3.D.f - Agriculture other including use of pesticides

Country Specifics

Background

Hexachlorobenzene (HCB) is one of the listed persistent organic pollutants covered by the the Aarhus Protocol on Persistent Organic Pollutants from 2009, Annex III[1], the Stockholm Convention[2] and Directive 2016/2284 (NECD), Annex I from 2016[3]. These conventions and directives oblige parties to reduce their emissions of dioxins, furans, polycyclic aromatic hydrocarbons (PAHs) and hexachlorobenzene (HCB) below their levels in 1990.

In Germany the application of HCB as a pesticide, in a pure form, has been prohibited since 1977 and thus no HCB emissions were reported before 2015. However, HCB can occur as an impurity in active substances e.g.:

Lindane (gamma-hexachlorocyclohexane, γ-HCCH),

DCPA (Dimethyl tetrachloroterephthalate also known as chlorthal-dimethyl or Dacthal),

PCP (Pentachlorphenol),

Atrazine (2-Chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine),

Simazine (2,4-Bis(ethylamino)-6-chloro-1,3,5-triazine),

Propazine (2,4-Bis(isopropylamino)-6-chloro-1,3,5-triazine) and PCNB (Pentachlornitrobenzol also known as quintozine).

Further active substances are chlorothalonil (fungicide), tefluthrin (insecticide) and picloram (herbicide). These active substances are continued to be used in approved pesticides in Germany (cf. Table I, Pesticides). Tefluthrin is not emission relevant due to the application method. The pesticide is applied on seed in closed storage buildings (communication by Syngenta Agro, 2015 [4)]). Thus, it is not considered in the amount of reported HCB emissions.

Table 1a, Chlorothalonil (above) & Table 1b (below), Picloram: Overview of plant protection products and their trade names, chemical agents, intended applications and approval numbers; last revision, 2020

Chemical agent	Plant protection product	Approval number	Application for	Meanwhile not approved in Germany
Chlorothalonil	BRAVO 500	043138-00	Wheat	•
	Sambarin	033705-00	Wheat	•
	Pugil 75 WG	004486-00	Wheat	•
	AMISTAR Opti	005748-00	Wheat, barley und rye	
	Tattoo C	005805-00	Potatoes	•
	CREDO	006542-00	Wheat, barley	•
	Simbo Extra	004124-00	Wheat, barley	•
	ZAKEO Opti	005748-61	Wheat, barley und rye	
	Daconil 2787 Extra	023138-00	Golf course greens, tees, and fairways, ornamental turfgrass and ornamental herbs, shrubs and trees.	

Chemical agent	Plant protection product	Approval number	Application for	Meanwhile not approved in Germany
Picloram	EFFIGO	005866-00	Rapeseed (winter), maize, round cabbage	
	Barca 334 SL	008772-00	Rapeseed (summer/winter)	
	Belkar	008778-00	Rapeseed (winter)	
	Gajus	008943-00	Rapeseed (winter)	
	Gala 334 SL	008772-60	Rapeseed	
	GF-2545	008089-00	Rapeseed (winter)	
	Runway	006872-00	Rapeseed (winter)	

Sources: https://apps2.bvl.bund.de/psm/jsp/index.jsp, https://www.proplanta.de/Pflanzenschutzmittel/Liste/

HCB has never been contained in co-formulants of approved pesticides (communication of the Federal Office of Consumer Protection and Food Safety (BVL, 2015) [5)].

In the past, some applicants listed maximum HCB concentrations in technical active substances in certain lindane-containing substances. The concentrations given amounted to ≤ 0.1 g/kg, a level oriented to the detection limits of the analysis method used at the time. Substances conforming to that maximum concentration were approved only through 1989 or 1990 (in one case, through 1995). Obligations to report substance quantities sold did not take effect until 1998. For the other relevant active substances, the BVL has no information on HCB as an impurity.

Methodology

The emissions were calculated in keeping with the method proposed in the EMEP (2019) [6] (3Df/3I-5, chapter 3, Tier 1 approach).

Epest = Σmpest_i • EFpest_i

To estimate the emission of HCB which is present as an impurity, an impurity factor (IF) has to be considered in the calculation:

Epest = Σmpest_i • IFj,i • EFpest_i

where:

Epest = total HCB emission of active substance (in mg a-1, unit conversion reported in kg a-1), mpest = mass of individual active substance applied (kg a-1), IFj,i = impurity factor of the jth active substance in the ith active substance (mg kg-1) EFpest= EF for individual active substance (volatile fraction of applied amount of the active substance).

