06	2.43E-06	1.66E-06	5.36E-07	2.84E-07	1.82E-07	9.79E-08	6.32E-08	4.50E-08	2.44E-08	1.58E-08
		10		3.88E-03	1.15E-05	5.09E-06	3.03E-06	2.07E-06	6.71E-07	3.55E-07	2.28E-07	1.22E-07	7.90E-08	5.63E-08	3.05E-08	1.97E-08
		20		7.76E-03	2.30E-05	1.02E-05	6.06E-06	4.14E-06	1.34E-06	7.10E-07	4.55E-07	2.45E-07	1.58E-07	1.13E-07	6.10E-08	3.95E-08
		30	>1 000 000	1.16E-02	3.44E-05	1.53E-05	9.10E-06	6.21E-06	2.01E-06	1.07E-06	6.83E-07	3.67E-07	2.37E-07	1.69E-07	9.14E-08	5.92E-08
		50		1.94E-02	5.74E-05	2.54E-05	1.52E-05	1.03E-05	3.35E-06	1.78E-06	1.14E-06	6.12E-07	3.95E-07	2.81E-07	1.52E-07	9.87E-08
		80		3.10E-02	9.19E-05	4.07E-05	2.43E-05	1.66E-05	5.36E-06	2.84E-06	1.82E-06	9.79E-07	6.32E-07	4.50E-07	2.44E-07	1.58E-07
		100		3.88E-02	1.15E-04	5.09E-05	3.03E-05	2.07E-05	6.71E-06	3.55E-06	2.28E-06	1.22E-06	7.90E-07	5.63E-07	3.05E-07	1.97E-07
		200		7.76E-02	2.30E-04	1.02E-04	6.06E-05	4.14E-05	1.34E-05	7.10E-06	4.55E-06	2.45E-06	1.58E-06	1.13E-06	6.10E-07	3.95E-07
		300		1.16E-01	3.44E-04	1.53E-04	9.10E-05	6.21E-05	2.01E-05	1.07E-05	6.83E-06	3.67E-06	2.37E-06	1.69E-06	9.14E-07	5.92E-07
		500	1 000 000	1.94E-01	5.74E-04	2.54E-04	1.52E-04	1.03E-04	3.35E-05	1.78E-05	1.14E-05	6.12E-06	3.95E-06	2.81E-06	1.52E-06	9.87E-07
		800		3.10E-01	9.19E-04	4.07E-04	2.43E-04	1.66E-04	5.36E-05	2.84E-05	1.82E-05	9.79E-06	6.32E-06	4.50E-06	2.44E-06	1.58E-06
	mg TEQ / year	3		1.16E+00	3.44E-03	1.53E-03	9.10E-04	6.21E-04	2.01E-04	1.07E-04	6.83E-05	3.67E-05	2.37E-05	1.69E-05	9.14E-06	5.92E-06
		5		1.94E+00	5.74E-03	2.54E-03	1.52E-03	1.03E-03	3.35E-04	1.78E-04	1.14E-04	6.12E-05	3.95E-05	2.81E-05	1.52E-05	9.87E-06
		8		3.10E+00	9.19E-03	4.07E-03	2.43E-03	1.66E-03	5.36E-04	2.84E-04	1.82E-04	9.79E-05	6.32E-05	4.50E-05	2.44E-05	1.58E-05
		10		3.88E+00	1.15E-02	5.09E-03	3.03E-03	2.07E-03	6.71E-04	3.55E-04	2.28E-04	1.22E-04	7.90E-05	5.63E-05	3.05E-05	1.97E-05
		15	100 000	7.76E+00	2.30E-02	1.02E-02	6.06E-03	4.14E-03	1.34E-03	7.10E-04	4.55E-04	2.45E-04	1.58E-04	1.13E-04	6.10E-05	3.95E-05
		30		1.16E+01	3.44E-02	1.53E-02	9.10E-03	6.21E-03	2.01E-03	1.07E-03	6.83E-04	3.67E-04	2.37E-04	1.69E-04	9.14E-05	5.92E-05
