




Dioxin Emission Measurements

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Objectives

- **Support to emission inventory**
 - Better emission factors for relevant sources
 - Identification of unknown hot-spots
 - Check of emission factors from UNEP Toolkit
- **Support capacity building in CCs**
 - Committing measurement tasks to local laboratories
 - Supervision of sampling by recently formed local groups

- The measurement program carried out within this project had two major goals:
- To obtain additional dioxin emission data from countries not yet covered so far by dioxin emission measurement activities and for not yet investigated emission sources, respectively
 - To help countries with emerging activities in emission control to obtain experience in dioxin emission sampling and – if appropriate laboratories are available – analysis.


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Procedure

- **Query to national experts**
 - Request for proposals of facilities
 - Request for information on laboratories
- **Selection of facilities from proposals**
- **Selection of companies/laboratories**
 - In principle at least one facility per country
 - At least in countries with measurement laboratories
- **Call for tender**
- **Selection of appropriate offer**
- **Commission of measurements**

CCs experts were asked to support the measurement program by supplying information on potentially relevant emission sources in their countries. For these sources, a questionnaire had to be answered covering plant information and technical data needed for an initial campaign planning and cost calculation. Most importantly, the plant operator's permits for the measurements had to be provided at this early stage, too. Waste incinerators in particular had to be ignored (already regulated by the so-called waste incineration directive 2000/76/EC).

Moreover, CCs experts were additionally asked to provide information on local companies that might be able to carry out the sampling campaign and/or the analytical work.

From the proposals obtained, facilities to be measured were selected according to their potential relevance. This was assessed by the estimated absolute dioxin emission per year or by its relative importance for the respective CC.

A campaign design was outlined for each of the selected plants, depending on the technical structure of the facility (e.g. number of lines and stacks). This outline served as basis for a specific call for offers which was sent to the indicated companies. CC based companies and laboratories were preferred whenever possible with respect to the capacity building goal of the project. In case no local company or laboratory existed foreign institutes were asked to take over these tasks.

Special report templates were provided to the companies committed with emission measurements. This was done to assure a high and equal quality of the results and completeness of data needed to assess the compliance of sampling and analysis methods with current standards (e.g. CEN 1948, 1-3 in connection with ISO 9096).

Facility proposals and identified laboratories

Suggested facilities

- 10 out of 13 countries responded
- 1 to 3 proposals per country

- 8 proposals from Poland

Identified laboratories

- Cracaw University/Emipro (PL)
- TESO (CZ)
- Tubitak (TR)

Overall, 31 facilities located in 10 of the CCs were proposed for emission measurements. No proposals were received from Hungary, Romania and Slovenia. Of the proposed facilities, 16 were selected for measurement campaigns, but finally only 13 of these campaigns could be realised due to insufficient support by some plant operators.

Due to the procedure of information gathering the result of identified laboratories in CCs give not necessarily a complete picture of the situation in the CCs. Particularly in case that no proposals for measurements had been made also no indication on laboratories was given.

Proposed and selected (*) facilities

- **Energy production**
 - Power plants (brown coal *, heavy fuel oil *)
- **Steel industry**
 - Pig iron tapping *
 - Iron sintering *
 - Furnaces (Scrap melter, EAF & ladle, Converter)
- **Non-ferrous metals**
 - Sec. Aluminium *
 - Sec. Zinc (oxide sintering *, recovery *, electrolytically melting *)
- **Cement industry** (dry *, wet *)
- **Other** (Shale oil production, Industrial bark combustion *)

