

# Final Report

## Evaluation of the Occurrence of PCDD/PCDF and POPs in Wastes and Their Potential to Enter the Foodchain

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## Glossary

ADI	Acceptable daily intake
Ah-receptor	Aryl hydrocarbon receptor
BCF	Bioconcentration factor
b.w.	Body weight
COR	Carry-over rate
CPP	Citrus pulp pellets
d.m.	Dry matter
FDA	Food and Drug Administration
f.w.	Fresh weight
HCB	Hexachlorobenzene
HCH	Hexachlorocyclohexane
I-TEF	International Toxicity Equivalency Factor
I-TEQ	International Toxicity Equivalent
LD <sub>50</sub>	Lethal dose, where 50 % of the organisms are killed
LOAEL	Lowest observed (adverse) effect level
MSWI	Municipal solid waste incinerator
NOAEL	No observed (adverse) effect level
OECD	Organization for Economic Cooperation and Development
PCB	Polychlorinated biphenyls
PCDD	Polychlorinated dibenzo- <i>para</i> -dioxins
PCDF	Polychlorinated dibenzofurans
PCP	Pentachlorophenol
PCT	Polychlorinated terphenyls
POPs	Persistent organic pollutants
TCDD	Tetrachlorodibenzo- <i>p</i> -dioxin
TDI	Tolerable daily intake
TEF	Toxicity Equivalency Factor
TEQ	Toxic Equivalent
UN-ECE	United Nations Economic Commission for Europe
UNEP	United Nations Environment Programme
WHO	World Health Organization

**EU Member States**

A	Austria
B	Belgium
D	Germany
DK	Denmark
E	Spain
F	France
FIN	Finland
GR	Greece
I	Italy
IRL	Ireland
L	Luxembourg
NL	Netherlands
P	Portugal
S	Sweden
UK	United Kingdom

**Units**

t	(metric) ton	$10^6$ g
kg	kilogram	$10^3$ g
g	gram	$10^0$ g
mg	milligram	$10^{-3}$ g
$\mu$ g	microgram	$10^{-6}$ g
ng	nanogram	$10^{-9}$ g
pg	picogram	$10^{-12}$ g

# 1 STUDY SCOPE AND OBJECTIVES

## 1.1 Background

Two recent studies focussing on polychlorinated dibenzo-*p*-dioxin and polychlorinated dibenzofuran (PCDD/PCDF) emission fluxes at the European and the international levels revealed current gaps. The first study is the report prepared on the behalf of DG XI at the North Rhine–Westphalia State Environment Agency, entitled “Identification of Relevant Industrial Sources of Dioxins and Furans in Europe (The European Dioxin Inventory)”, from 1997. The second is the report published by United Nations Environment Programme (UNEP), prepared by UNEP Chemicals Geneva, Switzerland, entitled “Dioxin and Furan Inventories, National and Regional Emissions of PCDD/PCDF” from 1999. In addition to European data, it includes also data from the US, Canada, Australia and Japan.

Among the conclusions of both studies it was stated, that PCDD/PCDF emissions into the atmosphere are fairly well documented, whereas insufficient information exists about other pathways of PCDD/PCDF and other POPs into the foodchain and the environment. In particular, data about the amount and fate as well as the dioxin content of wastes is often not available.

As recently highlighted by the Belgium episode of food contamination by PCB, PCDD and PCDF, the contamination of wastes and their industrial use within the feeding stuff industry may threaten public health. It has been calculated that the consumption of 30-40 meals of highly contaminated chicken or eggs (dioxin levels of around 1,000 pg I-TEQ per g fat) will double the body’s PCB and dioxin burden.

## 1.2 Objective

The objective of this study is to evaluate the current state of knowledge concerning PCDD/PCDF and POPs in wastes and their mass fluxes into feeding stuff. Furthermore, it should aim at clearly identifying data gaps in order to allow an appropriate planning of monitoring activities in that field.

The study should allow a first estimate of the relevance of that pathway and to which extent the elimination of certain contaminated wastes going into feeding stuff might reduce the overall daily intake of PCDD/PCDF and POPs.

### 1.3 Approach

1. Identification of type and mass fluxes of wastes and other additives used in the industrial production of feedingstuff in Europe.
2. Collection of available data on PCDD/Fs and POPs for each type of waste identified under 1, using literature and national databases.
3. If possible on the basis of the collected data, calculation of the fluxes of PCDD/PCDF and POPs into in feedingstuff along with the different types of waste streams.
4. Calculation of the human daily intake of PCDD/PCDF and POPs related to the transfer of PCDD/PCDF and POPs from waste reuse in the feedingstuff production.
5. Comparison of the human daily intake calculated under 4 with the daily intake along with the terrestrial (air – plant - terrestrial animals and their products) and marine foodchain.
6. Estimate of the possibility to lower the human daily intake of PCDD/PCDF and POPs through the elimination of certain contaminated wastes going into feedingstuff production.

## 2 METHODOLOGY AND REPORT STRUCTURE

After an introduction, this report starts with an overview on POPs characteristics (chapter 3) providing a definition of the term POPs in the international context and brief characteristics of the major representatives of this class of compounds. Further, information on the toxicity of these compounds, and when existing, guidelines and regulations concerning tolerable daily intake are provided.

Chapter 4 addresses major legislative initiatives to regulate POPs in the issues of concern: waste management, feedingstuff production, and food industry.

Chapter 5 gives an overview of the importance of the dietary intake and concentrations detected in humans.

The recent feedstuff and food contaminations are briefly summarized in chapter 6, which include the citrus pellet contamination originating in Brazil, the Belgian chicken accident, the dioxin contamination of clays, the Brandenburg case of the contamination during green fodder drying, and the most recent choline chloride case.

Chapter 7 outlines the most important findings and steps in the aquatic and terrestrial food-chains. Carry-over from feedstuffs to animal tissues or milk and eggs will be described. Such knowledge is later on used for the evaluation of sensitive steps, which can be affected by contaminants.

Chapter 8 describes the industrial production of feedingstuffs, gives consumption and production figures. Data on the contamination of feedingstuff ingredients are provided and PCDD/PCDF fluxes into feedingstuff industry are calculated.

Chapter 9 attempts to identify which exposure pathways within the feedingstuff/food complex contribute to the human dietary intake.

Chapter 10 concludes on the main findings.

Chapter 11 highlights major gaps in knowledge.

Chapter 12 gives recommendations for monitoring, future research and legislative action.

The report terminates with a list of key references in chapter 13.

As most information is available for PCDD/PCDF, most of the data and the discussion around these data and conclusions will deal with this class of compounds.



### 3 PCDD/PCDF AND POPs

#### 3.1 POPs in General

In science and in daily language, POPs stands for Persistent Organic Pollutants. In general, the term POPs does not have a clear definition and includes chemical compounds that are highly resistant to most forms of degradation and, therefore, have relatively long half-lives. POPs are often chlorinated and characterised by low water solubility and high lipid solubility. Due to their affinity for lipids they can easily travel throughout the food chain and bioaccumulate in the fatty tissues of top-level predators, including humans. Most of the POPs are semi-volatile compounds, and are distributed to different degrees between the gaseous, particulate and aqueous phases in the atmosphere, thereby facilitating their long range transport. POPs have been detected in air, soil, sediment, vegetation, animals and humans all over the world, even in locations that are remote and often thousands of miles away from any known sources.

Laboratory investigations and environmental impact studies have shown that POPs can cause birth defects, various cancers, immune system dysfunction, neurobehavioural effects, and reproductive abnormalities in wildlife. Although the effects of POPs on human health are still quite unclear, there is growing concern that even low-dose, long-term exposures may cause significant adverse health effects. Furthermore, emerging evidence indicates that many POPs act as endocrine disruptors *i.e.* they can alter endocrine-regulated functions resulting in toxic effects, particularly on the developing fetus.

Although some natural sources of POPs are known to exist, most of these compounds originate from anthropogenic activities. The class of POPs includes organochlorine pesticides such as DDT, HCH, toxaphene and chlordane, as well as industrial organochlorines such as the PCBs that have been employed extensively for a variety of industrial purposes. In contrast, POPs like PCDD/PCDF are formed unintentionally as by-products in a wide range of manufacturing and combustion processes.

Many countries have banned or severely restricted the use of the most dangerous POPs. However, it is thought that many of these compounds have been or continue to be employed in large quantities. DDT and HCH are still used in some developing tropical countries for agricultural and public health reasons, *e.g.* the control of malaria. Existing stockpiles of POPs are another problem particularly in countries that lack appropriate disposal facilities. There are still a lot of active PCB-containing transformers and capacitors all over the world, and finally evaporation of POPs residues from soils that were heavily treated years ago (*e.g.* by toxaphene) is suspected to be another important present-day source.

As for PCDD/PCDF, advances in pollution control have sharply reduced the release of these compounds from some major sources in many developed countries. However, in most parts of the world, including even those countries where such controls are available, PCDD/PCDF emissions are an ongoing concern.

Since June 1996, sufficient evidence was achieved for the international community, namely IFCS (Intergovernmental Forum on Chemical Safety) to recommend a global action plan on

POPs. In its decision 19/13 C of February 7, 1997, the Governing Council of the United Nations Environment Programme (UNEP) requested the Executive Director of UNEP to convene an Intergovernmental Negotiating Committee (INC) with a mandate to prepare an international legally binding instrument for implementing international action initially on twelve POPs, which were on a global level of most concern to humans, wildlife and the environment. Since this time, the acronym POPs primarily refers to these twelve POPs, which are sometimes named the “dirty dozen”. The 12 UNEP POPs are:

- eight chlorinated pesticides: aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, mirex and toxaphene;
- two industrial chemicals: HCB<sup>1</sup> and PCB;
- two unwanted by-products: PCDD and PCDF<sup>2</sup>.

The aims of the future POPs Convention are:

- Measures to reduce or eliminate releases of all of the POPs
- Process to add more POPs
- Technical and financial assistance.

Until July 2000, four rounds of talks have taken place to negotiate the future POPs treaty. The first meeting of the Intergovernmental Negotiating Committee (INC) was held in Montreal (Canada) in July 1998, the second INC took place in Nairobi (Kenya) in January 1999, INC-3 was held in September 1999 in Geneva (Switzerland) and INC-4 in March 2000 in Bonn (Germany). The final INC-5 will be held in Johannesburg (South Africa) in December 2000. The Diplomatic Conference is scheduled for May 21-23, 2001 in Stockholm (Sweden) to adopt and sign the convention and final act.

Based on experiences with similar agreements, the POPs Convention may enter into force in the year 2004 once 50 ratifications will be obtained.

With respect to measures on the 12 substances, the present status of the negotiations can be briefly summarized as follows:

- 10 deliberately produced POPs proposed for elimination – but with differing time frames
- Interim DDT use to be limited to vector control
- Some progress made on measures on dioxins and furans
- Process for adding new POPs was accepted
- Technology transfer and financial mechanism issues are still unresolved.

For the ten deliberately produced POPs the measures to reduce or eliminate releases are presently proposed as follows:

- aldrin, endrin, toxaphene - at entry into force of the convention

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<sup>1</sup> Note: HCB was also used as a pesticide

<sup>2</sup> Note: at the last round of negotiating talks (Bonn, March 20-25, 2000), the European Commission proposed to add HCB (a contaminant in certain agrochemicals and a by-product of combustion processes) and coplanar and mono-ortho PCBs to the list of by-products.



- chlordane, dieldrin, heptachlor, mirex, HCB - some critical uses may be permitted, but reviewed at specified dates
- DDT: elimination of production for all except public health uses (e.g. malaria) but review the need for remaining uses to see when production may be completely halted.
- PCBs: elimination of production for all new uses but permit continued use of PCBs in equipment, and phase out “as soon as possible” may specify a deadline
- By-products (dioxins, furans, HCB, non-ortho and mono-ortho substituted PCB):
  - goal is not yet agreed
  - “minimization, elimination”
  - agreement on reducing releases
- POPs wastes:
  - strategies for identification of articles, products and wastes
  - environmentally sound waste destruction
  - concern for dioxin and furan generation and POPs release to environment
  - technical & financial assistance for less developed countries

One of the PCDD, namely 2,3,7,8-TCDD is the most toxic synthetic compound known; for the dioxins, the mode of toxic action has been widely elucidated and finally, the analysis of PCDD/PCDF is on an extreme high standard and methods for their determination are standardized. Information on the other ten POPs will be incorporated whenever possible.

As can be seen from the chemicals subject to the POPs convention, all intentionally produced POPs are “old” chemicals, which have been banned in most countries and especially in the Member States of the EU. Consequently, the primary concern on these substances is the identification of stocks and its environmentally sound disposal as there are no new inputs. In this context, it should be noted that these chemicals can be imported into Member States of the European Union from countries where no destruction capacity exists. Further, mobilization from old sources can still occur, *e.g. via* revolatilization from contaminated soils, remobilization with sediments or leakages from storage locations.

In contrast to these “old” pesticides” and to PCB, PCDD/PCDF are still being produced and there will be sources present in the future. One of the tasks of the future POPs Convention will be a continuous minimization of releases and elimination of PCDD and PCDF sources.

PCDD/PCDF always occur as mixtures of congeners. Although all PCDD/PCDF are lipophilic, semi-volatile, bioaccumulative and most are toxic to animals, the physical and chemical properties between congeners varies about several orders of magnitude. These properties have been characterized quite well and thus, PCDD/PCDF congeners became model substances to study biological effects, environmental fate and behavior and formation. All these facts resulted in a widespread public attention and attracted a great deal of research. As a result, large databases have been generated in many industrialized countries.

In the following section, major characteristics of the other POPs are summarized. Part of this information was taken from Ritter *et al.* (1995) and Fisher (1999).

**Aldrin** and **Dieldrin** are pesticides used to control soil insects and to protect wooden structures from termites. Besides, dieldrin was also used in public health protection to control several insect vectors.

Aldrin is readily and rapidly converted to dieldrin in many organisms. Therefore, aldrin residues are rarely found in environmental matrices, and aldrin bioaccumulates mainly as its conversion product. Thus the levels of dieldrin reflect the total concentration of both compounds. Food, especially dairy products and animal meats, is the primary source of human exposure to dieldrin. Volatilisation from soils and regions where there was significant usage is an important source in ambient air (Harner *et al.* 1998).

**Chlordane** is a broad-spectrum contact insecticide that had been employed on agricultural crops, and on lawns and gardens. It has also been used extensively in the control of termites.

Chlordane was banned in many countries, and its use is severely restricted or limited to non-agricultural uses in several others. Because of these agricultural restrictions, food is probably not a major pathway of human exposure. Sources of chlordane in ambient air include volatilisation from soils as well as long range transport from places where it is still in use. Very high chlordane concentrations detected in the indoor air of residences in the United States (Wiberg *et al.* 1997) indicate that volatilisation from termiticide treated houses may be another significant source in certain areas.

**DDT** received widespread usage on a variety of agricultural crops. While much of the agricultural use has ceased, DDT is still being produced in considerable amounts and used for vector control, particularly against the malaria-transmitting *Anopheles* mosquito. It will, however, take time to replace DDT with non-pesticide alternatives for vector control, and thus DDT will remain an exception: banned or severely restricted on the one side, but essential for public health in many developing countries on the other side.

DDT and its metabolites have been detected in foods around the world, which is thought to be the primary pathway of human exposure.

**Endrin** is a foliar insecticide used mainly on field crops such as cotton and grains. It has also been employed against mice and voles. Endrin is very persistent in the environment with a half-life in soil up to 12 years. It enters the atmosphere by volatilisation, and can contaminate surface water from soil run-off. The main exposure pathway of endrin to the general population is *via* residues in food.

**Hexachlorobenzene (HCB)** is a fungicide used for seed treatment, particularly for the control of bunt, a fungal disease of cereal grasses such as wheat and rye. It is also a by-product of the manufacture of industrial chemicals including carbon tetrachloride, perchloroethylene, trichloroethylene and pentachlorobenzene and a known contaminant in certain agrochemicals, *e.g.* pentachlorophenol and dicloram and may be present as an impurity in others. HCB is also a byproduct of the manufacture of industrial chemicals. Finally, HCB is a by-product of combustion processes.

Some countries have documented HCB as a raw material for synthetic rubber, a PVC plasticizer, and a rubber peptizing agent in the production of nitroso- and styrene-rubbers. It is also used as a chemical intermediate in dyes, as well as in manufacturing process of pentachlorophenol in Europe and in the preservation of wood.

HCB is a by-product or waste material in the production of tetrachloroethylene, trichloroethylene, carbon tetrachloride, chlorine, chlorinated solvents, dimethyl tetrachloroterephthalate, vinyl chloride, atrazine, propazine, simazine, pentachloronitrobenzene and mirex.

Also as a waste material from pyrotechnic production, sodium chlorate production, aluminum manufacturing

- Possibly used in synthetic rubber production
- Has been found in treated waste water from non-ferrous metal manufacturing plants
- Ingredient in several pesticides

Might be emitted in gases from waste incineration facilities.

High bioconcentration factors (BCF) have been documented in fish and invertebrates. It is transferred in water through food chains, such as algae, snails, plankton, water fleas, mosquitoes and fish. Its presence has been detected and documented in human adipose tissue of non-occupationally exposed individuals. Bioconcentration factors seem to be higher in humans than in rodents by several orders of magnitude. HCB has been detected in foods of all types.

IARC classified HCB as a Group 2B compound, which means a probable human carcinogen with sufficient data in animals).

**Heptachlor** is a non-systemic stomach and contact insecticide, used primarily against soil insects and termites, as well as against cotton insects, grasshoppers, some crop pests, and malarial mosquitoes.

Heptachlor is metabolised in animals to heptachlor epoxide, whose toxicity is similar to that of heptachlor, and which may also be stored in animal fat. Heptachlor epoxide concentrations in ambient air are attributed to microbial activity in heptachlor containing soils and water (Wiberg *et al.* 1997).

**Mirex** is a stomach insecticide with little contact activity. Its main use was against fire ants in the United States. It has also been used to control leaf cutters in South America, harvester termites in South Africa, Western harvester ants in the United States, and mealybug of pineapple in Hawaii. Mirex has also been employed industrially as a fire retardant in plastics, rubber, paint, paper, and electrical goods.

Mirex is considered to be one of the most stable and persistent pesticides, with a half-life of up to 10 years. It is insoluble in water and has been shown to bioaccumulate and biomagnify. The primary source of human exposure to mirex is food, especially meat, fish, and wild game.

**Polychlorinated biphenyls (PCB)** comprise a class of 209 individual compounds (congeners), which carry between one and ten chlorine atoms. There are two major sources of PCB:

- Commercial production, and
- by-product in combustion processes as thermodynamically stable compounds.

Polychlorinated biphenyls (PCB) were produced by chlorination of biphenyl about 60 years ago with an estimated world production of about 1.5 million tons (Rantanen 1992).

PCB were marketed with respect to percentage of their chlorine content (by weight) and were available under several trade names. Depending on the degree of chlorination of the PCB, their physico-chemical properties, like non-flammability or non-electric conductivity, brought about a wide field of application. Thus, PCB have been used as dielectric fluids in transformers and capacitors, as pesticide extenders, adhesives, dedusting agents, cutting oils, flame retardants, heat transfer fluids, hydraulic lubricants, sealants, paints, and in carbonless

copy paper. Some of their applications resulted in a direct or indirect release of PCB into the environment. Relatively large amounts were released due to inappropriate disposal practices, accidents and leakages from industrial facilities. A summary of the present status of PCB in use, in storage, and amounts that have been destroyed are given in section 8.3.3.

In the technical product and in environmental compartments as well as in biota, polychlorinated biphenyls (PCB) occur as mixtures of congeners. Depending on the degree of chlorination, the physical and chemical properties vary greatly. Generally, the water solubility and vapor pressure decrease as the degree of substitution increases, and the lipid solubility increases with increasing chlorine substitution. PCB in the environment may be expected to associate with the organic components of soils, sediments, and biological tissues, or with dissolved organic carbon in aquatic systems, rather than being in solution in water. PCB volatilize from water surfaces in spite of their low vapor pressure, and partly as a result of their hydrophobicity; atmospheric transport may therefore be a significant pathway for the distribution of PCB into the environment.

Some PCB, namely those with no chlorine in the ortho positions (= coplanar PCB) or those with only one chlorine in one of the four ortho positions (= mono-ortho chlorinated PCB) exhibit dioxin-like toxicity. Thus, in 1997, a WHO expert group has assessed the dioxin-like toxicity of PCB and established toxicity equivalency factors (TEFs) for PCB (see Table 1) (WHO 1997, van den Berg *et al.* 1998). The toxicity of 2,3,7,8-TCDD has been set to 1 in his scheme.

Table 1: TEFs for PCB (WHO 1997, van den Berg *et al.* 1998)

Congener	Humans/Mammals	Fish	Birds
<b>Coplanar or non-ortho-substituted</b>			
3,4,4',5-TCB (81)	0.0001	0.0005	0.1
3,3',4,4'-TCB (77)	0.0001	0.0001	0.05
3,3',4,4',5-PeCB (126)	0.1	0.005	0.1
3,3',4,4',5,5'-HxCB (169)	0.01	0.00005	0.001
<b>Mono-ortho substituted</b>			
2,3,3',4,4'-PeCB (105)	0.0001	<0.000005	0.0001
2,3,4,4',5-PeCB (114)	0.0005	<0.000005	0.0001
2,3',4,4',5-PeCB (118)	0.0001	<0.000005	0.00001
2',3,4,4',5-PeCB (123)	0.0001	<0.000005	0.00001
2,3,3',4,4',5-HxCB (156)	0.0005	<0.000005	0.0001
2,3,3',4,4',5'-HxCB (157)	0.0005	<0.000005	0.0001
2,3',4,4',5,5'-HxCB (167)	0.00001	<0.000005	0.00001
2,3,3',4,4',5,5'-HpCB (189)	0.0001	<0.000005	0.00001

**Toxaphene** is a complex mixture of several hundred components. Most of these components are polychlorinated bornanes. The theoretically possible number of congeners exceeds 30,000. In the environment, however, most of the components of toxaphene are degraded and only few are accumulated in biota (Vetter and Oehme, 2000). The complex composition of toxaphene is reflected in the difficulties to establish a uniform nomenclature. Currently, the mostly used codes are the so-called "Parlar numbers" (Parlar *et al.* 1995) and the so-called "AV-codes" by Andrews and Vetter (1995).

Toxaphene was introduced in 1949, and became the most heavily used organochlorine pesticide in the United States until its ban in 1982 (Saleh, 1991). High production rates were

also reported for Brazil, the former Soviet Union and the former German Democratic Republic as well as for Central America (Voldner and Lie, 1993). Over the years it has become one of the most widely applied pesticides. Voldner and Lie (1993) estimated a global usage of 1.3 million tons from 1950 to 1993.

Toxaphene is particularly efficient against pests in cotton, soybeans, peanuts and maize. It has also been used by fisheries managers in Canada and in the United States as a piscicide to rid lakes of undesirable fish in the early 1960's (Saleh, 1991).

Present-day sources of toxaphene include evaporation of residues from soils that were treated years ago, and air transport from countries that still use toxaphene and similar products. There are indications of continuous usage in e.g. Mexico, the former Soviet Union, Africa and South America (Fishbein 1997). Toxaphene bioaccumulates readily in aquatic species and occurs as a contaminant especially in fish and seafood.

## 3.2 PCDD/PCDF

Polychlorinated dibenzo-*p*-dioxins (dioxins, PCDD) and polychlorinated dibenzofurans (furans, PCDF) are two groups of planar, tricyclic ethers which have up to eight chlorine atoms attached at carbon atoms 1 to 4 and 6 to 9. In total, there are 75 possible PCDD congeners and 135 possible PCDF congeners giving a total of 210 congeners. Dioxins and furans are generally very insoluble in water, are lipophilic and are persistent. PCDD and PCDF have never been produced intentionally but are unwanted byproducts of many chemical industrial processes and of all combustion processes. Almost all possible 210 congeners are released from these sources and, due to chemical, physical, and biological stability and long-range transport, are ubiquitous and have been detected in all environmental compartments. Due to the persistence of the 2,3,7,8-substituted congeners and the lipophilicity of these compounds, PCDD/PCDF accumulate in fatty tissues and in carbon-rich matrices such as soils and sediments.

### 3.2.1 Sources

Since the first overview on formation and sources of PCDD/PCDF was published in 1980 (Esposito *et al.* 1980), several updates are available in the international literature. The findings can be summarized as follows (Hutzinger and Fiedler 1993):

- PCDD/PCDF have never been produced intentionally but occur as trace contaminants in a variety of industrial and thermal processes.
- Due to their chemical, physical and biological stability PCDD/PCDF are able to remain in the environment for long times. As a consequence dioxins from so-called "primary sources" (once formed in industrial or combustion processes) can be transferred to other matrices and enter the environment. Such "secondary" sources are sewage sludge/biosludge, compost, or contaminated areas (*e.g.* Kieselrot in Germany).

- Enzymatic reactions can dimerize chlorophenols to PCDD/PCDF. However, compared to chemical-industrial and combustion sources, biological formation seems to be negligible.

### 3.2.2 Primary Sources of Dioxins

#### *3.2.2.1 Industrial-Chemical Processes*

Primary sources of environmental contamination with PCDD/PCDF in the past was due to production and use of chloroorganic chemicals, including the pulp and paper industry. In wet-chemical processes the propensity to generate PCDD/PCDF during synthesis of chemical compounds decreases in the following order:

Chlorophenols < Chlorobenzenes < Aliphatic chlorinated compounds < Inorganic chlorinated compounds

Factors favorable for the formation of PCDD/PCDF are high temperatures, alkaline media, presence of UV-light, and presence of radicals in the reaction mixture/chemical process (Hutzinger and Fiedler 1991, 1993). An overview on dioxin concentrations in chemicals shows that the concentrations can vary by several orders of magnitude.

Changes in the industrial processes resulted in reduction of PCDD/PCDF concentrations in the products: *e.g.* an estimate for Germany says that until 1990 about 105 g I-TEQ have been introduced through use of the dye pigment Violet 23 (chloranil produced by old process as intermediate). Application of a new process *via* hydroquinone will reduce the annual input to about 3 g I-TEQ (BGA/UBA 1993).

In Germany there exist exclusively sulfite mills which presently do not use molecular chlorine. Dioxin levels detected in German pulp were below 0.1 ng TEQ/kg d.m. (BGA/UBA 1993). The analysis of imported sulfate (Kraft) pulps gave concentrations in the range between 0.2 and 1.3 ng TEQ/kg d.m. Presently the import of Kraft pulp to Germany stands at 3 million tons, so that the total import of dioxins via Kraft pulp is between 0.6 and 3.9 g I-TEQ. Dioxin levels in paper products from fresh fibers generally has less than 1 ng TEQ/kg d.m. In recycling paper, however, average dioxin concentrations are between 5 to 10 ng TEQ/kg.

#### *3.2.2.2 Thermal Processes*

Whereas in the past, the chemical industry and to a lesser extent the pulp and paper industry were considered to be the main source of dioxins and also the cause of today's contaminated sites in Germany, today's dioxin input is due to thermal processes. There is still a considerable focus on waste incineration but based on the requirements set in the 17<sup>th</sup> Ordinance of the Federal Ambient Air Control Act, the annual input from MSWI *via* exhaust gases of about 400 g TEQ per year in 1988/89 is reduced to less than 4 g TEQ since 1997.

The process by which PCDD/PCDF are formed during incineration are not completely understood nor agreed upon. Three possibilities have been proposed to explain the presence of dioxins and furans in incinerator emissions:

1. PCDD/PCDF are already present in the incoming waste - in Germany representative measurements gave about 50 ng I-TEQ/kg waste - and are incompletely destroyed or transformed during combustion. Not relevant for modern MSWIs.
2. PCDD/PCDF are produced from related chlorinated precursors (= pre-dioxins) such as PCB, chlorinated phenols and chlorinated benzenes.
3. PCDD/PCDF are formed *via de novo* synthesis. This is, they are formed from the pyrolysis of chemically unrelated compounds such as polyvinyl chloride (PVC) or other chlorocarbons, and/or the burning of non-chlorinated organic matter such as polystyrene, cellulose, lignin, coal, and particulate carbon in the presence of chlorine-donors.

From the knowledge gained from MSWIs it can be concluded that PCDD/PCDF can be formed in other thermal processes in which chlorine-containing substances are burnt together with carbon and a suitable catalyst (preferably copper) at temperatures above 300 °C in the presence of excess air or oxygen. Preferentially dioxin formation takes place in the zone when combustion gases cool down from about 450 °C to 250 °C (*de novo* synthesis). Possible sources of the chlorine input are PVC residues as well as chloroparaffins in waste oils and inorganic chlorine.

### 3.2.3 Secondary Sources of PCDD/PCDF = Reservoirs

Dioxin reservoirs are present as sewage sludge, compost, and liquid manure, which can be used for fertilization in agriculture and gardens. A compilation of German data is given in Table 2. A first survey of German sewage sludges where potentially contaminated sludges should be targeted gave a mean concentration of 202 ng TEQ/kg d.m.; in 1990, most sludges were in the range 50-60 ng TEQ/kg d.m. The legal limit concentration for application on agricultural land is 100 ng I-TEQ/kg d.m. Composting of the total organic fraction from municipal waste collection results in a highly contaminated compost, not suitable for application in house gardens or in agriculture (mean concentration: 38 ng TEQ/kg d.m.). Compost from bio-waste, kitchen wastes, or green wastes give better qualities in the range of 14 ng I-TEQ/kg d.m. Such a mean value, however, is close to the guideline concentration of 17 ng I-TEQ/kg d.m.

Table 2: PCDD/PCDF in sewage sludge and compost. Data from Germany

Sewage Sludge	Limit value	100 ng I-TEQ/kg dm
	Survey 1986/87	202 ng I-TEQ/kg dm
	Survey 1990	50-60 ng I-TEQ/kg dm
Compost	Limit Value/Guideline	17 ng I-TEQ/kg dm
	All wastes	38±22 ng I-TEQ/kg dm
	Biowaste	14±9 ng I-TEQ/kg dm

So far, hardly any country did a reservoir inventory for PCDD/PCDF, which means that there is almost no knowledge about the total amounts of PCDD/PCDF present in sinks such as

sediments of harbors, rivers, lakes, and oceans, landfills, contaminated soils from (chemical) production sites. Although these reservoirs may be highly contaminated with PCDD/PCDF, the chemical-physical properties of these compounds imply that dioxins and furans will stay absorbed to organic carbon of soils or other particles. On the other hand, mobilization can occur in the presence of lipophilic solvents (→ leaching into deeper layers of soils and/or groundwater) or in cases of erosion or run-off by rain from topsoil (→ translocation into the neighborhood). Experience has shown that PCDD/PCDF transport due to soil erosion and run-off does not play a major role for environmental contamination and human exposure (Fiedler 1995).

Other reservoirs include the former use of PCDD/PCDF-contaminated products such as 2,4,5-T (2,4,5-trichlorophenoxyacetic acid), polychlorinated biphenyls (PCB), and pentachlorophenol/-phenate (PCP/PCP-Na).

Although there are estimates of the total amount of these compounds produced for various purposes, it seems to be impossible to deduce from these numbers a quantitative impact of PCDD/PCDF to the environment or humans (Fiedler 1995).

### 3.2.4 Toxic Equivalency Factors (TEFs)

For regulatory purposes so-called Toxicity Equivalency Factors (TEF) have been developed for risk assessment of complex mixtures of PCDD/PCDF (NATO/CCMS 1988). The TEF are based on acute toxicity values from *in vivo* and *in vitro* studies. This approach is based on the evidence that there is a common, receptor-mediated mechanism of action for these compounds. Although the scientific basis cannot be considered as solid, the TEF approach has been adopted as an administrative tool by many agencies and allows to convert quantitative analytical data for individual PCDD/PCDF congeners into a single Toxic Equivalent (TEQ). As TEFs are interim values and administrative tools, they are based on present state of knowledge and should be revised as new data gets available. Today's most commonly applied TEFs were established by a NATO/CCMS Working Group on Dioxins and Related Compounds as International Toxicity Equivalency Factors (I-TEF) (NATO/CCMS 1988). However, in 1997, a WHO/IPCS working group re-evaluated the I-TEFs and established a new scheme (Table 3).

