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Environmental and food contamination with polychlorinated biphenyls and selected POPs

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Abstract

The paper deals with the sources and pathways of the contamination of environment, domestic animals and foodstuffs by polychlorinated dibenzo-p-dioxins, dibenzofuran (PCDD/F and polychlorinated biphenyls as well as selected substitutes for PCBs. The main PCDD/F and PCB exposure sources in the environment including sinks and reservoirs are indicated. Current findings on causal relationships between the basic contamination of environmental compartments and (bio)magnification in the food chain are based on the results of research projects of the Federal Environmental Agency achieved in the last five years.

Introduction

A detailed report was given on dioxins and dioxin-like PCBs belonging to the group of the so-called POPs (**p**ersistent **o**rganic **p**ollutants) in the framework of a subject priority on dioxins (UBA 2011) in the journal UMID already in 2011. Many of these substances fulfil, at the same time, also the PBT criteria (**p**ersistent, **b**ioaccumulative, **t**oxic) according to the REACH Regulation (EU 2006).

In the last few years it was reported that food of an animal origin exceeded the maximum EU content for PCDD/F or the sum of PCDD/F and PCB more frequently. This referred to animal products of cattle, sheep, layers/eggs, game and fish. Notably the dioxin-like PCBs enrich distinctly stronger in particular in meat. It is striking that beef of extensively kept beef cattle, in particular from sucker cow husbandry, exceeds the maximum level for the total content of dioxins and dl-PCBs. A risk-oriented program „Federal Control Plan“ of the Federal Office for Consumer Protection and Food Safety (BVL), among others, goes into the problems of PCB contamination of beef from extensive farming (BVL 2013). It was not always possible to clearly identify the causes of the contamination situation. The Federal Environmental Agency (UBA) in close cooperation with the Federal Ministry for the Environment, Nature Conservation, Construction and Reactor Safety (BMUB) initiated several research projects to get onto the track of the sources and sinks, the pathways and the exposition of foodstuffs.

Information on POPs in environment and the food sector

The subject page of dioxins of the homepage of UBA allows a quick access to the problems. Here, the main sources for input pathways of dioxin and PCB contamination into environment are indicated. Table 1 lists selected scientific publications, workshops, completed research projects of UBA and background papers on this subject.

When dealing with the problems of dioxins and PCBs UBA makes also the contamination of man a subject of discussion. In this connection, the following problems are in the centre: How do dioxins get into man, what is the level of dioxin contamination of man in Germany, which effects have dioxins on man, which measures have been taken to reduce the dioxin contamination? The background paper „Dioxins and Dioxin-like PCBs in Environment and the Food Chains“(UBA 2017) and the „Data on Environment” (DzU) provide further information on dioxins and polychlorinated biphenyls in environment and foodstuffs.

Title	Completion	Promotional reference	Link
Evaluation of the research demand to clarify the causes for contamination of specific foodstuffs with dioxins and PCBs	10/2009	FKZ 3709 63 224	http://www.dioxindb.de/dokumente/Endbericht-16-10-09.pdf
Consideration of exposition and assessment of the transfer of dioxins, dioxin-like PCBs and PCB – literature study	09/2011	FKZ 3709 72 228	https://www.umweltbundesamt.de/en/publikationen/expositionsbetrachtung-beurteilung-des-transfers
Determination of wastes potentially containing POPs and recycling substances – derivation of limits	04/2015	FKZ 3712 33 342	https://www.umweltbundesamt.de/publikationen/ermittlung-von-potentiell-pop-haltigen-abfaellen
Analysis and assessment of trends of the contamination of environment and foodstuffs with selected POPs and extension of the data stock of the POP dioxin data base of the federal government and the laender with the aim to clarify pathway-related causes	12/2015	FKZ 3712 65 407 1	https://www.umweltbundesamt.de/publikationen/analyse-trendabschaetzung-der-belastung-der-umwelt
Allocation and quantification of the dioxin input via the air pathway by means of considering emission and immission congener patterns	03/2016	FKZ 3712 65 407 2	https://www.umweltbundesamt.de/publikationen/zuordnung-quantifizierung-der-dioxineintraege-auf
POP and Hg emissions from waste management plants	04/2016	FKZ 3712 42 313 1	https://www.umweltbundesamt.de/publikationen/pop-hg-emissionen-aus-abfallwirtschaftlichen
Closing workshop on causes, pathways & trends of POPs in environment	11/2016	-	https://www.umweltbundesamt.de/service/termine/abschluss-ws-zu-ursachen-pfaden-trends-von-pops-in
Answers to frequently asked questions to hexabromocyclo-dodecane (HBCD) – background paper	12/2016	-	https://www.umweltbundesamt.de/publikationen/answers-to-frequently-asked-questions-to
Dioxins and dioxin-like PCBs in environment and food chains – background paper	02/2017	-	https://www.umweltbundesamt.de/publikationen/dioxine-dioxinahnliche-pcb-in-umwelt-nahrungsketten
Evaluation of monitoring data of POPs, POP candidates and substitutes to clarify the causes, pathways and trends of environmental pollution	08/2017	FKZ 3715 65 423 0	https://www.umweltbundesamt.de/publikationen/evaluierung-von-monitoringdaten-zu-pops-pop

