

Regulatory measures in the Federal Republic of Germany to reduce the exposure of man and the environment to dioxins

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1 Introduction

The Minister for the Environment of the Federal Republic of Germany initiated in 1990 the international symposium "Health Effects and Safety Assessments of Dioxins and Furans" [1]. In connection with this symposium in Karlsruhe, a public hearing of experts on dioxins and furans was organised by the Federal Health Office and the Federal Environmental Agency. One of the main conclusions was [2]: With regard to average intake, humans are currently exposed to background levels of dioxin on the order of 2 pg TEQ¹ per kg body weight per day. According to the knowledge currently available, no impairment to the health can be assumed at an intake in the range of 1 to 10 pg per kg body weight and day. This is in accordance with a statement of a working group of the World Health Organisation. They considered a life-long daily exposure of 10 pg TCDD per kg body weight to be the maximum tolerable value for man.

However, changes in biochemistry, enzyme induction and other impacts occur in the range of current human exposures. The margin of exposure between background levels and levels where effects are detectable in humans is small. An adequate safety margin in accordance with the principles of preventive health protection is no longer given when the above mentioned intake of 10 pg per kg body weight and day applies.

¹ Throughout this paper, concentrations of dioxins will be presented as TEQ (Toxic Equivalents according to NATO/CCMS)

Reasons of precaution make it imperative to reduce the daily intake of 2 to less than 1 pg TEQ per kg body weight. It is a generally recognised fact that this can only be achieved in the long term due to the longevity of dioxins and their ubiquitous distribution. There is no doubt that this objective requires a minimisation of new dioxin discharges into the environment. As a consequence, the Federal Ministry for the Environment has started a number of initiatives to reduce the dioxin emissions (Tab. 1).

2 Sources and regulatory measures to reduce the dioxin emissions

At the opening of the international dioxin symposium in Karlsruhe in 1990 the Minister for Environment for the first time presented to the public a draft ordinance on incinerators for waste and similar combustible materials. The limit value for emissions of 0.1 nanogramme TEQ per m³ waste gas which was submitted for discussion at that time caused surprise and doubts. This value was considered too low to be realistic and hardly technically feasible or only with disproportionate expenditure. Almost one year later, on 1 December 1990, the Ordinance [3] entered into force despite resistance, prescribing the limit value mentioned above. Only two years later, the first new installation passed the critical test.

Based on the requirements of this Ordinance, effective dioxin minimization measures are applied at these plants. New plants have to comply with the emission limit of 0.1 ng TEQ per m³ immediately, existing plants by 1994 or 1996 at the latest. In the past, the average dioxin concentration in the waste gas of waste incinerators was 8 ng TEQ per m³. As a result, municipal incinerators in western Germany emitted a total of about 400 g TEQ per year. Due to the emission limit provided in the Ordinance, dioxin emission from these plants will be reduced drastically, by more than 99%. Whereas interest was often focused on waste incineration, attention will increasingly focus in the future on other thermal processes (Tab. 2):

Very high contamination levels have been ascertained in soil in the vicinity of cable smouldering plants. An extremely high concentration of far more than 100 ng TEQ per m³ waste gas has been reported. In Germany, the last cable smouldering plant was shut down in 1990. Only cold cable-stripping processes are now in use.

In the waste gas of plants for metallurgical treatment of iron ore, particularly in sinter plants, up to 43 ng TEQ per m³ were determined. Measurements on various sinter plants have shown an average dioxin emission level of 2 ng TEQ per m³. However, according to the high waste gas volume of 100.000 to 1.000.000 m³ per hour, even these plants with relatively low emissions are important sources with respect to dioxins. To reduce these emissions, the commonly used waste gas treatment system is the electrostatic precipitator. In a pilot study, financially supported by the Federal Ministry for Environment, a sinter plant was equipped in addition with a highly efficient fabric-filter for dust removal. Together with further measures a distinct reduction of the dioxin emission level is possible.

Extremely high concentrations have been also reported for copper recovery plants. Using primary measures and simple waste gas cleaning techniques, it was possible to reduce the emissions to values around 2 ng TEQ per m³.

The technology generally used for the melting of secondary aluminium in rotary drum type kilns is likely to cause dioxin emissions due to the well known formation mechanisms. Somewhat extended ranges of emissions, varying between 0.1 and 22 ng TEQ per m³, may result from different feedstock, aggregates and operational conditions. An arithmetic mean value of approximately 4 ng TEQ per m³ has been derived from 30 analysis.