		50		1.94E+01	5.74E-02	2.54E-02	1.52E-02	1.03E-02	3.35E-03	1.78E-03	1.14E-03	6.12E-04	3.95E-04	2.81E-04	1.52E-04	9.87E-05
		80		3.10E+01	9.19E-02	4.07E-02	2.43E-02	1.66E-02	5.36E-03	2.84E-03	1.82E-03	9.79E-04	6.32E-04	4.50E-04	2.44E-04	1.58E-04
		100		3.88E+01	1.15E-01	5.09E-02	3.03E-02	2.07E-02	6.71E-03	3.55E-03	2.28E-03	1.22E-03	7.90E-04	5.63E-04	3.05E-04	1.97E-04
		200		7.76E+01	2.30E-01	1.02E-01	6.06E-02	4.14E-02	1.34E-02	7.10E-03	4.55E-03	2.45E-03	1.58E-03	1.13E-03	6.10E-04	3.95E-04
		300	10 000	1.16E+02	3.44E-01	1.53E-01	9.10E-02	6.21E-02	2.01E-02	1.07E-02	6.83E-03	3.67E-03	2.37E-03	1.69E-03	9.14E-04	5.92E-04
		500		1.94E+02	5.74E-01	2.54E-01	1.52E-01	1.03E-01	3.35E-02	1.78E-02	1.14E-02	6.12E-03	3.95E-03	2.81E-03	1.52E-03	9.87E-04
		800		3.10E+02	9.19E-01	4.07E-01	2.43E-01	1.66E-01	5.36E-02	2.84E-02	1.82E-02	9.79E-03	6.32E-03	4.50E-03	2.44E-03	1.58E-03
	g TEQ / year	3		1.16E+03	3.44E+00	1.53E+00	9.10E-01	6.21E-01	2.01E-01	1.07E-01	6.83E-02	3.67E-02	2.37E-02	1.69E-02	9.14E-03	5.92E-03
		5		1.94E+03	5.74E+00	2.54E+00	1.52E+00	1.03E+00	3.35E-01	1.78E-01	1.14E-01	6.12E-02	3.95E-02	2.81E-02	1.52E-02	9.87E-03
		8		3.10E+03	9.19E+00	4.07E+00	2.43E+00	1.66E+00	5.36E-01	2.84E-01	1.82E-01	9.79E-02	6.32E-02	4.50E-02	2.44E-02	1.58E-02
		10	1 000	3.88E+03	1.15E+01	5.09E+00	3.03E+00	2.07E+00	6.71E-01	3.55E-01	2.28E-01	1.22E-01	7.90E-02	5.63E-02	3.05E-02	1.97E-02
		15		7.76E+03	2.30E+01	1.02E+01	6.06E+00	4.14E+00	1.34E+00	7.10E-01	4.55E-01	2.45E-01	1.58E-01	1.13E-01	6.10E-02	3.95E-02
		30		1.16E+04	3.44E+01	1.53E+01	9.10E+00	6.21E+00	2.01E+00	1.07E+00	6.83E-01	3.67E-01	2.37E-01	1.69E-01	9.14E-02	5.92E-02
		50		1.94E+04	5.74E+01	2.54E+01	1.52E+01	1.03E+01	3.35E+00	1.78E+00	1.14E+00	6.12E-01	3.95E-01	2.81E-01	1.52E-01	9.87E-02
		80		3.10E+04	9.19E+01	4.07E+01	2.43E+01	1.66E+01	5.36E+00	2.84E+00	1.82E+00	9.79E-01	6.32E-01	4.50E-01	2.44E-01	1.58E-01
		100		3.88E+04	1.15E+02	5.09E+01	3.03E+01	2.07E+01	6.71E+00	3.55E+00	2.28E+00	1.22E+00	7.90E-01	5.63E-01	3.05E-01	1.97E-01