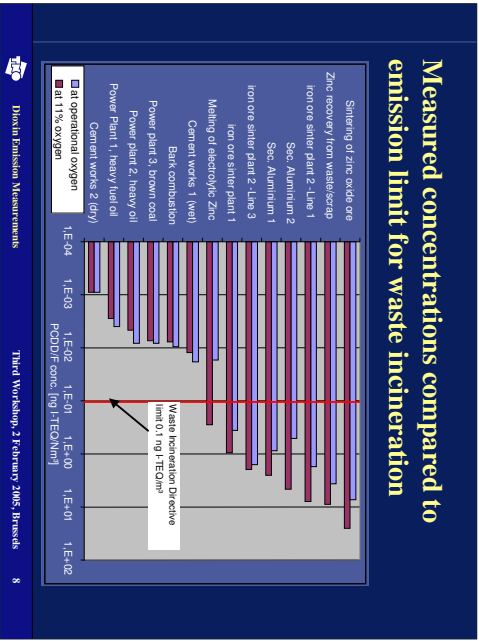
Measurement organisation (UTA)				
Country	Facility	Sampling	Analysis	Support
Bulgaria	Power plant (brown coal)	TUBITAK (TR)	TUBITAK (TR)	Casew University (PL)
Cyprus	Power plant (heavy fuel oil)	UBA (AT) and Cyprus	UBA (AT) and Cyprus	Cyprus Government
Cyprus	Cement production (dry)	UBA (AT) and Cyprus	UBA (AT) and Cyprus	Cyprus Government
Czech Rep.	Pig iron tapping	TESO (CZ)	TESO (CZ)	No
Estonia	Cement production (wet)	DK-Tetnik (DK)	ERGO (DE)	Estonian Gov.
Malta	Power plant (heavy oil)	TESO (CZ)	TESO (CZ)	No
Poland	Iron ore sintering (2s)	EMIPRO (PL)	Casew Univ. (PL)	No
Poland	Secondary Zinc (3s)	EMIPRO (PL)	Casew Univ. (PL)	No
Slovakia	Bank combustion	TESO (CZ)	TESO (CZ)	No
Turkey	Sec. Aluminium (2s)	TUBITAK (TR)	EMIPRO (PL)	Casew University (PL)
		EMIPRO (PL)	TUBITAK (TR)	



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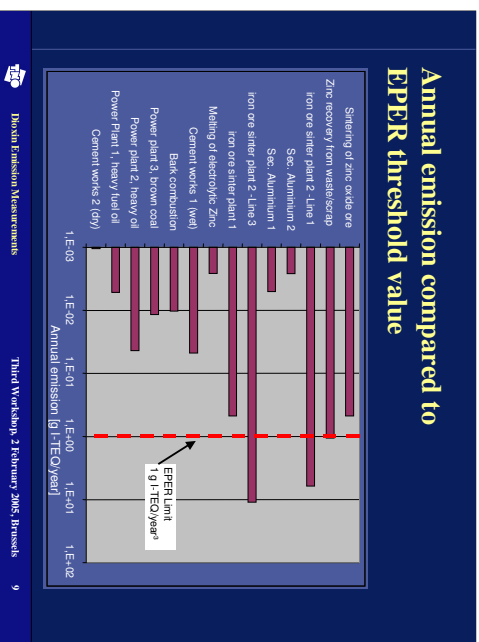
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To compare the results of different installations the dioxin and furan concentrations have been calculated referring to an oxygen concentration of 11 % in the flue gas. This reference oxygen content was chosen since it is required in the waste incineration directive to check compliance with the emission limit of 0.1 ng l-TEQ/Nm³ applied to waste incinerators. Therefore, re-calculation of the measured flue gas concentrations to 11 % oxygen content allows to use the waste incinerator limit value as an orientation value to compare with.

Clearly, a number of facilities, all belonging to the metallurgical sector, exceed the limit set for waste incineration facilities.

The highest concentration levels were found at secondary zinc processing facilities. Such findings correspond to similar experiences made in Western European countries (particularly in Germany and France) where secondary zinc producing facilities were among the most important emission sources.

However, none of the concentrations measured in the Candidate Countries appear to be surprisingly high when compared to the range of results taken from previous measurement data compilation given in the European Dioxin Inventory.



The figure shows the estimated annual emissions for the measured facilities in comparison to the threshold limit of 0.1 g TEO/year set for the European Pollutant Emission Register (EPER).

Obviously, most of the measured facilities would not be subjected to registration in the EPER (unless such registration would be necessary due to emissions of other compounds). Only in case of the zinc recovery plant and one of the iron ore sinter plants the EPER threshold for dioxins and furans might be exceeded.

