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 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 reported until the 2016 reporting. 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). Two of these active substances are continued to be used in approved pesticides in Germany (cf. Table I). 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]). In 2022, analyses were carried out for HCB contamination in the crop protection product Force 20 CS. HCB contamination could not be detected. Thus, it is not considered in the amount of reported HCB emissions.

Table I, Chlorothalonil (above) & Table Ib (below), Picloram: Overview of plant protection products and their trade names, chemical agents, intended applications and approval numbers; last update September 2022

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://www.bvl.bund.de/SharedDocs/Downloads/04_Pflanzenschutzmittel/Beendete_PSM.html?nn=11031326, 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. However, publications in recent years have included data from 1977 onward (BVL 2022) [6]. Therefore, data on the active ingredients atrazine, simazine, propazine, and quintozine are also available and will be included in the 2023 submission.

Methodology

The emissions were calculated in keeping with the method proposed in the EMEP (2019) [7] (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 [8] (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, picloram, lindane compiled by the BVL[9] were used (reports pursuant to § 64 of the Plant Protection Act (PflSchG, 2012 [10]); (cf. Table II, domestic sales)[11]. Since mid-2020, domestic sales of all active substances have been published.

Table II, Published data on domestic sales of active substances from 1987 until 2021 in t/a

HCB Impurities

The HCB quantities are calculated in light of the maximum permitted concentrations of HCB impurities established by legal acts of the EU [12] 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 substance chlorothalonil. However, with the implementation of Directive 91/414/EEC [13], 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, [14]) 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 [15]) is considered for the years 1990 until 1999 for Germany.

Directive 2005/53/EC [16], 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 [17]). According to the current FAO Specifications and Evaluations for Agricultural Pesticides, Chlorothalonil (2020)[18] continues to be reported at 40 mg/kg (see Table 1, p. 18).

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).

According to information from the BVL (October 2021, personal communication), the maximum content of HCB in chlorothalonil was increased from 10 to 40 mg/kg in the products “AMISTAR Opti” and “CREDO” due to subsequently applied for active substance sources. Likewise, an additional potential active substance source (production site) was also reported retroactively. For the years 2001 to 2017, the value of 40 mg/kg (for the reporting 2022) is used for the maximum content of HCB. For the years from 2018 onwards, the information from the authorisation holders (Syngenta Agro, 2015) is used for the maximum concentration of 10 mg/kg, as only the product “AMISTAR Opti” was still on the market.

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 [19] and the HCB impurity is still set to 50 mg/kg (FAO, 2012 [20]). For 2020, the same amount as for previous years is assumed.

Lindane

The data on lindane sales were compared by the BVL with historical data from the former GDR statistics and published since 2020 (see Table II). For the years after 1997 no data are available because the application of lindane was phased out in 1998.

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)[21)] (cf. Table III).

Table III: Maximum concentrations of HCB impurities in relevant active substances, in mg per kg

Impurity content	1990-1994	1995-1997	1998 - 1999	2000	2001 - 2003	2004 - 2017	2018 - 2020
Chlorothalonil	300	300	300	170	40	40	10
Picloram	50	50	50	50	50	50	50
Lindane	100	50	n/a	n/a	n/a	n/a	n/a

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.The maximum HCB quantities used in the 2022 submission correspond to the emissions and are presented under the chapter 'Recalculations'.

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 [22)]) 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).