Table 1: Survey of the research projects and background information on POPs of German Environment Agency

Inventories of the atmospheric input into environment

The actual atmospheric background load and the load following thereof for environment and finally also for foodstuffs shows that also in future there will be underestimated and unnoticed sources and input pathways, in particular, of dl-PCBs. Figure 1 shows a temporal trend course of dioxin and furan emissions in Germany during the last 25 year, subdivided according to various source categories.

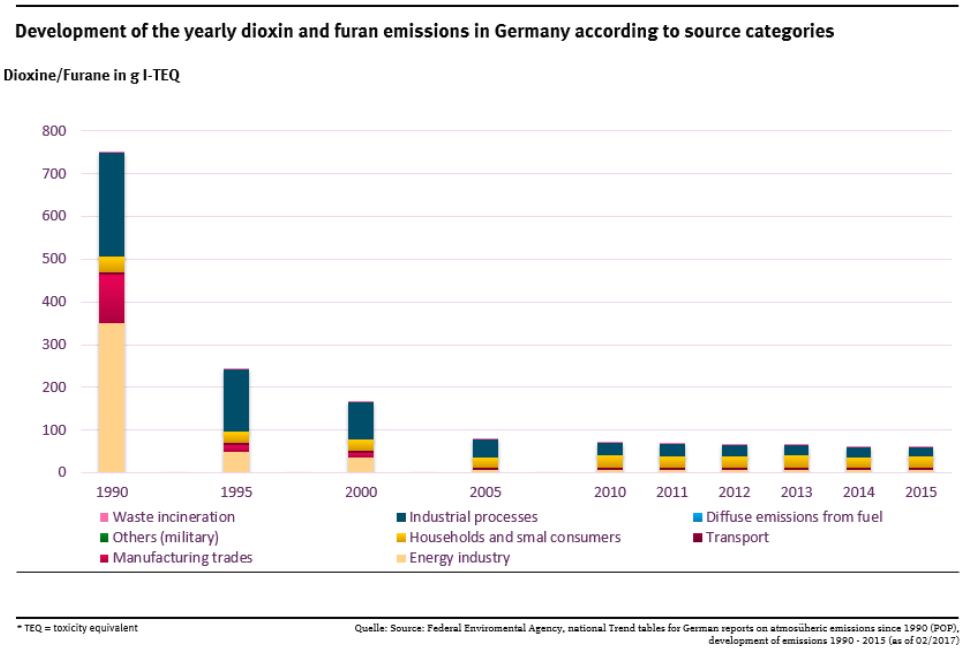

Figure 1: Development of the yearly dioxin and furan emissions in Germany according to source categories Source: Federal Environmental Agency 2017

PCB emissions result from industrial processes and energy industry, yet also from former open uses as e.g. PCB containing materials used in buildings. Figure 2 gives a survey of the various source categories (Source: German Environment Agency 2017)