The term TEF was defined to be an order of magnitude estimate of the toxicity of a compound relative to the toxicity of 2,3,7,8-TCDD that is derived using careful scientific judgement after considering all available data. The relative potency of a compound obtained in a single *in vivo* or *in vitro* study will be referred to as a relative potency (REP) value. TEFs, in combination with chemical residue data can be used to calculate toxic equivalent (TEQ) concentrations in various media, including animal tissues, soil, sediment and water. TEQ concentrations in samples containing PCDD, PCDF and PCB are calculated using the following equation:

$$\text{TEQ} = ([\text{PCDD}_i \times \text{TEF}_i] \text{ n}) + ([\text{PCDF}_i \times \text{TEF}_i] \text{ n}) + ([\text{PCB}_i \times \text{TEF}_i] \text{ n})$$

Substantial evidence indicated that the TEF approach is equally valid for human risk assessment as for wildlife, although wildlife risk assessments usually attempt to estimate population-level effects (unlike traditional human risk assessments, which focus on protecting individuals) because effects on populations are of greater ecological relevance than are effects



on individuals. The criteria used for including a compound in a wildlife TEF scheme are the same as those used for human TEFs. Compounds must:

- show a structural relationship to the PCDD and PCDF;
- bind to the Ah receptor;
- elicit dioxin-specific biochemical and toxic responses; and
- be persistent and accumulate in the food chain.

Table 3: International Toxicity Equivalency Factors (I-TEFs) for PCDD/PCDF (NATO/CCMS 1988) and WHO-TEFs for PCDD/PCDF (WHO 1997, van den Berg *et al.* 1998)

Congener	I-TEF	WHO-TEF		
		Humans/Mammals	Fish	Birds
2,3,7,8-Cl <sub>4</sub> DD	1	1	1	1
1,2,3,7,8-Cl <sub>5</sub> DD	0.5	1	1	1
1,2,3,4,7,8-Cl <sub>6</sub> DD	0.1	0.1	0.5	0.05
1,2,3,7,8,9-Cl <sub>6</sub> DD	0.1	0.1	0.01	0.01
1,2,3,6,7,8-Cl <sub>6</sub> DD	0.1	0.1	0.01	0.1
1,2,3,4,6,7,8-Cl <sub>7</sub> DD	0.01	0.01	0.001	<0.001
Cl <sub>8</sub> DD	0.001	0.0001	-	-
2,3,7,8-Cl <sub>4</sub> DF	0.1	0.1	0.05	1
1,2,3,7,8-Cl <sub>5</sub> DF	0.05	0.05	0.05	0.1
2,3,4,7,8-Cl <sub>5</sub> DF	0.5	0.5	0.5	1
1,2,3,4,7,8-Cl <sub>6</sub> DF	0.1	0.1	0.1	0.1
1,2,3,7,8,9-Cl <sub>6</sub> DF	0.1	0.1	0.1	0.1
1,2,3,6,7,8-Cl <sub>6</sub> DF	0.1	0.1	0.1	0.1
2,3,4,6,7,8-Cl <sub>6</sub> DF	0.1	0.1	0.1	0.1
1,2,3,4,6,7,8-Cl <sub>7</sub> DF	0.01	0.01	0.01	0.01
1,2,3,4,7,8,9-Cl <sub>7</sub> DF	0.01	0.01	0.01	0.01
Cl <sub>8</sub> DF	0.001	0.0001	0.0001	0.0001

For all non-2,3,7,8-substituted congeners, no TEF has been assigned.

### 3.2.5 Toxicity

Human exposure to 2,3,7,8-TCDD or other PCDD congeners due to industrial or accidental exposure has been associated with chloracne and alterations in liver enzyme levels in both children and adults. Changes in the immune system and glucose metabolism have also been observed in adults. Infants exposed to PCDD and PCDF through breast milk exhibit alterations in thyroid hormone levels and possible neurobehavioural and neurological deficits.

The extraordinary potency of 2,3,7,8-TCDD and related 2,3,7,8-substituted PCDD has been demonstrated in many animal species. The lethal dose of 2,3,7,8-TCDD, however, varies more than 5000-fold between the guinea-pig, the most sensitive, and the hamster, the least sensitive species. In all mammalian species tested so far, lethal doses of 2,3,7,8-TCDD result in delayed death preceded by excessive body weight loss ('wasting').

Other signs of 2,3,7,8-TCDD intoxication include thymic atrophy, hypertrophy/hyperplasia of hepatic, gastrointestinal, urogenital and cutaneous epithelia, atrophy of the gonads, subcutaneous oedema and systemic haemorrhage.

In tissue culture, 2,3,7,8-TCDD affects growth and differentiation of keratinocytes, hepatocytes and cells derived from other target organs. Toxicity of 2,3,7,8-TCDD segregates with the Ah receptor, and relative toxicity of other PCDD congeners is associated with their ability to bind to this receptor. PCDD cause suppression of both cell-mediated and humoral immunity in several species at low doses. PCDD have the potential to suppress resistance to bacterial, viral and parasitic challenges in mice.

### 3.2.5.1 *Effects on Reproduction*

Most studies on reproductive effects of PCDD in humans concerned paternal exposure, usually long after high exposure had occurred. Most studies have a limited power to detect elevations in specific birth defects. The studies also showed discordant results concerning an increase in the risk of spontaneous abortions. Some studies have shown alterations in hormone levels and sperm characteristics after PCDD exposure.

2,3,7,8-TCDD is both a developmental and reproductive toxicant in experimental animals. The developing embryo/fetus appears to display enhanced sensitivity to the adverse effects of PCDD. Perturbations of the reproductive system in adult animals require overtly toxic doses. In contrast, effects on the developing organism occur at doses > 100 times lower than those required in the mother. Sensitive targets include the developing reproductive, nervous and immune systems. Perturbation of multiple hormonal systems and their metabolism due to PCDD exposure may play a role in these events.

One effect that has been observed recently is the altered sex ratio (increased females) seen in the 6 years after the Seveso, Italy, accident (Mocarelli *et al.* 1996, 2000). Particularly intriguing in this latest evaluation is the observation that exposure before and during puberty is linked to this sex ratio effect. Other sites have been examined for the effect of TCDD exposure on sex ratio with mixed results, but with smaller numbers of offspring (US-EPA 2000).

### 3.2.5.2 *Genetic Effects*

In human studies after in-vivo exposure, there have been no unequivocal reports of effects of 2,3,7,8-TCDD or other PCDD congeners upon the frequencies of chromosomal aberrations. In animal studies *in vivo* and in cultured human and animal cells *in vitro*, 2,3,7,8-TCDD gave conflicting results with regard to several genetic endpoints, such as DNA damage, gene mutations, sister chromatid exchange and cell transformation.

Experimental data indicate that 2,3,7,8-TCDD and probably other PCDD and PCDF are not direct-acting genotoxic agents.

### 3.2.5.3 *Carcinogenicity*

Four epidemiological studies of high-exposure industrial cohorts in Germany, the Netherlands and the United States found an increase in overall cancer mortality.

In these cohorts, the blood lipid 2,3,7,8-TCDD levels estimated to the last time of exposure were 2000 ng/kg (mean) (up to 32 000 ng/kg) in the United States cohort, 1434 ng/kg

geometric mean (range, 301-3683 ng/kg) among accident workers in the Dutch cohort, 1008 ng/kg geometric mean in the group of workers with severe chloracne in the BASF accident cohort in Germany and measurements up to 2252 ng/kg in the Boehringer cohort in Germany. These calculated blood 2,3,7,8-TCDD levels in workers at time of exposure were in the same range as the estimated blood levels in a two-year rat carcinogenicity study. In rats exposed to 100 ng/kg b.w. 2,3,7,8-TCDD per day, hepatocellular carcinomas and squamous-cell carcinomas of the lung were observed. Estimated blood levels were 5000-10 000 ng/kg 2,3,7,8-TCDD. In the same study, in rats exposed to 10 ng/kg b.w. 2,3,7,8-TCDD per day, hepatocellular nodules and focal alveolar hyperplasia were observed. Estimated blood levels were 1500-2000 ng/kg 2,3,7,8-TCDD. These results indicate parallel tumorigenic responses to high exposure to 2,3,7,8-TCDD in both humans and rats.

In view of the results mentioned above, it should be noted that the present background levels of 2,3,7,8-TCDD in human populations (2-3 ng/kg) are 100 to 1000 times lower than those observed in this rat carcinogenicity study. Evaluation of the relationship between the magnitude of the exposure in experimental systems and the magnitude of the response (i.e., dose-response relationships) do not permit conclusions to be drawn on the human health risks from background exposures to 2,3,7,8-TCDD.

### Overall evaluation

2,3,7,8-Tetrachlorodibenzo-*para*-dioxin is carcinogenic to humans (IARC 1997).

In making the overall evaluation, the Working Group took into consideration the following supporting evidence:

- (i) 2,3,7,8-TCDD is a multi-site carcinogen in experimental animals that has been shown by several lines of evidence to act through a mechanism involving the Ah receptor;
- (ii) this receptor is highly conserved in an evolutionary sense and functions the same way in humans as in experimental animals;
- (iii) tissue concentrations are similar both in heavily exposed human populations in which an increased overall cancer risk was observed and in rats exposed to carcinogenic dosage regimens in bioassays.

Other polychlorinated dibenzo-*para*-dioxins are not classifiable as to their carcinogenicity to humans.

Dibenzo-*para*-dioxin is not classifiable as to its carcinogenicity to humans.

In its recent Dioxin Reassessment, US-EPA basically follows the IARC classification (US-EPA 2000) and concludes that “under EPA’s current approach, TCDD is best characterized as a “human carcinogen.” This means that, based on the weight of all of the evidence (human, animal, mode of action), TCDD meets the stringent criteria that allows EPA and the scientific community to accept a causal relationship between TCDD exposure and cancer hazard. The guidance suggests that “human carcinogen” is an appropriate descriptor of carcinogenic potential when there is an absence of conclusive epidemiologic evidence to clearly establish a cause-and-effect relationship between human exposure and cancer, but there is compelling carcinogenicity data in animals and mechanistic information in animals and humans demonstrating similar modes of carcinogenic action. The “human carcinogen” descriptor is suggested for TCDD because all of the following conditions are met: Occupational epidemiologic studies show an association between TCDD exposure and increases in cancer at all sites, in lung cancer, and perhaps at other sites, but the data are

insufficient on their own to demonstrate a causal association. There is extensive carcinogenicity in both sexes of multiple species of animals at multiple sites (IARC 1997).

### 3.2.6 Health Risk Assessment and Tolerable Daily Intake (TDI)

1990, a WHO working group concluded that 90% of the daily dioxin intake (from background contamination) results from ingestion. Especially, foodstuffs of animal origin are responsible for the daily intake of approximately 2 pg TEQ/(kg b.w.·d). All other foodstuffs, especially the „non-fatty" ones, are of minor importance in terms of PCDD/PCDF intake.

At the meeting on dioxins, held at Bilthoven, in the Netherlands, in 1990, WHO experts established a tolerable daily intake of 10 picograms/kilogram body weight for TCDD, said to be the most toxic dioxin. Since then, new epidemiological data has emerged, notably concerning dioxins' effects on neurological development and the endocrine system, and WHO thus convened an expert consultation to re-evaluate the tolerable daily dose of dioxins to which humans can be exposed. At the end of the meeting, the specialists agreed on a new tolerable daily intake range 1 to 4 picograms/kilogram body weight. The experts, however, recognized that subtle effects may already occur in the general population in developed countries at current background levels of 2 to 6 picograms/kilogram body weight. They therefore recommended that every effort should be made to reduce exposure to the lowest possible level.

The background documents for the experts' meeting discussed carcinogenic and non-carcinogenic effects of dioxins on humans and animals, the risks for young children, transmission mechanisms, general exposure to dioxins and the compounds of the same nature, as well as current means of evaluating these risks in different countries.

Human background exposure to PCDD, PCDF and PCB predominantly occurs through the diet, with food from animal origin being the major source. Information from food surveys in industrialized countries indicates a daily intake of PCDD and PCDF in the order of 50-200 pg I-TEQ/person day, or 1-3 pg I-TEQ/kg b.w. day for a 60 kg adult. If dioxin-like PCBs are also included, the daily total TEQ intake can be a factor of 2-3 higher. Recent studies from countries which started to implement measures to reduce dioxin emissions in the late 80s clearly show decreasing PCDD/PCDF and PCB levels in food and consequently a lower dietary intake of these compounds by almost a factor of 2 within the past 7 years.

Compared to adults, the daily intake of PCDD/PCDF and PCB for breast fed babies is 1-2 orders of magnitude higher. The latest WHO field study showed higher mean levels of PCDD/PCDF and PCB in human milk in industrialized areas (10-35 pg I-TEQ/g milk fat) and lower levels in developing countries (< 10 pg I-TEQ/g milk fat). There is clear evidence of a decrease in PCDD/PCDF levels in human milk between 1988 and 1993, with the highest rates of decrease in areas with the highest initial concentrations (WHO 1996).

Recognizing that additional compounds can possess “dioxin-like” activity, the consultation concluded that the use of TCDD alone as a measure of exposure to PCDD, PCDF and PCB would severely underestimate the risk to humans from exposure to these compounds. Therefore, the daily intake (TDI) in humans of PCDD, PCDF, *non-ortho* PCBs and *mono-ortho* PCB will be expressed in units of TCDD equivalents (TEQs) applying the recently established WHO TEFs (van Leeuwen and Younes 1998).

Epidemiological evidence from the most highly 2,3,7,8-TCDD- exposed cohorts studied produces the strongest evidence of increased risks for all cancers combined, along with less strong evidence of increased risks for cancers of particular sites. It was noted, however, that the general population is exposed to levels of dioxins which are several orders of magnitude lower than those experienced by the industrial populations or the population at Seveso.

Non-cancer endpoints were evaluated among groups exposed to dioxins, dioxin-like and non-dioxin-like polychlorinated aromatic compounds in a variety of exposure scenarios. Among children exposed *in utero* to background levels, effects include subtle developmental delays and thyroid hormone alterations. Of the many effects evaluated in exposed adult populations, many were transient effects disappearing after the end of exposure. A few conditions appear to be in excess among the exposed cohorts when compared to unexposed referent groups including alterations in metabolic parameters, as well as mortality from cardiovascular and non-malignant liver disease.

The consultation discussed the applicability of mechanistic and curve-fitting models for risk assessment purposes. It noted that the outcome of the models strongly depends on the assumptions used, and that discrepancies may exist between the prediction of effects and the actual data, leading to caution in the use of models. Therefore, a more traditional approach using body burden calculations and empirical observations was preferred for the current risk health evaluation.

For the purposes of risk assessment of human exposure to dioxin-like compounds, the consultation focused on the most sensitive effects which are considered adverse (hormonal, reproductive and developmental effects) seen at low doses in animal studies. These effects occur at body burdens in rats and monkeys in the range of 10-50 ng/kg b.w.

Human daily intakes corresponding with body burdens similar to those associated with adverse effects in animals can be estimated to be in the range of 10-40 pg/kg b.w. day.

Since body burdens have been used to scale doses across species, the consultation concluded that the use of an uncertainty factor to account for interspecies differences in toxicokinetics is not required. However, the estimated human intake was based on LOAELs and not on NOAELs. In addition the consultation noted that although for many parameters humans might be less sensitive than animals, still uncertainty remains regarding animal to human susceptibilities. Furthermore, differences exist in the half lives of elimination for the different components of a TEQ mixture. To account for all these uncertainties, a composite uncertainty factor of 10 was recommended.

Based on the range of estimated daily human intakes for the most sensitive responses in animal studies (10-40 pg/kg b.w.), and applying this uncertainty factor of 10 a TDI range of 1-4 pg TEQ/kg body weight was established.

The consultation recognized that subtle effects might already be occurring in the general population in developed countries at current background levels of exposure to dioxins and dioxin-like compounds. It therefore recommended that every effort should be made to reduce exposure to the lower end of this range.



## 4 LEGISLATION AND GUIDELINES

### 4.1 European Union

Presently, the European Union (EU) comprises 15 Member States<sup>3</sup> and directives released by the Council of the EU define minimum requirements and have to be transposed into national legislation, normally within two years and then become legally binding.

There are several EU Directives, which address feedingstuffs and other that address PCDD, PCDF or other POPs. As this study does not have the intention to control or verify if and to what extent EU Directives have been transposed into national legislation, it is assumed that all EU Directives have been realized in national legislation in the respective Member States. Table 4 gives a compilation of these EU Directives, which give numeric values or detailed information. In addition, there are other Directives, which indirectly address e.g. PCDD/PCDF, such as the Directives on Existing and New Municipal waste incinerators, which specify operating conditions (89/429/EEC Existing Municipal Waste Incinerators 89/369/EEC on New Municipal Waste Incinerators) or the Directives on Water Emissions, e.g. 76/464/EEC Pollution Caused by Discharge into the Aquatic Environment, which prohibits organohalogen discharge to water, 86/280/EEC on Limit Values and Quality Objectives for Discharges of Certain Dangerous Substances Included in List 1 of the Annex to Directive 76/464/EEC, which specifies water quality values for PCP concentrations, and 80/68/EEC on Protection of Groundwater Against Pollution, which prohibits the discharge of organohalogen to groundwater.

85/467/EEC on Restrictions on the Marketing and Use of Dangerous Substances (Amendment No. 6) prohibits all use of PCBs and PCTs, 91/173/EEC on Restrictions on the Marketing and Use of Certain Substances and Preparations (Amendment No. 9) limits the use of PCP to 0.1% of total content.

In the European Union, PCB have been regulated since 1975. EU Directives address various aspects of PCB disposal, e.g., Directive 75/439/EEC of 16 June 1975 on the disposal of waste oils, which lays down 50 ppm as the maximum limit for the PCB or PCT content of regenerated oils or oils used as fuel. Perhaps the two most important Directives are European Council (EC) Directive 85/467/EEC on the prohibition of the production, use and marketing of PCB terphenyls)<sup>4</sup> and EC Directive 96/59/EC on the disposal of PCB.

Whereas the 1985 directive sets a clear request to phase out any new uses of PCB and also does not allow PCT as alternatives to PCB, the latter directive approximates the regulations of

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<sup>3</sup> Austria, Belgium, Denmark, Finland, France, Germany, Greece, Italy, Ireland, Luxembourg, The Netherlands, Portugal, Spain, Sweden, United Kingdom

<sup>4</sup> With regard to these regulations PCB is defined as:

1. polychlorinated (trichloro- to decachloro) biphenyls (PCB),
2. polychlorinated terphenyls (PCT),
3. monomethyltetrachloro-, monomethyldichloro-, and monomethyldibromodiphenylmethane, and
4. mixtures and formulations of the above compounds.

the Member States on the controlled disposal of PCB, the decontamination or disposal of equipment containing PCBs and/or the disposal of used PCBs in order to eliminate them completely on the basis of the provisions of this directive.

According to Directive 96/59/EC, Member States shall take the necessary measures to ensure that used PCB are disposed of and PCB and equipment containing PCB are decontaminated or disposed of as soon as possible. The equipment and the PCB contained therein, which are subject to inventory, decontamination and/or disposal shall be effected at the latest by the end of the year 2010. The Directive aims at the elimination of polychlorinated biphenyls and polychlorinated terphenyls (PCBs) and at the decontamination of equipment containing them. This equipment must be inventoried, labeled and reported to the Commission by September 1999 and inventories must be updated. Equipment containing PCB, which has not yet been decontaminated must be kept in good working order to avoid leaks.

The PCB disposal must be licensed in accordance with Directive 75/442/EEC. If PCB are being incinerated, the standards set in the Directive on incineration of hazardous waste (EU 1994) - *inter alia* a limit value of 0.1 ng I-TEQ/m<sup>3</sup> (@ 11 % oxygen, temperature 273 K, pressure 101.3 kPa, 11%, dry gas) for dioxins and furans – have to be met. Disposal plans for inventoried PCB drawn up by the Member States have to be communicated to the Commission by September 1999. These plans should possibly also cover unregistered equipment possibly via the use of administrative and economic incentives established along with rigorous controls.

Table 4: EU Directives addressing POPs and/or feedingstuffs

EU Directive	Description
<b>Feedingstuffs</b>	
<b>98/60/EC</b> Citrus Pulp Pellets as Feedingstuffs (Amendment to 74/63/EEC)	Sets an upper-bound detection limit of 500 pg I-TEQ/kg. In force since July 1, 1998
<b>2439/1999/EC</b> and <b>739/2000/EC</b>	maximum limit for dioxin content of 500 pg WHO-TEQ/kg for most additives belonging to the group “binders, anti-caking agents and coagulants (applies from March 1, 2000; to be re-examined before October 2000)
<b>91/516/EC</b>	the use of “wood, sawdust and other materials derived from wood treated with wood protections products” is prohibited in compound feedingstuffs
<b>POPs-Related Directives</b>	
<b>94/67/EC</b> Incineration of Hazardous Waste	Emission limit value of 0.1 ng I-TEQ/m <sup>3</sup> for hazardous waste incinerators. In force since Dec. 31, 1996
Draft Waste Incineration Directive	Proposes an emission limit value of 0.1 ng I-TEQ/m <sup>3</sup> for all waste incinerators and for stationary sources with co-combustion of waste, e.g. cement kilns; sets a limit value of 0.5 ng I-TEQ/L or 150 ng I-TEQ/t of waste for releases to water
<b>82/501/EEC</b> Seveso Directive I	Sites qualify as Major Accident Hazard if 2,3,7,8-TCDD stored reaches 1 kg or hexachlorodibenzo- <i>p</i> -dioxin qualifying quantity of 100 kg
<b>96/82/EC</b> Seveso Directive II	Sites qualify as Major Accident Hazard if total dioxin stored reaches 1 kg



EU Directive	Description
<b>85/467/EEC</b> on PCBs/PCTs	Prohibition of placing PCB products on market for use in closed systems (>50 mg PCB/kg)
<b>96/59/EC</b> on the disposal of polychlorinated biphenyls and polychlorinated terphenyls (PCB/PCT)	Sets a time limit for PCB in use to the year 2010

## 4.2 Basel Convention

The transboundary movements of hazardous wastes are regulated by the Basel Convention (Basel 2000), which entered into force on May 5, 1992. By mid 2000, 136 States were Parties to the Convention, including the EU. The text of the conventions requires wastes to be managed and disposed of in environmentally sound manner by:

- reducing transboundary movements to minimum
- treating/disposing hazardous wastes close to source
- minimizing hazardous waste generation.

In the convention, PCB and other polyhalogenated aromatic compounds are classified under Category A3180 under the new Annex VIII as follows:

*Wastes, substances and articles containing, consisting of or contaminated with polychlorinated biphenyl (PCB), polychlorinated terphenyl (PCT), polychlorinated naphthalene (PCN) or polybrominated biphenyl (PBB), or any other polybrominated analogues of these compounds, at a concentration level of 50 mg/kg or more.*

## 4.3 German Regulation

In 1993, the BLAG (Bund-Länder Arbeitsgruppe DIOXINE, Germany) proposed guideline concentrations for PCDD/PCDF in dairy products as shown in Table 5. A maximum permissible concentration of 6 pg I-TEQ/g milk fat has been established by the Dutch authorities.

Table 5: Proposed guidelines for PCDD/PCDF in milk fat and recommended actions

PCDD/PCDF-contamination in pg I-TEQ/g milk fat	Recommended Action
< 0.9	Target value to be met. Only to be achieved by long-term reduction of PCDD/PCDF release into the environment.
> 3.0	Investigate sources and start measures to minimize release. If no short term measures to reduce emissions are possible, it is recommended to the farm to change pattern of land use. Recommendation not to distribute milk and dairy products directly to the consumer.
> 5.0	Milk and dairy products no longer marketable



## 5 DIETARY INTAKE

In 1998/99, the European Commission together with DETR from the UK sponsored a study on dioxins and health (AEA 1999). In this study, the exposure of EU citizens to PCDD/PCDF and related compounds has been assessed to provide a basis for the development of possible policies to control releases into the environment, in order to meet recommended guidelines for acceptable exposure. It was found that attention has focused on the foodchain, which is the most important route of human exposure to PCDD/PCDF; for other POPs only very limited information could be obtained.

### 5.1 Concentrations in Foodstuffs

Table 6 shows the availability, in the EU Member States, of data concerning the concentrations of PCDD/Fs in various foodstuffs. Finland, the Netherlands, Germany and the UK have the largest amount of numerical data, while the Spanish data set consists of a small number of samples for each food type and the Swedish data is from 1991 but is being updated. No data could be identified for Greece, Luxembourg or Portugal (King *et al.* 1999, AEA 1999).

Table 6: Foodstuff concentration data availability in the EU Member States (King *et al.* 1999)

	A	B	D	DK	E	EL	F	FIN	I	IRL	L	NL	P	S	UK
Foodstuffs in background locations															
Cows' milk		x	x	x	x			x		x		x		x	x
Dairy products			x	x	x			x	x			x		x	x
Eggs			x		x			x				x		x	x
Fish			x	x	x			x				x		x	x
Meat			x	x	x			x				x		x	x
Poultry			x		x							x			x
Fats and oils					x							x			x
Cereals					x			x				x			x
Fruits and vegetables			x		x			x	x			x			x
Fish oil dietary supplements					x										x
Foodstuffs in areas of contamination															
Cows' milk	x	x	x				x			x					x
Other							x								x
Total diet exposure estimate			x	x	x		x	x				x		x	x

An abundance of data exists for concentrations of PCDD/PCDF in cows' milk. Likewise, there is relatively good coverage for dairy products, meats and fish. These are the fatty foods likely to contain higher concentrations of PCDD/PCDF. Few samples of cereals, fruits and vegetables have been analyzed, due to the assumption that concentrations would be insignificant as fat levels are low. However, these foods have been found to contribute significantly to exposure in some regions with high consumption rates, especially in the Mediterranean diet. Analysis of these food types is increasing, and is becoming more reliable as analytical techniques continue to improve.

Figure 1 shows the measured concentrations of PCDD/PCDF in foodstuffs. It has been compiled from data on background concentrations and includes the most recent data available

for each foodstuff in each country. The data points represent mean or median values for sample sets, and are given as pg I-TEQ/g fat or fresh weight according to food type. This figure does not include foods from areas of known contamination. The pattern is as expected, with foods of animal origin having higher concentrations than those of plant origin. The highest concentrations measured were in fish and meat, but these food types also show the widest concentration ranges. The fish data in particular have a very wide range because of the differences in fat content and ages of fish analyzed. Fruits and vegetables have the lowest concentrations, with a mid point of 0.1 pg I-TEQ/g fresh weight. The milk and milk products, poultry and eggs have similar concentrations with mid points in the ranges of 0.75-1.7 pg I-TEQ/g fat, and the fats and oils, and bread and cereals categories have slightly lower concentrations with equal mid points of 1.2 pg I-TEQ/g fat weight and fresh weight respectively.

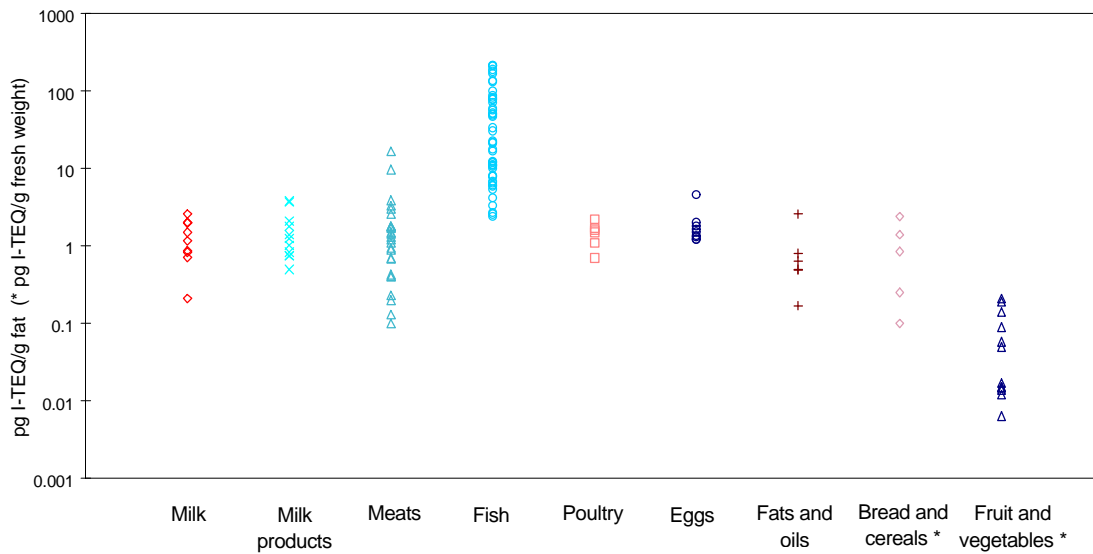


Figure 1: Concentrations of PCDD/PCDF in foods (King *et al.* 1999)

## 5.2 Total Dietary Exposure

The estimates of total dietary intake of PCDD/PCDF in Table 7 have been recalculated from original data assuming an average bodyweight of 70 kg, and show a range of 0.93-3.0 pg I-TEQ/kg b.w. day, with Spain having the highest exposure and the Netherlands the lowest, albeit in different years. These estimates are therefore all within or below the range of the TDI recently recommended by the WHO, of 1-4 pg TEQ/kg b.w. day. However, the values in Table 7 only include exposure to PCDD/PCDF, whereas the WHO TDI also includes PCB (King *et al.* 1999, AEA 1999).

Table 7: Total dietary exposure estimates across the EU (King *et al.* 1999, AEA 1999)

Year	D 1995	DK 1995	E 1996	F nd	FIN 1991	NL 1991	S 1990	UK 1992
Average total diet exposure (pg I-TEQ/d)	69.6	171	210	n.d.	95	65	126.5	69
Average daily exposure (pg I-TEQ/kg b.w./d)	0.99	2.44	3.0	2.21*	1.36	0.93	1.81	0.99
Daily exposure of high level consumer				5.66*		2.3		1.5-2.2

\* unknown average bodyweight assumption (preliminary estimate); nd = no data available / not known

Issues of comparability of exposure estimates are important. First, the data do not all relate to the same year, and second, the estimates are calculated using different methods and with data of varying qualities. In particular, the Spanish estimate includes consumption of cereals, fruit and vegetables, which contribute a total of 43 % of the exposure. These foodstuffs are rarely included in PCDD/F analysis and this may partly explain the higher values calculated for Spain.

In the Netherlands, the UK and France some analysis of variations in consumption has been considered, in order to assess elevated levels of exposure in high consumers (also in Table 7).

Figure 2 shows the relative contributions of different food types to overall dietary exposure to PCDD/Fs in the countries where these data are available. The chart shows the dominance in most countries of fish, meat products, milk and milk products. Fruit and vegetables are also important in France and Spain, and cereals in the UK, although the latter data are very uncertain.