The dioxin concentration in the exhaust gas of domestic fireplaces is relatively low. Values between 0.1 and 0.5 ng TEQ per m³ were analysed. However, due to the great number of fireplaces, the amount of annual emission is of importance. The 1989 annual

emission, calculated for the western Germany was up to 13 g. Up to 20 g TEQ per year are assumed for Germany as a whole.

In crematoriums, coffins of various designs and materials are incinerated. They often include printed plastics and in many cases also deodorants, such as dichlorobenzene. A fairly wide range of emission values has been recorded, with data up to 8 ng TEQ per m³.

Work is currently being done to examine whether these installations are able - after reasonably long transitional periods - to comply with a target value of 0.1 ng TEQ per m³ waste gas. A working group of representatives from federal and Länder ministries and agencies and other experts has been convened for that purpose by the Federal and Länder Ministers for the Environment. The report [4] and the recommendations were accepted by the Ministers for the Environment at the Conference in November 1994.

In the past, an impact of dioxins to the environment was due to the so-called scavengers [5]. In order to achieve a transformation of lead oxide to volatile lead halogenides, leaded petrol contained dichloroethane or dibromoethane as additives. During combustion, brominated and mixed-halogenated dibenzodioxins and -furans are produced, amounting to about 50 g TEQ per year in total. A contribution towards the objective of reducing the dioxin emissions was the ban on the additive of scavengers to leaded petrol.

The possibility of the formation of dioxins in the pulp industry is known. In Germany a series of experiments were carried some years ago at the Federal Health Office. Different types of paper were investigated. Furthermore, the carryover of dioxins from filter paper into coffee and the migration of dioxins from paperboard cartons into milk was measured. As a consequence, the dioxin levels in paperboard cartons have been significantly reduced to a level lower than 1 ppt TEQ by manufactures. Today, the formation and occurrence of dioxins due to the production of pulp in Germany is only of minor importance. All mills use the sulfite process for pulping and almost no chlorinated substances are used for bleaching. Therefore, the formation of dioxins in the German pulp industry is negligible.

Furthermore, mention must be made of the Ordinance on Sewage Sludge [6]. The Ordinance on Sewage Sludge in its revised version of 15 April 1992 is also helping to reduce dioxin discharges into the environment. For the first time, it introduced a dioxin limit value for sewage sludges used as fertilizer in agriculture, horticulture or forestry. Accordingly, fertilization with sewage sludge containing more than 100 ng TEQ per kg of dried residue is prohibited. This measure - although it primarily serves the purpose of environmental protection - has far-reaching secondary repercussions. By limiting the dioxin content in sewage sludge, it also interrupts the path of dioxin transmission via the soil, plants, animals and food to the human body. Considering that more than 90 % of the dioxin intake by humans originates from food, the positive effects of the Sewage Sludge Ordinance are self-evident.

Prohibition of certain chemicals

Most of these measures to protect man and environment reduce emissions at the "end of the pipe"; this is an approach which must gradually be changed. Therefore, the production of chemicals, preparations, products and the material flows are increasingly to be taken into account and included in the formulation of environmental protection measures.

In the past, certain chemicals containing chlorine were an important source of dioxins (Tab. 1). The ban on PCB of 18 July 1989 [7] was an essential step in protection from hazardous substances. Before the ban, environmental contamination of more than 4 kg TEQ per year was caused by the use of polychlorinated biphenyls.

By banning the production and the use of pentachlorophenol [8], a source that has accounted for an input of dioxins into the environment of the western part of Germany of more than 1 kg TEQ per year in the past, has been eliminated.

Another step in the protection from hazardous substances was the Ordinance on the

Prohibition of Certain Chemicals. This Ordinance has set stringent limit values for 8 PCDD/PCDF in substances, preparations and articles placed on the market. This regulation of dioxin-contents in chemicals is currently being amended (Tab. 3). The First Ordinance to amend the Ordinance of the Prohibition of Certain Chemicals of 5. July 1994 [9] increased the number of controlled chlorinated dioxins from 8 to 17 and reduced the limit values. Furthermore, for the first time, limit values for polybrominated dibenzodioxins and dibenzofurans substituted in the 2,3,7,8-position are included in the list of the regulated compounds.