16 Annex I Optimal number of measurements

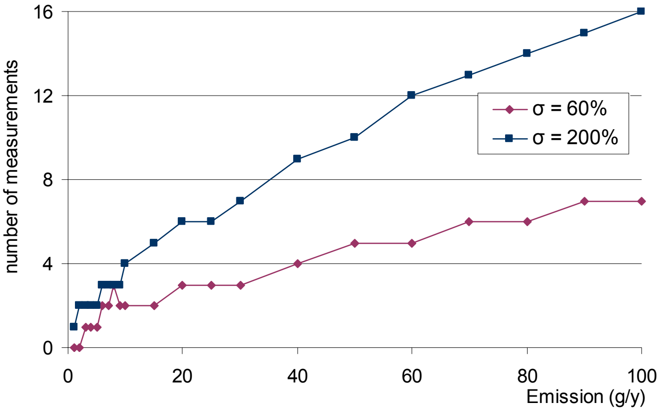
Optimal number of measurements

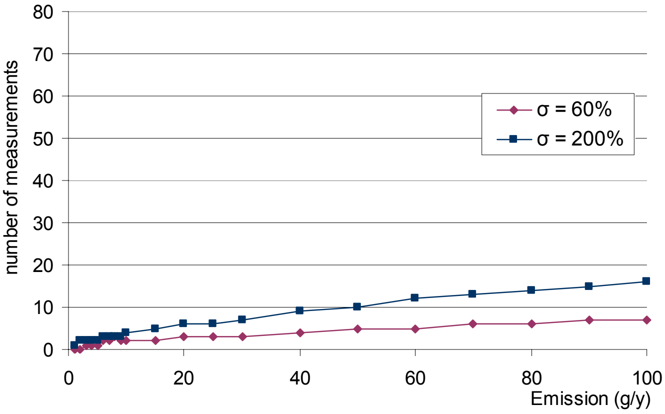
Measurement cost : 3000€ Probability coefficient : 1.96			Parameters							
		σ_{rel}	60%				200%			
		AC [€/(gTEQ/year)]	1 000	10 000	100 000	1 000 000	1 000	10 000	100 000	1 000 000
		MC/(AC*1.96*σ_{rel})	2.5510	0.2551	0.0255	0.0026	0.7653	0.0765	0.0077	0.00077
Yearly emission	1	µg TEQ/year	-	-	-	-	-	-	-	-
	2		-	-	-	-	-	-	-	-
	3		-	-	-	-	-	-	-	-
	4		-	-	-	-	-	-	-	-
	5		-	-	-	-	-	-	-	-
	6		-	-	-	-	-	-	-	-
	7		-	-	-	-	-	-	-	-
	8		-	-	-	-	-	-	-	1
	9		-	-	-	-	-	-	-	1
	10		-	-	-	-	-	-	-	1
	15		-	-	-	-	-	-	-	1
	20		-	-	-	-	-	-	-	1
	25		-	-	-	-	-	-	-	1
	30		-	-	-	1	-	-	-	1
	40		-	-	-	1	-	-	-	1
	50		-	-	-	1	-	-	-	1
	60		-	-	-	1	-	-	-	1
	70		-	-	-	1	-	-	-	1
	80		-	-	-	1	-	-	1	1
	90		-	-	-	1	-	-	1	1
	100		-	-	-	1	-	-	1	1
	150		-	-	-	1	-	-	1	1
	200		-	-	-	1	-	-	1	1
	250		-	-	-	1	-	-	1	1
	300		-	-	1	1	-	-	1	1
	350		-	-	1	1	-	-	1	1
	400		-	-	1	1	-	-	1	1
	450		-	-	1	1	-	-	1	1
	500		-	-	1	1	-	-	1	1
	600		-	-	1	1	-	-	1	1
	700		-	-	1	1	-	-	1	1
	800		-	-	1	1	-	1	1	1
	900		-	-	1	1	-	1	1	1
	1	mg TEQ/year	-	-	1	1	-	1	1	1
	2		-	-	1	1	-	1	1	1
	3		-	1	1	1	-	1	1	2
	4		-	1	1	1	-	1	1	2
	5		-	1	1	1	-	1	1	2
	6		-	1	1	1	-	1	1	3
	7		-	1	1	1	-	1	1	3
	8		-	1	1	1	1	1	1	3
	9		-	1	1	2	1	1	1	3
	10		-	1	1	2	1	1	1	4
	15		-	1	1	2	1	1	1	5
	20		-	1	1	3	1	1	1	6
	25		-	1	1	3	1	1	1	6

Yearly emission	30	mg TEQ/year	1	1	1	3	1	1	2	7
	40		1	1	1	4	1	1	2	9
	50		1	1	1	5	1	1	2	10
	60		1	1	1	5	1	1	3	12
	70		1	1	1	6	1	1	3	13
	80		1	1	1	6	1	1	3	14
	90		1	1	2	7	1	1	3	15
	100		1	1	2	7	1	1	4	16
	150		1	1	2	10	1	1	5	21
	200		1	1	3	12	1	1	6	26
	250		1	1	3	13	1	1	6	30
	300		1	1	3	15	1	2	7	34
	350		1	1	4	17	1	2	8	37
	400		1	1	4	18	1	2	9	41
	450		1	1	4	20	1	2	10	44
	500		1	1	5	21	1	2	10	47
	600		1	1	5	24	1	3	12	54
	700		1	1	6	27	1	3	13	59
	800		1	1	6	29	1	3	14	65
	900		1	2	7	31	1	3	15	70
	1	g TEQ/year	1	2	7	34	1	4	16	75
	2		1	3	12	54	1	6	26	120
	3		1	3	15	70	2	7	34	157
	4		1	4	18	85	2	9	41	190
	5		1	5	21	99	2	10	47	220
	6		1	5	24	111	3	12	54	249
	7		1	6	27	123	3	13	59	249
	8		1	6	29	135	3	14	65	249
	9		2	7	31	146	3	15	70	249
	10		2	7	34	157	4	16	75	249
	15		2	10	44	205	5	21	99	>250
	20		3	12	54	249	6	26	120	>250
	25		3	13	62	249	6	30	139	>250
	30		3	15	70	249	7	34	157	>250
	40		4	18	85	>250	9	41	190	>250
	50		5	21	99	>250	10	47	220	>250
	60		5	24	111	>250	12	54	249	>250
	70		6	27	123	>250	13	59	249	>250
	80		6	29	135	>250	14	65	249	>250
	90		7	31	146	>250	15	70	249	>250
	100		7	34	157	>250	16	75	249	>250
minimum emission to require measurement (mg TEQ/year)			**30**	**3.0**	**0.30**	**0.03**	**8.0**	**0.80**	**0.08**	**0.008**