A modeled emission factor is used for Germany (see description of Emission factors). According to the definition of the Tier 2 Approach [7] (EMEP Guidebook 2019) the method can be described as Tier 2.

Activity data

As activity data, domestic sales of pesticides with the active substances chlorothalonil and picloram compiled by the BVL (BVL, 2019 [8] were used (reports pursuant to § 64 of the Plant Protection Act (PflSchG, 2012 [9]); cf. Table II, domestic sales. For 2019, the same amount of pesticides used is assumed as for 2018 was used. The data will not be updated until submission 2022.

Table II (last update 12/08/2021): Published data on domestic sales of active substances, in t/a, 1990 - 2019, [10]

	1990-2001	**2002**	**2003**	**2004**	**2005 - 2015**	**2016 - 2017**	**2018 - 2019**
Chlorothalonil, in t/a	No published data	25-100	100-250	25-100	250-1000	1000-2500	250-1000
Picloram, in t/a	No published data	Not specified	Not specified	Not specified	2.5-10[(1)] 1.0 – 2.5[(2)]	2.5 - 10	2.5 - 10

1) The quantity data are for the years 2007 and 2011-2015. 2) The quantity data are for the years 2005, 2006, 2008, 2009 and 2010.

The quantities sold domestically are assumed to be equivalent to the quantities used. The specific sales data used in the calculation are considered to be business and operational secrets and thus have to be kept confidential.

HCB Impurities

The HCB quantities are calculated in light of the maximum permitted concentrations of HCB impurities established by legal acts of the EU [11] defines, for certain active substances and in connection with their approval, maximum levels of impurities that are of toxicological or ecotoxicological concern or that are of special concern due to the environmental risks they pose. Since the implementing regulation is a directly applicable law, the maximum levels are binding throughout Europe. In addition, in special cases the BVL may define maximum levels for impurities that the regulation does not cover. Conformance with such maximum levels is then included as a necessary condition for approval of relevant pesticides.)). The approach is a highly conservative one that probably overestimates the actual emissions. The BVL has no information regarding the actual concentrations of impurities, either past or present, in pesticides placed on the market.

Chlorothalonil

Before 2006 there was no legal regulation in Germany on the maximum content of HCB in the active ingredient chlorothalonil. However, with the implementation of Directive 91/414/EEC [12)], manufacturers had to analyse their technical active substance for possible relevant impurities and, where appropriate, indicate a maximum level. These maximum levels had to be maintained. Information about the levels specified for chlorothalonil for the years 1990 and 1999 for Germany are not known. As described in the FAO specification (2015, p. 49, [13)]) Chlorothalonil was reviewed by IPCS (INTERNATIONAL PROGRAMME ON CHEMICAL SAFETY) in the Environmental Health Criteria (EHC) series in 1996. The limit for HCB in the FAO specification in 1998 for chlorothalonil was 0.3 g/kg and manufacturer stated in that report that the company had improved the manufacturing process (see FAO Specification, 2015, p. 51) . Thus, a maximum HCB concentration of 300 mg/kg (IPCS, 1996 [14)]) is considered for the years 1990 until 1999 for Germany.

Directive 2005/53/EC [15)], which entered into force on 1 March 2006, established a maximum permitted HCB concentration of 10 mg/kg in chlorothalonil as a technical active substance. Due to a review by the FAO 288/2005 (see FAO 2015, p.22 and p. 51) and taking into account the results of batch samples testing the impurity the max. concentration was raised again up to 0.04 g/kg. Thus, the standard was raised to 40 mg/kg in Directive 2006/76/EC [16)]).

For the years as of 2000, the specified maximum HCB concentrations in chlorothalonil differ considerably from pesticide to pesticide – in some cases despite the EU-regulation, the values differ from year to year for the same pesticide. For the year 2000 an interim value was calulated by linear interpolation. (170 mg/kg). For the years 2001 to 2004, the value of 40 mg/kg is used.

The quantities of pesticide active substances sold, and reported pursuant to Art. 64 Plant Protection Act were used as a basis for deriving a weighted average for the maximum concentrations for 2000, 2005, 2010 and 2013 (cf. Table IV, concentrations of impurities). The average was used to calculate the relevant HCB quantities for the period between 2005 and 2008. For the later years starting from 2009 onwards the information on the maximum concentration of 10 mg/kg is assumed which is indicated by the authorisation holders (Syngenta Agro, 2015). For 2019, the same quantity is assumed as for 2018. The data will be updated with submission 2022.