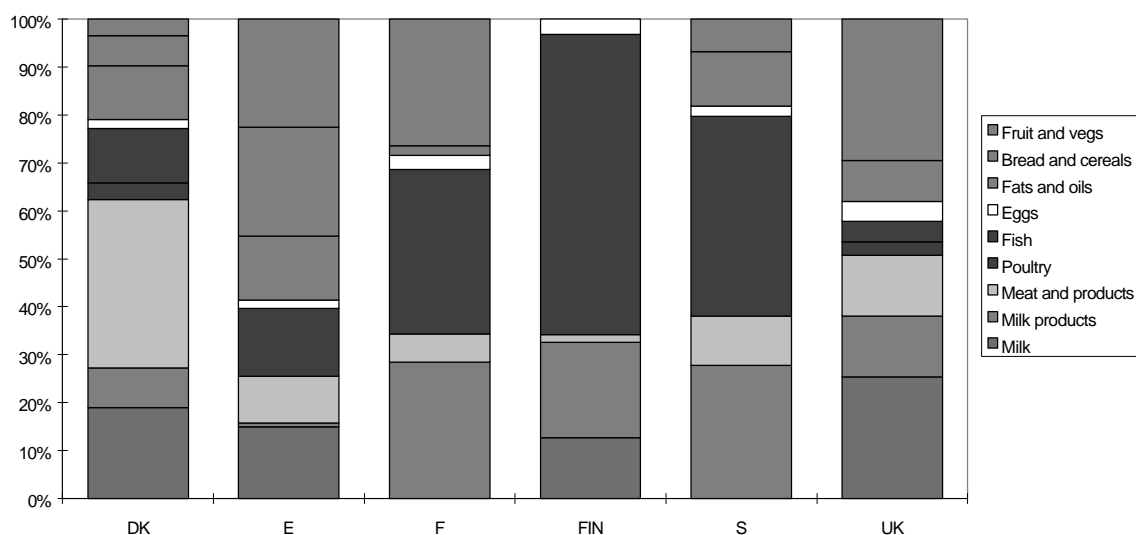


Figure 2: Breakdown of total dietary exposure by food type (King *et al.* 1999)

Variations in exposure by age have also been analyzed. In general, total exposure increases with age in childhood. However, when normalized by body weight it is found to decrease with age. In relation to the Tolerable Daily Intake (TDI), which considers body weight, this

implies that children may be at risk of over exposure at a young age. In the Netherlands the median intake was found to increase with age in childhood from 36.4 pg I-TEQ/day at the age of 1, to 70.4 pg I-TEQ/day at the age of 20. In adult life intake remained roughly constant. In Spain a similar pattern was found, although with higher values, with an increase in daily intake from 179 pg I-TEQ at 3-6 years to 184-214 pg I-TEQ at 16-20 years. However, in terms of intake per kg body weight exposure declines with increasing age. This has been shown in the UK, where those children of 1.5-2.5 years and 5-16 years having average intake ranges at 2.4-3.7 and 1.1-1.8 pg I-TEQ/kg b.w. day respectively compared with adults' exposure, which was estimated at 1.0-1.5 pg I-TEQ/kg b.w. day.

Time trend analysis was possible for Germany, the Netherlands and the UK. In the Netherlands a duplicate diets survey was undertaken in the periods 1978, 1984-1985 and 1994. A significant downward trend through time was found. For Germany, the average daily intake was found to have fallen by 45 % from 127 pg I-TEQ in 1989 to 70 pg I-TEQ in 1995. Exposure has also fallen in the UK from 240 pg I-TEQ/day in 1982, to 125 in 1988 and has fallen further to 69 pg I-TEQ/day in 1992.

Data from Germany as shown in Table 8 show the decrease in dioxin and furan concentrations in the foodstuffs comparing the two periods 1986-1991 and 1992-1996. The calculations are based on daily intake of major food categories as follows:

- ⇒ 28 g milk fat (milk, cheese, butter, *etc.*)
- ⇒ 33 g meat fat
- ⇒ 4 g egg fat
- ⇒ 1 g fish fat
- ⇒ 28 g vegetable oil
- ⇒ 6 g oil from bread and bakery products
- ⇒ 250 g vegetables
- ⇒ 130 g fruit

In general a decrease in contamination of major food categories and consequently in the daily dioxin intake can be observed. The decrease is most dramatic for dairy products, meat and fish, whereas eggs, vegetables and others stayed approximately on the same level. The overall decrease was more than 50 % for both, the contamination in foodstuffs and in the daily intake. From Table 8 follows that in more recent years – at least in Germany – fish did not play such an important role in the daily intake as did in the mid 1980s. On the other hand, eggs gained importance (increase from 5 % to 8 %). For both comparative periods, dairy products were the most important foodstuffs to contribute to the dioxin exposure in Germany (approximately one third).

Table 8: PCDD/PCDF concentrations in major foodstuffs and daily intake for Germany; comparison over 15 years

Category	Daily Intake 1986-1991   1992-1996 (pg I-TEQ/g)		Daily Intake 1986-1991   1992-1996 (pg I-TEQ/person-d)		Daily Intake 1986-1991   1992-1996 (%)	
	Milk	1.1-2.2	0.7	41.7	19.3	33%
Meat	0.3-2.7	0.3-0.7	33.1	13.8	26%	23%
Eggs	1.5	1.3	5.9	5.1	5%	8%
Fish	31-43	10.4	33.9	10.4	27%	17%
Fruit	15	ND	2.0	(2.0)	2%	3%
Vegetables	15	15	3.7	3.7	3%	6%
Others			7.0	(7.0)	5%	11%
Total Intake			127.3	61.3	100%	100%
Intake per kg			1.82	0.88		

### 5.3 Contribution of PCB to the TEQ

PCB data in food were only available for three countries. As can be seen in Table 9, the share of the coplanar and mono-ortho substituted PCB to the total TEQ is around 50 %.

For some countries data are available to compare exposure to PCDD/PCDF and PCB. In the Netherlands the contributions of these two groups to total TEQ exposure was roughly equal, with the median daily exposure of adults at 71 and 77 pg TEQ for PCDD/PCDF and PCB respectively. Similar results were found in Spain, where the PCB intake contributed 48-62 % of the total TEQ intake. In Sweden this contribution was 49-57 % of TEQ, and in the UK it was 38-43 %. The total exposures shown in Table 7 therefore represent roughly 50 % of total TEQ exposure (King *et al.* 1999, AEA 1999).

Table 9: Contribution of PCDD/PCDF and PCB to the total TEQ across European Member States (King *et al.* 1999, AEA 1999)

	Contribution (%) to Total TEQ	
	PCDD/PCDF	PCB
UK: Mean total dietary exposure	63	37
NL: Median total dietary exposure	48	52
S: Mean total dietary exposure	43-51	49-57

### 5.4 Human Milk and Tissue Levels

The WHO co-ordinated study of PCDD/PCDF concentrations in breast milk was the only substantial source of comparable data on human body burden of PCDD/PCDF relating to the majority of the EU Member States. By definition that study considered only young women. There were very few comparable data on concentrations in children, teenagers, men or older women.

Between 1988 and 1993 the average PCDD/PCDF concentration in breast milk in the EU decreased by around 35 %, with a slightly higher decrease in rural areas and slightly lower in industrial areas. Measurements taken in Germany between 1988 and 1996 showed that the average concentrations of PCDD/PCDF in the blood of adult males decreased by around 64 % (AEA 1999).

## **5.5 Conclusions**

Large variations exist in the availability of data to assess human exposure to PCDD/PCDF in individual Member States. Using the available data it has been shown that the products of fish and animal origin make the largest contribution to overall exposure, but also cereals and vegetables can contribute more than has previously been expected. Exposure has been estimated to be in the range 0.93-3.0 pg I-TEQ/kg b.w. day for PCDD/PCDF, which have been estimated to contribute roughly 50 % of total TEQ exposure if PCB are also included. As the recommended TDI for total TEQ is 1-4 pg TEQ/kg b.w. day there may be considerable exceedances of this intake across Europe. However, human exposure to PCDD/PCDF has declined in recent years and evidence shows that body burdens have also declined (AEA 1999).



## 6 RECENT ACCIDENTS OF DIOXIN AND PCB CONTAMINATION IN FEEDSTUFFS AND FOODS

Since 1997, several cases of feedingstuff and food contamination with PCDD, PCDF and PCB have occurred in Europe. The first of these was the citrus pellets case, which was first reported in 1997, with major effects in Germany. The second was the Belgian Chicken accident in 1999, which originated from Belgium but then spread all over Europe and many countries outside the European Union. Three smaller “accidents” have been recognized in mainly in Germany involving dioxin-containing clay, drying of green fodder and recently the choline chloride case. All these three happened in 1999/2000. This section gives a short summary on the present status of information on these five cases. Most of the information was compiled by Malisch and presented at a UNEP workshop in Seoul, Korea (2000).

### 6.1 Citrus Pulp

#### 6.1.1 The Findings

From mid-1997 until March 1998, elevated concentrations of PCDD/PCDF in milk have been detected by German Food Control laboratories. During this time period and on average, twice the concentrations were detected in milk samples: Starting from a level of about 0.6 pg I-TEQ/g fat in summer 1997, the average concentration from a limited number of randomly collected dairy samples (n=27) increased to 1.41 pg I-TEQ/g fat (median concentration was 1.06 pg I-TEQ/g fat) in different regions of Germany in February 1998. The concentrations found were in a range which was found in the early 1990s before dioxin-reducing action has taken place in Germany. The highest concentrations was detected in a cow's milk sample which gave 7.86 pg I-TEQ/g fat and thus exceeded the concentration of 5 pg I-TEQ/g fat, the maximum permissible concentration to place milk products on the market. Although, primarily, this observation was made in Germany first, later the same observation was found in the 12 Member States of the EU, e.g. a butter sample from the Netherlands gave 1.96 pg I-TEQ/g (Malisch 1998). Consequently, comprehensive work started to localize the source with a first emphasis on pesticides, disinfectants, and detergents used at dairy farms, drugs used in veterinary medicine, feedstuffs, *etc.*). Whereas feedstuff samples typically had concentrations in the range from 100 to 300 pg I-TEQ/kg, a compound feed for milk production, designated as “183”, which had been found at two different dairy farms, had about 1,800 pg I-TEQ/kg (1,827 and 1,825 pg I-TEQ/kg on farm 1, 1,652 and 1,661 pg I-TEQ/kg on farm 2; the sample collected at the manufacturer had 1,828 pg I-TEQ/kg) (Malisch 1998).

With these findings, the individual components of the compound feedstuffs have been analyzed and finally, citrus pulp pellets (CPP), which were used as additives were detected as the source. All other components were in the range of normal background contamination (Table 10) (Malisch 1998).

Table 10: PCDD/PCDF concentrations in compound feedstuff "183" (Malisch 1998)

Component	pg I-TEQ/kg
Maize	103
Molasses	73
Rape	122
Palm seed	39
Citrus pulp # 1	5,887
Citrus pulp #2	7,400

The results of PCDD/PCDF analyses of cow's milk samples and of feedstuffs that were fed to Table 11. The nine farms shown in Table 11 were among the biggest dairy farms providing milk to Baden-Württemberg's consumers. The last three columns in Table 11 show the amount of feed fed per day and cow. The highest dioxin contamination of milk was found on Farm 1 with 4.83 pg I-TEQ/g milk fat where the cows were fed up to 8 kg per day of the compound feed "183", which contained 25 % of citrus pulp. Five farms showed dioxin contamination in milk above 1.5 pg I-TEQ/g fat. These farms fed between 3 and 5 kg of compound feeds containing contaminated citrus pulp. All other dioxin concentrations in cow's milk were below 0.9 pg I-TEQ/g fat. Of these, two farms each did feed compound feed (which did not contain citrus pulp) whereas the two remainder did not use any compound feed. These results gave the final evidence that citrus pulp was the source for the milk contamination.

Table 11: Compound feed as dioxin source on different farms

Farm	Milk pg I-TEQ/g fat	Prod- ucer	Compound Feed		With Citrus Pulp	Max. Amount Fed	Cereals Fed	Soy- bean Fed
			Product	pg I-TEQ/kg				
1	4.83	R	"183"	1826	yes	8 kg		-
2	2.80	R	"183"	1657	yes			
3	2.75	R	"Lak."	1940	yes	4 kg	1-2 kg	1-2 kg
4	2.20	C	"718"	726	yes	5 kg	3 kg	1 kg
5	2.13	R	"183"	2290	yes	5 kg	1 kg	-
6	1.52	R	"183"	567	yes	3-4 kg	Max. 8 kg	1 kg
7	0.89	C	"625"	62		5 kg		
8	0.73	D	"9716"	53		10 kg	2 kg	
9	0.62	-	-				5 kg	0.5 kg
10	0.59	-	-				5 kg	2 kg

Assuming that the contribution of the other single components of the compound feed to the dioxin contamination is negligible, a content of about 25 % citrus pulp in the compound feed can be calculated.

In the State of Baden-Württemberg (Germany), 14 samples of citrus pulp used by the 6 biggest feed producers were analyzed in March 1998: all samples were contaminated at about the same level and exhibited the same pattern of PCDD and PCDF congeners. The average contamination was about 7,000 pg I-TEQ/kg with a range from about 4,600 to 10,100 pg I-TEQ/kg. By far, the predominant congener was Cl<sub>8</sub>DF at a level of about 450,000 pg/kg, followed by 1,2,3,4,6,7,8-Cl<sub>7</sub>DF with about 40,000 pg/kg; Cl<sub>8</sub>DD, which is usually the highest single congener was determined with about 10,000 pg/kg. Within the PCDD, the

concentrations decreased from Cl<sub>8</sub>DD to Cl<sub>7</sub>DD but also showed high concentrations of Cl<sub>4</sub>DD and Cl<sub>5</sub>DD (this is in contrast to the pentachlorophenol (PCP) pattern, which is also dominated by Cl<sub>8</sub>DD followed by Cl<sub>7</sub>DD).

To protect consumers in the EU Member States, the EU set tolerances of 500 pg WHO-TEQ/kg for citrus pellets in feedstuffs (EU Directive 98/60/EC).

### 6.1.2 The Production Process

The cutting and filtration of oranges generates three products: juice, citrus pulp, and orange oil. All remaining solids of the fruit (core, peel, seeds) are designated as citrus pulp. Citrus pulp is quite acidic and has a pH of about 2-3. To raise the pH to about 6-7 lime is added. After drying in open systems, the citrus pulp product is being sold to the feedingstuff industry.

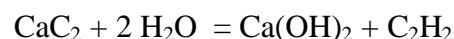
Possible sources of PCDD/PCDF contamination are:

- Pesticides in the orange peel (*e.g.* dicofol; bromopropilate);
- Formation of PCDD/PCDF during the drying process through contamination of the burning material (use of chlorinated additives to fuel oil such as perchloroethylene; sugar cane bagasse-fired drying);
- Ingredients such as lime.

The dioxin analysis found that lime was the source with contaminations up to 2.5 million pg I-TEQ/kg. The dioxin and furan pattern in the lime was very similar to the pattern found in citrus pulp.

The lime production took place in Brazil, where in 1998, nearly 6 millions tons of lime were produced. In Brazil there are different classes of lime manufacturers: “integrated manufacturers” who mine limestone and produce lime and “converters” who use lime and/or chemical products as raw material to produce hydrated lime (Ca(OH)<sub>2</sub>).

The dioxin-contaminated lime came from a “converter” who received the lime from a chemical company as a byproduct of the synthesis of acetylene (for the production of PVC). About 1 million tons of lime was found on the area of the chemical company. The dioxin contamination is not obvious from the synthesis process, *e.g.* there is no chlorine involved and there are some questions to be answered before drawing final conclusions:



### 6.1.3 Measures to Control the PCDD/PCDF Content in CPP

1. Legal measures in Brazil:

- Tolerances of 500 pg I-TEQ/kg in CPP and lime
- Exclusion of lime of “not virgin origin” from CPP production;
- Regulations for production and marketing, monitoring programs and inspection and sampling.

## 2. Supervision program:

- Sampling of CPP and lime on all production steps including shipment to Europe
- Analyses of representative samples in registered laboratories
- Responsibility for the appropriate supervision and registration of all involved companies by the Ministry of Agriculture, Brasilia

## 6.2 Belgian Chicken Accident

In brief, the chronological order of facts was as follows:

- Mid-January 1999: storage tank for animal fat is badly contaminated with PCB (and furans); the fat is supplied to feedstuff producer;
- March 1999: discovery of health problems in poultry production (marked reduction in egg hatchability, increased mortality of chicken);
- End of May 1999: results of analyses of feedstuff samples, hens (mother hens) and breeding eggs show high levels of PCDD/PCDF;
- May/June 1999: Storm breaks in the media over the perceived negligence;
- The starting point of the crisis is being detected: about 107 t fat was contaminated with PCB (mid January);
- From this, about 90 t were used for production of feedstuff for poultry; remaining fat also for production of milk and meat;
- Affected amounts and types of feedstuff by mid-June: 20,000 t for poultry, 6,000 t for pigs, 400 t for cattle;
- Affected number of farms by mid-June: 446 poultry farms, 746 pig farms, 393 cattle farms;
- Number of suspected farms at beginning of October: 505 poultry farms, 1626 pig farms, 411 cattle farms; from these 25 under restriction on October 6, 1999;
- Affected food categories: poultry, eggs, milk, beef and pork.

The first analysis of PCDD/PCDF were about 1,000-times above background and gave the following results:

- Poultry feed was contaminated with 811,000 pg WHO-TEQ/kg product;
- Poultry fat contained 775 and 1,009 pg WHO-TEQ/g fat (2 samples);
- Egg fat: 266 and 713 pg WHO-TEQ/g fat (2 samples)

First, only the contamination with PCDD/PCDF was known. When a very intensive search for dioxin-contaminated food began, the capacity to perform these analyses was very limited; *e.g.* in Belgium there was not a single laboratory to perform this kind of analysis- By mid June, it was discovered that about 25 L of PCB-containing transformer oil was the source of the contamination. It is suspected that PCB transformer oil, mainly a mixture of Aroclors 1254 and 1260, has been disposed of together with animal fat in a disposal unit for recycling. Consequently, an intense PCB screening was performed and the final report from Belgium summarizes that results of more than 60,000 analyses for PCB and 800 for PCDD/PCDF have been generated.

Major findings from the Final Report by Belgium are:

- The peak of PCB/dioxin contamination occurred in poultry feedstuff in January 1999 with a mean PCB level of about 350,000 ng/g fat;

- Between February and March, the levels of contamination dropped by more than 100 times.
- In April, no sample of feedstuff was found to exceed the Belgian PCB tolerance of 1,000 ng/g fat

In response to the Belgian crisis, the German Ministry for Health issued emergency regulations and set maximum permissible concentrations for PCDD/PCDF (on June 10, 1999, BAnz 1999) and once a commercial PCB mixture was proven to be the source of the “dioxin” contamination, also limit values for the six most abundant PCB congeners<sup>5</sup> were issued (on June 24, 1999). These limit values were applicable only for this Belgian crisis and for foods originating from Belgium. The concentrations were as shown in Table 12.

Table 12: Tolerance values for PCDD/PCDF and for six marker PCB in Germany applicable to foods from Belgium

Foodstuff	PCDD/PCDF Maximum Concentration (pg WHO-TEQ/g fat)	PCB Maximum Concentration (ng/g fat)
Eggs	5	200
Poultry	5	200
Beef	6	200
Pork	2	100
Milk	3	100

valid only for this particular accident (Belgian dioxin crisis)

By mid-July 1999, the following conclusions were drawn by the Commission:

- maximum contamination was in January
- contamination became public at end of May
- at that time, still some food samples with significantly increased dioxin contamination on the market, but far below the extremely high contamination found in January
- in comparison to CPP contamination: probably much less number of samples affected, but these with much higher dioxin content

Estimated costs for Belgium were:

- roughly 1 billion US\$ in direct costs
- about 3 times more indirect costs
- costs for analyses negligible

### 6.3 Caolinitic Clay

In 1997, the FDA in the United States discovered elevated concentrations of PCDD/PCDF in poultry samples. Ball clay was found to be the source of the contamination. Especially affected were eggs and catfish. Ball clay is being used as a feed additive mainly to soybean meal as a flowing or anti-caking agent. The source of the clay was found to be a bentonite mine in Mississippi. The reason for the occurrence of PCDD/PCDF in clay has been unknown for a long time.

<sup>5</sup> These are: PCB IUPAC numbers 28, 52, 101, 138, 153, 180

In 1999, similar food contamination occurred in Europe with caolinitic clay as the source for the PCDD/PCDF contamination. Here, the clay was used as an anti-caking agent in feedstuffs, too. The origin of the clay was a mine in Germany. Interestingly, the PCDD/PCDF pattern in the clays from Mississippi and from Germany and consequently in the feedstuffs were very similar. The pattern was dominated by Cl<sub>8</sub>DD and had almost no PCDF. In addition, the same pattern was found in sediments from the East coast of Australia.

Preliminary conclusion direct towards natural formation of PCDD/PCDF. Possibly, geological processes formed this unique pattern of dioxins over time from organic material and chlorine

The impact in foods by application of mineral feed does not seem to result in a significant increase of dioxin content of food samples (milk) as the mineral product is added at a rate of only about 0.5 to 1 % of daily feed ratio. On the other hand, the use of clay as an anti-caking agent in poultry feed caused significant contamination of food. The data were as follows:

- feedstuff: 8600 pg WHO-TEQ/kg
- eggs: 7-42 pg WHO-TEQ/g fat
- poultry meat: up to 50 pg WHO-TEQ/g fat
- Commission Regulation (EC) No. 2439/1999 and 739/2000:

For consumer protection, the EU set a maximum limit for the dioxin content of 500 pg WHO-TEQ/kg for most additives belonging to the group “binders, anti-caking agents and coagulants. This regulation applies from March 1, 2000 and should be re-examined before October 2000. The EU concludes that “Contaminated additives should be avoided as much as possible. An unacceptable degree of contamination of feedingstuffs should be prevented”.

The use of caolinitic clay is common also in cosmetic and pharmaceutical products. However, so far, no elevated dioxin concentrations have been detected in these products.

It should be noted that not all clays are contaminated with PCDD/PCDF and most clay is “dioxin-free”.

## 6.4 Brandenburg Case (Drying Case)

In the year 1999, the Chemisches Untersuchungsamt Freiburg (CVUA Freiburg) repeated detected elevated dioxin levels in egg samples produced in the German state “Brandenburg” in its routine analyses. The source could be identified in the same year when it was found that the direct drying of green feedstuff (dried greens) contained high concentrations of PCDD/PCDF. The elevated concentrations were caused by drying green fodder in an open system with all kinds of wood being burnt. The firing materials included waste wood with chemical contamination from former paintings or use of wood preservatives. Some more information on the drying process is given in section 8.2.3.1.

## 6.5 Choline Chloride Case

The latest of the dioxin feedstuff contamination occurred in spring 2000, when elevated dioxin concentrations were found in choline chloride premixtures for feedstuff (2000). It was

found that the additive choline chloride originated from Belgium and the premix was manufactured in Spain. The final product was sold to Germany. The analyses of two products gave 14 and 50 ng WHO-TEQ/kg product (for PCDD/PCDF only), respectively. Typically, this premixture is added at a rate of 1 % in the compound feed. The pure chemical, choline chloride, was not contaminated with PCDD/PCDF. Further investigations showed that the carrier of the choline chloride was the source of the contamination. Typical carriers are corn cob meal, rice husks or almond husks, and pine sawdust. In this case, pine sawdust was heavily contaminated with dioxins and furans exhibiting the PCP pattern.

Following the provisions of the Commission Decision 91/516/EC, the use of “wood, sawdust and other materials derived from wood treated with wood protections products” is prohibited in compound feedingstuffs.





## 7 PCDD/PCDF AND POPs IN THE FOODCHAINS

Living organisms are characterized by their ability to bioaccumulate, either directly from the surrounding medium through oral, percutaneous, or sometimes respiratory courses (bioconcentration), or indirectly *via* food through different trophic levels in a foodchain (biomagnification). However, it should be noted that opinions about the correct usage of the terminology 'bioconcentration' and 'biomagnification' differ.

The traditional measure of a chemical's potential to accumulate in an organism is the bioconcentration factor (BCF), which is defined as the concentration of a chemical in an organism or tissue divided by its concentration in the surrounding medium, *e.g.* water (for aquatic organisms) or air (for plants). BCFs are also used to show the movement from feedingstuffs to foodstuffs along agricultural food chains (eq. 1).

$$\text{BCF} = \frac{\text{contaminant concentration in meat (milk, eggs) (pg / g fat)}}{\text{contaminant concentration in feedingstuffs (pg / g fat)}} \quad (1)$$

Besides, biomagnification factors (BMF) are employed in order to express the increase in concentration from food to consumer, or (especially in aquatic food chains) from one foodchain level to the next. They are calculated as the contaminant concentration in an organism or tissue divided by the contaminant concentration in the food, or the contaminant concentration at the next lowest food chain level (compare eq. 1).

For monitoring and predicting contaminant levels in foodstuffs, carry-over rates (COR) are more useful than BCFs, because they take both the feedingstuff intake and the foodstuff output into account (eq. 2).

$$\text{COR} = \frac{\text{contaminant flux in milk (or meat) (pg / day)}}{\text{contaminant flux in feed (pg / day)}} \quad (2)$$

It should be noted that carry-over rates assume that livestock animals are at steady-state with respect to contaminants whenever they are applied. True steady-state conditions are, however, not attained at any time, and changes in the body fat depot, *e.g.* throughout the lactation cycle of cows may play an important role in the storage and release of contaminants.

### 7.1 Aquatic Foodchain

Aquatic foodchains or food webs are rather complex, and often comprise several trophic levels and various active and passive links. In the classical paradigm of the aquatic foodchain phytoplankton is the primary producer of basic nutrients for zooplankton, which is followed by fish of different trophic levels (*e.g.* coarse fish, predatory fish). Top-level predators may be marine mammals, fish-eating birds *etc.*, and humans.

It has been well documented that organic contaminants bioconcentrate and biomagnify in aquatic biota, and may undergo subsequent transport from organism to organism along the

food chain. This often leads to high concentrations at high trophic levels, which may threaten the health of these animals or those who consume them. Transfer of various POPs through the water-plankton-fish-bird foodchain *e. g.* has been found responsible for adverse health effects in birds, and even regional extirpation of certain species.

POPs are hydrophobic compounds with low water solubility that show a strong tendency to partition into organic phases. Contaminant uptake by aquatic organisms can occur through different pathways. One possible route for uptake is sorption to the outer surface followed by passive diffusion into lipid tissues. This should, however, only be of importance for organisms with a high surface to mass ratio, like microorganisms. Major pathways into higher aquatic animals are respiration and ingestion. Because of the low oxygen content of water relative to air, fish and many other aquatic organisms must pass large quantities of water, and the equilibration of chemicals between water and body by transport *via* the respiratory organs can be very fast. Depending on the trophic level the animal belongs to, food can, however, be responsible for the vast majority of the exposure. Exposure may also occur by sediment ingestion. Benthic organisms, *e.g.* ingest and process sediments as a food source.

Letcher *et al.* (1996) investigated part of the polar bear's food chain, and analyzed arctic cod, ringed seal blubber and polar bear fat for various chlorinated hydrocarbon contaminants. They observed increases in concentration from cod to seal blubber, and also from seal blubber to bear fat – except for  $\Sigma$ DDT and 4,4'-DDE. Biomagnification factors for  $\Sigma$ DDT and 4,4'-DDE, a metabolite of the insecticide 4,4'-DDT, were less than 1 from seal to bear, which was attributed to biotransformation.

Table 13: Biomagnification factors for the polar bear food chain (Letcher *et al.* 1996) (Ratio of tissue concentration at one food chain level to those at the next lowest level at lipid weight)

Compound	Cod to seal blubber	Seal blubber to bear fat
$\Sigma$ HCH	1.4	1.6
$\Sigma$ DDT *	17.1	0.6
4,4'-DDE	38.5	0.8
$\Sigma$ PCB	7.8	15.1
PCB 153	26.6	47.3

\* sum of 4,4'-DDT, 4,4'-DDD and 4,4'-DDE

Especially PCB 153 exhibited high biomagnification factors at both steps. One reason for this may be the resistance of PCB 153 to metabolic degradation, which has been observed in aquatic organisms as well as in terrestrial animals and humans.

Dewailly *et al.* (1993) conducted a study on humans potentially exposed to PCB through the aquatic foodchain in the Arctic. They analyzed breast milk of Inuit women from northern Quebec in Canada, and showed that levels of PCB were similar to those in beluga blubber from that area, and seven times higher than in southern Quebec women.

Testing the relationship between bioaccumulation of conservative organochlorine compounds and steps of the Arctic marine foodchain, Norstrom (1994) found that the logarithm of the concentration of total chlordanes, total PCB and PCB 153 was linearly correlated to trophic levels. On the basis of the regression equations obtained, he defined an overall biomagnification factor between unit trophic levels in the Arctic marine ecosystem for non-

metabolizable organochlorines of 6.6 based on lipid weight. A field study on the bioaccumulation of various organochlorines, including PCB, HCB and DDT, and nitro-musks in fish of different trophic levels and fish otter in northern Germany indicated, that accumulation is much higher in top level organisms than in organisms at lower levels. The ratio of accumulation within the aquatic foodchain sediment-fish-otter was 1 : 6 : 15, and from coarse fish to predatory fish 1 : 5; both calculated, however, on a dry weight basis (Willitzkat, 2000).

A study on farm raised catfish from the U.S. by Cooper *et al.* (1996) suggests that the major source of PCDD in catfish is from fish meal feed and not from the uptake of environmental contamination, *e.g.* sediment. But, although a lot of data exists about PCDD/PCDF concentrations of different waters, aquatic organisms and sediments, to our knowledge there are no investigations on bioaccumulation and biomagnification of these compounds through various trophic levels within the aquatic ecosystem.

It is important to note that the usage of fish meal and fish oil as protein source for livestock partly combines the terrestrial and the aquatic food chain at a high trophic level, probably leading to a significant additional biomagnification.

## 7.2 Terrestrial/Agricultural Foodchain

Dairy products and beef are the source of about half of the exposure of the general population to PCDD/PCDF. Tracing PCDD/PCDF back through the agricultural food chain, it has been found that a major contribution to the dairy cow's uptake occurs *via* the consumption of grass and grass products such as hay and silage. Therefore, the accumulation of PCDD/PCDF in grassland is one of the key processes determining human exposure.

Organic chemicals can be deposited on plant surfaces via wet deposition, via dry deposition of chemicals bound to atmospheric particles, or via diffusive transport of gaseous chemicals in the air to the plant surfaces. Each of these processes is governed by a different set of plant properties, environmental parameters, and atmospheric concentrations. Investigations with native grassland cultures showed that dry gaseous deposition plays the dominant role for the accumulation of the lower chlorinated PCDD/PCDF, whereas dry particle-bound deposition played an important role in the uptake of the PCDD/PCDF with 6 and more chlorine atoms. There was also some evidence indicating an input of the higher chlorinated PCDD/PCDF from wet deposition (Welsch-Pausch *et al.* 1995; Welsch-Pausch 1998).

An evaluation of the PCDD/PCDF fluxes along the pathway atmosphere into and within an agricultural ecosystem was made by Welsch-Pausch and McLachlan (1998). The annual fluxes of PCDD/PCDF were calculated from measurements conducted at a dairy farm (800 hectares) in northern Germany in 1996. The results indicated that roughly 15 % of the total annual deposition to the farm is captured in the feed crops, while the major part is transferred directly to soil. The retention efficiency of the different feed crops was variable, with grassland contributing 85 % of the total PCDD/PCDF flux in feed, corn 15 % and grain virtually none. While particle-bound deposition accounted for the majority of the atmospheric flux into the ecosystem, the vast majority of this went directly to soil. Gaseous deposition dominated the transfer into crops and hence into the foodchain.

The overall transfer of the annual atmospheric deposition into milk was very low, reaching a maximum of 3 % for 2,3,7,8-Cl<sub>4</sub>DD, 1,2,3,7,8-Cl<sub>5</sub>DD and 2,3,4,7,8-Cl<sub>5</sub>DF and falling to below 0.1 % for many of the other congeners. These low transfer rates are due to a combination of low retention of deposition by crops, incomplete absorption of the PCDD/PCDF in the cows and metabolism within the animals. A significant fraction of the PCDD/PCDF left the cow barn with the manure. Nevertheless, spreading this manure on the fields only increases the annual input into the soils by about 10 %.

For Cl<sub>8</sub>DD the total output exceeded the input by a factor of three, indicating a source of this compound within the cow barn. Several authors have reported formation of the higher chlorinated PCDD during composting processes and sewage sludge digestion. Thus, the most likely reason for the unexpectedly high Cl<sub>8</sub>DD output seemed to be biogenic formation. Laboratory experiments were conducted to establish whether Cl<sub>8</sub>DD is formed during fermentation of corn silage or stable manure, but no evidence of this was found. There is, however, some evidence in the literature suggesting that Cl<sub>8</sub>DD is formed in the digestive tracts of cows.

As schematic drawing summarizing all these findings is shown in Figure 3.