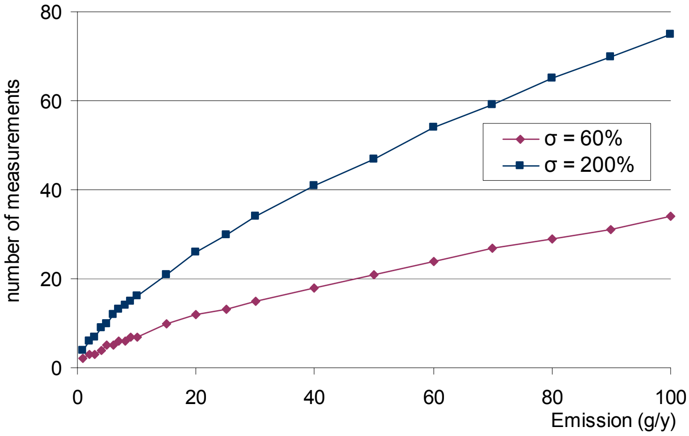
Adapted scale ***Same scale***

Optimal number of measurements as a function of plant emission (**Acceptable cost = € 1,000/gTEQ**)

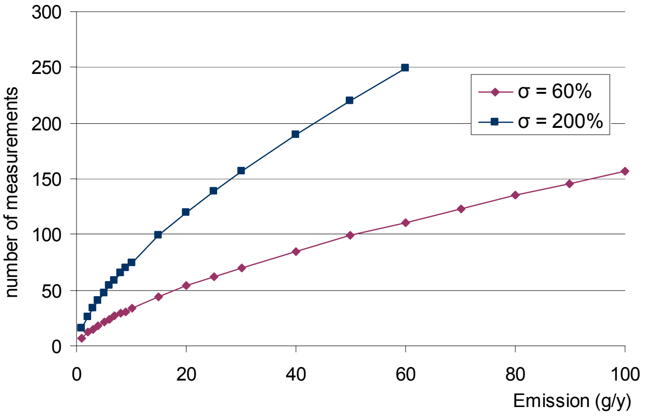


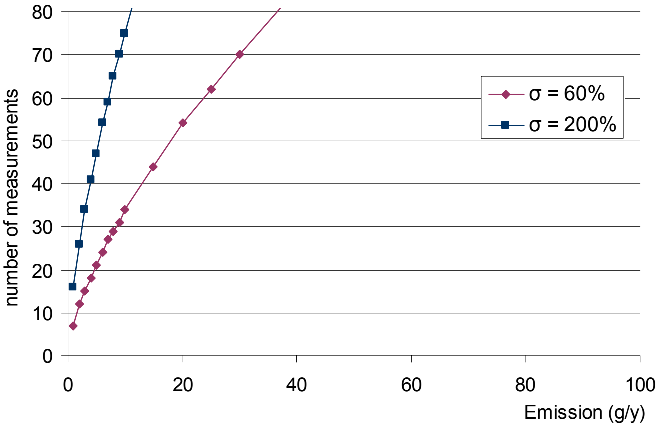


Optimal number of measurements as a function of plant emission (**Acceptable cost = € 10,000/gTEQ**)



Optimal number of measurements as a function of plant emission (**Acceptable cost = € 100,000/gTEQ**)





17 Annex J Case Studies

The purpose of this annex is to provide with some examples of plants which have made large investments to reduce significantly their emissions, after having performed measurements which indicated very high emission levels.

The three presented plants were indeed very large emitters (Recytech in France, Contimelt and Sidmar in Belgium) and the intensity of their efforts can by no way be representative of the amount of investments that could be realized by other plants.