Picloram

For picloram, a maximum concentration of 50 mg/kg has been specified for some pesticides. Relevant pesticides were introduced in Germany beginning in 2006. Picloram was added to Annex I with the Commission Directive 2008/69/EC [17)] and the HCB impurity is still set to 50 mg/kg (FAO, 2012 [18)]). For 2019, the same quantity is assumed as for 2018. The data will be updated with submission 2022.

Lindane

The HCB quantities in lindane were determined with the help of historically reported lindane-quantity data (cf. Table III) of the former former Federal Biological Office for Agriculture and Forestry (Biologische Bundesanstalt für Land- und Forstwirtschaft; BBA), Institute of Pesticide Technology Assessment (Institut für Folgenabschätzungen im Pflanzenschutz, Kleinmachnow). Those data are based on information that producers provided voluntarily. For the years after 1997 no data are available because the application of Lindan was phased out in 1998.

Table III: Domestic sales of Lindane, in t/a

	1990	**1991**	**1992**	**1993**	**1994**	**1995**	**1996**	**1997**
Lindane	119.34	126.28	73.05	46.59	36.67	25.97	36.57	28.74

For lindane, a maximum concentration of 100 mg/kg was specified for the years 1990 through 1994. For the years after 1994 a lower concentration (50 mg/kg) was assumed which is based on compiled information of Bailey (2001)[19] (cf. Table IV). *Table IV: Maximum concentrations of HCB impurities in relevant active substances, in mg per kg*

Impurity content	**1990**	**1995**	**2000**	**2001**	**2002**	**2003**	**2004**	**2005**	**2009 - 2019**
Chlorothalonil	300	300	170	40	40	40	40	13.33*	10
Picloram	50	50	50	50	50	50	50	50	50
Lindane	100	50	n/a	n/a	n/a	n/a	n/a	n/a	n/a
n/a: not applicable; *weighted average									

In recent years, the total HCB quantities in pesticide active substances (cf. Table V) have been affected primarily by sales of chlorothalonil.

While this results from the large quantities of chlorothalonil-containing pesticides sold, it is also due to the high chlorothalonil concentrations in such pesticides and to the high permitted maximum HCB concentrations (0.3 g/kg), in chlorothalonil as a technical active substance, that applied prior to 2000. Due to the revised data, changes in HCB quantities occur. The maximum HCB quantity for picloram, in the period under consideration, were lower, respectively, than the relevant quantities for chlorothalonil. For this reason, fluctuations in sales of picloram have very little impact on maximum HCB quantities.

Table V: Maximum HCB quantities in domestically sold active substances in pesticides [kg] from 1990 until 2019

	1990	**1991**	**1992**	**1993**	**1994**	**1995**	**1996**	**1997**	**1998**	**1999**
Max. HCB Amount	107.12	137.98	55.65	29.68	26.71	17.98	26.58	24.24	5.01	44.98
	2000	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**	**2008**	**2009**
Max. HCB Amount	18.58	0.79	1.00	9.60	1.59	11.43	12.07	9.88	9.59	5.25
	2010	**2011**	**2012**	**2013**	**2014**	**2015**	**2016**	**2017**	**2018**	**2019**
Max. HCB Amount	6.30	6.68	5.48	5.84	10.22	9.03	11.70	14.39	8.80	8.80

Emission factor

The HCB emission factor was modeled by using the Pesticide Leaching Model (PELMO 3.31) which is also used for the European registration process of pesticides. The one-dimensional pesticide leaching model has been extended to predict the pesticide volatilisation after agricultural applications under field conditions (Ferrari et al., 2005 [20]) however, it is also able to calculate the behaviour of impurities in the products. The model was developed by the Fraunhofer Institute for Molecularbiology and Applied Ecology (IME).

Due to its volatility behaviour in the presence of water vapor even at low temperatures, ambient HCB is usually found in the vapour phase and appears to volatilize from plant and soil surfaces during the first 24 hours after application (Klein, M., 2017) [21]. As a test substance chlorothalonil was used in the simulation. The simulation conditions are defined after annual applications in potatoes 14 days before harvest. A detailed description of the input parameters is available (Klein, M., 2017). It is assumed that the HCB volatilisation of the impurity in picloram is the same.