In view of the flue gas concentrations that were shown to exceed the waste directive limit value this result might be surprising. However, most of these non-ferrous metal facilities are not operated continuously and therefore have quite low operation times.

Emission factors compared with UNEP Toolkit and Bref documents

No	Plant type	EF measured	EF UNEP Toolkit Specific operation	UNEP Toolkit Total range	BREF Docu-ment
1	Iron ore sintering	0.43	0.3	0.3 - 20	< 0.5
2	Iron ore sintering (2-lines)	2.2 - 4.3	5	0.3 - 20	< 0.5
3	Zinc oxide ore sintering	110	100	0.3 - 1000	< 10
4	Zinc recovery by rotary kiln	130	100	0.3 - 1000	< 10
5	Melting of zinc (electrolytic)	0.04	0.3	0.3 - 1000	< 10
6	Sec. Aluminium production	3.74	150	0.5 - 150	< 10
7	Sec. Aluminium production	0.52	150	0.5 - 150	< 10

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One of the motivations to carry out an emission measurement program within the project was to obtain some emission factors (EFs) from facilities located in the countries of interest. Emission factors have been calculated from the measurement results by using typical production or throughput capacities. The emission factors obtained are compared with the range of emission factors given by the UNEP Toolkit in relation to different flue gas cleaning technologies or input materials.

The figure shows the result of the comparison between the emission factors calculated for the measured facilities with toolkit factors which have been chosen according to the technical information provided within the measurement reports. Comparison of the measured emission factors with those given in the Reference Documents on Best Available Technologies (BREF) for the specific branches of industry reveals that emission factors given in the BREFs are in some cases a factor 10 lower. This is the case for sintering (iron ore and zinc oxide ore) and zinc recovery in the metal industry. In most other cases measured EFs are lower than given in the BREF (if available).

It can be concluded that implementation of IPPC Directory can reduce dioxin emission from certain facilities in the metal industry with a factor of 10 by using Best Available Techniques.

Emission factors compared (continued)

No	Plant type	EF measured	EF UNEP Toolkit		BREF Document
			Specific operation	Total Range	
8	Public power plant (heavy fuel oil; 4 boilers)	1.3 – 10.3	2.5	0.5 – 35	n.a.
9	Public power plant (brown coal)	0.8	10	0.5 – 35	< 0.5
10	Public power plant (heavy fuel oil)	12	2.5	0.5 – 35	n.a.
11	Cement production (wet)	0.07	0.05	0.05 – 5	< 0.2
12	Cement production (dry)	0.002	0.05	0.05 – 5	< 0.2
13	Pulp & paper industry (black combustion)	3.8	50	50 – 500	n.a.

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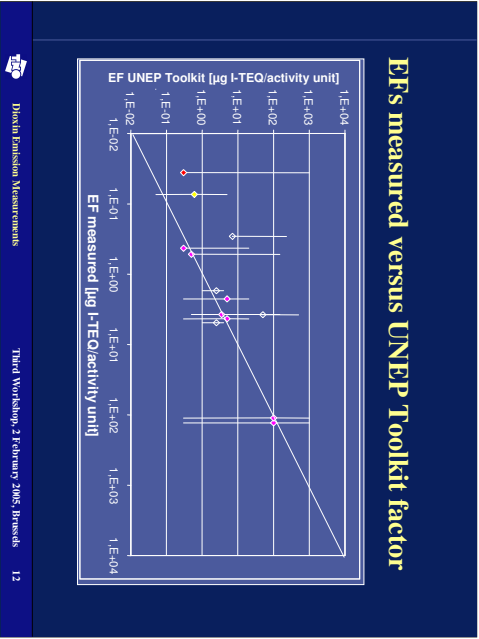
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(continued)

An evaluation of uncertainties in measured concentrations shows that on-site sampling conditions did not allow to carry out the sampling as exactly required. It is difficult to assess whether the actual conditions really influence the particular results or not. It might be reasonable to assume however, that at least the order of magnitude of these results is correct.

For the uncertainty in analytical procedures duplicates of samples and blanks have been analysed by other laboratories. With a few exceptions most results compared well to each other.