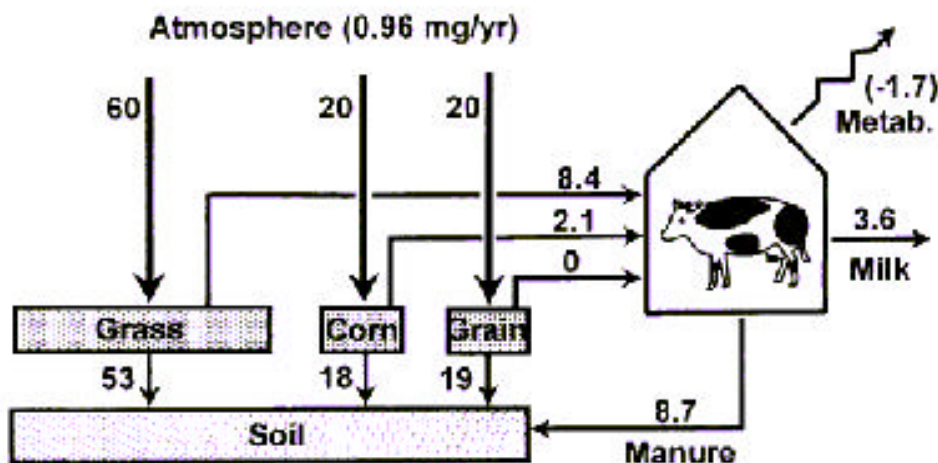


Figure 3: Overview on fluxes in the agricultural foodchain

### 7.3 Carry-over of PCDD/PCDF and Other POPs from Feed to Livestock

So far, investigations on the carry-over behavior of POPs have mainly concentrated on the transfer of PCDD/PCDF *via* the „grass-cow-milk” pathway. Little is known about transfer into other livestock animals, and to our knowledge no data has been generated to determine the carry-over from industrially produced feedingstuffs into animals.

### 7.3.1 Carry-over to Cattle

#### 7.3.1.1 Carry-over from Feed to Milk

Carry-over rates (CORs) from feedingstuffs contaminated with only background concentrations of PCDD/PCDF, to milk were determined by Welsch-Pausch and McLachlan (1998) and McLachlan and Richter (1998) (Table 14).

Table 14: Carry-over rates for PCDD/PCDF from feed into cow milk

	Welsch-Pausch and McLachlan (1998)	McLachlan and Richter (1998)
2,3,7,8-Cl <sub>4</sub> DD	0.34	0.38
1,2,3,7,8-Cl <sub>5</sub> DD	0.31	0.39
1,2,3,4,7,8-Cl <sub>6</sub> DD	0.127	0.33
1,2,3,6,7,8-Cl <sub>6</sub> DD	0.21	0.33
1,2,3,7,8,9-Cl <sub>6</sub> DD	0.110	0.16
1,2,3,4,6,7,8-Cl <sub>7</sub> DD	0.028	0.034
Cl <sub>8</sub> DD	0.0121	0.0068
2,3,7,8-Cl <sub>4</sub> DF	0.0083	
1,2,3,7,8-Cl <sub>5</sub> DF	0.0107	
2,3,4,7,8-Cl <sub>5</sub> DF	0.26	0.40
1,2,3,4,7,8-Cl <sub>6</sub> DF	0.094	0.24
1,2,3,6,7,8-Cl <sub>6</sub> DF	0.098	0.187
2,3,4,6,7,8-Cl <sub>6</sub> DF	0.089	0.189
1,2,3,4,6,7,8-Cl <sub>7</sub> DF	0.0146	0.034
1,2,3,4,7,8,9-Cl <sub>7</sub> DF	0.023	
Cl <sub>8</sub> DF	0.0053	

The data from Table 14 allow to make a rough classification of the CORs into three groups: The first group consists of the two lower chlorinated dibenzo-*p*-dioxins and one dibenzofurans, namely 2,3,7,8-Cl<sub>4</sub>DD, 1,2,3,7,8-Cl<sub>5</sub>DD, and 2,3,4,7,8-Cl<sub>5</sub>DF. For these three congeners about 30–40 % are transferred from feed to milk. The 2,3,7,8-substituted Cl<sub>6</sub>DD and Cl<sub>6</sub>DF make up the second group: the congeners of these two homologue groups are excreted in the milk at a rate of around 20 % compared to the intake. The hepta- and octachlorinated PCDD and PCDF form the third group; of these not more than 4 % of the ingested congeners find their way into the milk. Overall, about 30 % of the most toxic congeners taken up by the cow are excreted *via* the milk.

Generally, Table 14 shows that the CORs decrease with increasing degree of chlorination, indicating that absorption through the gut also decreases. This decrease in absorption was attributed to the greater hydrophobicity of the higher chlorinated PCDD/PCDF, which inhibits their transport across aqueous films in the digestive tract of the cow.

Thomas *et al.* (1999) performed a PCB input/output balance study investigating five cows which were fed a natural background contaminated diet and kept under typical U.K. winter husbandry conditions for 15 weeks. Input/output balances (*i.e.* milk and fecal output fluxes divided by the dietary intake flux) of around 100 % were found for the unmetabolized, higher

chlorinated PCB (*e.g.* PCB 153, PCB 138, PCB 180). This dropped, however, to about 20 % for the readily metabolized, lower chlorinated congeners (*e.g.* PCB 28, PCB 33).

These findings are also reflected in the average CORs from feed to milk (Table 15). PCB in milk were dominated by the hexachlorinated congeners 138 and 153 and the pentachlorinated congener 118. For all PCB analysed an overall transfer rate to milk of 27 % was determined. Most of the heavier congeners, however, were excreted in the milk at a much more higher rate (about 70 %) than the lower chlorinated ones (about 10 %) (Thomas *et al.* 1999).

Table 15: Average carry-over rates for PCB from feed into cow milk

PCB	Av. CORs	Std. dev. (%)	PCB	Av. CORs	Std. dev. (%)	Previously reported CORs
18	0.03	71	151	0.00	0	
31	0.05	76	149	0.05	38	
28	0.04	69	153	0.83	17	0.78 *, 0.71 **
33	0.03	72	141	0.06	41	
37	0.06	32	138	0,74	17	0.63 * , 0.75 **
52	0.00	0	128	0.65	25	
49	0.00	0	167	0.91	29	
47	0.25	18	156	0.76	19	
74	0.45	17	187	0.09	23	
66	0.18	18	183	0.65	17	
60	0.00	0	180	0.67	15	0.63 * , 0.68 **
101	0.05	14	170	0.65	18	
110	0.02	29	194	0.00	0	
118	1.09	22				
105	0.00	0	Σ PCB	0.27	17	

There is a good agreement between the results of this study and the CORs for PCB 153, PCB 138 and PCB 180 reported by McLachlan (1993) \* and by Heeschen and Blüthgen (1986) \*\*.

Table 16  
feed to milk determined by McLachlan (1992) and Heeschen and Blüthgen (1985).

Table 16: Carry-over rates for other POPs from feed into cow milk

Substance	McLachlan (1992)	Heeschen and Blüthgen (1985)
ã-HCH	0.04	0.03
á-HCH	0.21	0.09
HCB	0.79	
<i>p,p'</i> -DDE	0.80	
<i>p,p'</i> -DDT	0.04	

### 7.3.1.2 Carry-over from Feed to Beef

There are only few data about the carry-over from feed to beef.

In a feeding experiment with growing bulls six PCB congeners (PCB 28, PCB 52, PCB 101, PCB 138, PCB 153, PCB 180) were added to the feed rations of the animals in concentrations of 0, 10, and 30 ng of each congener/g air-dried feed (Vemmer *et al.* 1992). The bulls were intensively fattened with maize silage and concentrate over a fattening period from 160 to 600 kg live weight. At the end of the experiment the animals were slaughtered and analyzed for the quantity of PCB in the whole bodies. It was found that about 50 % of the total amount of PCB 138, PCB 153 and PCB 180 administered were retained in the body of the bulls, whereas no residues of PCB 28, PCB 52 and PCB 101 could be detected.

The analysis of muscles, liver, kidney, pelvic cavity-kidney fat, stomach-intestine fat, subcutaneous adipose tissue and bones of growing bulls in a very similar feeding experiment (Vemmer *et al.* 1993) showed a close relation between dietary intake and tissue concentrations for PCB 138, PCB 153 and PCB 180. Again, no accumulation of PCB 28, PCB 52 and PCB 101 in the tissues of the bulls could be detected.

Except for liver, PCB contents of about 10 ng of PCB 138, PCB 153 and PCB 180 per g feed led to comparable concentrations in all tissues analyzed (Table 17). As it can be seen in Table 17, the PCB concentrations of tissue fat were approximately 20 times higher than the concentrations in feed.

Table 17: Concentrations of PCB 138, PCB 153 and PCB 180 in various tissues of growing bulls (ng/g fat), slaughtered at a live weight of 600 kg (means and standard deviations)

	PCB 138	PCB 153	PCB 180
Concentration of feed (ng/g air-dried feed)	10.18	9.84	11.64
Muscle	222.3 ± 58.3	211.3 ± 61.1	199.6 ± 52.3
Liver	1,153.9 ± 310.0	714.5 ± 221.0	681.8 ± 50.6
Kidney	211.8 ± 70.2	181.1 ± 55.4	203.4 ± 58.7
Pel. cavity-kidney fat	214.3 ± 75.1	182.4 ± 67.0	189.8 ± 61.8
Stomach-intestine fat	233.6 ± 55.7	203.7 ± 51.0	212.9 ± 50.5
Subcut. adipose tissue	195.5 ± 43.5	166.9 ± 41.9	164.3 ± 36.4
Bones	251.2 ± 60.1	221.6 ± 62.9	237.1 ± 35.2

In a parallel experiment the authors demonstrated that an increasing PCB dosage in the feed (up to 30 ng/g feed) resulted in an almost linear increase in most of the tissues. They established the regression equations for the relationship between the PCB contents of feed and the PCB contents of kidney fat as shown in Table 18.

Table 18: Relationship between PCB concentrations of air-dried feed and PCB concentrations of kidney fat

PCB 138	$y = 0.497 + 20.895 x ; r = 0.975$
PCB 153	$y = -0.314 + 18.586 x ; r = 0.970$
PCB 180	$y = -4.848 + 17.330 x ; r = 0.968$

(x = ng/g air-dried feed; y = ng/g tissue fat)

It has, however, to be considered that this experiment does not necessarily reflect normal feeding conditions. PCB contents of grass and maize silage measured on a dairy farm in northern Germany *e.g.* were in the range of 30 to 70 pg/g d.m. for PCB 28 and PCB 52, and of 120 to 200 pg/g d.m. for the hexachlorinated congeners, PCB 153 and PCB 138. Concentrations of grain and rape were even lower, and did not exceed 15 pg/g d.m. (Welsch-Pausch, unpublished data). That means, that levels of basic feedingstuffs would be more than three orders of magnitude lower than feed levels in these experiments. Therefore, an extrapolation from the findings of Vemmer *et al.* to background situations may be problematical. Besides, bioavailability of the PCB may also influence the transfer behavior. In the feeding studies of Vemmer *et al.* wheat meal was used as a carrier for the PCB which may result in a better resorption compared to the resorption, *e.g.* from grass or straw.

To our knowledge there are no investigations on the carry-over from feed to beef for PCDD/PCDF or other POPs

### 7.3.2 Carry-over to Pigs

In a feeding experiment Vemmer *et al.* (1991) investigated the PCB transfer from feed to the whole body of 50 fattening pigs. PCB (PCB 28, PCB 52, PCB 101, PCB 138, PCB 153, PCB 180) were added to the feedingstuffs from the 1<sup>st</sup> to the 15<sup>th</sup> experimental week (at concentrations of about 30 ng of each congener/g air-dried feed). There was no further application from the 16<sup>th</sup> to the 25<sup>th</sup> week. Two pigs were slaughtered at a time in a seven days interval. On average, only 8 % of the total amount of PCB 28 administered, and about 30 % of PCB 52 and of PCB 101, were recovered in the whole body. Interestingly, the concentrations of these congeners in the carcass began to decrease again after the application of PCB had ceased. As for PCB 138, PCB 153 and PCB 180, about 80 % of the total amount administered were obtained in the body. In contrast to the lower chlorinated PCB, no decrease could be detected for these compounds during the second period of the experiment when animals were fed a PCB free diet. The authors, therefore, concluded that PCB 138, PCB 153 and PCB 180 have to be viewed with concern because of their high transfer potential from feed to pig.

Vemmer *et al.* (1989) reported another feeding experiment in which PCB (PCB 28, PCB 52, PCB 101, PCB 138, PCB 153, PCB 180) were added to the diet of five groups of fattening pigs in different concentrations (0, 5, 10, 20, 30 ng of each congener/g air-dried feed) over a fattening period of about 100 days. The pigs were slaughtered at a live weight of about 100 kg, and PCB contents were analyzed in subcutaneous adipose tissue, flare fat, muscles, liver and kidney. For all PCB congeners, there was a close relationship between dietary intake and tissue concentrations. The heavier compounds, PCB 138, PCB 153 and PCB 180, showed the highest accumulation in the tissues. PCB 28 gave the lowest residues, whereas PCB 52 and PCB 101 had intermediate accumulation factors. Table 19 shows the results of the linear regressions of the PCB concentration in subcutaneous adipose tissue fat (ng/g), *e.g. versus* the PCB concentration in air-dried feed (ng/g) in the range of 5 to 30 ng/g feed, which were derived from dose-efficiency curves.



Table 19: Relationship between PCB concentrations in subcutaneous adipose tissue fat and PCB concentrations in air-dried feed (Vemmer *et al.* 1989)

PCB 28	$\ln y = 0.2495690 + 0.6872597 \ln x$
PCB 52	$y = 2.0900 + 2.4389 x$
PCB 101	$y = -4.0038 + 3.2110 x$
PCB 138	$y = 6.6955 + 5.6703 x$
PCB 153	$\ln y = 2.218282 + 0.879270 \ln x$
PCB 180	$y = 5.0739 + 5.3575 x$

(x = ng/g air-dried feed; y = ng/g fat)

According to these regressions a concentration of 10 ng/g air-dried feed of PCB 153 would give a food stuff concentration (adipose tissue) of about 70 ng/g fat.

However, as it has already been discussed above (compare Chapter 7.3.2), the results of the feeding studies presented here must be used judiciously when going to background situations.

To our knowledge there are no investigations on the carry-over from feed to pork for PCDD/PCDF or other POPs

### 7.3.3 Carry-over to Chickens and Eggs

Besides meat, milk and milk products eggs play an important role in human nutrition and thus can be important contributors for POPs intake of humans *via* food. In Germany, an average contribution of 5 % to the PCDD/PCDF exposure of the general population was estimated (Beck *et al.* 1989). This estimation was based on PCDD/PCDF levels usually detected in eggs of hens kept in cages without soil contact. Eggs from chickens allowed to forage on soil showed, however, elevated PCDD/PCDF concentrations, and soil was found to be a main exposure to chickens (Petreas *et al.* 1996; Schuler *et al.* 1997; Harnly *et al.* 2000).

Comprehensive investigations have shown that there exist distinct differences in the PCDD/PCDF contamination of eggs dependent on the type of housing for the laying hens. The results of these investigations are shown in Table 20. Table 20 clearly demonstrates that the majority of PCDD/PCDF levels in eggs from chickens housed in elevated wire cages is below 2 ng I-TEQ/kg fat. Only a very small number of samples ranged up to 2.3 ng I-TEQ/kg fat. In contrast, eggs from laying hens kept on ground and from foraging chickens raised on fields show a broader range of contamination. In both cases a considerable number of samples revealed PCDD/PCDF levels above 2 ng TEQ/kg fat. The highest level was found to be 23.4 ng I-TEQ/kg fat. Moreover, these studies revealed that the concentrations and congener profiles of PCDD and PCDF in eggs of chickens appear to be related to the soil on which they are raised. As a consequence, chicken eggs, especially from laying hens kept on contaminated ground or from free foraging chickens may contribute considerably to human dioxin body burden. Consequently, egg samples very often are characterized by high concentrations of Cl<sub>8</sub>DD indicating that the soil contamination may be transferred into the animal. In cases of very high dioxin contamination, concentrations up to several hundred pg I-TEQ/g lipid (*e.g.* 300 pg I-TEQ/g lipid in Baden-Württemberg and 219 pg I-TEQ/g in Hamburg) have been reported.

Table 20: Germany: PCDD/PCDF concentrations in eggs (Fürst 1998). Concentrations in pg I-TEQ/g lipid. \* Median

Method Keeping	N	Min	Max	Mean	Source
Caged, housing in elevated wire cages	20	0.56	2.30	1.16*	Fürst <i>et al.</i> 1993
	69	0.23	6.04	1.36	CLUA Freiburg 1995
Chicken kept on ground	11	1.03	23.4	1.81*	Fürst <i>et al.</i> 1993
	32	0.19	5.57	1.63	CLUA Freiburg 1995
Free Foraging	23	0.38	11.4	1.91*	Fürst <i>et al.</i> 1993
	31	0.49	22.8	4.58	CLUA Freiburg 1995

The transfer of PCDD/PCDF from soil into chicken eggs was investigated in an exposure study by Petreas *et al.* (1991). There was only little variation in PCDD/PCDF concentrations of the eggs after 30, 60 and 80 days, respectively. Thus, it can be assumed that a relatively fast equilibrium between the concentration in the soil ingested with feed and the concentration in the eggs is reached. The results were confirmed by a second study, which clearly showed that the accumulation factors were inversely correlated with the degree of chlorination (Petreas *et al.* 1996).

Table 21 summarizes the egg/soil ratios (mean of samples collected on days 30, 60 and 80) reported by Petreas *et al.* (1991), and compares them to the soil-to-egg transfer rates determined by Schuler *et al.* (1997)

Table 21: PCDD/PCDF transfer from soil to eggs

	Petreas <i>et al.</i> (1991) (egg concentration (pg/g fat) / soil concentration (pg/g))	Schuler <i>et al.</i> (1997) (egg concentration (pg/g lipids) / soil concentration (pg/g))
2,3,7,8-Cl <sub>4</sub> DD	n. c.	1.2
1,2,3,7,8-Cl <sub>5</sub> DD	0.41	2.4
1,2,3,4,7,8-Cl <sub>6</sub> DD	0.52	1.5
1,2,3,6,7,8-Cl <sub>6</sub> DD	0.53	1.6
1,2,3,7,8,9-Cl <sub>6</sub> DD	0.36	0.8
1,2,3,4,6,7,8-Cl <sub>7</sub> DD	0.30	0.4
Cl <sub>8</sub> DD	0.14	0.1
2,3,7,8-Cl <sub>4</sub> DF	0.25	3.3
1,2,3,7,8-Cl <sub>5</sub> DF	1.37	4.4
2,3,4,7,8-Cl <sub>5</sub> DF	0.67	0.8
1,2,3,4,7,8-Cl <sub>6</sub> DF	0.61	0.9
1,2,3,6,7,8-Cl <sub>6</sub> DF	0.53	1.0
2,3,4,6,7,8-Cl <sub>6</sub> DF	0.26	0.6
1,2,3,7,8,9-Cl <sub>6</sub> DF	n. c.	0.1
1,2,3,4,6,7,8-Cl <sub>7</sub> DF	0.22	0.2
1,2,3,4,7,8,9-Cl <sub>7</sub> DF	0.16	0.1
Cl <sub>8</sub> DF	0.09	0.1

n. c. not calculated

Although there are several differences between these two studies (maybe due to the study design, since the results of Petreas *et al.* are from a laboratory experiment, whereas Schuler *et al.* conducted a field study), certain common trends can be recognized: Table 21 shows that

the quotients (egg/soil) decrease by more than one order of magnitude from the lower chlorinated to the higher chlorinated congeners. Similar observations were reported for the transfer of PCDD/PCDF from feed into dairy milk (see Chapter 7.3.1.1). These findings were attributed to a better resorption of the lower chlorinated PCDD/PCDF when compared to the higher chlorinated ones. Generally milk shows extraordinarily low concentrations of 2,3,7,8-Cl<sub>4</sub>DF and 1,2,3,7,8-Cl<sub>5</sub>DF due to a relatively fast metabolism of these two congeners in the cow. In contrast, the patterns observed in the eggs of both studies indicate a metabolism rate, which is more or less similar to the rates of the other 2,3,7,8-substituted compounds.

A survey of PCB and PCDD/PCDF congeners in eggs and poultry meat conducted by Lovett *et al.* (1998) in England and Wales showed that the environment in which poultry live influences both, the eggs as well as the meat. They reported that the PCB and PCDD/PCDF concentrations of poultry products from a site close to an incinerator were appreciably greater than those detected elsewhere. The contrast was, however, less marked for poultry meat than for eggs. Petreas *et al.* (1996) confirmed that PCDD/PCDF bioconcentrate less in female than in male chickens. Eggs presumably present an elimination pathway for female chicken to 'clear' their body concentrations, comparable to cow milk for cows.

Ueberschär (1993) reported a PCB feeding study with laying hens. PCB (PCB 28, PCB 52, PCB 101, PCB 138, PCB 153, PCB 180) were added to the diet of the hens in different concentrations (0, 10, 20, 40 and 80 µg of each congener/kg feed).

Table 22: PCB uptake and residues in laying hens

		PCB 28	PCB 52	PCB 101	PCB 138	PCB 153	PCB 180
Feed concentration	µg/kg	81	72	89	95	98	70
Uptake with feed	µg	1700	1510	1870	2000	2060	1470
PCB in eggs	%	48	4	4	68	72	96
PCB in feces	%	7.9	6.6	4.7	7.1	7.6	8.8
PCB in tissue	%	21	1.3	1.7	25	24	29

Table 22 shows that the major part of the PCB administered was transferred to the eggs. Less than 10 % were found in the feces, and up to 30 % remained in the tissue of the laying hens. The amount of excretion *via* feces was very similar for all PCB congeners analyzed. Surprisingly, PCB 28 displayed a transfer behavior comparable to the higher chlorinated congeners, PCB 138, PCB 153 and PCB 180.



## 8 PRODUCTION OF FEEDINGSTUFFS AND ADDITIVES

### 8.1 Definitions and Classifications

Feedingstuffs are of major importance for the European agriculture, more precisely for the production of food of animal origin for human consumption. Feedingstuffs can be either of animal and vegetable origin. In the latter group, feedingstuffs of plant origin can be either fed directly to the food-producing animal like grass, corn or other grains or can be ingredients of feedingstuff mixtures. Besides these “natural” components, the feedingstuff industry is also a major recycler utilizing by-products from industrial processing of raw materials of vegetable and animal origin, products from the removal of dead animal bodies as well as slaughter house waste in its production processes. Thus, secondary resources can make a significant contribution to the energy and nutrient supply of livestock.

Due to the wide range of feedingstuffs and feedingstuff mixtures offered by the industry and to avoid confusion of terms, brand names, *etc.* *Council Directive 79/373/EEC of April 2, 1979 on the marketing of compound feedingstuffs* (and its corresponding *Amendments*) gives definitions for feedingstuffs. For the marketing of feedingstuffs *Council Directive 79/373/EEC* applies the following definitions, which will also be followed by this study:

**Feedingstuffs** are (Article 2 [a]): “products of vegetable or animal origin in their natural state, fresh or preserved, and products derived from the industrial processing thereof, and organic or inorganic substances, used singly or in mixtures, whether or not containing additives, for oral animal feeding”.

**Compound feedingstuffs** are (Article 2 [b]): “mixtures of feed materials, whether or not containing additives, for oral animal feeding in the form of complete or complementary feedingstuffs”.

**Complete feedingstuffs** are (Article 2 [d]): “mixtures of feedingstuffs which, by reason of their composition, are sufficient for a daily ration”.

**Complementary feedingstuffs** are (Article 2 [e]): “mixtures of feedingstuffs which have a high content of certain substances but which, by reason of their composition, are sufficient for a daily ration only if used in combination with other feedingstuffs”.

**Mineral feedingstuffs** are (Article 2 [f]): “complementary feedingstuffs composed mainly of minerals and containing at least 40 % crude ash”.

**Feed materials** are (Article 2 [k]): “various products of vegetable or animal origin, in their natural state, fresh or preserved, and products derived from the industrial processing thereof, and organic or inorganic substances, whether or not containing additives, which are intended for use in oral animal feeding, either directly as such or after processing, in the preparation of compound feedingstuffs or as carriers of pre-mixtures”.

There exists a great variety of components. Table 23 is an attempt to classify components according to its type, origin or treatment, respectively. According to Table 23, feedingstuffs can be divided into three major categories, namely basic feedingstuffs, concentrates, and by-products.

Table 23: Classification of components of animal feed – basic feedingstuffs

Type	Origin / Treatment	Components
Basic feedingstuffs	Green forage cultivation	Permanent grassland Forage crops Catch crops Green maize Beet leaves
	Silage	Maize silage Green forage silage Sugar beet pulp
	Roughage preparation	Hay Straw
	Hot-air drying	Dried greens (cobs; briquettes) Dried sugar beet shreds Dried fruit pulp
	Root crops	Forage beet Sugar beet Potatoes Cassava roots (tapioca)

Table 23 (cont'd.): Classification of components of animal feed - concentrates

Type	Origin / Treatment	Components
Concentrates	Grain growing	Barley Oat Wheat Rye Triticale Grain maize
	Oilseed and pulse Cultivation	Broad bean Pea Lupine Sunflower Rape

Table 23 (cont'd.): Classification of components of animal feed - by-products from food industry

Type	Origin / Treatment	Components
By-products from the food industry	Oil and fat production	Soy products Linseeds and linseed products Rape oil-meal Peanut oil-meal Cottonseed residues Sunflower oil-meal Copra Palm kernel oil Olive pulp
	Sugar production	Filter press mud Sugar beet shreds Molasses
	Beverage production	Distiller's wash Brewer's grain Malt sprouts Brewer's yeast Citrus pulp Fruit pulp
	Starch production	Potato pulp Potato protein Maize gluten
	Flour production	Feeding meal Semolina Bran shorts Aspiration dust
	Animal origin	Dairy products Fish meal Fish oil Carcass meal Meat- and -bone-meal Grease / Animal fats Blood meal
	Baker's ware industry	By-products and Baker's ware
	Canning industry	Fruit and vegetable by-products
	Canteens and restaurants	Kitchen-refuse waste food

Table 23 has been amended by “olive pulp”., although presently there is no information how much pulp is generated from olive production nor if the pulp is being used in the feedingstuff industry. A separate section on olive pulp (8.3.1.2) will address possible implications and give arguments for adding this category.

### 8.1.1 Additives

Trend analysis has shown that animal feeding increasingly uses increasing amount of additives. The inclusion of a given additive in a compound feedingstuff is authorized only if the additive

- has a favorable effect on the characteristics of the feedingstuff to which it is added or on livestock production; and
- does not endanger animal or human health, nor harm the consumer of livestock products.

Table 24 shows a list of the major groups of additives and its major representatives permitted for incorporation in the production of feedingstuffs according to *Council Directive 70/524/EEC*.

Table 24: Additives used in feedingstuff production

Additive	Major Representatives
Antibiotics (growth promoters)	Avilamycin Favophospholipol Salinomycin sodium
Antioxidants	L-ascorbic acid Butylated hydroxyanisole
Aroma and appetizing substances	Saccharine Neohesperidine-dihydrochalcone
Binders, anti-caking agents and coagulants	Bentonite-montmorillonite Kaolinitic clays Sepiolite
Emulsifiers, stabilizers and thickeners	Aginic acid Lecithins Sodium alginate
Colouring agents including pigments	Canthaxanthine Luteine
Coccidiostats and other medicinal substances	Nifursol Amprolium
Preservatives	Formic acid Formaldehyde
Acidity regulators	Ammonium carbonate Calcium carbonate
Trace elements	Iron, Copper Jodine
Vitamins	Vitamins A, B, D, <i>etc.</i> Choline chloride
Enzymes	Alpha-amylase Endo-1,3(4)-beta-glucanase
Microorganisms	<i>Bacillus cereus</i> <i>Bacillus licheniformis/ subtilis</i>

Additives are employed to improve both the feedingstuffs in which they are incorporated and the livestock production. For this reason, antibiotics are also regarded as additives, since, when used in small quantities, they have a physiological nutritional effect. Further, certain purely medical substances such as coccidiostats are regarded as additives at the present, since



in most Member States they are used for collective prophylaxis, principally in poultry-farming.

The dioxin and furan concentrations that have been found in the above mentioned compounds is given in Section 8.4.1.

It should be noted that processing of agricultural plants for the non-food sector to obtain, *e.g.*, fibers, oils, and fats for the cosmetic or pharmaceutical industries, can generate a variety of wastes and residues suitable for use in the feedingstuff industry. An interesting example of these “unconventional” feedstuffs is glycerine from the “organic diesel” production.

## 8.2 Industrial Production of Feedingstuffs

### 8.2.1 General

Success in livestock production depends to a large extent on the use of suitable, good-quality feedingstuffs. Only high quality products can produce successful results. Industrially produced compound feedingstuffs are particularly relevant in agricultural practice. For example, on the basis of grain units about 25 % of the feedingstuffs consumed in Germany, are compound feedingstuffs originating from industrial processes, like finishing, recycling and re-using.

Table 25 reveals that the biggest compound feedingstuff producers in the EU are France, Germany, Spain, the Netherlands, the United Kingdom and Italy, providing about 80 % of the total annual production in the year 1999 (FEFAC 2000).

Table 25: Compound feedingstuff production in 1999 in the EU\* (x 1,000 tons)

	Cattle	Pigs	Poultry	Milk-Substitutes	Others	Total
Germany	6,896	6,857	4,280	182	535	<b>18,750</b>
France	4,100	6,900	9,540	520	2,190	<b>23,250</b>
Italy	3,380	2,250	4,280	160	1,050	<b>11,120</b>
Netherlands	3,570	8,900	3,850	750	780	<b>15,858</b>
Belgium	1,263	3,536	1,563	53	162	<b>6,577</b>
United Kingdom	4,437	2,500	3,921	13	1,393	<b>12,264</b>
Ireland	2,155	706	491	10	390	<b>3,752</b>
Denmark	1,336	3,504	670	6	115	<b>5,630</b>
Spain	3,500	7,700	4,100	60	1,120	<b>16,480</b>
Portugal	1,130	1,230	1,350	-	220	<b>3,930</b>
Austria	183	70	390	4	137	<b>784</b>
Sweden	1,170	610	500	7	150	<b>2,437</b>
Finland	500	325	247	-	154	<b>1,226</b>

\* Data from Luxembourg and Greece were not available.

### 8.2.2 Raw Materials

The industry offers a multitude of compound feedingstuffs, which are the basis for an intensive and profitable animal production. Especially the big pig and poultry farms depend almost exclusively on the feeding with compound feedingstuffs.

Feeding studies are conducted to determine the requirements of fat, protein, carbohydrate, vitamins, minerals, *etc.* of production animals at different ages, and it is up to the industry to choose among a variety of raw materials to meet these requirements. Information on formulae of compound feedingstuff mixtures is normally not available. As a further complication, it is often difficult to compose quantitatively and qualitatively the ingredients used in compound feedingstuff. This fact is caused by the nature of the products employed, of the complexity of the mixtures made or the manufacturing methods adopted.

*Council Directive 79/373/EEC* of April, 2 1979 on the marketing on compound feedingstuffs requires “to provide the user with accurate and meaningful information on the compound feedingstuffs at his disposal”, and “at least the levels of analytical constituents having a direct effect on the quality of the feedingstuff should be declared”. Thus, declarations by compound feedingstuff producers are normally restricted to the contents of crude protein, crude oils and fats, crude fiber, crude ash, various vitamins, amino-acids, trace elements, and to categories of ingredients (according to *Commission Directive 91/357/EEC*), which may be indicated instead of individual components. For the identification and evaluation of POPs fluxes within the feedingstuff industry and users, such declarations are of no use. Further, the use of individual components in the compound feedingstuffs depend on world market prices and as these are highly variable, only snapshots on a few components with potential POPs relevance can be done.