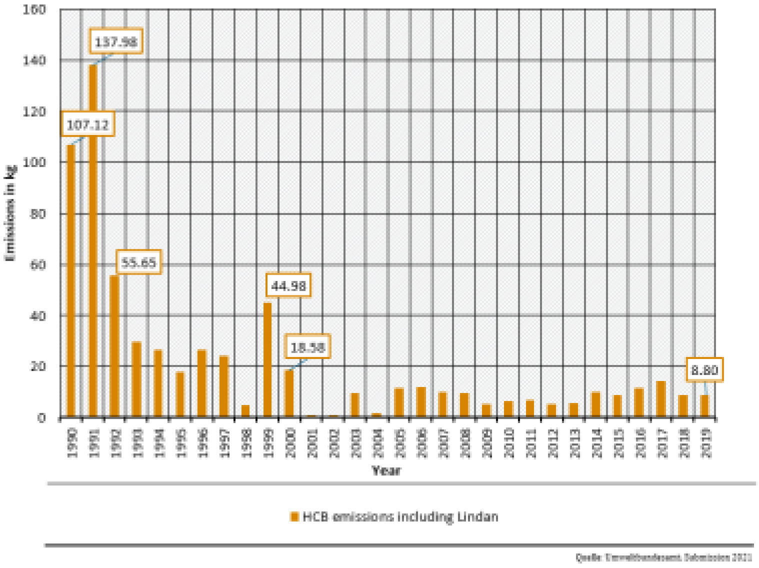
The result of the emission factor is 1 or 100% and represents a fraction that has to be multiplied with the concentration of the applied compound.

Trend discussion for Key Sources

The following chart give an overview of the emission trend of HCB (see Picture 1). The HCB emissions were calculated and updated for the years 2017 and 2018. The value for 2019 was updated. HCB emissions are mainly dominated by the proportion of chlorothalonil. According to the information of the BVL, a possible explanation for the increase of HCB emissions from 2005 onwards would be the renewed approval of Bravo 500. Possibly the first “sell-out” took place in 2014, because the approval end of “Bravo 500” was originally 30.04.2016 with a sales period until 30.10.2016 and a use-by period for users until 30.10.2017.

The end of the EU active substance approval for chlorothalonil was later extended to 31.10.2018 and again to 31.10.2019, and accordingly also the approvals for the pesticides in Germany. According to the Implementing Regulation (EU) 2019/677 [22], the BVL revoked the last three approvals for plant protection products containing chlorothalonil as of 31 October 2019. There was a sales deadline of April 30, 2020 (see https://www.bvl.bund.de/SharedDocs/Fachmeldungen/04_pflanzenschutzmittel/2019/2019_06_19_Fa_Widerruf_Chlorthalonil.html of June 19, 2019).

Picture 1: Annual trend of HCB emissions in Germany in the sector agriculture, in kg



Recalculations

No recalculations were made from 1990 until 2016. Only the domestic sales in 2017 were updated.

Uncertainty

For the calculation of emissions consumption figures (i. e. statistical figures) are used. Therefore, a standard error of HCB content is assumed as 2.5 % for the emission inventory. The 95% confidence interval is therefore 5 %. A normal distribution is assumed.

The uncertainty for the emission factor was determined using the PELMO model. For this purpose, the applied amounts of HCB on the plant surface were calculated with a vapour pressure reduced by a factor of 10. In addition, the meteorological conditions for modelling were selected in such a way that a range of possible emission factors for different locations was distributed across Europe (from Porto, Portugal, to Jokioinen in Finland). This results in a minimum and maximum emission factor. The maximum range was 30 %; the arithmetic mean was 10 % uncertainty (personal communication, Klein, 2017). A conservative approach and thus 30 % uncertainty is chosen for the calculation of uncertainties. This results in a total uncertainty for HCB emissions of 30.4 %.

Planned improvements

No improvements are planned for the next submissions.

1)

Aarhus Protocol on Persistent Organic Pollutants (2009), United Nation: Aarhus Protocol on Long-range Transboundary Air Pollution, Persistent Organic Pollutants, 1998 - Amendment - (on Annexes V and VII) Decision 2009. Status In force (since Dec 13, 2010), Annex III.

2)

Stockholm Convention (2001): The Stockholm Convention on Persistent Organic Pollutants, opened for signature May 23, 2001, UN Doc. UNEP/POPS/CONF/4, App. II (2001), reprinted in 40 ILM 532 (2001)

[hereinafter Stockholm Convention]. The text of the convention and additional information about POPs is available online at the United Nations Environment Programme's (UNEP's) POPs website

3)

Directive 2016/2284/EU: Directive (EU) 2016/2284 of the European Parliament and of the Council of 14 December 2016 on the reduction of national emissions of certain atmospheric pollutants, amending Directive 2003/35/EC and repealing Directive 2001/81/EC (Text with EEA relevance).

4)

Syngenta Agro (2015), Dep. „Zulassung und Produktsicherheit", personal communication

5)

BVL (2015) (Bundesamts für Verbraucherschutz und Lebensmittelsicherheit Braunschweig): persönliche Mitteilung der Wirkstoffdaten, 2015.