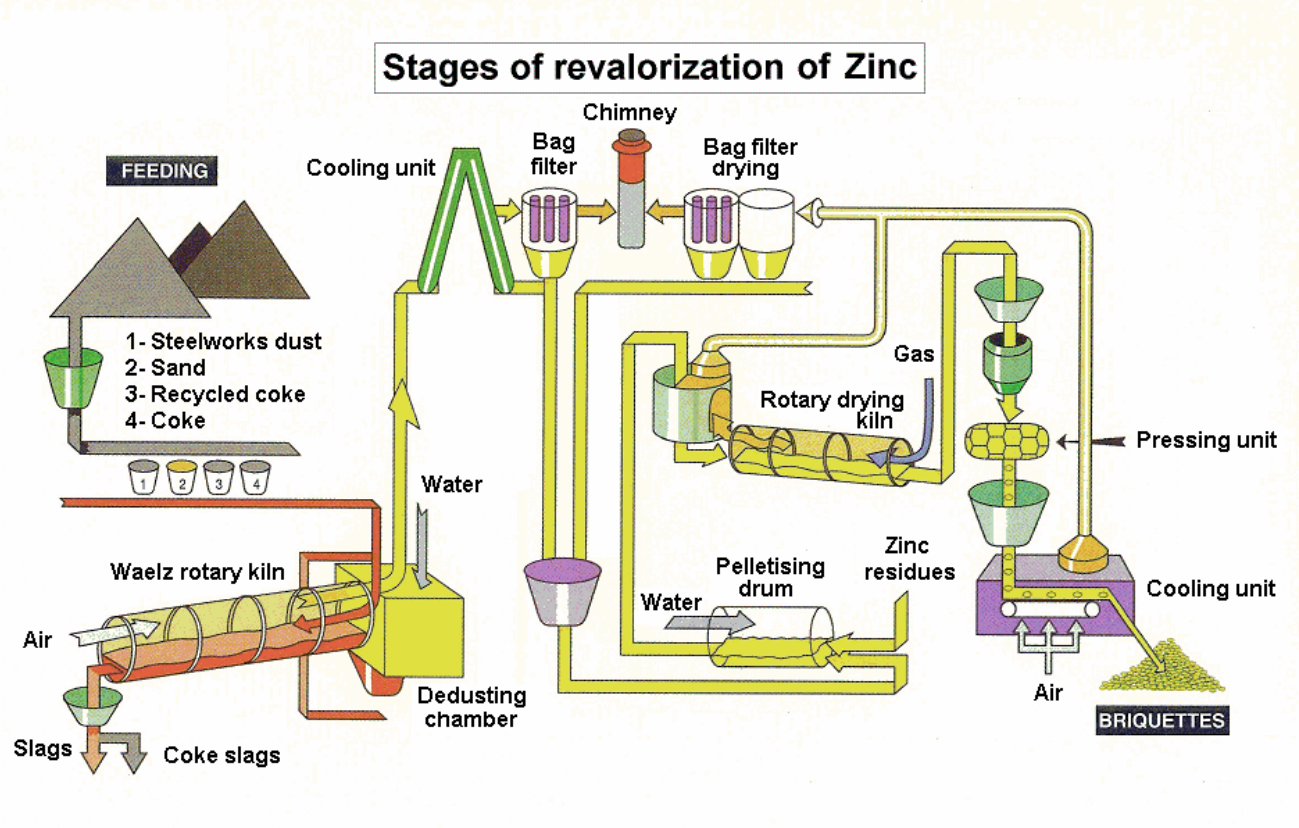
17.1 Recytech

Plant Description

Recytech operates a Waelz process in Fouquières-lez-Lens (France – Pas-de-Calais) as a joint venture operated by Metaleurop and BUS.

The plant recovers a crude zinc oxide from zinc containing dust, e.g. originating from a steel converter or a blast furnace. The iron oxide is converted into a slag.

Process Description



The raw materials (zinc containing dust and sludge, coke and sand) are mixed in well-defined proportion and introduced in the Waelz kiln. As its name infers, they are treated while tumbling in a rotary kiln; burners situated at the discharge end heat it in countercurrent. The coke in the batch reduces the metal oxides. Zinc and lead volatilize. An excess of air in the kiln induce re-oxidation of zinc and lead on one the hand and of CO to CO_2 on the other hand.

The maximum temperature of the kiln exceeds 1200°C.

Off-gases leave the kiln at approximately 750°C. They first pass through a sedimentation chamber to separate coarse dust, which is recycled. They are then gradually cooled, using water sprays, in order to allow their filtration at low temperature.

During the successive cooling steps, dioxins are formed.

In 1998, a spot measurement was performed, following a request from the Prefecture for establishing an inventory of industrial dioxin emissions.
The results were surprisingly high: 205 g I-TEQ/year, if the spot measurement result (134.6 ng/Nm³) are representative for the 8000 hours of functioning per year.

At the same time, independently of the dioxin measurement requirement, Recytech was studying the possibility of increasing their capacity of treatment by way of the absorption of mercury by adapted adsorbents.
After pilot plant testing by Rheinbraun, lignite coke was selected as an adsorbent, which also absorbs dioxins.

An action plan was developed to reduce dioxin emissions as soon as possible.

I. quenching of flue gas and injection of lignite coke
II. fixed bed filter treatement of part of the gas effluent
III. filter for the treatment of dusts from Waelz furnace

Quenching of flue gas and injection of lignite coke

Generally, an adsorbent (fine coke powder) is injected into the gas flow and the resulting gas flow moves the adsorbent towards the filter where the dust and the coke adsorbent are separated simultaneously from the gas. Adsorption proceeds during co-current flow and is increased in the layer of coke and dust that is retained on the filter sleeves. To enhance efficiency, a good mixing of coke and gas must be realized. Moreover, the temperature must be well controlled to avoid ignition. In metallurgical plants, there is an increased danger of coke explosion. For that reason, a mixture of inert dust and coke is often the preferred adsorbent.

In the Recytech case, the most expensive element for this treatment, i.e. the filter, already existed.