The Association of German Compound Feedingstuff Producers published the following data (as displayed in Table 26) on the consumption of raw materials during the marketing season 1997/1998:

Table 26: Consumption of raw materials by compound feedingstuff producers in Germany; marketing season 1997/1998 (Mischfutter-Tabellarium 1999)

Raw Material	Amount (x 1,000 tons)
Wheat	2,555
Rye	622
Barley	1,262
Oats	66
Maize	971
Triticale	805
Field pea	293
Field bean	32
Other pulses	75
Rape seed	5
Sunflower seed	23
Oil-cake/coarse meal of soy beans	1,971
Oil-cake/coarse meal of rape seeds	1,251
Oil-cake/coarse meal of other oil seeds	1,252
Maize gluten	1,306
Flour products	1,531
Cassava products	67
Fish meal / carcass meal / blood meal	405
Fruit pulp	534
By-products from sugar production	1,032
Other feedingstuffs	2,298
<b>Total</b>	<b>18,356</b>

The major ingredients used by German compound feedingstuffs producers were grain (34 %), oil-cake and coarse meal of pulses and oil seeds (24 %), flour products and maize gluten (together 15 %), as well as by-products from sugar production (6 %).

The figures provided by the Association of European Compound Feedingstuff Producers (FEFAC 2000) for 1998 show a similar distribution (Table 27), with grain making up 40 % and oil-cakes and coarse oil-meal making up 25 % of the total amount of about 120 Mio. tons of raw materials processed. By-products from the food industry also play an important role (15 %).

Table 27: Consumption of raw materials by European compound feedingstuff producers in 1998

Raw Material	Amount (x 1,000 tons)
Grain	48,748
Tapioca (starchy food of cassava roots)	2,739
By-products of food industry	17,475
Oils and fats	2,118
Oil-cakes and coarse oil-meal	30,212
Animal meal	2,759
Dairy products	1,598
Dried feed	2,400
Pulses	4,033
Minerals and vitamins	3,397
Other raw materials	4,737
<b>Total</b>	<b>120,216</b>

During the processing of raw materials of plant and animal origin in the food industry, by-products and residues are generated in large quantities. They occupy a firm position in the compound feedingstuff production (see Table 26 and Table 27), and rough estimates revealed that almost 20 % of the energy and protein consumption of the animal production sector in Germany is supplied *via* by-products suitable for feed (Flachowsky and Kamphues 1996).

The following Table 28 gives guide values for the amounts of by-products generated from selected raw materials during foodstuff production.

Table 28: Quantities of by-products generated within the production of selected foods (Flachowsky and Kamphues 1996)

Parent material	Main products	By-products	Quantity of parent material (in %)
Wheat	Flour (75-80 % extraction rate)	Bran Bran shorts and feed meal Germ	12-15 5-8 2-4
Maize	Starch	Gluten feed	30-40
Barley	Beer	Brewer's grains Yeast	25-35 5-6
Oil seeds	Oil	Press cake	60-90
Potatoes	Starch	Pulp	20-30
Sugar beet	Sugar	Shreds (moist, dry) Molasses	20-30 15-25
Fruit	Fruit juice	Marc (Pulp)	15-30
Livestock	Meat	Slaughtering by-products	30-60
Food	Meals	Food residues	50-160 g/meal

The variation shown on the very right column is mainly due to the production process itself. The quantity of by-products from oilseed processing *e.g.* varies between 60 and 90 %, depending on the degree of oil removal and the degree of milling, respectively.

Food residues from canteens, restaurants, *etc.* have a high potential for the re-utilization in feedingstuffs as they have a high nutritional value and are being generated in sufficient

quantities. On average, *per capita* and year 50-100 kg of food residues are generated in Germany. This means, that annually about 6 Mio. tons of food residues can be generated (Flachowsky and Kamphues 1996).

### 8.2.3 Treatment and Processing in General

There exists a multitude of different techniques employed for the treatment and processing of feedingstuffs. The most important ones are summarized in Table 29.

Table 29: Treatment and processing techniques

Treatment / Process	Technique	Feedingstuff
Cleaning	Separating and sieving	Grain, pulses, compound feedingstuff components
	Washing and mechanical cleaning	Root crops, beet leaves
Mechanical Treatment and processing	Chopping	Green forage, dried forage, hay, straw
	Shredding and mashing	Beets, potatoes
	Milling and grinding	Grain, pulses, oilseeds, by-products from the vegetable oil and fat production (e.g. oil cakes, expeller)
	Scouring (husking)	Grain, pulses, oilseeds
	Pressing of grinded and chopped materials	Hay, straw, dried green forage
Biological treatment	Germination (enzyme activation)	Grain, pulses, oilseeds
	Soaking (enzyme activation)	Grain (rye, barley)
	Enzymatic treatment	Grain, pulses, raw fiber rich materials, slaughter-house waste
	Ensiling	Green forage, maize
Chemical treatment	Water extraction (removal of soluble non-starchy-polysaccharides)	Barley, rye
	NaOH-treatment (Soda grain-processing)	Grain
	Treatment with formaldehyde	Oilseed extraction residues (e.g. coarse meal of rape and soy)
	Alkaline treatment with NaOH, KOH <i>etc.</i> (enhancement of digestibility)	Straw
	Hydrolysis with acids, e.g. HCl, H <sub>2</sub> SO <sub>4</sub> (feeding of non-ruminants)	Straw

Treatment / Process	Technique	Feedingstuff
Thermal and hydro-thermal treatment	Hot-air drying	Green forage, grain, sugar beet shreds, fruit pulp
	Toasting	Oilseed extraction residues ( <i>e.g.</i> coarse meal of rape and soy)
	Steam sterilization	Raw materials for animal and fish meal production, food residues
	Pelleting	Compound feedingstuffs
	Extruding, expanding	Feedingstuffs for piglets and poultry, protein feedingstuffs for ruminants

In most cases the production processes *per se* do not generate PCDD and PCDF; however, experiences have shown that a dioxin and furan contamination entering a process or an equipment can be transferred into products and processes further down the production lines. Very often also cleaning or extraction steps in a process generate dioxins and furans, *e.g.* if UV-light is present or strong alkali is being applied. Within the group of the feedingstuff treatment techniques and technologies potential sources of PCDD/PCDF occurrence may be:

- Spillage or leakage of hydraulic liquids (containing PCB or chlorinated benzenes) from equipment;
- Oil spraying for dust control in the feedingstuff production;
- Transfer of PCDD/PCDF or other POPs contamination during transport; *e.g.* transport containers are usually not cleaned between transports so that transfer from a former load can occur. Examples in the past have been the transfer of halogenated scavengers used in leaded gasoline which was transferred into unleaded gasoline and diesel (subsequently, higher PCDD/PCDF emissions have been measured in automobile exhaust than in later periods when laded gasoline was no longer available on the EU market);
- Dead volumes can serve as catchment locations for contaminants, *e.g.* in caolinite mills where the contamination from highly contaminated batches was transferred into the next batches.

Problems that have been associated in the past with the formation of PCDD/PCDF are described in the following sections (8.2.3.1 –Hot Air Drying, 8.2.3.2 – Cereal Cleaning, and 8.2.3.3 – Breeding and Storage).

### 8.2.3.1 Hot-Air Drying

Huge amounts of greens, such as grass, beet leaves or lucerne as well as grain and pulp are dried in hot-air drying plants, *esp.* in France, Denmark and Germany.

The consumption figures of dried greens for Germany (data for the other EU Member States is not available) mounted up to 468,009 tons in 1999. Of these, 340,902 tons were produced domestically, 23,779 tons have been exported and 150,886 tons have been imported (Bundesfachverband Landwirtschaftlicher Trocknungswerke Deutschland e.V.). The import of dried greens into Germany for the year 1999 looks as shown in Table 30. The total imports were 138,343 tons from EU Member States and 12,543 tons from other countries.

Table 30: Import of dried greens into Germany in the year 1999 (Bundesfachverband Landwirtschaftlicher Trocknungswerke Deutschland e. V.)

From:	Import (tons):	From:	Import (tons):
France	80,532	Poland	690
Denmark	38,279	Czech Republic	5,522
Netherlands	18,092	Slovak Republic	170
Belgium	188	Hungary	39
Italy	115	USA/Canada	378
Great Britain	10	Australia	2,620
Austria	1,101	Others	1,479
Switzerland	1,681		

Presently, there are 72 hot-air drying plants operating in Germany; the plants run on a variety of fuels. A summary of the number of plants and fuels being utilized in 1999 is shown in Table 31.

Table 31: Types of fuels used in German hot-air drying plants and annual production figures (Bundesfachverband Landwirtschaftlicher Trocknungswerke Deutschland e.V.)

Type of fuel	No. of Drying Plants	Production Figures (1999)
Fuel oil	13	39,072 tons
Gas	36	225,586 tons
Biomass	11	46,736 tons
Coal	12	29,508 tons

There are two types for hot-air drying devices: direct and indirect drying. In direct drying systems, the hot fumes are directly passed through the drying drum, whereas in indirect drying heating the drum is performed from outside. Due to a better efficiency, most of the drying plants use the direct process as shown in Figure 4. The grass is fed to the drum via a chopper. Hot fumes from the burner are mixed with ambient air at the front end of the drum in order to achieve a drying gas temperature of approximately 300-500 °C. The process is set-up in such a way that the fumes and the grass are in direct contact and thus, if any PCDD/PCDF is contained in the fumes, these may adsorb and be absorbed into the grass. Depending on the fuel utilized, the PCDD/PCDF concentrations can be in the order of several ng I-TEQ/m<sup>3</sup> (see section 8.4.3). High concentrations of PCDD/PCDF can be expected if contaminated fuels, such as treated wood or waste wood or other combustible materials, such as textiles, leather or dried sludges are burnt.

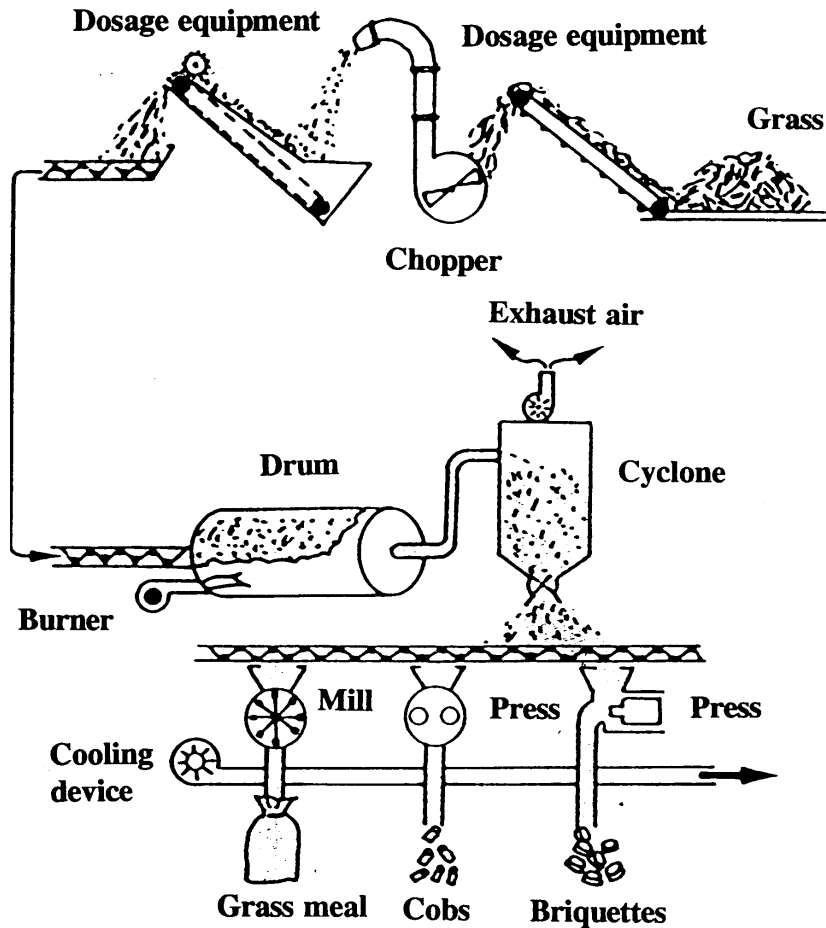


Figure 4: Schematic drawing of a plant for hot-air drying of feedingstuffs (Alsing 1995, adapted)

More research is required on the influence of the fuels employed, the importance of soil impurities in the fresh material, and finally on the emissions via exhaust air.

### 8.2.3.2 Cereal Cleaning

Grain processing is complex. The principle procedure is milling. Before the grain can be milled, it has to go through different grain cleaning machines. Usually, an aspirator is used as the first step of cleaning. In cereal cleaning there are two different principles: separating grain from weeds and other material in a jet of air according to different weight, and separating through shaking sieves according to different size of the material. A schematic drawing is provided in Figure 5.



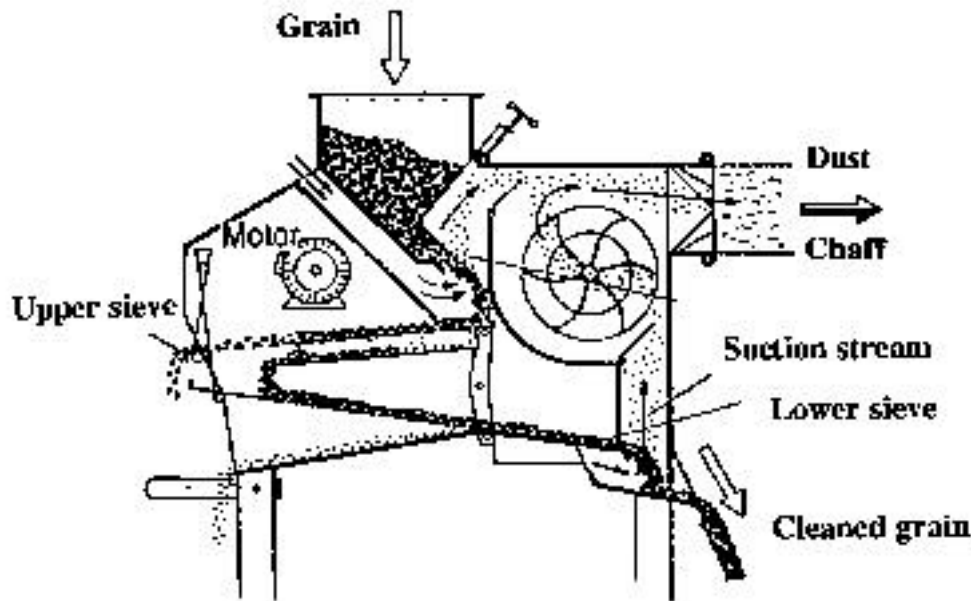


Figure 5: Schematic drawing of equipment to clean cereals (Alsing 1995, adapted)

The residues from this cleaning process, the so-called ‘aspiration dust’, are normally used for feedingstuff production. An analysis of ‘aspiration dusts’ for PCDD/PCDF (Schöppe *et al.* 1996) revealed high concentrations of PCDD and PCDF and thus, this fraction may represent a significant source of feedingstuff contamination (see Chapter 8.4.3).

### 8.2.3.3 Breeding and Storage – Impurities in Paints and Coatings

Within the agricultural foodchain and in aquaculture there are many containers and equipment that are treated with biocides and herbicides. Pentachlorophenol (PCP) for example, has been widely used in agriculture and farming and also polychlorinated biphenyls (PCB) have been used in construction business. The following section 8.3 highlights the use of chlorinated biocides, import and use patterns of PCP in the European Union’s Member States as well as the uses and stocks of PCB.

## 8.3 Products and Wastes with the Potential of POPs Contamination

Some POPs are or were commercially produced for given purposes. As most POPs (of the twelve) are no longer produced in the Member States of the European Union and many other countries, new products may play a minor role in the contamination of feedstuffs and foods. However, there are still many POPs, which are present in stocks or waiting final disposal. This section will address wastes with the potential to be contaminated with any of the twelve POPs. Further, wastes or waste fractions have been selected, which are not specifically excluded from use in the feedstuff production.

### 8.3.1 The European Waste Catalogue

The European Waste Catalogue categorizes wastes with the so-called EWC numbers. In this section (Table 32) we display several waste types of different origin contained in the EWC, which have the potential to be utilized in the feedingstuff production. It should be mentioned that Table 32 is an indicative list and waste numbers have been chosen to criteria such as:

- High energetic value or rich in nutrients
- High content of fibres
- Oily consistence and thus can be mixed up with edible oils and fats
- Potential of leakages or spillages during processing and transport.

Table 32: Wastes included in the European Waste Catalogue/Council Directive 75/442/EEC with the potential to be used in the feedingstuff industry.

EWC-No.	Type of Waste
<b>02</b>	<b>Waste from agricultural, horticultural, hunting, fishing, and aquaculture primary production, food preparation and processing</b>
<i>02 01</i>	<i>Primary production waste</i>
02 01 02	Animal tissue waste
02 01 03	Plant tissue waste
02 01 06	Animal feces, urine and manure (including spoiled straw), effluent, collected separately and treated off-site
02 01 07	Waste from forest exploitation
<i>02 02</i>	<i>Waste from the preparation and processing of meat, fish and other foods of animal origin</i>
02 02 02	Animal tissue waste
02 02 03	Materials unsuitable for consumption or processing
02 02 04	Sludges from on-site effluent treatment
<i>02 03</i>	<i>Waste from fruit, vegetables, cereals, edible oils, cocoa, coffee and tobacco preparation, processing, conserve production, tobacco processing</i>
02 03 01	Sludges from washing, cleaning, peeling, centrifugation and separation
02 03 03	Waste from solvent extraction
02 03 04	Materials unsuitable for consumption or processing
02 03 05	Sludges from on-site effluent treatment
<i>02 04</i>	<i>Wastes from sugar processing</i>
02 04 03	Sludges from on-site effluent treatment
<i>02 05</i>	<i>Wastes from the dairy products industry</i>
02 05 01	Materials unsuitable for consumption or processing
02 05 02	Sludges from on-site effluent treatment
<i>02 06</i>	<i>Wastes from baking and confectionery industry</i>
02 06 01	Materials unsuitable for consumption or processing
02 06 03	Sludges from on-site effluent treatment
02 07	Wastes from the production of alcoholic and non-alcoholic beverages (excluding coffee, tea and cocoa)
02 07 02	Waste from spirit's distillation
02 07 03	Waste from chemical treatment
02 07 04	Materials unsuitable for consumption or processing
02 07 05	Sludges from on-site effluent treatment

EWC-No.	Type of Waste
<b>03</b>	<b>Wastes from wood processing and the production of paper, cardboard, pulp, panels and furniture</b>
<i>03 01</i>	<i>Wastes from wood processing and the production of panels and furniture</i>
03 01 01	Waste bark and cork
03 01 02	Sawdust
03 01 03	Shavings, cuttings, spoiled timber/ particle board/ veneer
<i>03 03</i>	<i>Wastes from pulp, paper and cardboard production and processing</i>
03 03 01	Bark
03 03 06	Fibre and paper sludge
03 03 07	Rejects from paper and cardboard recycling
<b>04</b>	<b>Wastes from the leather and textile industry</b>
<i>04 01</i>	<i>Wastes from the leather industry</i>
04 01 01	Fleshing and lime split waste
04 01 08	Waste tanned leather (blue sheetings, shavings, cuttings, buffing dust) containing chromium
04 01 09	Wastes from dressing and finishing
<i>04 02</i>	<i>Wastes from textile industry</i>
04 02 01	Wastes from unprocessed textile fibres and other natural fibrous substances mainly of vegetable origin
04 02 02	Wastes from unprocessed textile fibres mainly of animal origin
04 02 04	Wastes from unprocessed mixed textile fibres before spinning and weaving
04 02 05	Wastes from processed textile fibres mainly of vegetable origin
04 02 06	Wastes from processed textile fibres mainly of animal origin
04 02 08	Wastes from processed mixed textile fibres
04 02 10	Organic matter from natural products ( <i>e.g.</i> grease, wax)
<b>13</b>	<b>Oil wastes (except edible oils)</b>
<i>13 01</i>	<i>Waste hydraulic oils and brake fluids</i>
13 01 01	Hydraulic oils containing PCB's or PCT's
13 01 02	Other chlorinated hydraulic oils (not emulsions)
13 01 07	Other hydraulic oil
13 01 08	Brake fluids
<i>13 02</i>	<i>Waste engine, gear and lubricating oils</i>
13 02 01	Chlorinated engine, gear and lubrication oils
13 02 02	Non-chlorinated engine, gear and lubrication oils
13 02 03	Other engine, gear and lubrication oils
<i>13 03</i>	<i>Waste insulating and heat transmission oils and other liquids</i>
13 03 01	Insulating and heat transmission oils and other liquids containing PCB's or
13 03 02	Other chlorinated insulating and heat transmission oils and other liquids
13 03 03	Non-chlorinated insulating and heat transmission oils and other liquids
<b>19</b>	<b>Wastes from waste treatment facilities, off-site waste water treatment plants and the water industry</b>
<i>19 01</i>	<i>Wastes from incineration or pyrolysis of municipal and similar commercial, industrial and institutional waste</i>
19 01 06	Aqueous liquid waste from gas treatment and other aqueous liquid wastes
19 01 07	Solid wastes from gas treatment
<i>19 05</i>	<i>Wastes from aerobic treatment of solid wastes</i>
19 05 01	Non-composted fraction of municipal and similar waste
19 05 02	Non-composted fraction of animal and vegetable waste
<i>19 06</i>	<i>Wastes from anaerobic treatment of wastes</i>

EWC-No.	Type of Waste
19 06 01	Anaerobic treatment sludges of municipal and similar wastes
19 06 02	Anaerobic treatment sludges of animal and vegetal wastes
19 08	<i>Wastes from waste water treatment plants not otherwise specified</i>
19 08 03	Grease and oil mixture from oil / waste separation
19 08 04	Sludges from treatment of industrial waste water
19 08 05	Sludges from treatment of urban waste water
<b>20</b>	<b>Municipal Wastes and similar commercial, industrial and institutional wastes including separately collected fractions</b>
20 01	<i>Separately collected fractions</i>
20 01 08	Organic compostable kitchen waste ( including frying oil and kitchen waste from canteens and restaurants)
20 01 09	Oil and fat
20 03	<i>Other municipal waste</i>
20 03 02	Waste from markets

The *Commission Decision 91/516/EEC* established a list of ingredients (wastes) whose use is prohibited in compound feedingstuff production:

1. Faeces, urine as well as separated digestive tract content resulting from the emptying or removal of the digestive tract, irrespective of any form of treatment or admixture;
2. Leather and leather waste;
3. Seed and other plant propagating materials which, after harvest, have undergone specific treatment with plant protection products for their intended use (propagation), and any derived by-products;
4. Wood, sawdust and other materials derived from wood treated with wood protection products;
5. Sludge from sewage plants treating wastewaters.

Furthermore, the use of protein products obtained from *Candida* yeasts cultivated on *n*-alkanes in feedingstuffs is prohibited by the *Commission Decision 85/382/EEC*.

Despite these prohibitions and as the Belgian chicken accident has shown, illegal utilization of the above mentioned substances, mixtures or wastes in the feedingstuff production cannot be ruled out. It has been reported, that the sludge from the factory-owned purification plant was mixed with animal meal for many years in a French compound feedingstuff factory. A similar case has been recognized in Germany (<http://www.spiegel.de>).

Some wastes from the EWC catalogue with a high potential of being used in the feedingstuff industry will be discussed in the sections below.

### 8.3.1.1 *Animal Waste*

Breeding of animals and processing of their products can cause various types of wastes:

- losses from breeding and fattening (e.g. eggs, chicken, dead animal bodies, etc.);
- slaughter-house wastes;
- wastes from the meat producing and finishing industries;
- wastes from treatment and processing of skins, feathers, wool, bristles, etc.

Most of these animal wastes get to the rendering industry. It is estimated that over 12 Mio. tons of material are processed in the rendering industry in the EU per year (Table 33).

Table 33: Estimates of amounts of animal wastes processed in the rendering industry in the EU in 1995 (Böhm 1997)

	x 1,000 tons
Belgium	350
Denmark	720
Germany	2,191
Finland	65
France	3,000
Greece	16
United Kingdom	1,300
Ireland	300
Italy	1,650
Netherlands	970
Austria	250
Portugal	100
Sweden	119
Spain	1,100
<b>Total</b>	<b>12,313</b>

The rendering industry in the EU supplied about 3.2 Mio tons of animal meals and about 1.3 Mio tons of animal fats in 1995 (Table 34). Main producers were France (32 %), Germany (18 %) and Italy (15 %).

Table 34: Production figures for animal meals and animal fats in the EU in 1995 (Böhm 1997)

	Production of animal meals (tons)	Production of animal fats (tons)
Belgium/Luxembourg	147,000	64,000
Denmark	189,226	78,964
Germany	549,578	244,832
Finland	24,000	8,500
France	714,350	319,980
Greece	5,000	no data
United Kingdom	360,000	125,000
Ireland	89,000	49,000
Italy	459,000	160,000
Netherlands	295,400	79,000
Austria	76,949	26,500
Portugal	30,000	12,000
Sweden	40,800	34,500
Spain	369,000	142,500
<b>Total</b>	<b>3,259,303</b>	<b>1,345,279</b>

Disposal and processing of animal waste and its placing on the market is regulated by the Council Directive 90/667/EEC. For prevention of pathogens animal waste must be heated to a temperature of at least 133 °C for 20 minutes at a pressure of 3 bar.

### 8.3.1.2 Used Oils and Fats

In Germany and perhaps in Europe, there exist a number of specialized companies dealing with the disposal of used oils and fats. Besides these, there is a considerable grey and black market of collectors. For the year 1995, it has been estimated that a total of 300,000 tons of waste oils and fats were available on the market in Germany. Of these, approximately 200,000 t/a have been collected and were made available for other uses, among these by the feedingstuff industry to a large extent. As a general trend it can be expected that low prices will result in minor qualities.

The major providers of used oils were as follows (no quantitative numbers available):

- Frying and roasting fats from canteens, restaurants, *etc.*;
- Frying and cooking fats from households;
- Frying and cooking fats from the food industry;
- Hydraulic oils on basis of vegetable oils;
- Residues from slaughter and fats from animals;
- Residual fats from food, and
- Fats from decanters.

### 8.3.1.3 Olive Pulp

The reason for inclusion of olive pulp is that of the worldwide olive oil production of about 2.4 million tons per year, 78 % (about 1.9 million tons) are produced in the European Union <sup>6</sup>. In the Mediterranean region more than 95 % of the world's olives are harvested; the highest yield is achieved in Spain and more than 200 million of the world's nearly 800 million olive trees are cultivated in Spain (IMPROLIVE 2000). Based on these economic data it can be assumed that olive pulp as well as other residues from the oil and fat production, can be used in the feedingstuff industry. Especially the pulp can be used as fertilizer or fodder.

The olive oil production is also a producer of large amounts of waste: about 400 kg of liquid waste are produced per ton of processed olives. Actually, the IMPROLIVE project, funded by the EU, suggests to recycle wastes from the olive oil production for fertilizer production and livestock feeding.

#### 1. Fertilizer

Research at the Laboratory for Microbiology of the Athens University has shown that margine is a good substrate for a certain microbial fauna. It is especially useful to produce fertilizer for agricultural purposes. Under aerobic conditions the margine content helps the qualitative breeding of nitrogen-consuming bacteria, especially of the so-called acetobacter.

#### 2. Livestock feeding:

Just like the use as fertilizer, the dried oil wastes are used without previous treatment as livestock feeding, due to their nutrients properties. Nevertheless, in this case, as well, the process might be improved by means of a biological treatment, controlling this way the fodder characteristics (absence of pollutants and suitability).

Further, treatment of the sludges <sup>7</sup> by white rot fungi seems to be a method to dispose the solid wastes from olive pulp production. From white rot fungi it is known that they can break down phenolic structure and also lower chlorinated aromatic hydrocarbons. However, the same extracellular enzymes can also very efficiently dimerize chlorophenols to form dibenzodioxins and dibenzofurans as has been shown in sewage sludge and compost (Öberg *et al.* 1993, Wagner *et al.* 1990).

Although the EU project concludes that "The use of organic waste as compost or fodder provides only limited market opportunities which in particular is due to the risks of pollution and market disadvantages when competing with products not using waste as raw material." These possibilities should be further evaluated.

As presently there is no information available from this sector, we placed the issue of the olive oil production and associated processes as a priority for research. It should be already

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<sup>6</sup> Other main producers are Tunisia (170 000 tons), Turkey (190 000 tons), Syria (110 000 tons) and Morocco (70 000 tons).

<sup>7</sup> In Spain, 30 Mio tons of sludge are generated annually from the olive oil production. For comparison the total amount of municipal sewage sludge in Germany amounts to 55 Mio m<sup>3</sup> per year (for a 80 Mio population). The sludge is heavily polluted by fats, harmful substances and solids. In the production areas the sludges are usually discharged into evaporation basins and dried by solar radiation during the summer months

noted at this point that the whole industry involves many small producers and thus, at least in Spain, exhibit a very scattered pattern.

Further, few data from Spain indicate that PCDD/PCDF concentrations in pulses and cereals are higher than have been reported elsewhere. The results of PCDD/PCDF analyses are given in Section 8.4.5.

Harvest residues such as rice straw has a potential to contain PCDD/PCDF. Although no analytical data exist to our knowledge, it is known at least from the United States that PCP and its derivatives have been applied in rice paddies. It can be expected that the dioxin contamination will transfer to the outer parts of the plants. After harvest, these residues may either stay on the field, be burnt (attention: high dioxin formation potential!) or being used in various industries, *e.g.* furniture, household goods or in the feedingstuff industry. Once again, there exist a potential to transfer dioxin contamination into another sector but no hard data are available.

#### 8.3.1.4 *Agricultural and Industrial Wastes with High Fibre Content*

Harvest residues like straw from grain and pulse cultivation are used as feedingstuffs mainly due to their high content of fibres. Especially rice straw has a potential to contain PCDD/PCDF. Although no analytical data exists to our knowledge, it is known at least from the United States that PCP and its derivatives have been applied in rice paddies. It can be expected that the dioxin contamination will transfer to the outer parts of the plants. After harvest, these residues may either stay on the field, be burnt (attention: high dioxin formation potential!) or be used in various industries, *e.g.* furniture, household goods or in the feedingstuff industry. Once again, there exists a potential to transfer dioxin contamination into another sector, but no hard data is available.

Generally, chemical treatment techniques are employed to enhance the digestibility and thus the feed value of straw (Table 28). There is, however, no information on possible consequences for the contaminant content of this feedingstuff.

Industrial wastes rich in fibre and therefore suitable for feeding purposes are generated above all by the wood processing and paper industry. 20-30 % of the dry mass uptake of ruminants *e.g.* can be accomplished through cellulose and other by-products from the paper industry (Jeroch *et al.* 1993). Besides, saw dust and wood shavings may serve as fillers in compound feedingstuffs. Wood, sawdust and other materials derived from wood treated with wood protection products, or pulp from the processing of recycling paper (see chapter 3.2.2.1) are examples for potential sources of feedingstuff contamination.

#### 8.3.2 Pentachlorophenol

Pentachlorophenol is still an issue in the EU. According to information from OSPAR (2000), production of PCP and PCP-Na was ceased in the EU in 1992. However, both chemicals are being imported from the United States of America into the European market. Further, there are indications that imports may also come from Southeast Asia. In 1996, a total of 378 tons of PCP-Na and 30 tons of PCP have been imported into EU Member countries. Of the 378 tons of PCP-Na, 126 went to France, 108 tons to Portugal and 144 tons to Spain. 28 of the 30



tons of imported PCP went to the UK to be transformed into 46 PCP-L (pentachlorophenyl laureate), the remainder 2 tons went in equal amounts to two distributors in the EU. Of 46 tons of PCP-L, 5-10 tons were used domestically in the UK, 5-10 tons were exported to France and the rest exported to customers outside the EU.

In the USA, there are still two producers, which export PCP and PCP-Na to Europe. According to their information, the production numbers declined slightly within the last years. The PCP is being sold to the UK for the manufacture of PCP-L, which in turn is then being used exclusively as a preservative in the textile industry. The production numbers are given in Table 35.

Table 35: Export of PCP and PCP-Na of two U.S. producers (metric tons per year)

Compound / Year	1996	1997	1998	1999
PCP	75	15	30	15
PCP-Na	397	385	341	324

Some PCP-Na is used in the treatment of construction timber. The major use of PCP-Na occurs mainly in southwest France, northeast Spain and Portugal for sapstain control of freshly cut timber (OSPAR 2000). Especially low quality pine for the fabrication of non-returnable pallets/pallet boards is often treated with PCP-Na accounting for almost 90 % of the total PCP, PCP-Na and PCP-L usage in 1996.