6)

EMEP (2019): EMEP/EEA air pollutant emission inventory guidebook – 2019, EEA Report No 13/2019, https://www.eea.europa.eu/publications/emep-eea-guidebook-2019.

7)

Tier 2 is similar to Tier 1 but uses more specific emission factors developed on the basis of knowledge of the types of processes and specific process conditions that apply in the country for which the inventory is being developed. Tier 2 methods are more complex, will reduce the level of uncertainty, and are considered adequate for estimating emissions for key categories.

8)

BVL (2019) (Bundesamts für Verbraucherschutz und Lebensmittelsicherheit Braunschweig): persönliche Mitteilung der Wirkstoffdaten, 2019.

9)

PflSchG (2012): Gesetz zur Neuordnung des Pflanzenschutzgesetzes, Bundesgesetzblatt (BGBl), Jahrgang 2012, Teil I, Nr. 7, § 64.

10)

BVL (2019) (Bundesamts für Verbraucherschutz und Lebensmittelsicherheit Braunschweig): Absatz an Pflanzenschutzmitteln in der Bundesrepublik Deutschland, Ergebnisse der Meldungen gemäß § 64 Pflanzenschutzgesetz, https://www.bvl.bund.de/DE/Arbeitsbereiche/04_Pflanzenschutzmittel/01_Aufgaben/02_ZulassungPSM/03_PSMInlandsabsatzAusfuhr/psm_PSMInlandsabsatzAusfuhr_node.html

11)

Commission Implementing Regulation (EU) No 540/2011 ((COMMISSION IMPLEMENTING REGULATION (EU) No 540/2011 of 25 May 2011 implementing Regulation (EC) No 1107/2009 of the European Parliament and of the Council as regards the list of approved active substances. http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex%3A32011R0541

12)

Council Directive 91/414/EEC of 15 July 1991 concerning the placing of plant protection products on the market, https://eur-lex.europa.eu/legal-content/en/ALL/?uri=CELEX:31991L0414

13)

FAO (2015): FAO (Food and Agriculture Organization of the United Nations) Specifications and Evaluations for Chlorothalonil, p 51. http://www.fao.org/agriculture/crops/thematic-sitemap/theme/pests/jmps/ps-new/en/

14)

IPCS (1996), Chlorothalonil. Environmental Health Criteria, 183. 145pp. WHO, Geneva, Switzerland. ISBN 92-4-157183-7. C12138614.7.

15)

Directive 2005/53/EC: Commission Directive 2005/53/EC of 16 September 2005 amending Council Directive 91/414/EEC to include chlorothalonil, chlorotoluron, cypermethrin, daminozide and thiophanate-methyl as active substances 2005/53/EC C.F.R. (2005).

16)

Directive 2006/76/EC: Commission Directive 2006/76/EC of 22 September 2006 amending Council Directive 91/414/EEC as regards the specification of the active substance chlorothalonil (Text with EEA relevance) 2006/76/EC C.F.R. (2006

17)

Directive 2008/69/EC: Commission Directive 2008/69/EC of 1 July 2008 amending Council Directive 91/414/EEC to include clofentezine, dicamba, difenoconazole, diflubenzuron, imazaquin, lenacil, oxadiazon, picloram and pyriproxyfen as active substances 2008/69/EC C.F.R. (2008).

18)

FAO (2012): FAO (Food and Agriculture Organization of the United Nations)Specifications and Evaluations for Picloram, Table 2, p. 23.

http://www.fao.org/agriculture/crops/thematic-sitemap/theme/pests/jmps/ps-new/en/

19)

Bailey, R. E., (2001): Global hexachlorobenzene emissions. Chemosphere, 43(2), 167-182.

20)

Ferrari, F., Klein, M., Capri, E., & Trevisan, M. (2005). Prediction of pesticide volatilization with PELMO 3.31. Chemosphere, 60 (5), 705-713

21)

Klein, M. (2017), Calculation of emission factors for impurities in organic pesticides with PELMO. Personel communication. Description available, Umweltbundesamt, FG V 1.6,Emissionssituation.

22)

Regulation (EU) 2019/677: Commission Implementing Regulation (EU) 2019/677 of 29 April 2019 concerning the non-renewal of the approval of the active substance chlorothalonil, in accordance with Regulation (EC) No 1107/2009 of the European Parliament and of the Council concerning the placing of plant protection products on the market, and amending Commission Implementing Regulation (EU) No 540/2011, http://data.europa.eu/eli/reg_impl/2019/677/oj