According to these regulations, the following substances, as well as preparations and articles are not allowed to be placed on the market:

- if the sum of the concentrations of the chemical compounds listed in No. 1 of the column 1 of Tab. 3 exceeds a value of 1 µg per kg or
- if the sum of the concentrations of the chemical compounds listed in No. 1 and 2, - the so-called "dirty dozen" - exceeds a value of 5 µg per kg or
- if the sum of the concentrations of the chemical compounds listed in Nos. 1, 2 and 3, that are all congeners substituted in 2,3,7,8-position, exceeds a value of 100 µg per kg.

According to the present stage of knowledge, a comparable toxicity and the same spectrum of action of the chlorinated compounds must be assumed for the polybrominated dibenzodioxins and dibenzofurans. Investigations of the toxicity have shown that the brominated congeners tested up to the present display an active potency similar to the corresponding chlorinated compounds. The polybrominated dibenzodioxins and dibenzofurans are thus treated fundamentally in the same manner as the

² In the Ordinance of the Prohibition of Certain Chemicals, the concentrations of dioxins are not presented as TEQ. The limit values are determined by summing the concentrations of the listed individual congeners.

corresponding chlorinated compounds. For this reason limit values are also specified for brominated congeners to the extent permitted by present scientific knowledge and analytical abilities. The limiting values for polybrominated dibenzodioxins and dibenzofurans listed in No. 4 is 1 µg per kg and 5 µg per kg for the sum of the concentrations of the chemical compounds listed No. 4 and 5.

The Ordinance has been in force since 5 July 1994. However, transition periods of three to five years were set *inter alia* for anthraquinone pigments, dyes and pigments which are produced with chloranil as an intermediate product, as well as for chloranil itself if it is used as a catalyst in the production of dyes and pigments. The Ordinance does not apply to intermediate substances or to certain products which are already regulated by other legislations, for example drugs, pesticides, foodstuffs or marketing for a proper waste disposal and for purposes of research or testing of properties or as a control substance for analytical investigations.

4 Recommendations of a Federal State and Länder Working Group on dioxins

In their report on present developments, the Federal Health Office and the Federal Environmental Agency, have proposed a number of additional measures [2]. Because of both their diversity and the implications which their implement action would entail, close cooperation between the Federal government and the governments of the Länder, that is the federal constituent states, are required. This was also the position expressed by the Conference of Federal and Länder Ministers for the Environment at its annual meeting in 1990. It was decided to establish a Joint Working Group on dioxins which has been commissioned

- to initiate and coordinate nationwide measuring programmes,
- to document and evaluate the data collected up to now,
- to initiate research,
- and to deduce, on the basis of these data, preliminary, nationally applicable guidelines and/or limit values for different environmental media.

The first report of the Joint Working Group was published in 1992 by the Ministry for Environment [10]. The report contained the following reference values and recommended action for agricultural and horticultural land uses (Tab. 4) :

- For preventive reasons, the working group considers, it a long term objective to reduce dioxin concentration to below 5 ng TEQ per kg of soil used for agricultural purposes.
- Cultivation of foodstuffs is not restricted in the case the soil contains 5 - 40 ng per kg. However, critical land uses, for example grazing management, should be avoided if increased dioxin levels are analysed in foodstuffs.
- Limitations on the cultivation of certain feedstuffs and foodstuffs might be necessary if the dioxin contamination were to exceed 40 ng TEQ per kg soil. And unlimited cultivation is recommended only of plants with minimum dioxin transfer, for example corn.

Guideline values were also established for redevelopment measures for children playgrounds and for urban areas (Tab. 4):

- Remediation of contaminated soil is required in playgrounds if the soil contains more than 1.00 ng TEQ per kg. Remediation means sealing, decontamination or exchange of the soil.
- This action is required in urban areas if the soil is contaminated with more than 1.000 ng TEQ per kg.
- In industrial areas redevelopment measures are required if the soil is contaminated with more than 10.000 ng TEQ per kg.

The reference values and recommendations for action as proposed by the Joint Working Group were discussed at the Conference of Ministers for the Environment in November 1991. The recommendations have already been translated into governmental decrees in a number of Länder.