This figure shows a graph of the result of the comparison between the emission factors calculated for the measured facilities with toolkit factors which have been chosen according to the technical information provided within the measurement reports.

It is obvious that some measured emission factors are in very good agreement with the appropriate toolkit EFs (blue dots); however, there are also large deviations. Unfilled dots represent the power generation sources with emission factors related to produced energy ($\mu\text{g I-TEQ/TJ}$) rather than material input usually given in in $\mu\text{g I-TEQ/ton}$.

To deal with the uncertainty in choosing the appropriate toolkit EFs the range of emission factors in the Toolkit for the source type the facilities in general belong to are also given ("error bars").

It can be seen that for one of the data points (yellow dot) showing a higher toolkit than measured EF an alternative toolkit factor could be chosen which are in better agreement with the measurements.

Contrarily, in case of the data indicated by red dots the measured emission factors are considerably lower (higher) than even the lowest (highest) factor given in the toolkit.


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Conclusions

Measurement program


- Generally relevant plants
 - Sinter plants, cement production, secondary non-ferrous metals
- Relevant plants for specific countries
 - Combustion (heavy fuel oil, brown coal, bark)

Measurement results

- Metallurgical plants are important sources of dioxin
- Several plants exceed the level of 0.1 ng TEQ/m³
- Most plants keep emission under EPER threshold value

The emission measurement program comprised a number of potentially relevant sources for dioxins and furans like iron ore sinter plants and facilities in the non-ferrous metal industry. Beside these installations also industrial plants with particular importance for the specific country were investigated.

The results have shown again, as already known from the Western European dioxin inventory projects, that metallurgical plants are of particular importance for the release of dioxins and furans to air. Several of the measured facilities exceeded the orientation level of 0.1 ng I-TEQ/m³ that has been set as emission limit for waste incineration. Concerning the annual emissions, however, almost all installations kept the dioxin and furan EPER threshold value of 1 g I-TEQ/year.


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Conclusions (continued)

Comparison with UNEP Toolkit emission factors

- Acceptable to good agreement (differ less than factor 10)
- UNEP Toolkit factors seem to fit also for CCs
 - Under comparable process conditions
- Considerable range of uncertainty (factor 10)

Comparison with BREF documents

- Measured EFs are comparable to EFs given in BREFs
- Exception: some activities in metal industry (factor 10 higher)

Capacity building

- Verification of experienced laboratories (IUTA)
- Support "New" laboratories (sampling and analysis)

In general, the comparison between measured emission factors and UNEP toolkit factors showed acceptable to good agreement if the range of emission factors underlying the toolkit figures are taken into account. The measurements therefore do not indicate that applying the UNEP toolkit emission factors for releases to air would lead to significant over- or underestimations of the annual emissions. It should be noted however, that only a small fraction of existing emission sources were investigated. Hence, there is a considerable range of uncertainty when conclusions are drawn by scaling up these results to the situation in the entire region of the Candidate Countries.

Comparison of the measured emission factors with those given in the BREFs for the specific branches of industry show that in general they are comparable. This is not the case for sintering (iron ore and zinc oxide ore) and zinc recovery in the metal industry (factor 10 higher). In most other cases measured EFs are lower (factor 1 to 100) than in the BREFs (if available).

It can be concluded that implementation of IPPC Directory can reduce dioxin emission from certain facilities in the metal industry with a factor of 10 by using Best Available Techniques.

The measurements and analyses were carried out mostly by companies and institutes located in the area of interest; moreover, some joint sub-projects were established which involved experienced Western European laboratories and less experienced teams of local authorities.

For quality assurance reasons a number of samples have been additionally analysed by another laboratory (IUTA). In most cases, these samples comprised either the final extract solutions after clean-up in the laboratory that did the first analysis. Hence, only errors made during clean-up could not be identified.

From a comparison between the single PCDD/F concentrations found in the both laboratories it turned out that with a few exceptions most results were comparable.

Recommendation

- During the project it turned out that some plant operators did not want that measurement were performed at their plant. It could be an idea for the permit authorities to evaluate the reasons for this in view of the IPPC Directive to be complied with in 2010 for the New Member States.



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