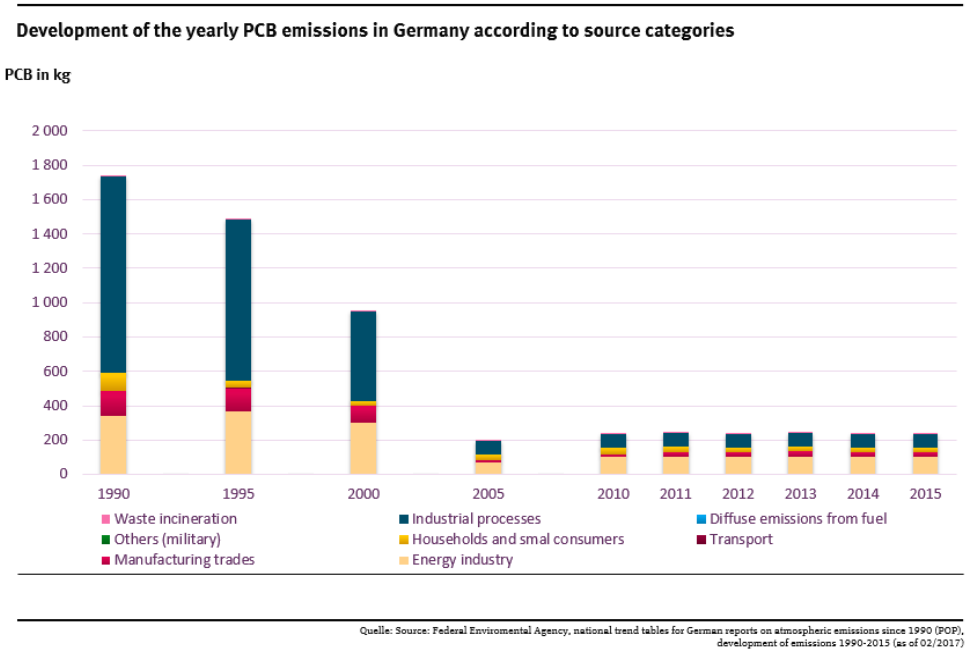

Figure 2: Development of the yearly PCB emissions in Germany according to source categories

Realizing the negative effects of chemicals with POP properties on man and environment the search for and the use of substitutes started. In the meantime, it has been stated that substitutes may have similar dangerous properties as the substances to be substituted. Substitutes such as chlorinated paraffins and specific brominated flame retardants (polybrominated diphenyl ether and HBCD) exist already ubiquitously in environment similar as PCN, PCB and dioxins.

There was a call for action and in the course of the research project „E**valuation of Monitoring Data on POPs, POP Candidates and Substitutes to Clarify the Causes, Pathways and Trends of Environmental Contamination"** (Potrykus et al. 2017) and the closing workshop "Causes, Pathways & Trends of POPs in Environment" (UBA 2016) the basic knowledge on specific POPs and POP candidates, in particular dl PCBs and selected PCB substitutes, especially SCCP, PBDE and HBCD, were investigated for the respective substances and substance groups and represented in detail. With the aim to better understand the causes of their ubiquitous existence in environment and the mechanisms and distribution pathways the connection between sources, pathways, sinks and their staying in environment were discussed.
To identify potential contaminators (sources and source processes) of environmental samples special methods of the so-called "Composition Data Statistics" (CoDa) have been applied in addition which so far have been only rarely applied and should be tested in the framework of the project.

Sources, sinks, pathways of environmental contamination

Based on hypotheses and assumptions on the transfer behaviour of PCDD/F, PCB and further POPs at the interface between environment and man research projects and investigation programs have been initiated on various levels. A study dealt with the „Determination of Wastes and Recycling Substances Potentially Containing POPs" and the „Derivation of Limits" (Potrykus 2015) to include further POPs in the list of the Stockholm Convention. This refers to

- Hexabromocyclododecane (HBCD),
- Hexachlorobutadiene (HCBD),
- Polychlorinated naphthalines (PCN),
- Pentachlorophenol (PCP) and
- Short-chain chlorinated paraffines (SCCP)

under the premise to find a reasonable balance between the promotion of circular economy for conserving natural resources and the protection of man and environment in managing wastes. The tense relationship between the two basic aims of waste policy shall be eased by fixing pollutant-specific limits. These limits have to correspond to the principle of proportionality in the same way as to the environment-political precautionary principle. It is essential for a proper fixing of the limits that a solid fact and data basis will exist for each individual contaminant. The annexes of the POP REGULATION (EC) no. 850/2004 (EU 2004) are the legal instrument for this.