In addition, the management of the device of dioxin abatement could be made by the existing teams. For further details, the literature must be referred to, including various MINIDIP studies.

The next table gives an overview of investments made and the results achieved:

Summary of Measures and Effects

	Date	*Measurement result*	*Cost*
Without abatement measure	Measurement : 07/05/1998	205 g I-TEQ/year	
I. *quenching of flue gas and injection of lignite coke*	Realization: 9-11/1998	~ 7 g I-TEQ/year	~ € 534,000
II. *fixed bed filter treatment of part of the gas effluent*	Realization: 12/1998		~ € 686,000
III. *filter for the treatment of dusts from the Waelz furnace*	Realization: 08/1999	~ 0.75 g I-TEQ/year	~ € 1,677,000
Total		Abatement > 99.6%	~ € 2,896,000

As stated before, even before aiming to reduce dioxin emissions, Recytech already aimed to make feasible an increasing of production capacity (from 80,000 ton/year to 100,000 ton/year from a technical point of view and to 200,000 ton/year according to administrative authorization) and to reduce mercury emission (from 76kg/year to 16kg/year).

Conclusions

Recytech was one of the largest source of dioxins in France.

The problem was studied by one of the MINIDIP partners, Rheinbraun, who demonstrated the possibilities of abatement using lignite coke (Herdofenkoks).

Since then, Recytech ended the production of "briquettes".
Indeed, the Imperial smelting of Metaleurop which was the majority user of briquette closed.
Consequently of what the fixed bed filter is not used any more.

Currently, Recytech :

- treats about 100,000 ton/year of steelworks dusts,
- uses 20,000 ton/year of coke and 10,000 ton/year of lime,
- produces 40,000 ton/year of Waelz oxide and 60,000 ton/year of slag for roads and construction,
- and emits much less than 5 ng TEQ/Nm³, the threshold value set by the Prefecture.

Similar plants at Freiberg and Duisburg were studied by FZ-K and VUB.

In this example, annual emissions could gradually be lowered from ca. 200 to less than 1 g TEQ/year.

This chain of events was triggered by a single measurement.

17.2 Contimelt

Plant Description of the installation

The Contimelt unit (Umicore Copper, today Cumerio) at the Olen factory has been operated since 1986 and is used for melting and refining copper and casting it into anodes, for use in electrolysis. The feed to the shaft furnace consists of blister copper, spent anodes from the electrolytic refinery and some other clean copper scrap.

The unit features heat recovery and the process gases are treated in an afterburner and a baghouse filter.

On the basis of the results of a "deposition monitoring" campaign in Flanders, mainly conducted around incinerator plants and industrial production sites, the Flemish Environmental Inspectorate (AMI) organized dedicated emission measurement campaigns for the ferrous and the non-ferrous metals industries.

At the Olen plant, the Contimelt unit was given top priority.

On July 1998, AMI requested Umicore to reduce emissions immediately to a level of 0.5 ng I-TEQ/Nm³ although at that time no standards for dioxin emissions were present in the Vlarem legislation.

Abatement measures

Spring 1999

One out of 12 compartments of the baghouse filter was adapted for the additional injection of activated carbon or lignite coke to capture dioxins.

It was shown that - by injecting an increased amount of lime with a proportion of 8% of added active carbon, and by strictly controlling the filter temperature - it was possible to reduce emissions to less than 1ngTEQ/Nm³.

Summer 1999

During the annual shutdown the gas circuit and the filter for the whole process were adapted for treating all the process gases with the above-mentioned mixture.

Autumn 1999

With some additional adaptations to the unit and process parameters, the emissions level finally reached 0.5 ngTEQ/Nm³ at the end of 1999

2000-2001

Further optimization further reduced emissions to the level of 0.2 – 0.3 ngTEQ/Nm³.

To minimize dioxin generation it was necessary to remove a heat exchanger.

The impact of changing parameters such as concentrations of active carbon (or lignite coke), injecting the adsorbent at two different points, adapting the load (blister copper and scrap), was measured.

The prevention of dioxin generation in the shaft by means of adding a reagent was tested but the results were not significant.

Summary

With additional activated carbon injection spread over two different points in the gas ducts and using a controlled dosing system, dioxin emissions have been reduced to 0.2 – 0.3 ngTEQ/Nm³ at the Contimelt unit.

It was necessary to double lime injection in order to guarantee the necessary fire protection level, given the flammability of the mixture of adsorbent and dust.

So, overall, emissions have been reduced by 98 - 99%.

For the period 1998 – 2002, about € 1.6 M were invested, not taking into account the supplemental work performed by Umicore staff, and about € 1 M for monitoring.

17.3 Sidmar

Plant Description

Sidmar is an integrated iron & steel plant. Its sintering plant is composed of two lines. Sinter plant Sifa1 has a daily production of 5,300 t, whilst sinter plant Sifa 2 produces 14,400 t per day. The total yearly production is 6,840,000 t. The waste gas flows are 500,000 and 1,100,000 Nm3/h, respectively.