At the end of 1993 the Working Group submitted its second report [11]. The focal point of this report was a documentation on the contamination of food by dioxins and the deduction of guidelines and maximum values for milk and dairy products together with recommendations for action. Food and foodstuff have been analyzed on dioxin since 1986. Altogether about 900 analyses have been performed, the majority on milk and dairy products. The data on dioxins in milk and dairy products in the Federal Republic of Germany can be summarized as follows: Around 200 milk probes have been analysed. The dioxin content varied between 0.14 pg TEQ per g milk-fat as a minimum and 5.61 at maximum. In the mean, the milk collected on single farms was contaminated with 1.09 pg TEQ per g fat. Similar data have been obtained in dairy products.

Maximum tolerable values for the contamination of food and foodstuff can be derived in a theoretical manner. Based on data of the body weight, the daily milk consumption and the values for the tolerable daily intake, the maximum tolerable values for dioxins in milk fat was calculated. At the end of the discussion, the Joint Working Group came to the following concept of action (Tab. 5):

- Based on an TDI value of 10 pg 2,3,7,8-TCDD per kg body weight per day, the maximum dioxin concentration in milk should not exceed 5.0 pg TEQ per g milk fat. A ban on trade in contaminated milk and dairy products is required if the dioxin contamination exceeds this value. However, from the data on the existing dioxin contents of milk it is obvious, that a limit value of 5 pg TEQ per g milk fat would cut off only cases of extreme contamination. This limit value would probably have no consequences at all and would not improve the consumer situation.
- To reduce the impact, measures are recommended if more than 3 pg TEQ per g milk fat are analysed. In this case, verification of the existence of dioxin sources and emission-reducing measures are required. Furthermore, it is recommended that direct supply of milk and dairy products to the consumer be stopped.

- Furthermore, the Joint Working Group elaborated an orientation value based on the principle of precaution. The value of 1 pg TEQ per kg body weight was also taken as a basis for these calculations. In this case, the target value for milk and dairy products would be about only 0.9 pg TEQ per g fat. From the data presented above, it is obvious that more than 50% of the milk and dairy products in Germany, as well as in other countries of Europe, exceed this value. An immediate implementation of the value of precaution into maximum amount for food would lead to non-assessable consequences in respect to the food supply on the population. Therefore, these values should be regarded as target values to be achieved. To reach this target, it is necessary to reduce the dioxin release into the environment.

In view of the public controversy on this issue and the large number of questions that are still unresolved, the Federal Minister for the Environment hosted a second international symposium in November 1992 [12], again linked to a public hearing on dioxins and furans [13,14]. At this hearing in Berlin, the reference values and recommendations for contaminated milk and dairy products were discussed and the reference values proposed were numerically confirmed. However, till today, these proposed measures are recommendations for action, but they are not legally binding. Nevertheless, they are brought to bear by those responsible for environment and health in the governments of the Länder as the basis for the political decisions to protect human and the environment. In the case of a number of hazardous incidents (fire at a plastic store for example) in the recent past in which dioxin contamination of the environment was to be feared, recommendations for actions were made on the basis of the recommendations contained in the above-mentioned report of the Joint Working Group.

5 Results of the regulatory measures

The regulatory measures have reduced the exposure of man and the environment to dioxins (Tab. 6). Whereas in the past, the chemical industry and chemical products (PCB, PCP) were considered the main sources and cause of today's contaminated sites in

Germany, it must be assumed on the basis of the information available, that today's input of dioxins are mainly caused by thermal processes. Of the thermal processes, the waste incineration played a role in the past. In the future, more attention should be given to industrial thermal processes (sinter plants, aluminium remelting plants, copper recovery etc.) to reduce the exposure of man and the environment to dioxins.

A good substrate for studying background contamination is breast milk. In western Germany, dioxins in human milk have been analyzed since 1985. The body burden is well known, since more than 2000 samples of breast milk have been analyzed over the last 9 years and documented by the Federal Health Office [15]. As to be seen (Tab. 7), a considerable reduction in the dioxin concentration is today becoming apparent, even in one of the final links in the food chain, namely breast milk. This is due to measures taken in the past, in the eighties. It is to assume, that the measures, recommendations and the Ordinances of the nineties will stabilise this positive trend.