In the last few years the foodstuff monitoring for dioxin-like (dl) PCB and also not dioxin-like (ndl) PCBs has been intensified as in 2006 the maximum EU contents for the sum of PCDD/F and dl PCB and in 2011 the maximum EU contents for the sum of the six ndl PCB congeners in foodstuffs were fixed. A duty of notification in the case of the maximum EU contents of dioxins for foodstuffs and feedstuffs being exceeded was adopted for laboratories in 2012 (MitÜbermitV 2012).

It was repeatedly stated that notably domestic animals from extensive farming (cattle, sheep, layers) or the foodstuffs got from them, also without a specific feedstuff contamination, exceed partly the maximum EU content for the sum of dioxins and dl PCB (PCDD/F-PCB-TEQ) and that this contamination comes, for the most part, from environment.
Man takes up PCDD/F and PCB basically through fatty foodstuffs coming from animals such as meat, milk products and eggs and fishery products. With its food intake a part of the population exceeds the tolerable daily intake (TDI) of 2 pg TEQ/kg body weight (kg) for the sum of PCDD/F and dioxin-like (dl) PCBs as well as the TDI for PCBs in total of 20 ng/kg and day (BfR 2010).

Thus, a new need for research and subsequently an extremely comprehensive research report on **„Analysis and assessment of the trend of contamination of environment and foodstuffs by selected POPs and extension of the data stock of the POP dioxin data base of the federal government and the laender with the aim of a pathway-related clarification of the causes“** (Weber et al. 2015) were the result. For the first time, the available information on sources, sinks and input pathways of PCB and PCDD/F was summarized and in connection with the exposition of domestic animals described in detail in this report. Figure 3 shows the connection between PCB contents in soil and PCB contents in plant growth. A maximum exceedance of the content may occur from soil contents of 6 ng WHO PCB TEQ/kg TS upwards assuming that 3 % of the soil share is taken up with feed.