From the above outlined use pattern of PCP and its derivatives it becomes obvious that the use of these chemicals in short-lived applications poses a potential threat to contaminate recycling operations with PCDD/PCDF. In the USA, virtually all PCP sold domestically today is used for pressure treatment of wood.

According to EU Directive 1999/51/EC, the anti-sapstain and the wood preservation use of PCP-Na and PCP will cease on December 31, 2008 in France, Ireland, Portugal, Spain and the UK. In the other EU Member States, where there are no bans of PCP and its derivatives, these uses will cease by December 31, 2000. Some countries, such as Austria, Denmark, Finland, Germany, the Netherlands, Norway, Sweden (and Switzerland as a non-EU Member State) have banned PCP and its derivatives through national legislation.

The first EU Directive to address PCP and its derivatives was Council Directive 91/173/EEC (of March 21, 1991), which prohibits the marketing of PCP-containing products to concentrations equal or greater than 0.1 % by mass (1,000 ppm). The Directive also gives a maximum concentration of 4 ppm (4,000,000 ng/kg PCP or formulation) for the sum of all Cl<sub>6</sub>DD isomers (sum of hexachlorinated dibenzo-*para*-dioxins). Council Directive 1999/51/EC lowered the maximum permissible concentration of Cl<sub>6</sub>DD to 2 ppm (2,000,000 ng/kg PCP or formulation).

### Conclusion and Recommendation:

The information on imports, uses and exports of PCP and its derivatives in the Member States of the European Union remains still unclear although presently, there is no production of PCP and PCP-Na ongoing. In addition to the uncertainty about present uses, there is import of PCP-treated wood, textiles and leather into the Member States of the EU. Data by Horstmann and McLachlan, Malisch and others have shown that these consumer goods may contain high concentrations of PCDD/PCDF caused by the impurities from commercial PCP and PCP-Na (AEA 1999, Task 2). The import of such materials cannot be controlled at the borders of the

EU Member States as there is no simple test to determine PCDD/PCDF concentrations. As these consumer goods and wood can end in recycling processes, there exists a potential to have dioxins and furans entering the foodchain; *e.g.* treated wood chips being used in chicken farming, treated wood being used a fuel for green fodder drying.

PCP-treated packaging materials, wood, cotton (bags), plastics may transfer the dioxin contamination into the feedingstuff packaged. Presently, there is no knowledge about the transfer of PCDD/PCDF from PCP-treated packaging materials into feedingstuffs. Also, there is no regulation within the EU to control the transfer of contaminants from packaging materials into food or feedstuffs. It has been shown in the past that the PCDD/PCDF contamination of paper-based milk cartons did transfer the contamination into the milk. As a countermeasure, the producers of paper used in the food-packaging industry committed themselves to supply only papers with less than 1 ppt TEQ (1 ng I-TEQ/kg).

As pentachlorophenol is presently used only in a limited number of countries, there seems to be no need for action on Community basis; however, countries still using PCP and its derivatives should be encouraged to initiate national legislation to cease the use of PCP and to eliminate this source of PCDD/PCDF. Lastly, it should be mentioned that PCP *per se* is toxic and is a POPs chemical under the POPs Protocol in the UN-ECE LRTAP Convention (UN-ECE 1999).

### 8.3.3 Commercial PCB Mixtures

This chapter briefly summarizes the present knowledge on how much PCB have been produced, what has been disposed of and which amounts of PCB are still in storage or in use.

The commercial production started about 60 years ago and the commercial products were available under several trade names, *e.g.* Clophen (produced by Bayer AG, Germany), Aroclor (by Monsanto, USA), Kanechlor (by Kanegafuchi, Japan), Santotherm (by Mitsubishi, Japan), Phenoclor and Pyralene (by Prodolec, France). The total amount produced world-wide is estimated at 1.5 million tons (Ivanov and Sandell 1992, Rantanen 1992).

The unwanted and accidental releases of PCB into the environment and subsequent exposures to PCB resulted in a cease out of production and new uses of PCB in western, industrialized countries. For example, in Japan, the production of PCB, marketed under the trade name "Kanechlor (KC)", was started by Kanegafuchi Chemical Co. Ltd. (Kaneka) in 1954 and in 1972, production, use and import were banned. In 1977, in the USA, the Monsanto industrial Chemical Company (the market leader with 98 % of PCB/PCT production) terminated production and export. In (West-)Germany the Bayer AG produced PCB under the trade name Clophen (A30 to A60). In 1972, the Bayer AG restricted their supply of PCB for use in closed systems (transformers, condensers, hydraulic fluid), which resulted in a total of 23,000 t of PCB in "open uses". In Germany, production of PCB was voluntarily stopped in 1983 (Fiedler 1998).

In 1998/99 UNEP sent out questionnaires to countries to ask about the status of PCB production, use and disposal. Although the data in this compilation cannot be more than a snapshot on the present information and the datasheets have not been reviewed, it gives some useful information.

Among the countries with responses are Vietnam and Bulgaria with no legislation on PCB. Bulgaria reported imports of 110 t of PCB in 1990 and 90 t in 1995.

The UNEP compilation found stockpiles of old PCB as shown in Table 36. There are about 70,000 tons of stockpiled PCB to be disposed of recently or in the near future. For example, in Germany, a total of 23,000 tons has been removed between 1994 and 2000 (the latest date to comply with national legislation was 31.12.1999).

Table 36: Stockpiles PCB by country and year (UNEP 2000)

Country	Tons of PCB	Reference Date
Canada	22,150	1990
Finland	300	1.1.1983
Germany	23,000	1994-2000
Japan	0.04	1996
Korea	38	
Mexico	7,100	
Russian Federation	12,780	1.1.1996
Slovak Republic	2,791	1.1.1998
Switzerland	2	1.1.1998
TOTAL	68,161.42	

Table 37 gives an overview on PCB that have been exported by countries without own destruction facilities.

Table 37: Waste PCB exported for destruction by country and year (UNEP 2000)

Country	Tons Exported	Reference Year
Chile	141	since 1992
Costa Rica	200	1997/98
Croatia	16.204	1997
Republic of Guinea	108	since 1982
Ireland	83	1996
Republic of Korea	94	1996
New Zealand	243	1997
Norway	752	
Slovenia	232	
Thailand	to France and UK	

Among the PCB producers was also the Slovak Republic, which reported a total PCB production of 21,482 tons between the years 1959 and 1984. Of these, 17,677 t have been exported under the trade name of Delor to the Czech Republic, the former German Democratic Republic of Germany and the member states of the COMECON. Further, 266 tons have been imported into the Slovak Republic. Presently, it is estimated that 4,071 t are still in use with the main use sectors as paint additives (1,433 t), heat exchangers (948 t), electric insulation (1,439 t) and others (241 t). Presently, there are 1,190 t of PCB stockpiled in facilities with capacitors and 1,601 t as waste (in a dump near the Chemko Stazke Co.).

The Republic of Korea like most other countries did never have a domestic production of PCB but imported 167 t as transformer oils (in the years 1963-1979) and lastly 63 t in 1998. In 1996, the country exported 94 t of pure PCB for destruction to facilities in the United

Kingdom and another 129.4 t from U.S. military bases have been exported to the U.K. for destruction in 1993.

Canada still has 10,781 t of high concentration PCB liquids in use. If low PCB concentration liquids would be included the total amount would be 12,556 t. In 1995, Canada has 2,953 PCB storage sites; of these 409 were federal and 2,544 were non-federal. The country estimates to have 141,452 t of PCB-containing waste.

Algeria reported 3,056 t of total imports, which are stockpiled now. Slovenia imported 3,688 t for use in the years 1962/1985. Of these, 67 t are stockpiled and 232 t have been exported for destruction. Croatia identified 405 enterprises using PCB transformer and condensers: 22,532 condensers carry 574 t of PCB wastes and 293 transformers carry 707 t of PCB wastes.

New Zealand imported PCB with a major use as ballast in fluorescent tube light fittings until 1977. In 1997, 243 t have been exported to France for destruction and 50 t are stockpiled as waste.

The Austrian inventory for 1995 reported PCB stockpiled at amounts 481-571 t from transformers and capacitors and 182.6 t of PCB-containing wastes. Disposal will be done by the end of the year 2015. Own destruction capacities are in the range of 1 t per year.

The People's Republic of China banned production of PCB in 1983. In the years 1965-1974, Trichlorobiphenyl (PCB<sub>3</sub>, a mixture  $\approx$  Aroclor 1242) and Pentachlorobiphenyl (PCB<sub>5</sub>, a mixture  $\approx$  Aroclor 1254) amounted to a production of 10,000 tons. In addition, in the 1970s and early 1980s, PCB have been imported from Belgium, France, Germany, and Japan for use by electric facilities (Wong 1999).

#### **8.4 Known PCDD/PCDF Contamination in Feedingstuffs and Potential Constituents**

This section summarizes results of PCDD/PCDF concentrations in feedingstuffs, its raw materials, additives or other products and wastes. The concentrations are listed on an I-TEQ and a WHO-TEQ basis. We found this necessary to list the data site by site as one of the recommendations from this study will be to switch from the International system to the WHO system. As most data are still published on an I-TEQ basis, we calculated the WHO-TEQ when congener-specific data were available. From the information shown below, "typical" concentrations will be chosen to calculate the influence of dioxin contamination on the feedingstuff and food production and finally levels in humans. As can be seen in the Tables from this section, there is not much of a difference between the values of the different schemes.

Unfortunately, for POPs other than dioxins and furans, there are almost no data available.

### 8.4.1 Feedingstuffs – Major Constituents

The basic constituents of feedingstuffs such as grain, silage, *etc.* normally do not pose a problem with respect to POPs and especially PCDD/PCDF concentrations.

Table 38: PCDD/PCDF concentrations in basic feedingstuffs

	I-TEQ	WHO-TEQ
Grass (Germany) <sup>a</sup> (pg/g d.m.)	0.11	0.12
Grass (Germany) <sup>b</sup> (pg/g d.m.)	0.13	0.14
Grass silage (Germany) <sup>b</sup> (pg/g d.m.)	0.34	0.37
Grass silage <sup>c</sup> (pg/g d.m.) / mean value; n = 39	0.17	-
Maize silage (Germany) <sup>b</sup> (pg/g d.m.)	0.096	0.10
Maize silage <sup>c</sup> (pg/g d.m.) / mean value; n = 26	0.081	-
Straw (Germany) <sup>b</sup> (pg/g d.m.)	0.11	0.12
Tubers and roots <sup>d</sup> (pg/g d.m.) / mean value; n = 2	-	0.036
Dried beet shreds <sup>e</sup> (pg/g d.m.)	0.56	0.51*

<sup>a</sup> McLachlan 1996 <sup>b</sup> Welsch-Pausch 1998 <sup>c</sup> Appuhn *et al.* 2000 <sup>d</sup> Malisch and Fürst 2000 <sup>e</sup> Schöppe *et al.* 1996; \* recalculated based on congener-specific data

Table 39: PCDD/PCDF concentrations in concentrates - grain

	I-TEQ	WHO-TEQ
Wheat (Germany) <sup>a</sup> (pg/g d.m.)	0.23	0.22*
Wheat (Germany) <sup>a</sup> (pg/g d.m.)	0.17	0.17*
Wheat (Germany) <sup>a</sup> (pg/g d.m.)	0.18	0.18*
Barley (Germany) <sup>a</sup> (pg/g d.m.)	0.14	0.13*
Barley (Germany) <sup>a</sup> (pg/g d.m.)	0.18	0.19*
Barley, cleaned (Germany) <sup>a</sup> (pg/g d.m.)	0.002	0.002*
Rye (Germany) <sup>a</sup> (pg/g d.m.)	0.19	0.19*
Rye (Germany) <sup>a</sup> (pg/g d.m.)	0.25	0.25*
Oat (Germany) <sup>a</sup> (pg/g d.m.)	0.15	0.15*
Triticale (Germany) <sup>a</sup> (pg/g d.m.)	0.068	0.066*
Cereals <sup>b</sup> (pg/g d.m.) / mean value; n = 21	0.015	-
Cereals and seeds <sup>c</sup> (pg/g d.m.) / mean value; n = 8	-	0.037
Cereals (Spain) <sup>d</sup> (pg/g f.w.)	0.25	-

<sup>a</sup> Schöppe *et al.* 1996 <sup>b</sup> Appuhn *et al.* 2000 <sup>c</sup> Malisch and Fürst 2000 <sup>d</sup> Schuhmacher *et al.* 1997

\* recalculated based on congener-specific data

Table 40: PCDD/PCDF concentrations in concentrates – oilseeds and pulses

	I-TEQ	WHO-TEQ
Rape – coarse meal (Germany) <sup>a</sup> (pg/g d.m.)	0.17	0.17*
Rape – coarse meal (Germany) <sup>a</sup> (pg/g d.m.)	0.42	0.42*
Rape – coarse meal (Germany) <sup>a</sup> (pg/g d.m.)	0.062	0.061*
Soya – coarse meal (Germany) <sup>a</sup> (pg/g d.m.)	0.19	0.19*
Soya – coarse meal (Germany) <sup>a</sup> (pg/g d.m.)	0.42	0.35*
Pulses (Spain) <sup>b</sup> (pg/g f.w.)	0.19	-

<sup>a</sup> Schöppe *et al.* 1996 <sup>b</sup> Schuhmacher *et al.* 1997

\* recalculated based on congener-specific data

### 8.4.2 Additives

In the recent months, feedingstuffs additives attracted some attention when it was discovered that one of the additives, clay - used as anti-caking agent – was found to contain PCDD/PCDF (see Chapter 6.3). As a preventive measure the EU set a maximum limit of 500 pg WHO-TEQ/kg for the PCDD/PCDF content for additives belonging to the group ‘Binders, anti-  
*Commission Regulation (EC) No. 2439/1999 and 739/2000*).

This regulation applies from March 1, 2000 and should be re-examined before October 2000. In spring 2000, the EU concluded that “Contaminated additives should be avoided as much as possible. An unacceptable degree of contamination of feedingstuffs should be prevented”.

An investigation of various compound feedingstuffs and ingredients (Appuhn *et al.* 2000) suggests that there are other crucial additives. Seven samples out of a total of 35 additives (*e.g.* vitamins and antibiotics) analyzed showed PCDD/PCDF concentrations above 500 pg I-TEQ/kg d.m. Since the congener pattern of these samples were similar to that of kaolinitic clay, which is probably used as a carrier, clay was supposed to be the cause for the occurrence of PCDD/PCDF in these additives, too.

Table 41: PCDD/PCDF concentrations in additives

	I-TEQ	WHO-TEQ
Bentonite <sup>a</sup> (pg/g)	0.19	0.20
Damoline <sup>a</sup> (pg/g)	0.14	0.14
Magnesite <sup>a</sup> (pg/g)	0.08	0.10
Magnesite <sup>a</sup> (pg/g)	0.05	0.05
Zeolite <sup>a</sup> (pg/g)	0.05	0.05
Sepiolite <sup>a</sup> (pg/g)	0.21	0.27
Sepiolite <sup>a</sup> (pg/g)	0.25	0.33
Sepiolite <sup>a</sup> (pg/g)	0.11	0.16
Ball clay (USA) <sup>b</sup> (pg/g)	730	720
Ball clay (USA) <sup>b</sup> (pg/g)	1000	1200
Kaolin <sup>a</sup> (pg/g)	193.24	232.31
Kaolin <sup>a</sup> (pg/g)	388.21	460.59
Kaolin (USA) <sup>b</sup> (pg/g)	0.22	0.32
Kaolin (USA) <sup>b</sup> (pg/g)	0.94	0.50
Kaolin (USA) <sup>b</sup> (pg/g)	0.21	0.23
Kaolin (Germany) <sup>b</sup> (pg/g)	140	198

<sup>a</sup> Eljarrat *et al.* 2000 <sup>b</sup> Rappe and Anderson 2000

Data from final commercial compound feedingstuff mixtures will be presented in chapter 8.5

### 8.4.3 Dried Greens from Hot-Air Drying

Table 42 gives the results of PCDD/PCDF analysis from dried greens in dependence of the fuel used in the drying process. Highest concentrations have been detected when wood was used as a fuel. The results can be compared with the limit value established by the EU for the dioxin concentration for citrus pulp. For comparison, the dioxin contamination in these additives can be compared with the maximum permissible concentration of 500 pg I-TEQ/kg

or 0.5 pg I-TEQ/g (for easier comparison with the results in Table 42) as set for citrus pellets by *Commission Regulation (EC) No. 2439/1999* and *739/2000*. On this basis, it can be seen from Table 42 that two of the ten samples exceeded this limit and three more exhausted more than 80 % of the limit value.

Table 42: PCDD/PCDF concentrations in dried greens

	I-TEQ	WHO-TEQ
Dried greens / Denmark / Fuel: Wood <sup>a</sup> (pg/g d.m.)	2.40	2.41*
Dried greens / Denmark / Fuel: Oil <sup>a</sup> (pg/g d.m.)	0.13	0.12*
Dried greens / Netherlands / Fuel: Coal <sup>a</sup> (pg/g d.m.)	0.31	0.31*
Dried greens / Germany / Fuel: Coal, Wood <sup>a</sup> (pg/g d.m.)	1.1	1.1*
Dried greens / Germany / Fuel: Gas <sup>a</sup> (pg/g d.m.)	0.37	0.36*
Dried greens / Germany / Fuel: Wood <sup>b</sup> (pg/g d.m.)	0.48	-
Dried greens / Germany / Fuel: Gas <sup>b</sup> (pg/g d.m.)	0.42	-
Dried greens / Germany / Fuel: Gas <sup>b</sup> (pg/g d.m.)	0.41	-
Dried greens / Germany / Fuel: Gas <sup>b</sup> (pg/g d.m.)	0.30	-
Dried greens / Germany / Fuel: Oil <sup>b</sup> (pg/g d.m.)	0.36	-

<sup>a</sup> Schöppe *et al.* 1996, <sup>b</sup> Mayer 2000

\* recalculated based on congener-specific data

At the end of 1999, elevated levels of PCDD/PCDF in feedingstuffs have been detected in the State of Brandenburg in Germany. Investigations revealed that hot-air drying plants that used treated wood and certain plastic wastes as fuel did cause the contamination of the dried greens (see section 6.4).

This „accident“ showed that hot-air drying has a high potential for feedingstuff contamination. The type of feed material seemed to have a direct impact on the level of contamination of the feedstuffs.

#### 8.4.4 Aspiration Dusts from Cereal Cleaning

During the mechanical treatment of the cereals in the cleaning process, aspiration dust is generated (for process description, see section 8.2.3.2). The fine dust particles have been analyzed for PCDD/PCDF and it was found that the dusts contained quite high concentrations, namely 4 and 14 ng I-TEQ/kg (Table 43). In numerals this means that 125 g or 36 g of aspiration dust in one kilogram of feedingstuffs would result in a contamination at the tolerance level. As the major constituent of the feedingstuff may not be completely free of PCDD/PCDF it can be expected that a few grams of aspiration dust can exclude a feedingstuff from the market.

Table 43: PCDD/PCDF concentrations of aspiration dust (Schöppe *et al.* 1996)

	I-TEQ	WHO-TEQ
Aspiration dust (pg/g d.m.)	3.7	3.6 *
Aspiration dust (pg/g d.m.)	14.1	14.1 *

\* recalculated based on congener-specific data

### 8.4.5 Raw Materials of Plant Origin

Schuhmacher *et al.* (1997) have published PCDD/PCDF concentrations in foodstuffs from Spain, or more precisely from Catalonia. Of the 35 samples analyzed, there were some food categories included which normally are not analyzed for dioxins and furans or other lipophilic organic compounds (such as POPs) as it is supposed that these foodstuffs do not contain these contaminants. Some results are shown in Table 44. It can be seen that pulses and cereals contain quite high concentrations of PCDD/PCDF (Note: the results are on fresh weight basis).

Table 44: PCDD/PCDF in food categories from Spain/Catalunya

Food Category	Concentration (pg I-TEQ/kg f.w.)
Vegetables	140
Pulses	190
Cereals	250
Fruits	90

Also from Spain, analysis of retail fish oil dietary supplement capsules gave PCDD/PCDF concentrations of 2.11 pg I-TEQ/g fat and PCB at a concentration of 0.31 pg I-TEQ /g fat.

These examples show that there is demand for research to either confirm these results or reveal analytical deficiencies. The results especially the high concentrations for foods of plant origin are unique for Spain and have not been found in any other country; although it should be mentioned that most surveys of food baskets do not analyzed foodstuffs such as grains, cereals, and fruits for PCDD/PCDF.

### 8.4.6 Byproducts from Various Processes

Table 45: PCDD/PCDF concentrations in by-products from starch and flour production

	I-TEQ	WHO-TEQ
Wheat bran (Germany) <sup>a</sup> (pg/g d.m.)	0.018	0.013*
Gluten (Germany) <sup>a</sup> (pg/g d.m.)	0.11	0.10*
Gluten (Germany) <sup>a</sup> (pg/g d.m.)	0.19	0.19*
Tapioca (Thailand) <sup>a</sup> (pg/g d.m.)	0.71	0.68*
Tapioca (Thailand) <sup>a</sup> (pg/g d.m.)	0.05	0.05*

<sup>a</sup> Schöppe et al. 1996

\* recalculated based on congener-specific data

Table 46: PCDD/PCDF concentrations in by-products from beverage production

	I-TEQ	WHO-TEQ
Citrus pulp (Brazil) <sup>a</sup> (pg/g d.m.)	5.89	-
Citrus pulp (Brazil) <sup>a</sup> (pg/g d.m.)	7.4	-

<sup>a</sup> Malisch 1998



Table 47: PCDD/PCDF concentrations in animal meals

	I-TEQ	WHO-TEQ
Meat-and-bone-meal <sup>a</sup> (pg/g fat)	2.72	2.82
Meat-and-bone-meal <sup>a</sup> (pg/g fat)	8.50	6.77
Animal meal <sup>b</sup> (pg/g d.m.) / (pg/g fat)	0.26 / 0.93	0.25* / 0.89*
Animal meal <sup>b</sup> (pg/g d.m.) / (pg/g fat)	0.10 / 0.69	0.09* / 0.62*
Animal meal <sup>c</sup> (pg/g d.m.) / mean value; n = 46	0.06	-

<sup>a</sup> Eljarrat *et al.* 2000 <sup>b</sup> Schöppe *et al.* 1996 <sup>c</sup> Appuhn *et al.* 2000

\* recalculated based on congener-specific data

Table 48: PCDD/PCDF concentrations in animal fat

	I-TEQ	WHO-TEQ
Animal fat <sup>a</sup> (pg/g fat)	0.75	0.72
Animal fat <sup>a</sup> (pg/g fat)	0.69	0.66
Animal fat <sup>a</sup> (pg/g fat)	0.48	0.52
Animal fat <sup>a</sup> (pg/g fat)	0.54	0.59
Animal fat <sup>b</sup> (pg/g fat)	0.80	-
Animal fat <sup>b</sup> (pg/g fat)	2.31	-
Animal fat <sup>b</sup> (pg/g fat)	0.05	-
Animal fat <sup>b</sup> (pg/g fat)	1.0	-
Animal fat (Northern Europe) <sup>b</sup> (pg/g fat)	0.18	-
Bone fat <sup>b</sup> (pg/g fat)	1.4	-

<sup>a</sup> Eljarrat *et al.* 2000 <sup>b</sup> Schöppe *et al.* 1996

Table 49: PCDD/PCDF concentrations in fish meal

	I-TEQ	WHO-TEQ
Fish meal <sup>a</sup> (pg/g fat)	3.28	3.21
Fish meal <sup>a</sup> (pg/g fat)	2.77	2.82
Fish meal <sup>a</sup> (pg/g fat)	1.42	1.46
Fish meal <sup>a</sup> (pg/g fat)	2.62	2.47
Fish meal <sup>a</sup> (pg/g fat)	8.00	9.08
Fish meal (North Sea) <sup>b</sup> (pg/g fat)	6.5	-
Fish meal (South America) <sup>b</sup> (pg/g fat)	1.5	-

<sup>a</sup> Eljarrat *et al.* 2000 <sup>b</sup> Schöppe *et al.* 1996

Table 50: PCDD/PCDF concentrations in food residues

	I-TEQ	WHO-TEQ
Canteen food <sup>a</sup> (pg/g fat) / mean value; n = 50	0.37	-
Food – adults (Germany) <sup>b</sup> (pg/g fat) / (pg/g d.m.)	0.24-1.3 / 0.05-0.25	-
Food – children (Germany) <sup>c</sup> (pg/g fat)/(pg/g d.m.)	0.31-1.7 / 0.06-0.43	-

<sup>a</sup> R. Mayer 1999 <sup>b</sup> Schrey *et al.* 1995 <sup>c</sup> Schrey *et al.* 1996

#### 8.4.7 Impurities in Pentachlorophenol and Its Derivatives

Pentachlorophenol and its derivatives are classified as POPs in the POPs Protocol (Aarhus Convention) under the LRTAP Convention of the UN-ECE. They are not included in the initial list of the 12 POPs under negotiation for a global convention. Nevertheless, as the EU and its Member States are in the process to sign the Aarhus Convention, the marketing and use of PCP in the Member States are of importance for potential contamination of feedingstuffs.

Commercial mixtures of PCP and PCP-Na can have PCDD/PCDF contamination ranging from some  $\mu\text{g}$  I-TEQ/kg to 2 mg I-TEQ/kg or more depending on the manufacturing process and the compound.

Research by USDA (United States Department of Agriculture, Fries, 1997) has shown that cattle fed PCP-treated wood in their diet excreted  $\text{Cl}_8\text{DD}$  in high quantities. The amount excreted was almost four-fold greater than the amount that has been ingested. These results show that dioxins, present as contamination in the commercial product (PCP), are ingested but more importantly point to the possible *in vivo* formation of  $\text{Cl}_8\text{DD}$  from pre-dioxins, *i.e.* chlorinated phenoxyphenols and pentachlorophenol.

The choline chloride case (see section 6.5) is an example that PCP-contaminated wood can enter the feedingstuff industry.

#### 8.4.8 Impurities in Polychlorinated Biphenyls

The dual principle where the product itself is a POP and the fact that the POPs product is being contaminated with another POP exists for PCB. PCB are one class of POPs under the Aarhus Convention and will be under the Global POPs Convention.

Commercial PCB mixtures contain approximately 130 of the 209 possible PCB congeners. Of these, the dioxin-like PCB (more precisely, the 12 with TEFs assigned by WHO) are of minor importance. Nevertheless, PCB are contained in high concentrations from a few percent to almost 100 % in electrical equipment such transformers and capacitors.

Further, PCB are contaminated through the production process with PCDF. On a TEQ basis, the contamination ranges from 15,000 ng I-TEQ/kg to 1.5 mg I-TEQ/kg with the higher concentrations found in the higher chlorinated PCB mixtures, *e.g.* Clophen A60, Aroclor 1260. It can be assumed that during the use phase and under thermal stress, the biphenyls will close the rings and form PCDF resulting in an overall increase of the TEQ.

As has been shown in the recent Belgian chicken accident, a few kilogram of commercial PCB – 20 kg – caused a severe feedstuff poisoning (see section 6.2).

Further, due to the wide range of open application, *e.g.* in sealants, paints, flame retardants, *etc.*, it cannot be excluded that a PCB contamination present in buildings can transfer into raw materials or additives during storage or transport. Lastly, leakages and spillages of PCB-containing equipment as has been shown in the rice oil poisonings in Taiwan and Japan (Yucheng and Yusho accidents – Guo *et al.* 1994, Needham 1993 and Masuda 1994) cannot be excluded.

## Conclusion and Outlook

According to UNEP information, presently there seems to be no production of PCB. However, in many parts of the world, PCB are still in use with the major applications in transformers and capacitors. Large amounts of PCB contained in equipment have been decommissioned and the PCB have been disposed of, mainly through high temperature incineration. However, stocks of PCB and PCB-containing wastes have been accumulated and are awaiting disposal. International agreements, such as the Basel Convention regulate the environmentally sound destruction of PCB and allow transport across borders for destruction of toxic wastes.

Based on these findings there is a potential of the contamination of feedstuffs and foods with PCB to happen again. Within the EU, Germany, France, United Kingdom and Spain were former producers of PCB and thus may be required to take their old products back. Further, all EU Member States are OECD countries and thus are open for import of PCB wastes for destruction under the Basel Convention from developing countries and countries that do not have own destruction capacities. An example is Finland, which has the capacity to destroy PCBs in an environmentally sound manner (for the Basel Convention, see section 4.2).

To protect the environment and humans, existing regulations addressing PCB should be strongly enforced and any movement of PCB and PCB-containing equipment and wastes should be carefully monitored and documented to prevent any irregularities.

## 8.5 PCDD/PCDF Fluxes into the Compound Feedingstuff Industry

In this section 8.5 a rough estimate of the PCDD/PCDF fluxes into the EU compound feedingstuff industry will be given. The annual fluxes into this industrial sector *via* raw materials are calculated according to equation (3):

$$\text{Annual flux}_{\text{PCDD/PCDF}} = \text{Annual consumption of raw materials} \times \text{concentration} \quad (3)$$

The annual consumption data of raw materials by the European compound feedingstuff producers are shown in Table 27 and PCDD/PCDF concentrations of the different raw materials are compiled in chapter 8.4 - Known PCDD/PCDF Contamination in Feedingstuffs and Potential Constituents. Our calculation is done on the assumption that the water content of all components is negligible, except for “by-products from the food industry” and “others” for which we assume a water content of 50 %. Since there is no specification as to “dairy products”, we further assume, that this term refers to fresh as well as to dried dairy by-products, such as whey, skim milk, buttermilk and milk powders, respectively, with an average fat content of 2 %. Table 51 summarizes the data used for the calculation.

Table 51: Data base for the calculation of PCDD/PCDF fluxes into the EU compound feedingstuff industry

Raw Material	Annual consumption (x 1,000 tons)	Average PCDD/PCDF concentration (pg I-TEQ/g d.m.)	Assumption
Grain	<b>48,748</b>	<b>0.2</b> (range: 0.068–0.25/not cleaned)	d.m. = f.w.
Tapioca	<b>2,739</b>	<b>0.3</b> (range: 0.05 – 0.71)	d.m. = f.w.
By-products from food industry	<b>17,475</b>	<b>0.3</b> (estimated)	water content: 50 %
Oils and fats	<b>2,118</b>	<b>1</b> (range: 0.05-2.31/animal fat)	d.m. = fat
Oil cake/oil meal	<b>30,212</b>	<b>0.3</b> (range: 0.062-0.42)	d.m. = f.w.
Animal meal	<b>2,759</b>	<b>0.1</b> (range: 0.06 – 0.26)	d.m. = f.w.
Dairy products	<b>1,598</b>	<b>0.7</b> (pg I-TEQ/g fat) (range: 0.59-0.89/see Table 11)	fat content: 2 %
Dried feed	<b>2,400</b>	<b>0.6</b> (range: 0.13-2.4)	d.m. = f.w.
Pulses	<b>4,033</b>	<b>0.2</b> (average value from duplicates)	d.m. = f.w.
Minerals, vitamins	<b>3,397</b>	<b>0.2</b> (range:0.05-0.25/"clean" minerals)	d.m. = f.w.
Others	<b>4,737</b>	<b>0.2</b> (estimated)	water content: 50 %

The results of this calculation are shown in Figure 6.