Sifa 1 has an in-line cooling section and Sifa 2 has a circular cooler off-line. The off-gas is treated in huge electrofilters featuring 3 fields.

Measurement

In 1997, high dioxin emission values were recorded at the stacks of the sinter plants. Immediately, Sidmar started an intensive measuring test campaign, aiming to assess the effect of various "primary" measures for prevention of dioxin emissions[35]. Between 1998 and 2000, three laboratories in total took 530 dioxin measurements, some of these in duplicate. The measures taken simultaneously by two distinct, accredited laboratories show a poor correspondence, pointing at a possible stratification in the off-gases. The latter was confirmed during the MINIDIP project by a Computer Fluid Dynamics simulation of a typical sintering plant.

Based on the estimation that each measuring day costs € 2750 (between € 2500 and 3000), measurements costs from 1997 to 2000 exceeded € 650,000.

Abatement measures

In 1998, the influence of chlorides and VOC (volatile organic components) has been verified. This was based upon the assumption that the concentration of the building blocks, responsible for the formation of dioxins, had to be minimized. Therefore the input of oil contaminated mill scales, chloride rich channel water, electrostatic precipitator dust and so on have been reduced considerably in the framework of a systematic testing programme.

Some process parameters (such as the sintering layer height and the use of burnt lime, or the injection of lime in the waste gas) have also been investigated. The conclusion was that the chemical composition of the sintering blend is irrelevant.

In 1999, the research was mainly focused on the assumption that dioxins are generated in the sintering layer, rather than the downstream parts of the process. The final conclusion was that by adding burnt lime to the feed and optimizing the sintering process conditions (such as a better control of the burn-through point and improvement of the permeability of the batch) a reduction of 85% in dioxin emissions could be realized.

A further decrease in the dioxin emission was only possible using end-of-pipe technology. It was decided to build an industrial coal injection installation for further reduction of the dioxin emission.

Thanks to this systematic approach, Sidmar succeeded in reducing dioxin emissions to below the Vlarem II standard of 2.5 ng TEQ/Nm3 in 2000, and even below the target value of

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[35] Sidmar joined ARGE, the German research consortium that conducts research into the capture of unavoidable dioxin emissions in sinter plant waste gases by means of injecting adsorption agents

0.5 ng TEQ/Nm3, as was laid down in an order from the Aminal (environmental management of the Flanders Region) environmental inspectors. Sidmar was the first steelmaker to incorporate an injection installation into the waste gas ducts of its sinter plants. Injecting active carbon as adsorbent for dioxins has proved to be a great success, and Sidmar is now regarded as the benchmark for the European steel industry.

This success also did not escape the notice of the local green movement, and Sidmar shared equal first place with power generator SPE for of the "De Voldere" Prize from the Green Platform, an umbrella organization for green groups active in the Ghent Canal Zone.

Summary

Due to circumstances, mainly feed formulation, the original emission values from Sidmar were definitely higher than average for sintering.

When this became apparent, the local Inspectorate heavily tackled the enterprise, even though it spontaneously led to a vast measurement campaign, in which all conceivable parameters were systematically studied.

Following a steep learning curve, by selecting the more relevant parameters, the enterprise managed to reduce its emission values significantly, from an original value of 15 ng I-TEQ/Nm3 to the present values.

In Europe, this effort has been fairly unique.

For the sake of comparison, the rapidly growing integrated iron & steel industry in China has still to perform its very first measurement[36]! Conversely, Japanese iron & steelmakers employ thorough dust cleaning of the off-gases from the sintering plant, and a catalytic DeNOx, destroying dioxins.

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[36] Personal Communication from a Chinese Delegation, on visit in May 2005.

18 Annex K List of NoE Members

Table 36 List of NoE Members

Name	First Name	Country	Organsation
Angosto	Angel	Spain	Freelance
Andersson		Sweden	
Apfel	Jens	Germany	
Benestad	Christel	Norway	Norwegian Pollution Control Authority (SFT)
Bröker	Günter	Germany	LUA
Brouhon	Jean-Marc	Belgium	DGRNE (Walloon Region)
Buekens	Alfons	Belgium	VUB
Burcher	Michael G.	United Kingdom	European General Galvanizers Association
Bureš	Vladimir	Czech Republic	TESO Prague
Ceulemans	Michiel	Belgium	Umicore
Chung	Lynette	Belgium	Eurometaux
Continho	M.	Portugal	
Cwiakalski	Wlodzislaw	Poland	EmiPro Ltd. 30-663 Krakow ul.Wielicka 250
De Fré	Raf	Belgium	Vito
de Jong	Vincent	Netherlands	Alcontrol Laboratories
De Ridder	Ludo	Belgium	Umicore
DeCaevael	Bernard	Belgium	RDC
Dishovsky	Stefan	Bulgaria	Executive Environmental Agency
Dvarioniene	Jolanta	Lithuania	Institute of Environmental Engineering, Kaunas University of Technology
Dyke	Patrick	United Kingdom	PD Consulting
Ekdahl	Asa	Belgium	Eurofer
Esteban	Abad	Spain	SPANISH COUNCIL FOR SCIENTIFIC RESEARCH (CSIC)
Fabrellas	Begona	Spain	Environment and Technology, (CIEMAT). Ministry of Science
Fehérváry	Ákos	Hungary	Ministry of Environment and Water
Fiedler	Heidi	Switzerland	UNEP
Fisher	Ray	United Kingdom	Corus UK Ltd.
Forsgren	Christer	Sweden	Stena Metall AB
Fournelle	Raymond	Belgium	Arcelor