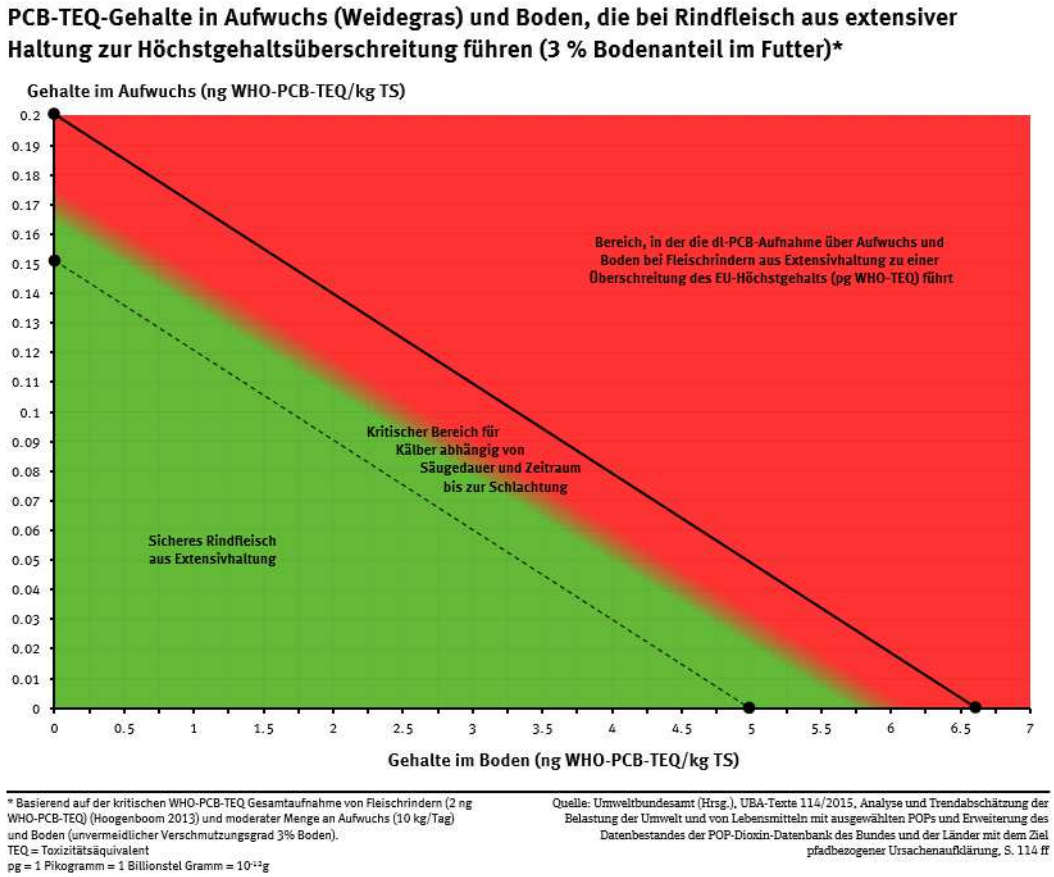

Figure 3: Connection between contaminant content of the soil and growth and secure beef production of extensively kept cattle

Legend:
PCB-TEQ contents in growth (pasture grass) and soil resulting in the case of beef from extensively kept cattle in an exceedance of the maximum content (3 % soil share in the feed)*

Content in growth (ng WHO-PCB-TEQ/kg TS) to content in soil (ng WHO-PCB-TEQ/kg TS)

Red area: Area where the dl PCB uptake through growth and soil of extensively kept beef cattle results in an exceedance of the maximum EU content (ng WHO-TEQ)
Red/green area: Critical area for calfs depending on the suckling period and the time up to being slaughtered
Green area: Secure beef from extensive farming

*based on the critical total WHO PCB TEQ uptake by beef cattle (2ng WHO PCB TEQ) (Hoogenboom 2013) and the moderate quantity of growth (10 kg/day and soil (unavoidable degree of pollution: 3 % of soil)
TEQ = toxicity equivalent
Pg = 1 picogram = 1 billionth gram = 10^{12} g

Source: German Environmt Agency (ed.), UBA-Texte 114/2015, **Analysis and assessment of the trend of contamination of environment and foodstuffs by selected POPs and extension of the data stock of the POP dioxin data base of the federal government and the laender with the aim of a pathway-related clarification of the causes. p. 115 ff.**

The illustration shows that the most important causes for the contamination of extensively kept cattle are the following:

- The input of dl-PCB takes place, on the one hand, through feed consisting, for the most part, of growth contaminated by atmospheric deposition (air pathway). On the other hand, when grazing the cattle takes up soil particles sticking to the grass which may amount up to a soil share of 3 % in the feed – depending on the type of soil.

- Local, yet also regional point sources may be the primary sources for an exposition for heards of cattle.

- In suckler cow husbandry the calf takes up dl-PCB through mother's milk. The descendants may not eliminate the dl PCB body load by supplying milk. That is why higher PCB contents are found in the beef of these descendants than in the beef of the suckler cows.

Extension of the data stock of the POP dioxin data base

The research project acquired data sets representing a potential for the contamination of feedstuffs and foodstuffs. This involves technical PCB mixtures, yet also sealant compounds and paints from open PCB applications. Also, a number of PCDD/F and PCBs formed unintentionally in chlorocarbons including pesticides and coloured pigments and a number of data sets on PCBs from thermal processes were included in the POP dioxin data base.
Partly suggestions were submitted on searching further PCDD/F and PCB data sets for a future completion of the POP dioxin data base. Thus, further aromatic chlorocarbons (e.g. pesticides, coloured pigments), yet also chlorinated paraffins, should be investigated for PCDD/F, PCBs, polychlorinated naphthalin (PCN) and other unintended POP contamination and the congener profiles and relative contents of POPs formed unintentionally should be included in the POP dioxin data base.

Statistical procedures for comparing congener profiles

Congener profiles are chemical fingerprints allowing to draw conclusions to the source. With the increasing number of data sets the idea arose to evaluate them also by means of statistical methods.