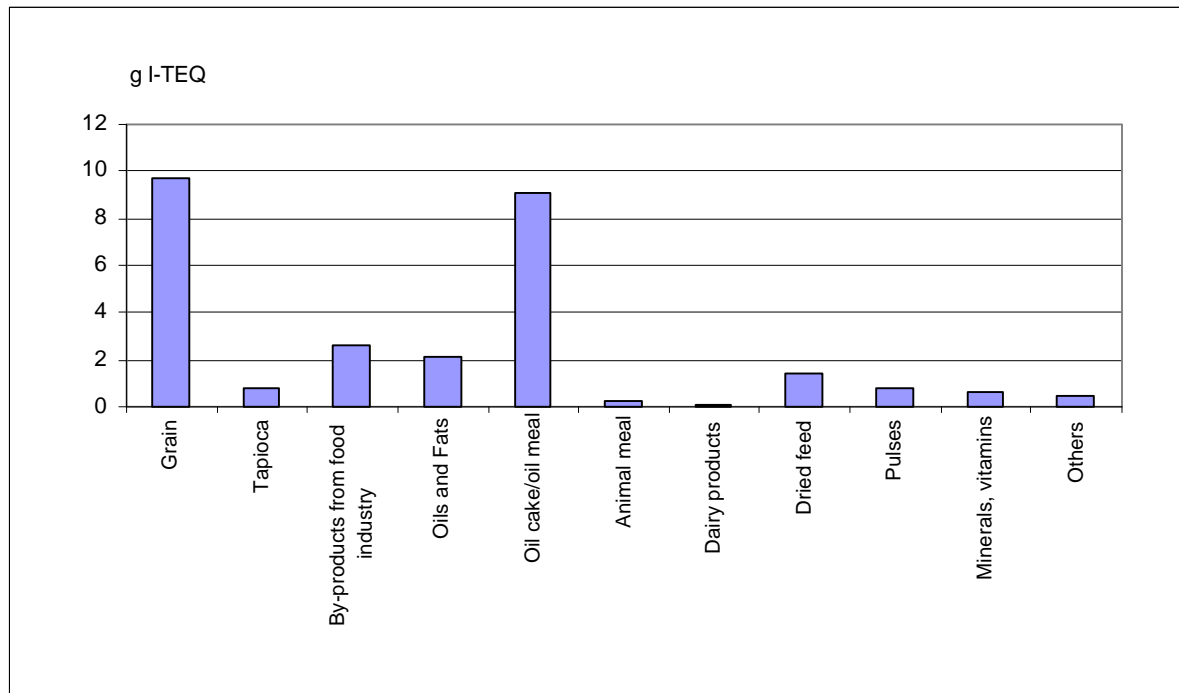


Figure 6: Annual PCDD/PCDF fluxes into the EU compound feedingstuff industry via raw materials

On the basis of actual consumption data and the most recent PCDD/PCDF concentrations available to us, it can be estimated that annually 28 g I-TEQ are transferred from raw materials into compound feedingstuffs. Main contributors are grain with almost 10 g I-TEQ and oil cake and oil meal together with about 9 g I-TEQ. By-products from the food industry contribute with about 2.6 g I-TEQ. Although on a mass basis, the flux from oils and fats into compound feedingstuffs is relatively small (less than 2 %), they represent a share of almost 8 % to the final PCDD/PCDF contamination in the final product, which is due to the high concentrations in these raw materials. For dried feed we assumed an average PCDD/PCDF concentration of 0.6 pg I-TEQ/g d.m. resulting in an input flux of 1.4 pg I-TEQ or a share of about 5 %. Replacing this average value by the PCDD/PCDF concentration of 2.4 pg I-TEQ/g d.m. found in dried greens from Denmark (worst case) would give an input flux of 5.8 pg, which means an increase of the total input from 28 to more than 32 pg I-TEQ, or by 15 %. This example demonstrates that raw materials, which are of minor importance as to their mass fluxes, may significantly influence the total PCDD/PCDF flux into the compound feedingstuff industry.

When looking at the fluxes into the European compound feedingstuff industry, it became obvious that almost 50 % of the total PCDD/PCDF inputs are from by-products, oil cake and oil meal and from oils and fats, *e.g.* primarily from recycled materials.

It should be noted that the above fluxes refer to European production of feedingstuffs and do not take into account imported or exported materials. At present, it was not possible for us to retrieve import and export statistics for compound feedingstuffs as statistical yearbooks do not provide more than data on import and export of single components such as wheat, potatoes, *etc.*

Taking the total amount of about 120 Mio. tons of compound feedingstuffs produced within the EU per year (Table 25) into consideration, the total input flux calculated above would give

an average PCDD/PCDF concentration of compound feedingstuffs of 0.23 pg I-TEQ/g, or 0.25 pg I-TEQ/g d.m. assuming a moisture content of compound feedingstuffs of 10 %. This is consistent with the results from various feedingstuff analyses ((Table 52).

Table 52: PCDD/PCDF concentrations in compound feedingstuffs

	I-TEQ	WHO-TEQ
Feedingstuff on vegetable basis <sup>a</sup> (pg/g d.m.)	0.61	0.70*
Feedingstuff on vegetable basis <sup>a</sup> (pg/g d.m.)	0.34	0.36*
Feedingstuff on vegetable basis <sup>a</sup> (pg/g d.m.)	0.35	0.38*
Cattle fattening feed <sup>a</sup> (pg/g d.m.)	0.09	0.09*
Calf starter <sup>a</sup> (pg/g d.m.)	0.45	0.44*
Supplementary feed for calves <sup>a</sup> (pg/g d.m.)	0.48	0.47*
Milk replacer <sup>a</sup> (pg/g d.m.)	1.0	0.99*
Compound feed <sup>b</sup> (pg/g d.m.) / mean value; n = 33	-	0.067
Complete feedingstuff for pigs <sup>c</sup> (pg/g d.m.) / mean value; n = 14	0.05	-
Complete feedingstuff for poultry <sup>c</sup> (pg/g d.m.) / mean value; n = 63	1.4	-
Complete feedingstuff for poultry/without kaolin <sup>c</sup> (pg/g d.m.) / mean value; n = 45	0.09	-

<sup>a</sup> Schöppe et al. 1996 <sup>b</sup> Malisch and Fürst 2000 <sup>c</sup> Appuhn et al. 2000

\* recalculated based on congener-specific data

Additional data with PCDD/PCDF concentrations found in mineral feed found in the literature are shown in Table 53.

Table 53: PCDD/PCDF concentrations in mineral feed

	I-TEQ	WHO-TEQ
Mineral feed for cattle <sup>a</sup> (pg/g d.m.)	0.60	0.62*
Mineral feed <sup>b</sup> (pg/g d.m.) / mean value; n = 22	-	0.126

<sup>a</sup> Schöppe et al., 1996 <sup>b</sup> Malisch and Fürst 2000

\* recalculated based on congener-specific data

## 9 HUMAN EXPOSURE RELATED TO FEEDINGSTUFFS

A summary of fluxes within the environment and potential entries of POPs and especially for PCDD/PCDF into the feedingstuff and food production is shown in Figure 7. Both, the terrestrial foodchain (on the left side) and the aquatic foodchain (on the right side) are effected by the industrial processes *via* the atmosphere and with water discharges, respectively. Contaminants released into air or water bioconcentrate and biomagnify in biota, and may undergo subsequent transport from organism to organism along these two foodchains (see Chapters 7.1 and 7.2). This often leads to high concentrations at higher trophic levels.

Humans as end-consumers are exposed to PCDD/PCDF and other POPs through agricultural products from the terrestrial foodchain (*e.g.*, dairy products, meat, vegetables, grains, *etc.*) and from the aquatic foodchain (*e.g.*, fish and shellfish). Livestock (and fish and shellfish from aquaculture) partially or exclusively reared on industrially manufactured feedingstuffs represent a third pathway for human exposure.

Figure 7 illustrates that whenever livestock is involved there are interferences between the terrestrial and the aquatic foodchains and industrial manufacturing as a third branch. The feedingstuff industry plays an important role in this network, receiving inputs from both foodchains as well as recycles and residues from various industrial processes, especially from the foodstuff industry as has been shown and discussed in Chapter 8. Besides, it has to be considered, that loops are being built up within this network, for example, by using animal waste as raw materials for compound feedingstuffs, or (not shown in Figure 7) by using sewage sludge and compost as fertilizers on farmland, which may represent an additional vector into vegetable products, but also into livestock *via* soil ingestion.

Whereas, a lot of work has been done on the aquatic and the agricultural foodchains, there is almost no information as to the effect of industrially manufactured feedingstuffs on human health. One aim of this study is to calculate the human daily intake related to the transfer from re-used material into industrially manufactured feedingstuffs and to compare this impact to the impact through the agricultural and the aquatic foodchain. From our findings presented in the previous chapters, and as it is illustrated in Figure 7, we have, however, to conclude, that a separate quantification of the influence of these three branches will not be possible due to interactions between the different compartments. Vegetable products, for example, are effected by industrial emissions into the environment as well as by industrial processing if they go to the foodstuff industry. In the following sections we will calculate the impact of some selected compound feedingstuff components to the final contamination in the end-product for PCDD/PCDF, which allows an indirect comparison between the three branches.

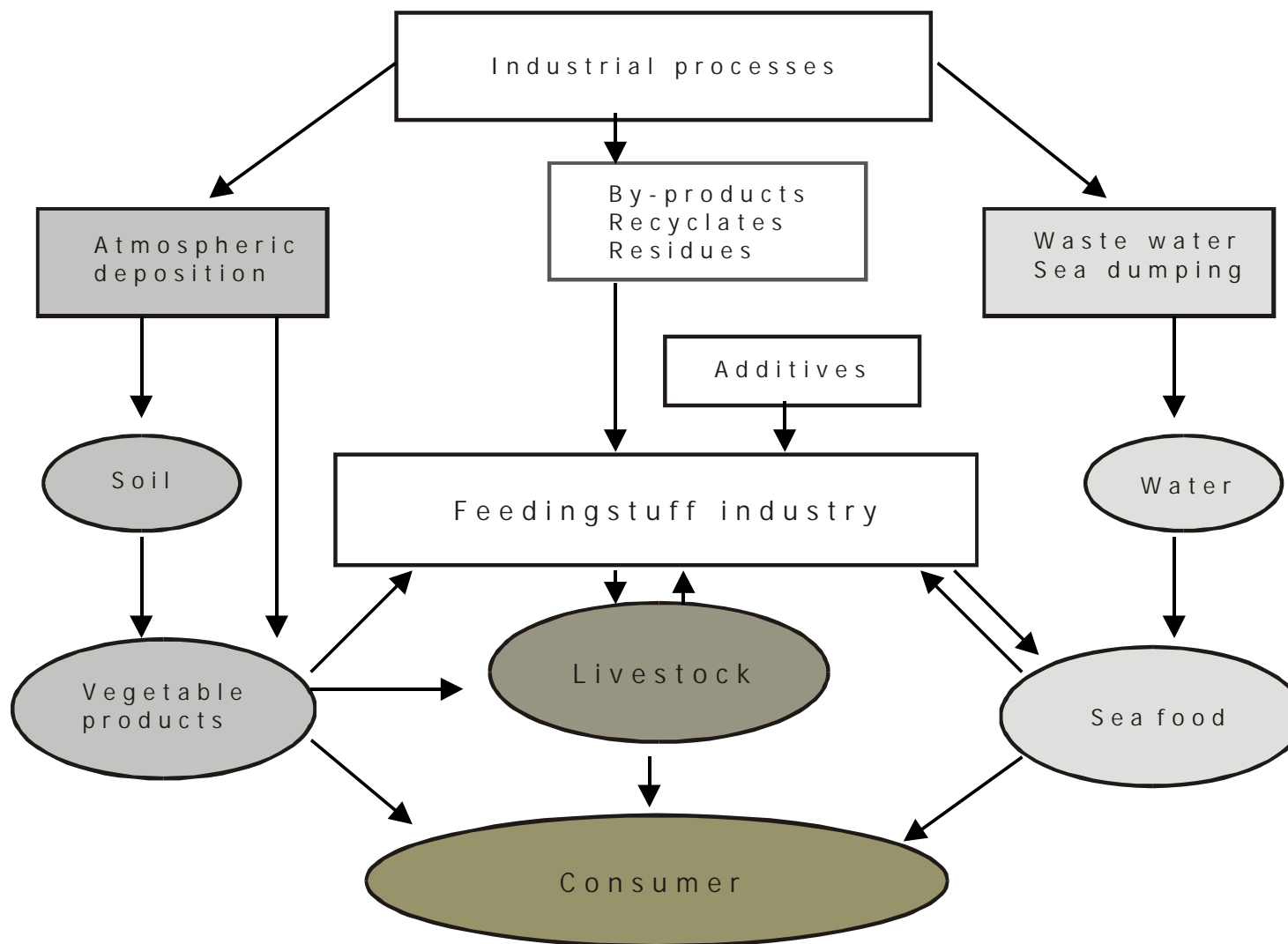


Figure 7: Fluxes in the environment and potential implications for POPs entering the feedingstuff and food production



## 9.1 Basic Assumptions

### 9.1.1 Model Compound Feedingstuff

Present regulations and agreements do not require a detailed declaration of the composition of compound feedingstuffs. As already discussed in section 8.2, declarations by compound feedingstuff producers are normally restricted to the contents of crude protein, crude oils and fats, crude fiber etc. EU Directive 91/375/EEC established categories of feedingstuff constituents which ‘may be used for the purpose of labelling compound feedingstuffs’. There are categories such as ‘Cereal grain’ or ‘Products and by-products of sugar production’ or ‘Fish products’, resulting in a declaration according to decreasing masses in the compound feedingstuff in a very general manner. Thus, for marketing issues of high quality products, the producer may declare explicitly what is contained in the compound feedingstuff, others may prefer not to do so.

Due to this unsatisfactory database, we created a model compound feedingstuff for the purpose of this study and the calculations to be done. The composition, as shown in Table 54, is mainly based on figures of the raw material consumption of the European and German compound feedingstuff producers (Table 26 and Table 27).

Table 54: Composition of the model compound feedingstuff used in this study

Ingredient	Share in Compound Feedingstuff
Grain	40 %
Oil cake and oil meal	25 %
By-products from food industry	14 %
Pulses	4 %
Dried feed	3 %
Animal meal and fish meal	3 %
Starchy food	2 %
Oils and fats	2 %
Others	7 %

Dairy products have been omitted in this composition, since they are mainly used for special feeds like milk replacers or starters.

We are aware, that our approach using only one type of model feed ignores differences in livestock feeding to a certain extend, and does not take into consideration that the composition of compound feedingstuffs also varies according to specialization of production (breeding, fattening, dairy farming, *etc.*).

For the calculation of the PCDD/PCDF content of this model feed (Table 55), we apply the average PCDD/PCDF concentrations of the different compound feedingstuff ingredients as presented and discussed in chapter 8.5, assuming background levels in all these components.

Table 55: PCDD/PCDF concentration in the model compound feedingstuff

Ingredient	Share %	Av. Concentration pg I-TEQ/g d.m.	Contribution to Model feed pg I-TEQ/g d.m.
Grain	40	0.2	0.08
Oil cake/meal	25	0.3	0.075
By-products/food industry	14	0.3	0.042
Pulses	4	0.2	0.008
Dried greens	3	0.6	0.018
Animal meal/fish meal	3	0.1	0.003
Starchy food	2	0.3	0.006
	2	1	0.02
Oils/fats (pg I-TEQ/g fat)			
Others	7	0.2	0.014
<b>Model Compound Feedingstuff</b>	<b>100</b>		<b>0.266</b>

The resulting concentration of our model compound feedingstuff of 0.26 pg I-TEQ/g d.m. is in good agreement with the results of compound feedingstuff analyses reported by various authors, which were in a range of 0.05-1.4 pg I-TEQ/g d.m. (Table 52), demonstrating the suitability of this model feed.

### 9.1.2 Transfer from Feedingstuffs to Foodstuffs and Impact on Human Daily Intake

The transfer of contaminants from feedingstuffs to human foodstuffs is normally described by carry-over rates (see Chapter 7). Since carry-over rates (CORs) for PCDD/PCDF from feed to eggs and from feed to meat (life-time CORs) are not available, we have to restrict the following calculations to the carry-over from feed to milk as model foodstuff. Although, the carry-over from feed to eggs and from feed to meat may be different compared to the carry-over from feed to milk, at a first step the contaminant input *via* feedingstuffs is generally the same for all these animal products. Hence, doubling the contaminant input means (if there is no saturation) doubling the fluxes into the different products, independent of the CORs. Calculating the effect from different PCDD/PCDF inputs *via* feed on milk reflects as well the effect on other animal products obtained from farming when compound feedingstuffs are used. Therefore, on the basis of the “milk data” derived, we will also give a rough estimate of the impact on meat, eggs and fish in the following.

Carry-over rates (CORs) from feed to milk can be calculated on the basis of daily fluxes by dividing the contaminant flux in the milk by the total contaminant input in feed (Chapter 7). Scientifically, CORs on TEQ-basis do not make sense as the different congeners behave differently. However, considering that about 30-40 % of the most toxic PCDD/PCDF congeners taken up by the cow are excreted *via* milk (Table 13), a COR of 0.3 for I-TEQs seems to be reasonable.

Typically a lactating cow consumes 12-14 kg d.m. of basic feedingstuffs (greens, hay, silage, *etc.*) and about 4-5 kg d.m. of compound feedingstuffs per day (Lexikon Landwirtschaft 1995). Using an average PCDD/PCDF concentration of 0.1 pg I-TEQ/g d.m. for basic feedingstuffs (Table 39) and the above calculated PCDD/PCDF concentration of 0.26 pg I-TEQ/g d.m. for compound feedingstuff (Table 56), gives a daily input flux into the cow with

the feed of 2,264 pg I-TEQ, as shown in Table 56. Applying a COR of 0.3, we obtain a daily PCDD/PCDF excretion into milk of 679.2 pg I-TEQ. For the output flux *via* milk we presumed a daily milk performance of 20 kg and a milk fat content of 4 %, which finally results in a milk concentration of 0.85 pg I-TEQ/g fat.

Table 56: PCDD/PCDF transfer from model feed to milk

Daily feed consumption:	
12 kg d.m. basic feedingstuffs x 0.1 pg I-TEQ/g d.m.	1,200 pg I-TEQ
4 kg d.m. compound feedingstuff x 0.26 pg I-TEQ/g d.m.	1,064 pg I-TEQ
<b>Daily PCDD/PCDF input flux</b>	<b>2,264 pg I-TEQ</b>
Carry-over to milk - COR = 0.3:	
<b>Daily PCDD/PCDF excretion into milk</b>	<b>679.2 pg I-TEQ</b>
Daily milk performance 20 kg = 0.8 kg milk fat	
<b>Resulting PCDD/PCDF milk concentration</b>	<b>0.85 pg I-TEQ/g fat</b>

Comparing the resulting milk concentration of 0.85 pg I-TEQ/g fat to concentrations measured in 1998 in Germany which were in a range of 0.5 to 1.8 pg I-TEQ/g fat (Fürst and Wilmers 1999), for example, indicates that our model feed and the assumptions made as to the carry-over from feed to milk are a suitable basis for the following calculations of the impact of certain compound feedingstuff components on human food and human daily intake.

Assuming a daily consumption of 28 g milk fat (Chapter 5.2), our 'model milk' would contribute 23.7 pg I-TEQ to the daily intake of an adult. For the following intake calculations we used consumption and intake data from Germany (as shown in Table 8) and replaced the contribution of milk of 19.3 pg I-TEQ by our calculated milk contribution of 23.7 pg I-TEQ. To estimate the impact of the PCDD/PCDF content of feedingstuffs on meat, eggs and fish, the intakes were adjusted accordingly. For fish we assumed, however, that only 30 % are from aquaculture *i.e.* directly influenced by industrially produced feeds.

Table 57: Estimated daily intake of PCDD/PCDF for an adult (b.w. = 70 kg)

Food group	Daily intake (pg I-TEQ)	Transfer: Model feed to milk	Transfer: Model feed to milk + meat, eggs, fish (estimated)
		Daily intake (pg I-TEQ)	Daily intake (pg I-TEQ)
Milk	19.3	<b>23.7</b>	<b>23.7</b>
Meat	13.8	13.8	<b>17.0</b>
Eggs	5.1	5.1	<b>6.3</b>
Fish	10.4	10.4	<b>11.1</b>
Fruit	2.0	2.0	2.0
Vegetables	3.7	3.7	3.7
Others	7.0	7.0	7.0
<b>Total</b>	<b>61.3</b>	<b>65.7</b>	<b>70.8</b>
(pg I-TEQ/kg b.w.)	0.88	<b>0.94</b>	<b>1.01</b>

The calculated contribution from milk of 23.7 pg I-TEQ leads to a daily intake of 0.94 pg I-TEQ/kg b.w. Assuming the same COR for meat, eggs and fish the daily intake results in 1.01 pg I-TEQ/kg b.w. However, it has to be noted that this is a very rough estimate, which probably reflects the impact on beef quite well due to the diet of cattle which is well represented by our model. Since pigs and chicken consume a higher share of concentrates

and/or compound feedingstuffs, the impact on these animals and on pork, poultry meat and eggs, respectively, is probably much more higher. Fish from aquaculture normally are fed industrially produced feedingstuffs only, which has a high content of animal meal and fish meal. Therefore, the impact on fish and fish products may differ significantly from our estimate.

## 9.2 Calculation of the Impact of Potentially Problematic Standard Raw Materials

### 9.2.1 Dried Greens

Dried greens seem to need special consideration. The annual flux of 28 g I-TEQ into the EU compound feedingstuff industry calculated in section 8.5 was based on a mean contamination of dried greens of 0.6 pg I-TEQ/g d.m. Assuming 3 % of dried greens containing 0.60 pg I-TEQ/g d.m. will give a PCDD/PCDF concentration in our model compound feed of 0.26 pg I-TEQ/g d.m. and result in a daily intake (model feed to milk) of 0.9 pg I-TEQ/kg b.w. (Table 58).

Table 58: PCDD/PCDF transfer from model feed to milk – impact of dried greens

Ingredient	Share %	Av. concentr. pg I-TEQ/g d.m.	Contribution to compound feed pg I-TEQ/g d.m.	Av. concentr. pg I-TEQ/g d.m. (Dried greens: Denmark/wood)	Contribution to compound feed pg I-TEQ/g d.m.
Grain	40	0.2	0.08	0.2	0.08
Oil cake/meal	25	0.3	0.075	0.3	0.075
By-products/food industry	14	0.3	0.042	0.3	0.042
Pulses	4	0.2	0.008	0.2	0.008
Dried greens	3	<b>0.6</b>	0.018	<b>2.4</b>	0.072
Animal meal/fish meal	3	0.1	0.003	0.1	0.003
Starchy food	2	0.3	0.006	0.3	0.006
Oils/fats (pg I-TEQ/g fat)	2	1	0.02	1	0.02
Others	7	0.2	0.014	0.2	0.014
Compound feedingstuff (pg I-TEQ/g d.m.)	100		<b>0.266</b>		<b>0.32</b>

*Transfer: Model feed to milk*

Daily contaminant flux in feed (pg I-TEQ)	2,264		2,480
Daily flux in milk (pg I-TEQ)	679.2		744
Milk concentration (pg I-TEQ/g fat)	0.85		0.93
Daily intake (pg I-TEQ/person)	<b>65.7</b>		<b>68.0</b>
Daily intake (pg I-TEQ/kg b.w.)	<b>0.94</b>		<b>0.97</b>

*Transfer: Model feed to milk + meat, eggs, fish (estimated)*

Daily intake (pg I-TEQ/person)	<b>70.8</b>		<b>75.7</b>
Daily intake (pg I-TEQ/kg b.w.)	<b>1.01</b>		<b>1.08</b>

If the calculation is being done using 2.4 pg I-TEQ/g d.m. as was the highest concentration found in dried greens from Denmark (fuel of drying plant: wood), the model compound feedingstuff would have a concentration of 0.32 pg I-TEQ/g d.m., which means an increase of about 20 %. The corresponding increase of the daily intake is, however, negligible.

### 9.2.2 Fish Meal

Fish meals are prepared from fish caught in different areas and hence can have highly variable PCDD/PCDF contents. Table 59 shows that using North Sea fish meal would result in a PCDD/PCDF concentration of 0.3 pg I-TEQ/g d.m. in the model feed, whereas the final concentration in the compound feedingstuff would be only 0.27 pg I-TEQ/g d.m. if the less contaminated fish meal from South America is being utilized.

Table 59: PCDD/PCDF transfer from model feed to milk – impact of fish meal

Ingredient	Share %	Av. concentr. pg I-TEQ/g d.m. (Fish meal, North Sea)	Contribution to compound feed pg I-TEQ/g d.m.	Av. concentr. pg I-TEQ/g d.m. (Fish meal, South America)	Contribution to compound feed pg I-TEQ/g d.m.
Grain	40	0.2	0.08	0.2	0.08
Oil cake/meal	25	0.3	0.075	0.3	0.075
By-products/food industry	14	0.3	0.042	0.3	0.042
Pulses	4	0.2	0.008	0.2	0.008
Dried greens	3	0.6	0.018	0.6	0.018
Animal meal/fish meal	3	<b>1.3</b>	0.039	<b>0.18</b>	0.0054
Starchy food	2	0.3	0.006	0.3	0.006
Oils/fats (pg I-TEQ/g fat)	2	1	0.02	1	0.02
Others	7	0.2	0.014	0.2	0.014
Compound feedingstuff (pg I-TEQ/g d.m.)	100		<b>0.302</b>		<b>0.268</b>

*Transfer: Model feed to milk*

Daily contaminant flux in feed (pg I-TEQ)	2,408		2,274
Daily flux in milk (pg I-TEQ)	722.4		682.1
Milk concentration (pg I-TEQ/g fat)	0.90		0.85
Daily intake (pg I-TEQ/person)	<b>67.3</b>		<b>65.9</b>
Daily intake (pg I-TEQ/kg b.w.)	<b>0.96</b>		<b>0.94</b>

*Transfer: Model feed to milk + meat, eggs, fish (estimated)*

Daily intake (pg I-TEQ/person)	<b>74.1</b>		<b>71.1</b>
Daily intake (pg I-TEQ/kg b.w.)	<b>1.06</b>		<b>1.02</b>

Although, this calculation shows that fish meal can be a significant source of PCDD/PCDF in the feedingstuff production depending on their origin, their effect on the daily intake, again, is of minor importance. However, it should be considered that some compound feedingstuffs, especially for poultry, can contain higher amounts of fish meal and might, therefore, be more problematic.

### 9.2.3 Aspiration Dust

Aspiration dust are residues from cereal and pulse cleaning, which are normally used for feedingstuff production. It was reported that these dusts contain quite high PCDD/PCDF concentrations (chapter 8.4.4) (Schöppe *et al.* 1996). Replacing 5 % of grain by aspiration dust with a PCDD/PCDF content of 14.1 pg I-TEQ/g d.m. found by Schöppe *et al.* (1996) would increase the concentration of the model feed more than threefold. As shown in Table 60 below, using aspiration dusts in feedingstuff production also leads to a considerable increase in the daily intake. If only the contribution *via* milk is considered, the daily intake will be increased by 44 %. Inclusion of the milk + meat, egg, fish pathway will double the daily intake to 88 %.

Table 60: PCDD/PCDF transfer from model feed to milk – impact of aspiration dust

Ingredient	Share %	Av. concentr. pg I-TEQ/g d.m.	Contribution to compound feed pg I-TEQ/g d.m.	Av. concentr. pg I-TEQ/g d.m. (35 % grain, 5 % aspir. dust)	Contribution to compound feed pg I-TEQ/g d.m.
Grain	40	0.2	0.08	0.2	0.07
Oil cake/meal	25	0.3	0.075	0.3	0.075
By-products/food industry	14	0.3	0.042	0.3	0.042
Pulses	4	0.2	0.008	0.2	0.008
Dried greens	3	0.6	0.018	0.6	0.018
Animal meal/fish meal	3	0.1	0.003	0.1	0.003
Starchy food	2	0.3	0.006	0.3	0.006
Oils/fats (pg I-TEQ/g fat)	2	1	0.02	1	0.02
Others	7	0.2	0.014	0.2	0.014
Aspiration dust	-	-	-	<b>14.1</b>	0.705
Compound feedingstuff (pg I-TEQ/g d.m.)	100		<b>0.266</b>		<b>0.961</b>

#### *Transfer: Model feed to milk*

Daily contaminant flux in feed (pg I-TEQ)	2,264		5,044
Daily flux in milk (pg I-TEQ)	679.2		1,513
Milk concentration (pg I-TEQ/g fat)	0.85		1.89
Daily intake (pg I-TEQ/person)	<b>65.7</b>		<b>94.9</b>
Daily intake (pg I-TEQ/kg b.w.)	<b>0.94</b>		<b>1.36</b>

#### *Transfer: Model feed to milk + meat, eggs, fish (estimated)*

Daily intake (pg I-TEQ/person)	<b>70.8</b>		<b>132</b>
Daily intake (pg I-TEQ/kg b.w.)	<b>1.01</b>		<b>1.90</b>

Since aspiration dust can contribute severely to the PCDD/PCDF contamination of feedingstuffs, the use of these “cleaning residues” has to be classified as critically.

### 9.2.4 Citrus Pulp

Elevated PCDD/PCDF concentrations were detected in German milk in 1997 and 1998. The source of this contamination was traced back to citrus pulp pellets from Brazil (0). Citrus pulp pellets are normally used as an energy source for dairy cows. In the following calculation we compare the effect of our basic model compound feed to the impact of a compound feed in which 15 % of grain was substituted by citrus pulp, both being comparable as to their energy supply (DLG-Verlags-GmbH, 1999). For citrus pulp we took an elevated PCDD/PCDF concentration of 7.4 pg I-TEQ/g, as it was reported by Malisch (1998).

The use of contaminated citrus pulp in our model causes a 5-fold increase of the compound feed concentration, and there is also a considerable increase in the daily intake. The resulting PCDD/PCDF concentrations of 1.3 pg I-TEQ/g d.m in compound feed. and 2.4 pg I-TEQ/ g fat in milk, *resp.*, are in very good agreement with measured data from feed and milk, which were affected by citrus pulp from Brazil (Table 9).

Table 61: PCDD/PCDF transfer from model feed to milk – impact of citrus pulp

Ingredient	Share %	Av. concentr. pg I-TEQ/g d.m. (basic model compound feed)	Contribution to Compound feed pg I-TEQ/g d.m.	Av. concentr. pg I-TEQ/g d.m. (25 % grain, 15 % citr. pulp)	Contribution to compound feed pg I-TEQ/g d.m.
Grain	40	0.2	0.08	0.2	0.05
Oil cake/meal	25	0.3	0.075	0.3	0.075
By-products/food industry	14	0.3	0.042	0.3	0.042
Pulses	4	0.2	0.008	0.2	0.008
Dried greens	3	0.6	0.018	0.6	0.018
Animal meal/fish meal	3	0.1	0.003	0.1	0.003
Starchy food	2	0.3	0.006	0.3	0.006
Oils/fats (pg I-TEQ/g fat)	2	1	0.02	1	0.02
Others	7	0.2	0.014	0.2	0.014
Citrus pulp	-	-	-	<b>7.4</b>	1.11
Compound feedingstuff (pg I-TEQ/g d.m.)	100		<b>0.266</b>		<b>1.346</b>

#### *Transfer: Model feed to milk*

Daily contaminant flux in feed (pg I-TEQ)	2,264		6,584
Daily flux in milk (pg I-TEQ)	679.2		1,975
Milk concentration (pg I-TEQ/g fat)	0.85		2.47
Daily intake (pg I-TEQ/person)	<b>65.7</b>		<b>111</b>
Daily intake (pg I-TEQ/kg b.w.)	<b>0.94</b>		<b>1.59</b>

#### *Transfer: Model feed to milk + meat, eggs, fish (estimated)*

Daily intake (pg I-TEQ/person)	<b>70.8</b>		<b>167</b>
Daily intake (pg I-TEQ/kg b.w.)	<b>1.01</b>		<b>2.39</b>

### 9.2.5 Clay

Kaolinitic clays are used as flowing or anti-caking agents as well as carriers for additives like antibiotics. Whereas “dioxin-free” clay contains 0.2 pg I-TEQ/g (Rappe and Andersson 2000), clay with a PCDD/PCDF concentration of 174 pg I-TEQ/g was found in a mine in Germany (Malisch 2000). In the calculation below (Table 62) we assume a share of 2 % of clay in the model feed, and compare the impact of contaminated clay to uncontaminated material.