Francois		Belgium	
Fullana	Andres	Spain	University of Alicante
Gemmill	Robert	United Kingdom	Environment Agency
Georghiades	Stelios	Cyprus	Department of Labour Inspection
Goksoyr	A.	Norway	
Gomes	Susanna	Portugal	
Grochowalski	Adam	Poland	Cracow Univerity of Technology
Haep	Stefan	Germany	IUTA
Helber	Joachim	Germany	IfG - Institut fuer Giessereitechnik GmbH
Henkelmann	Bernhard	Germany	GSF - National Research Center for Environment and Health, Institute of Ecological Chemistry
Hinshaw	Gary	United States	Environmental Assurance Monitoring, LLC
Hlinova	Yvonna	Czech Republic	Ministry of the Environment of the Czech Rep.
Hovemann	Andreas	Germany	Eurofins/GfA mbH
Joas	Anke	Germany	BiPRO
Johansson	Niklas	Sweden	Swedish EPA
Kahr	Gerhard	Austria	MonitoringSystems GmbH
Kasai		Japan	
Kenyeressy		Germany	
Kirchner	Günter	Germany	European Aluminium Refiners and Remelters
Kovacs	Gabor	Hungary	Ministry of Environment
Kube	Christine	Germany	IUTA
Kubica	Chrystina	Poland	NILU Polska
Kuipers	J.	Netherlands	
Kulczycka	J.	Poland	
Lambert	Catherine	Belgium	RDC
Lassen		Denmark	
Luthard	Peter	Germany	
Malinov		Bulgaria	
Marklund		Sweden	
Mason	Justin	Netherlands	BioDetection Systems BV
Narros		Spain	
Nordheim	Erik	Belgium	European Aluminium Association

Öberg	Tomas	Sweden	University of Kalmar
Paquot	Alexandre	Belgium	EU DG ENV
Pless-Mulloli	Tanja	United Kingdom	University of Newcastle
Potrykus	Alexander	Germany	BiPRO
Prévost	Franck	France	Ministère de l'Ecologie et du Développement Durable
Puncochar	Miroslav	Czech Republic	Czech Academy of Sciences
Quass	Ulrich	Germany	M-BBM
Ramos	I.	Spain	
Raptis	Sotirios	Austria	Voest-Alpine
Reinmann		Germany	Becker- Messtechnik
Ribeiro	Silva	Portugal	Universidade do Porto/Portugese Foundry Association
Rivera		Spain	
Sanalan	A.Teoman	Turkey	Ministry of Environment and Forestry
Schleicher	Ole	Denmark	FORCE technology
Schramm	Karl-Werner	Germany	GSF - National Research Center for Environment and Health, Institute of Ecological Chemistry
Schulz	Verena	Germany	Stahlinstitut VDEh
Sharifi	Vida	United Kingdom	SUWIC, Sheffield University
Smurthwaite	Michael	United Kingdom	Westech Instrument Services Ltd.
Spezzano	Pasquale	Italy	ENEA
Steiner	Thomas	Austria	MonitoringSystems GmbH
Swithenbank	Jim	United Kingdom	Sheffield University
Thomas	Jacqueline	Germany	Federal Environment Agency
Thompson	Kenneth Clive	United Kingdom	Alcontrol Laboratories
Tirler		Italy	
Varro	Tomas	Slovakia	Environment/Department Air Protection/Emission Monitoring
Vrancken	Karl	Belgium	Vito
Weber	Roland	Germany	
Weber	Theo	Luxemburg	Administration de l'environnement
Werner	Charles	Luxemburg	ProfilArbed SA
Wiesenberger	Herbert	Austria	Umweltbundesamt

Wikström	Evalena	Sweden	SP-energy technoloy
Woeldgen	Jean-Jaques	Belgium	EU DG Enterprise
Woodfield	Michael	United Kingdom	AEA Technology
Xhrouet	C.	Belgium	
Zerjav	Janko	Slovenia	Ministry of Environment and Spatial Planning

19 Quotations

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