6 Literature

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- [15] L. Alder, H. Beck, W. Mathar, R. Palavinkas: PCDDs, FCDFs, PCBs and other organochlorine compounds in human milk levels and their dynamics in Germany; 14th International Symposium on chlorinated dioxins, PCB and related compounds, November 21-25, 1994, Kyoto, Japan. Organohalogen Compounds, Vol. 21 (1994) 39-44

Tab. 1: Prohibition of certain chemicals and regulatory measures to reduce the exposure of the environment to dioxins

Ordinance on the Ban on Pentachlorophenol (PCP) of 12 December 1989

Ordinance on the Ban of Polychlorinated Biphenyls (PCB) of 18 July 1989

Ordinance of the Prohibition of Certain Chemicals of 6 July 1994:
limit values for dioxins in substances, preparations and articles

Ordinance on Combustion Plants of 23 November 1990:
Limit value for dioxins in exhaust gas: 0.1 ng TEQ/m³

19th Ordinance on the Federal Immission Control Act of 17 Januar 1992:
Ban on the additive of scavengers to leaded petrol

Ordinance on Sewage Sludge of 15 April 1992:
Limit value for dioxins in sewage sludge: 100 ng TEQ/kg dried residue

Tab. 2: Sources and emissions

Sources	emissions (ng TEQ/m ³)
cable smouldering	100
metallurgical treatment of iron (sinter plants)	45 - 0.5
aluminium remelting plants	22 - 0.1
crematories	8
copper recovery	2
home heating (oil, coal, wood)	0.5 - 0.1
burning processes of nonmetallic minerals industry	0.1
power stations	< 0.1
Target	0.1 ???

Tab. 3: Limit values for dioxins in substances, preparations and articles

1.	2,3,7,8-tetra-CDD	∑ No. 1
	1,2,3,7,8-penta-CDD	1 µg/kg
	2,3,7,8 -tetra-CDF	
	2,3,4,7,8-penta-CDF	
2.	1,2,3,4,7,8-hexa-CDD	∑ No. 1 and 2
	1,2,3,7,8,9-hexa-CDD	5 µg/kg
	1,2,3,6,7,8-hexa-CDD	
	1,2,3,7,8-penta-CDF	
	1,2,3,4,7,8-hexa-CDF	
	1,2,3,7,8,9-hexa-CDF	
	1,2,3,6,7,8-hexa-CDF	
	2,3,4,6,7,8-hexa-CDF	
3.	1,2,3,4,6,7,8-hepta-CDD	∑ Nos. 1,2 and 3
	1,2,3,4,6,7,8,9-octa-CDD	100 µg/kg
	1,2,3,4,6,7,8-hepta-CDF	
	1,2,3,4,7,8,9-hepta-CDF	
	1,2,3,4,6,7,8,9-octa-CDF	
4.	2,3,7,8-tetra-BDD	∑ No. 4
	1,2,3,7,8-penta-BDD	1 µg/kg
	2,3,7,8-tetra-BDF	
	2,3,4,7,8-penta-BDF	
5.	1,2,3,4,7,8-hexa-BDD	∑ No. 4 and 5
	1,2,3,7,8,9-hexa-BDD	5 µg/kg
	1,2,3,6,7,8-hexa-BDD	
	1,2,3,7,8-penta-BDF	

Tab. 4: Reference values and recommended action for land use and for remediation of soil

ng TEQ/kg soil	Recommended action
< 5	Target value
5 - 40	Unrestricted cultivation of foodstuffs; avoidance of critical land uses (e.g. grazing management) if increased dioxin levels are analysed in foodstuffs
> 40	Limitation to defined agricultural and horticultural land uses; unlimited cultivation only of plants with minimum dioxin transfer (e.g. corn)
> 100	Remediation of contaminated soil (sealing, decontamination or exchange) in playgrounds
> 1,000	Remediation of contaminated soil in urban areas
> 10,000	Remediation of contaminated soil also in industrial areas

Tab. 5: Dioxin contaminated milk and dairy products

pg TEQ/g milk fat	Proposed action
< 0.9	Desirable target
> 3.0	Verification of existence of PCDD/PCDF sources Measures to reduce the impact of dioxins Recommendation to stop direct supply of milk and dairy products to consumer
> 5.0	Ban on trade of contaminated milk and dairy products

Tab. 6: Emissions in the past, today and in the next future

sources	emissions (g TEQ per year)		
	in the past	today	1996
PCB	4.500	0	0
PCP	1.350	0	0
Municipal Waste Incineration	400	< 300	4
Scavenger	> 50	0	0
Domestic Furnaces	20	20	20
Industrial Thermal Processes	> 1.000	500	?

Tab. 7: Dioxins in human milk fat (pg TEQ/g) in Germany

L. Alder, H. Beck, W. Mathar, R. Palavinskas [15]