Table 62: PCDD/PCDF transfer from model feed to milk – impact of clay

Ingredient	Share %	Av. concentr. pg I-TEQ/g d.m. (Clay,uncontam)	Contribution to compound feed pg I-TEQ/g d.m.	Av. concentr. pg I-TEQ/g d.m. (Clay, contam.)	Contribution to compound feed pg I-TEQ/g d.m.
Grain	40	0.2	0.08	0.2	0.08
Oil cake/meal	25	0.3	0.075	0.3	0.075
By-products/food industry	14	0.3	0.042	0.3	0.042
Pulses	4	0.2	0.008	0.2	0.008
Dried greens	3	0.6	0.018	0.6	0.018
Animal meal/fish meal	3	0.1	0.003	0.1	0.003
Starchy food	2	0.3	0.006	0.3	0.006
Oils/fats (pg I-TEQ/g fat)	2	1	0.02	1	0.02
Others	5	0.2	0.01	0.2	0.01
Kaolinitic clay	2	<b>0.2</b>	0.004	<b>174</b>	3.48
Compound feedingstuff (pg I-TEQ/g d.m.)	100		<b>0.266</b>		<b>3.742</b>

#### *Transfer: Model feed to milk*

Daily contaminant flux in feed (pg I-TEQ)	2,264		16,168
Daily flux in milk (pg I-TEQ)	679.2		4,850
Milk concentration (pg I-TEQ/g fat)	0.85		6.06
Daily intake (pg I-TEQ/person)	<b>65.7</b>		<b>211.7</b>
Daily intake (pg I-TEQ/kg b.w.)	<b>0.94</b>		<b>3.03</b>

#### *Transfer: Model feed to milk + meat, eggs, fish (estimated)*

Daily intake (pg I-TEQ/person)	<b>70.8</b>		<b>380</b>
Daily intake (pg I-TEQ/kg b.w.)	<b>1.01</b>		<b>5.4</b>

Whereas the uncontaminated clay shows no effect on the PCDD/PCDF concentration of the compound feed and hence on the daily intake, the contaminated material exerts a strong influence on the feedingstuff and on human dietary exposure.

As shown in Table 62, the compound feed containing 2 % of the contaminated material would result in a milk contamination of 6 pg I-TEQ/g fat, which would exclude the milk to be marketed in Germany, where authorities set a tolerance level of 5 pg I-TEQ/g fat for milk and dairy products (see chapter 4.3).



### 9.3 Calculation of the Impact of Illegal Ingredients

The changes in the PCDD/PCDF contamination will become more dramatic if wastes are being mixed into compound feedingstuffs, as will be demonstrated in the following calculations.

#### 9.3.1 Sewage Sludge

Table 63 gives an example where only 1 % of highly contaminated sewage sludge (Fiedler 1996) is added to a feedingstuff mixture; the concentration of the compound feedingstuff increases dramatically.

Table 63: PCDD/PCDF transfer from model feed to milk – impact of sewage sludge

Ingredient	Share %	Av. concentr. pg I-TEQ/g d.m.	Contribution to compound feed pg I-TEQ/g d.m.	Av. concentr. pg I-TEQ/g d.m. (worst case)	Contribution to compound feed pg I-TEQ/g d.m.
Grain	40	0.2	0.08	0.2	0.08
Oil cake/meal	25	0.3	0.075	0.3	0.075
By-products/food industry	14	0.3	0.042	0.3	0.042
Pulses	4	0.2	0.008	0.2	0.008
Dried greens	3	0.6	0.018	0.6	0.018
Animal meal/fish meal	3	0.1	0.003	0.1	0.003
Starchy food	2	0.3	0.006	0.3	0.006
Oils/fats (pg I-TEQ/g fat)	2	1	0.02	1	0.02
Others	6	0.2	0.012	0.2	0.012
Sewage sludge	1	<b>20</b>	0.2	<b>5,000</b>	50
Compound feedingstuff (pg I-TEQ/g d.m.)	100		<b>0.464</b>		<b>50.264</b>

#### *Transfer: Model feed to milk*

Daily contaminant flux in feed (pg I-TEQ)	3,056	202,256
Daily flux in milk (pg I-TEQ)	916.8	60,676
Milk concentration (pg I-TEQ/g fat)	1.15	75.85
Daily intake (pg I-TEQ/person)	<b>74.1</b>	<b>2,165</b>
Daily intake (pg I-TEQ/kg b.w.)	<b>1.06</b>	<b>30.9</b>

#### *Transfer: Model feed to milk + meat, eggs, fish (estimated)*

Daily intake (pg I-TEQ/person)	<b>88.5</b>	<b>4,522</b>
Daily intake (pg I-TEQ/kg b.w.)	<b>1.26</b>	<b>64.6</b>

Whereas the calculation shown in the above Table 63 at the right side assumes a worst case situation with very high PCDD/PCDF concentrations in the sewage sludge, the calculation at the left side takes a concentration of 20 pg I-TEQ/g d.m. which is within the range of data reported by Rappe *et al.* (1997) and Eljarrat *et al.* (1997). In this case, the increase is less dramatic and leads only to a minor increase of the daily intake when compared to our model feedingstuff without sludge as shown in Table 57. Note, that 100 pg I-TEQ/g, is the limit value for sewage sludge application in some EU Member States as the default concentration.

### 9.3.2 Wood Chips

For the calculation of the impact of wood chips, which may be used *e.g.* as fillers in compound feedingstuffs, we assumed a PCDD/PCDF concentration of 250 pg I-TEQ/g d.m. Comparable concentrations are reported by Reichle *et al.* (1997) who analyzed different fractions of used woods. As shown in Table 64, contaminated wood increases the daily intake to 2.44 pg I-TEQ/kg b.w. and day for the milk only and to 4.19 pg I-TEQ/kg b.w. and day when meat, eggs and fish are included as well.

Table 64: PCDD/PCDF transfer from model feed to milk – impact of wood chips

Ingredient	Share %	Av. concentr. pg I-TEQ/g d.m.	Contribution to compound feed pg I-TEQ/g d.m.	Av. concentr. pg I-TEQ/g d.m. (1 % Wood chips)	Contribution to compound feed pg I-TEQ/g d.m.
Grain	40	0.2	0.08	0.2	0.08
Oil cake/meal	25	0.3	0.075	0.3	0.075
By-products/food industry	14	0.3	0.042	0.3	0.042
Pulses	4	0.2	0.008	0.2	0.008
Dried greens	3	0.6	0.018	0.6	0.018
Animal meal/fish meal	3	0.1	0.003	0.1	0.003
Starchy food	2	0.3	0.006	0.3	0.006
Oils/fats (pg I-TEQ/g fat)	2	1	0.02	1	0.02
Others	7	0.2	0.014	0.2	0.012
Wood chips	-	-	-	<b>250</b>	2.5
Compound feedingstuff (pg I-TEQ/g d.m.)	100		<b>0.266</b>		<b>2.764</b>

#### *Transfer: Model feed to milk*

Daily contaminant flux in feed (pg I-TEQ)	2,264		12,256
Daily flux in milk (pg I-TEQ)	679.2		3,676
Milk concentration (pg I-TEQ/g fat)	0.85		4.6
Daily intake (pg I-TEQ/person)	<b>65.7</b>		<b>170</b>
Daily intake (pg I-TEQ/kg b.w.)	<b>0.94</b>		<b>2.44</b>

#### *Transfer: Model feed to milk + meat, eggs, fish (estimated)*

Daily intake (pg I-TEQ/person)	<b>70.8</b>		<b>293</b>
Daily intake (pg I-TEQ/kg b.w.)	<b>1.01</b>		<b>4.19</b>

### 9.3.3 Waste Oil

For a potential waste oil contamination, we used a PCDD/PCDF contamination of 1,600,000 pg I-TEQ/g as was found for Aroclor 1260 or Clophen A60. A percentage of 0.05 % was derived from the Belgian chicken accident where a commercial PCB mixture of the Aroclor 1260 type resulted in a poultry feed contamination of more than 800 pg I-TEQ/g. The effects are dramatic as can be seen in Table 65.

Table 65: PCDD/PCDF transfer from model feed to milk – impact of fat contaminated with transformer oil

Ingredient	Share %	Av. concentr. pg I-TEQ/g d.m.	Contribution to compound feed pg I-TEQ/g d.m.	Av. concentr. pg I-TEQ/g d.m. <b>(0.05 % contam. fat)</b>	Contribution to compound feed pg I-TEQ/g d.m.
Grain	40	0.2	0.08	0.2	0.08
Oil cake/meal	25	0.3	0.075	0.3	0.075
By-products/food industry	14	0.3	0.042	0.3	0.042
Pulses	4	0.2	0.008	0.2	0.008
Dried greens	3	0.6	0.018	0.6	0.018
Animal meal/fish meal	3	0.1	0.003	0.1	0.003
Starchy food	2	0.3	0.006	0.3	0.006
Oils/fats (pg I-TEQ/g fat)	2	1	0.02	1	0.02
Others	7	0.2	0.014	0.2	0.014
Fat contaminated with PCB transformer oil	-	-	-	<b>1,600,000</b>	800
Compound feedingstuff (pg I-TEQ/g d.m.)	100		<b>0.266</b>		<b>800.266</b>

*Transfer: Model feed to milk*

Daily contaminant flux in feed (pg I-TEQ)	2,264		3,202,264
Daily flux in milk (pg I-TEQ)	679.2		960,679
Milk concentration (pg I-TEQ/g fat)	0.85		1,200
Daily intake (pg I-TEQ/person)	<b>65.7</b>		<b>33,665</b>
Daily intake (pg I-TEQ/kg b.w.)	<b>0.94</b>		<b>481</b>

*Transfer: Model feed to milk + meat, eggs, fish (estimated)*

Daily intake (pg I-TEQ/person)	<b>70.8</b>		<b>71,293</b>
Daily intake (pg I-TEQ/kg b.w.)	<b>1.01</b>		<b>1,018</b>

### 9.3.4 Leather Waste

To calculate the impact of leather waste, we replaced 1 % of “other” by 1 % leather waste in the compound feed mixture. Leather used for the production of clothing, shoes and furniture is often treated with PCP containing high concentrations of PCDD/PCDF (chapter 8.4.3). Analyses of leather samples showed PCDD/PCDF contents in the range of 3.1-6,400 pg I-TEQ/g (Fiedler 1996). For our model calculation we used a mean value of 800 pg I-TEQ/g.

As shown in Table 66 the model compound feed containing 1 % of the contaminated leather would result in a milk contamination of 13 pg I-TEQ/g fat, which would far exceed the tolerance level of 5 pg I-TEQ/g fat established by German authorities for marketable milk and dairy products (chapter 4.3).

Table 66: PCDD/PCDF transfer from model feed to milk – impact of leather waste

Ingredient	Share %	Av. concentr. pg I-TEQ/g d.m.	Contribution to compound feed pg I-TEQ/g d.m.	Av. concentr.pg I-TEQ/g d.m. (1 % Leather waste)	Contribution to compound feed pg I-TEQ/g d.m.
Grain	40	0.2	0.08	0.2	0.08
Oil cake/meal	25	0.3	0.075	0.3	0.075
By-products/food industry	14	0.3	0.042	0.3	0.042
Pulses	4	0.2	0.008	0.2	0.008
Dried greens	3	0.6	0.018	0.6	0.018
Animal meal/fish meal	3	0.1	0.003	0.1	0.003
Starchy food	2	0.3	0.006	0.3	0.006
Oils/fats (pg I-TEQ/g fat)	2	1	0.02	1	0.02
Others	7	0.2	0.014	0.2	0.012
Leather waste	-	-	-	<b>800</b>	8
Compound feedingstuff (pg I-TEQ/g d.m.)	100		<b>0.266</b>		<b>8.264</b>

*Transfer: Model feed to milk*

Daily contaminant flux in feed (pg I-TEQ)	2,264		34,256
Daily flux in milk (pg I-TEQ)	679.2		10,277
Milk concentration (pg I-TEQ/g fat)	0.85		12.85
Daily intake (pg I-TEQ/person)	<b>65.7</b>		<b>402</b>
Daily intake (pg I-TEQ/kg b.w.)	<b>0.94</b>		<b>5.7</b>

*Transfer: Model feed to milk + meat, eggs, fish (estimated)*

Daily intake (pg I-TEQ/person)	<b>70.8</b>		<b>783</b>
Daily intake (pg I-TEQ/kg b.w.)	<b>1.01</b>		<b>11.2</b>

As can be seen from the four examples of these illegal uses of ingredients, the high contaminations in these materials can have dramatic effects on the compound feedingstuff. In all cases the limit value – as set for PCDD/PCDF concentrations in milk in Germany – were reached (in the case of wood chips) or heavily exceeded (sewage sludge, waste oil, leather waste). The most efficient tools for intervention are legally binding restrictions on the use of these materials as is being executed in Switzerland for example where separate collection and recycling systems have been set up for used edible oils/fats and technical oils/fats.

## 9.4 Potential for Reduction Measures

### 9.4.1 Variation of Diet

In this section we will examine potentials for reduction of the PCDD/PCDF contents of feedingstuffs by variations of feed consumption and feed mixture for dairy cows, in all cases assuming a milk performance of 20 kg per day. The cow model has been selected as the carry-over rates from feed to cow's milk are the best studied. Nevertheless, it should be mentioned that the estimated effect should be much higher for animals fed on a higher percentage of compound or concentrate feed (= grain).

*Case 1* shows the typical case when green fodder (basic feedingstuff) is amended with a smaller portion of compound feedingstuff (including 50 % of recyclates). The calculation result in a PCDD/PCDF concentration in milk of 0.85 pg I-TEQ/g fat. Although the compound feedingstuff only covers one fourth of the mass ingested, the PCDD/PCDF share is close to 50 %.

In the second case (*Case 2*) we assumed that the cows are only fed basic feedingstuffs and thus replaced the 4 kg of compound feedingstuff by twice the amount (8 kg) of basic feed in order to keep up a milk performance of 20 kg (Tierische Erzeugung 1999). As shown in Table 66, there is, however, only a minor effect on the PCDD/PCDF content of milk. The milk concentration decreased only by about 13 %. This case represents the baseline situation when solely “natural” feedingstuffs without any industrially impacted ingredients are fed. It also shows that the whole system does not have a large potential for reduction.

Table 67: Model calculations for milk by modifying ingredients of compound feedingstuffs

<b>Case 1:</b>	
<u>Consumption:</u> 12 kg d.m. basic feedingstuff 4 kg d.m. compound feedingstuff	<u>PCDD/PCDF input flux via feed:</u> 12 kg d.m. x 0.1 pg I-TEQ/g d.m. = 1,200 pg I-TEQ 4 kg d.m. x 0.26 pg I-TEQ/g d.m. = 1,064 pg I-TEQ total <b>2,264 pg I-TEQ</b>
<u>Milk performance:</u> 20 kg milk = 0.8 kg milk fat	<u>PCDD/PCDF excretion into milk:</u> <b>679.2 pg I-TEQ</b> <u>PCDD/PCDF milk concentration:</u> <b>0.85 pg I-TEQ/g fat</b>
<b>Case 2:</b>	
<u>Consumption:</u> 20 kg d.m. basic feedingstuff	<u>PCDD/PCDF input flux via feed:</u> 20 kg d.m. x 0.1 pg I-TEQ/g d.m. = 2,000 pg I-TEQ total <b>2,000 pg I-TEQ</b>
<u>Milk performance:</u> 20 kg milk = 0.8 kg milk fat	<u>PCDD/PCDF excretion into milk:</u> <b>600.0 pg I-TEQ</b> <u>PCDD/PCDF milk concentration:</u> <b>0.75 pg I-TEQ/g fat</b>
<b>Case 3:</b>	
<u>Consumption:</u> 12 kg d.m. basic feedingstuff 4 kg d.m. compound feedingstuff/ recyclates substituted by grain	<u>PCDD/PCDF input flux via feed:</u> 12 kg d.m. x 0.1 pg I-TEQ/g d.m. = 1,200 pg I-TEQ 4 kg d.m. x 0.21 pg I-TEQ/g d.m. = 840 pg I-TEQ total <b>2,004 pg I-TEQ</b>
<u>Milk performance:</u> 20 kg milk = 0.8 kg milk fat	<u>PCDD/PCDF excretion into milk:</u> <b>612.0 pg I-TEQ</b> <u>PCDD/PCDF milk concentration:</u> <b>0.76 pg I-TEQ/g fat</b>
<b>Case 4:</b>	
<u>Consumption:</u> 12 kg d.m. basic feedingstuffs 4 kg d.m. compound feedingstuff/ recyclates subst. by grain/ all grain <b>cleaned</b>	<u>PCDD/PCDF input flux via feed:</u> 12 kg d.m. x 0.1 pg I-TEQ/g d.m. = 1,200 pg I-TEQ 4 kg d.m. x 0.05 pg I-TEQ/g d.m. = 202.5 pg I-TEQ total <b>1,402 pg I-TEQ</b>
<u>Milk performance:</u> 20 kg milk = 0.8 kg milk fat	<u>PCDD/PCDF excretion into milk:</u> <b>420.7 pg I-TEQ</b> <u>PCDD/PCDF milk concentration:</u> <b>0.53 pg I-TEQ/g fat</b>

In a third step (*Case 3*), the recyclates in the compound feed, *i.e.* oil cake and oil meal, by-products from the food industry, animal meal and fish meal as well as oils and fates, were substituted by uncleaned grain. The resulting milk concentration of 0.76 pg I-TEQ/g fat is

comparable to *Case 2*, reflecting the influence of environmental impacts. The exclusion of recyclates in the compound feedingstuff only reduces the concentration by 12 % compared with *Case 1*.

*Case 4* is based on the same assumptions as made in *Case 3*, however, all uncleaned grain was replaced by cleaned grain. Generally, simple cleaning processes can lead to a significant reduction of the PCDD/PCDF contamination of feedingstuffs. Analyzing around hundred individual feed samples of different origins, types and composition for their PCDD/PCDF contents, Schöppe *et al.* (1997) found that especially grain cleaning (presuming a cleaning grade > 95 %) can reduce the PCDD/PCDF concentration of compound feedingstuff up to 50 %. For the following calculation we used the values published by Schöppe *et al.* (1996) for cleaned grain. The substitution leads to a further reduction of about 30 % (compared with *Case 3*).

#### 9.4.2 Different Recyclates

Figure 8 shows the mass and PCDD/PCDF fluxes for the four recyclates in compound feedingsstuffs relevant for EU feedingstuff production (see chapter 8.2.2). These four constitute 43 % of the mass base and approximately 50 % of the PCDD/PCDF flux. The similarity of the mass flux and the PCDD/PCDF flux indicates already that recyclates do not overproportionally contribute to the dioxin load in compound feedingstuffs.

Oil cakes and oil meals have the highest share on a mass basis and also contribute to the dioxin load. However, the source of the PCDD/PCDF contamination therein is largely unknown and needs further investigation. Oils and fats contribute only 2 % on a mass basis and 7.5 % to the dioxin contamination.

The potential for reduction exists either for recyclates with high mass fluxes (*e.g.*, oil cakes) or high PCDD/PCDF concentrations (*e.g.*, oils and fats<sup>8</sup>). For small mass fluxes with high contaminations (oils and fats), the easiest way to reduce the PCDD/PCDF flux into compound feedingstuffs would be its exclusion. For large mass fluxes with low contaminations, source identification of the PCDD/PCDF and its elimination would be the most practicable approach.

It should be noted, that the low PCDD/PCDF load along with animal meal and fish meal is based on low average concentrations used for this calculation. However, due to the high variability of PCDD/PCDF concentrations in these recyclates (see Table 48 and Table 49) compared to other ingredients, they might actually contribute to a much higher extend to the PCDD/PCDF flux into the compound feedingstuffs.

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<sup>8</sup> It should be noted that fresh oils and fats are also used in the feedingstuff production, however, no data is available as to the share of fresh materials

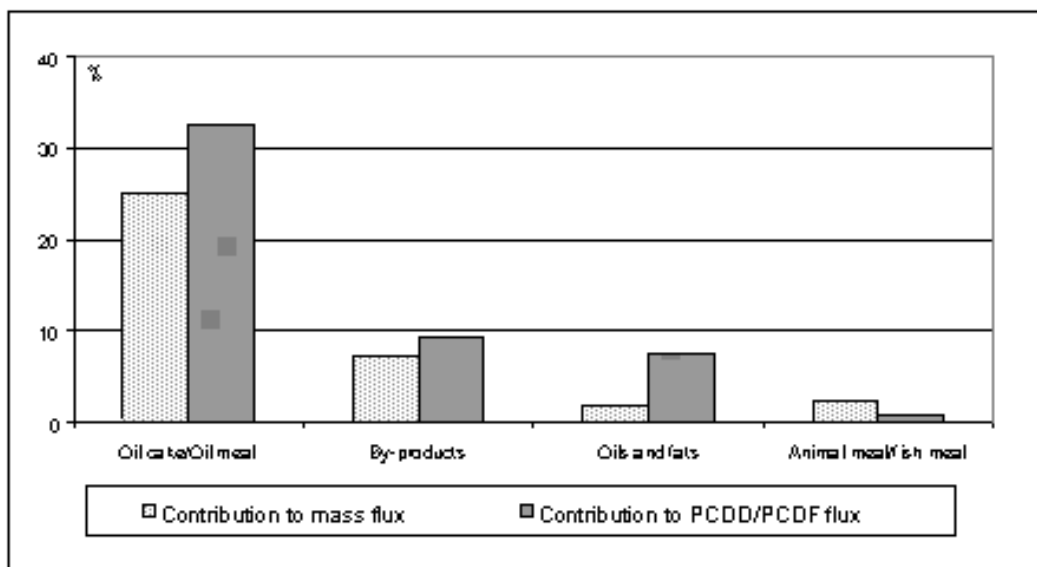


Figure 8: Fluxes of recyclates and related PCDD/PCDF fluxes into compound feedingstuffs





## 10 CONCLUSIONS

Industrially produced feedingstuffs (compound feedingstuffs) are particularly relevant in European agricultural practice (25 % contribution to feedingstuff consumption in Germany on a caloric base). The annual consumption of raw materials of the EU compound feedingstuff producers amounts to about 120 Mio. tons. Roughly 40 % thereof is covered by recyclates such as industrial by-products, used oils and fats, etc. (secondary resources).

Based on typical PCDD/PCDF concentrations in the various ingredients, the annual dioxin flux going into this industrial sector along with the raw materials was calculated at 28 g I-TEQ/year. No estimate could, however, be made for other POPs due to the lack of analytical data. Surprisingly, it was found that the PCDD/PCDF flux associated with recyclates is only slightly higher compared to the flux along primary raw materials like grain, pulses, greens etc. This indicates that recyclates are not of special concern under normal conditions. Nevertheless, episodes such as the Belgian chicken accident showed that severe contaminations can occur if highly contaminated materials enter the feedingstuff sector *via* the recycling industry, whether fraudulently or by accident.

Model calculations were done in order to link the above findings to the impact on human consumption:

- In the absence of fraudulent or accidental contamination of industrial feedingstuff ingredients, the human daily intake related to livestock reared on compound feedingstuff is only slightly higher compared to the intake related to livestock fed only native components such as greens, hay, grain etc. Limited reduction potential exists, however, within the recyclates such as used oils and fats and aspiration dust etc.
- Considerable reduction of human daily intake (approx. 30-40 % decrease in milk concentration) could be achieved by replacing uncleaned cereals commonly used in the preparation of compound feed as well as for direct livestock feeding through clean cereals, given that the residues (aspiration dust) are separated from the foodchain.
- Consequently the reduction potential for PCDD/PCDF fluxes would be higher for livestock reared on a higher share of compound feed or concentrates.

Quantification of the individual contributions of terrestrial, aquatic and industrial feedingstuff pathways to human exposure could not be made, because industrial feedingstuff production was found to be cross-linked with the other pathways.

Waste management is also food management since a lot of recyclates are fed to livestock. But waste management has not got that strict criteria applied to food management, *e.g.* a food producer would not be allowed to store or process toxic materials together with food.

In contrast the recycling industry manages in parallel potential recyclates such as edible oils and highly contaminated stuff such as hydraulic and transformer oils. This means that there is a high potential for cross-over between the different waste streams either by accident or fraudulently. As a consequence criteria applied to the food industry should also be applied to waste management whenever there is a crosslink to feedingstuff production.

## 11 MAJOR GAPS IN KNOWLEDGE

In order to assess the impact of PCDD/PCDF and POPs present in recyclates used in the feedingstuff preparation on human dietary exposure, data on the following parameters are essential:

- Raw material fluxes (including recyclates) into feedingstuffs for different livestock species;
- Related concentrations of PCDD/PCDF and POPs;
- Carry-over from feed to various livestock and livestock products, *resp.*
- Contribution of the various livestock and products to human diet.

During the study it became obvious that in general data from South European Member States are missing, both for production figures and levels of contamination along the foodchain. More data has been generated by North European Member States, but monitoring programs organized by the private sector, *e.g.*, the feedingstuff industry, and also by governmental authorities are hardly accessible. Moreover, the few data that have been published address PCDD/PCDF only. There is a lack of harmonized reporting and important accompanying information such as fat and water content, congener-specific data, etc. For other POPs the situation is even worse.

Concerning carry-over rates from feed to animals and animal products, so far, investigations have mainly concentrated on the transfer of PCDD/PCDF *via* the “grass-cow-milk” foodchain. Further, some studies have investigated the uptake of PCDD/PCDF and PCB by chicken.

Almost no information is available on the carry-over from feedingstuffs other than grass. Especially, the carry-over from inorganic ingredients of industrially manufactured feedingstuffs might be different due to different sorption properties as observed, *e.g.*, for clay. In addition, carry over rates for different species might differ due to specific metabolisms.

The availability of data on the contribution of livestock and its products to human diet in Member States is better.

But as long as the link to feedingstuff *via* the carry over rates cannot be quantified, no sound prediction of the impact of feedingstuff contaminated with PCDD/PCDF and POPs on human dietary intake can be obtained.

## 12 RECOMMENDATIONS

### 12.1 Monitoring

#### General Aspects

- Collect existing data on the composition of compound feedingstuffs used in the EU.
- Collect existing data from feedingstuff and foodstuff analyses for PCDD/PCDF and POPs from all Member States of the European Union. Fill data gaps by analyzing critical feedingstuffs and their ingredients, especially for the European Member States in Southern Europe.
- Include the determination of especially coplanar and mono-ortho substituted PCB in the PCDD/PCDF analysis of feedingstuffs, foodstuffs, foods and humans to determine the share of PCDD/PCDF vs. dioxin-like PCB when calculating the TEQ.
- Evaluate the need and the advantages of an European database containing POPs contaminations/concentrations in feedingstuffs. Several agencies, *e.g.* CLUA in Münster (Germany), Chemisches Untersuchungsamt in Freiburg (Germany), Dioxin Database of the German Federal Environment Agency or MAFF in the UK, have datasets which may serve as starting points for a central database.
- Evaluate the life-cycle of dioxin containing industrial products such as pentachlorophenol and its derivatives, pesticides etc. within the EU Member States by establishing import/export and use statistics and monitor the final disposal (importance should be given to recycling operations *e.g.* utilizing the calorific content of PCP-treated wood or other uses in textiles and leather).
- Determine the dietary intake of PCDD/PCDF and POPs for EU citizens with a diet consisting of potentially high contaminated foodstuffs such as fish, shellfish etc.

#### Specific cases of potential or known contamination

- Cooking oils and fats, since they tend to enrich organic contaminants from the foodstuff during cooking, and might be contaminated by waste oils.
- Animals fats and oils, since they are “natural” sinks for organic contaminants.
- Animal meals and fish meals, since highly variable concentrations were found.

## 12.2 Research

### Raw Materials

- Quantify feedingstuff related fluxes of raw materials including recyclates within the EU.
- Evaluate the „fat flow” within Europe, as well as exports and imports.
- Evaluate the possible implications from dioxin-contaminated clay in the production of feedingstuffs.
- Investigate the origin of the dioxin contamination in clay.
- Investigate the importance of aspiration dust.
- Evaluate which components subject to contamination can be omitted in the production of feeding stuffs or can be replaced by components that are not vulnerable for contamination with PCDD/PCDF and POPs.

### Processing of feedingstuffs

- Investigate the hot-air drying process and evaluate the influence of different types of fuel used in the direct drying process on the resulting PCDD/PCDF concentration of the dried feed.
- Investigate the use and contamination level of olive pulp in feedingstuff production.
- Investigate potential emissions into the environment from direct drying plants and cereal cleaning installations (*via* aspiration dust).
- Investigate if the process of a fat melting plant has a potential to generate PCDD/PCDF

### Carry-over rates from feedingstuff to livestock

- Determine the carry-over rates for various livestock, including fish and shellfish from aquaculture.
- Determine the carry-over rates for industrially produced feedingstuffs.
- Determine the carry-over from clay and other mineral ingredients
- Determine the carry-over rates for POPs other than PCDD/PCDF and PCB.
- Assess the carry-over from secondary sources like disinfectants, treated woods in farm building and fences, surface coatings of storage tanks; *etc.*

### Analytical aspects

- Validate bio- and immunoassays as well as fast chemical screening methods for monitoring purposes.
- Conclude on harmonized analytical procedures for clay and other mineral matrices with critical extraction properties.

## **12.3 Regulatory Aspects**

The recent accidents involving dioxin- and PCB-contaminated food and feedings stuffs in the Member States of the European Union have clearly demonstrated the vulnerability of our societies originating from polluted foodstuffs: The effects have been dramatic in many ways and have effected a multitude of sectors.

Regulatory measures should, therefore, first of all address waste management since most of the recent cases occurred through interferences within the recycling industry and linked to feedingstuff production. A number of accidental as well as fraudulent feedingstuff contaminations were only possible because highly contaminated waste streams (*e.g.* transformer oils) are being processed close to low contaminated waste streams (*e.g.* cooking oils and fats) which are used for feedingstuff production. Strict separation (as already initiated in Switzerland) should, therefore, be recommended by law.

By-products such as PCDD/PCDF are regulated by EU Directives and in some Member States there exists national legislation that goes beyond the requirements in the EU Directives (AEA 1998). Further, EU Member States as well as the European Commission are signatories to several global and regional Conventions such as the Basel Convention, OSPAR, HELCOM, UN-ECE POPs Protocol, and may ratify the Rotterdam Convention (PIC Convention) and actively participate in the negotiations for the POPs Convention. Lastly, WHO recommended a TDI of 1-4 pg TEQ/kg b.w. and day for the intake of PCDD/PCDF and dioxin-like PCB and recommends to take all efforts to lower the exposure of the general population to below 1 pg TEQ/kg b.w. and day.

- (a) Control the enforcement of existing legislation and obligations under international agreements;
- (b) Consider to move from regulation of emissions only, *e.g.* PCDD/PCDF air emissions from hazardous waste incinerators, to life-cycle considerations (as has started in the draft Directives for municipal solid waste incinerators) as exists in Japan (where ALL emissions are included and the emission is regulated on a  $\mu\text{g}$  TEQ per ton of waste incinerated basis);
- (c) Update numerals in EU Directives by moving from I-TEFs to WHO-TEFs for PCDD/PCDF AND include coplanar and mono-ortho substituted PCB.
- (d) Adopt the WHO-TDI of 1-4 of TEQ/kg body weight and day and thus include coplanar and mono-ortho substituted PCB. Take this recommendation for actions to reduce the daily intake to the target of 1 pg TEQ/kg body weight and day;

- (e) Although the future POPs Convention will address monitoring of POPs it has not yet specified the methods, the matrices nor the frequency of analyses. There is an urgent need for validating analytical methods for the determination of POPs. Methods for the analysis of PCDD/PCDF have been established with the Method 1948, similar approaches and minimum requirements should be established for the analysis of PCDD/PCDF in food and feedingstuffs. There is much greater demand to establish and validate methods for the analysis of PCB; here all three groups of PCB should be addressed:
- i) coplanar PCB \*
  - ii) mono-ortho substituted PCB \*
  - iii) 6 or 7 indicator PCB or
  - iv) total PCB.

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\* (i) and (ii) should be included in the determination of the (overall dioxin) TEQ; the two combined will have 12 PCB congeners analyzed, which have got a TEF in the WHO scheme

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