The project "**Allocation and quantification of the dioxin input via the air pathway by means of considering emission and ambient air congener patterns**" (Quass et al, 2016) aimed at evaluating the information on immissions, depositions and emissions of PCDD/F and PCBs existing at the federal government and in the laender with regard to the underlying source processes. In this connection, data stocks available in the POP dioxin data base of the Federal Government as well as additional data stocks collected in the Federal Laender in the framework of the project were used. Thereby, the main emphasis was put on city measuring points distant from sources and not immediately near the emittents. The available data were investigated by means of cluster and distance analyses of the substance profiles (congener or homologue patterns) for similarities and differences. In addition, appropriate partial data stocks were subjected to a factor analysis with positive matrix factorization (PMF). The factors found were subsequently compared by means of a specially developed procedure applying a multivariant similarity analysis with emission profiles. Comprehensive recommendations for a more appropriate procedure in monitoring PCDD/F and PCB ambient air concentrations, depositions and emissions were derived from the results and in the sense of an improved identification of the sources in the study (Quass et al 2016: 44 ff.).

Results

The results of these research projects contribute to finding more easily contamination sources and causes in environment and foodstuffs in future. They allow to quickly clarify the causes and to derive measures for reducing the contamination of environment by POPs and their substitutes.

Yet, the clarification of the causes of input of dioxins, PCBs and their substitutes into environment and the food chain is as previously a complex problem. Finding and quantitatively recording of sources, pathways and sinks is often associated with a high demand for clarification and research.

Web pages

Dioxin data base of the federal government and the laender:
http://www.dioxindb.de (Access on: 06.03.2018).

DzU – Data on environment: dioxins and polychlorinated biphenyls (PCB) in foodstuffs:
https://www.umweltbundesamt.de/daten/chemikalien/dioxine-polychlorierte-biphenyle-pcb-in (Access on 6.03.2018).

DzU – Data on environment: dioxins and polychlorinated biphenyls (PCB) in environment:
https://www.umweltbundesamt.de/daten/chemikalien/dioxine-polychlorierte-biphenyle-pcb-in-der-umwelt (Access on: 06.03.2018).

UBA – Federal Environmental Agency (2017): website dioxins
https://www.umweltbundesamt.de/themen/chemikalien/dioxine (Access on: 06.03.2018).

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BfR – Federal Institute of Risk Assessment (2010): Uptake of environmental contaminants through foodstuffs, results of the research project LexUKon
http://www.bfr.bund.de/cm/350/aufnahme_von_umweltkontaminanten_ueber_lebensmittel.pdf (Access on: 06.03.2018).

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https://www.bvl.bund.de/SharedDocs/Downloads/01_Lebensmittel/02_BUEp_dokumente/buep_berichte_archiv/BUEp_Bericht_2011.pdf?__blob=publicationFile&v=4 (Zugriff am: 06.03.2018).

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EU – European Union (2004): REGULATION (EC) no. 850/2004 OF THE EUROPEAN PARLIAMENT and the COUNCIL OF April 29, 2004 on persistent organic pollutants and on changing Directive 79/117/EEC.
http://eur-lex.europa.eu/legal-content/DE/TXT/PDF/?uri=CELEX:32004R0850&from=DE (Access on: 06.03.2018).

MitÜbermitV (2012): Regulation on obligations to communicate and transmit information on substances undesired for reasons of health (Communication and Transmission regulation) of December 28, federal law gazette 2012 I: 58. https://www.gesetze-im-internet.de/mit_bermitv/index.html (Access on 06.03.2018).

Potrykus A, Zettl E, Milunov M et al. (2017): Evaluation of monitoring data on POPs, POP candidates and substitutes to clarify causes, pathways and trends of environmental pollution. UBA-Texte 65.
https://www.umweltbundesamt.de/publikationen/evaluierung-von-monitoringdaten-zu-pops-pop (Access on: 06.03.2018).

Potrykus A, Milunov M, Weißenbacher J (2015): Determination of wastes and recycling substances potentially containing POPs – derivation of limits. UBA-Texte 34.
https://www.umweltbundesamt.de/publikationen/ermittlung-von-potentiell-pop-haltigen-abfaellen (Access on: 06.03.2018).

Quass U, Meyer J, Kuhlbusch T (2016): Allocation and quantification of the dioxin input via the air pathway by means of considering emission and immission congener patterns UBA-Texte 23. https://www.umweltbundesamt.de/publikationen/zuordnung-quantifizierung-der-dioxineintraege-auf (ACCESS on: 06.03.2018).

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