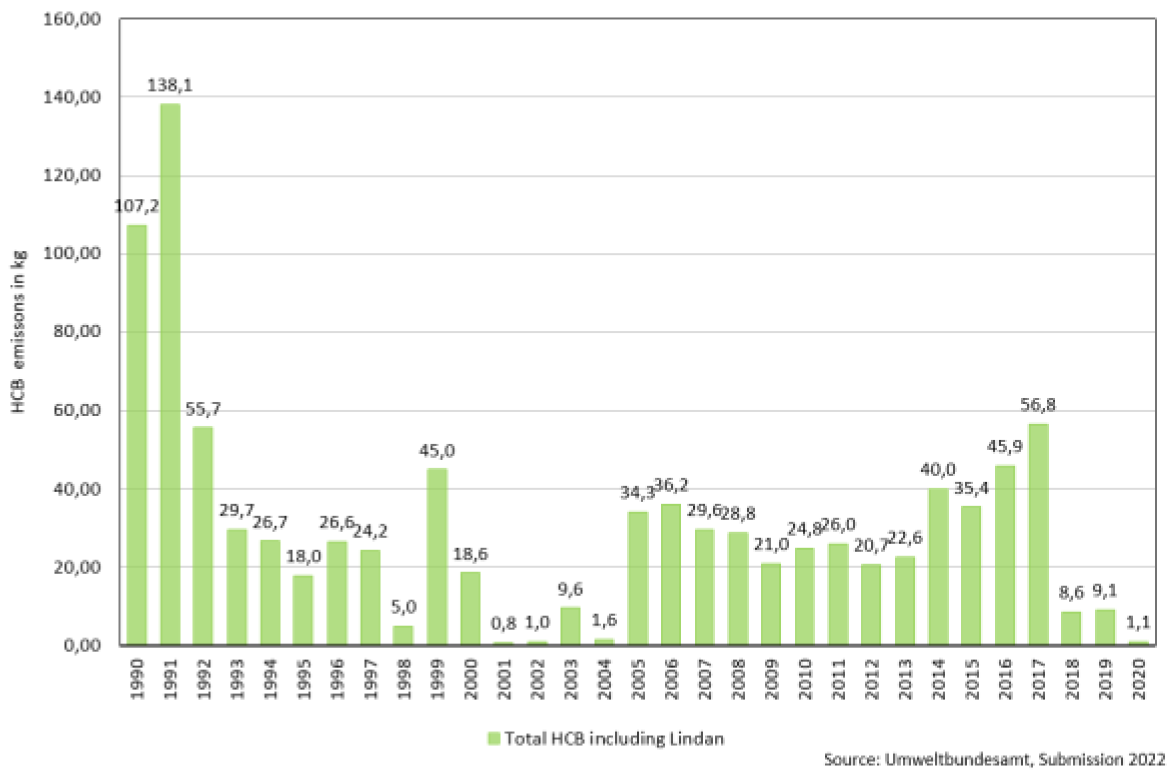
Due to its volatility behaviour in the presence of water vapor even at low temperatures, ambient HCB is usually found in the vapour phase and appears to volatilize from plant and soil surfaces during the first 24 hours after application (Klein, M., 2017) [23)]. As a test substance chlorothalonil was 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). HCB emissions were fully recalculated up to 1990. HCB emissions are mainly dominated by the share of chlorothalonil. According to the BVL (2021a), a possible explanation for the increase in HCB emissions from 2005 onwards would be the re-approval of “Bravo 500” in December 2004 against Septoria in wheat and then for the first time against phytophthora in potatoes. It is possible that the first “sell-out” took place in 2014, as the end of approval for “Bravo 500” was originally 30.04.2016 with a sales deadline of 30.10.2016 and a phase-out period for users until 30.10.2017. The end of the EU active substance authorisation for chlorothalonil was later extended to 31.10.2018 and again to 31.10.2019, and with it the authorisations for the plant protection products in Germany. With the Implementing Regulation (EU) 2019/677 23), the BVL revoked the last three approvals for plant protection products containing chlorothalonil on 31 October 2019[24)]. A sell-off period until 30 April 2020 applied. Often, in the last years before the end of the approval, the remaining stocks are brought onto the market, which leads to higher sales than in previous years.

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



Recalculations

Recalculations were made for the complete time series due to the changes and new information given by the BVL for the amount of domestic sales of the active substances. The following Tables IV a) - c) show the differences between the data for submission 2021 and the current data and are given in tonnes per year and in percentage.

Tables IV a) - c): Recalculation of the activity data: lindane, chlorothalonil and picloram.

a)

Active Substance	Unit	1990	1991	1992	1993	1994	1995	1996	1997
Lindane_SUB 2022	t	120.4	127.4	73.7	47.0	37.0	26.2	36.9	29.0
Lindane_SUB 2021	t	119.3	126.3	73.0	46.6	36.7	26.0	36.6	28.7
Difference	t	1.0	1.1	0.7	0.4	0.3	0.2	0.3	0.2
Difference	%	0.9	0.9	0.9	0.9	0.8	0.7	0.9	0.8

b)

Active Substance	Unit	2019
Chlorothalonil_SUB 2022	t	911.8
Chlorothalonil_SUB 2021	t	860.8
Difference	t	50.9
Difference	%	5.9

c)

Active Substance	Unit	2019
Picloram_SUB 2022	t	7.5
Picloram_SUB 2021	t	3.9
Difference	t	3.5

Active Substance	Unit	2019
Difference	%	90.0

Due to the changes in the input data and the assumptions on the maximum quantities of HCB, the emissions also change. The following Table V shows the differences between the data for submission 2021 and the current data and are given in kg per year and in percentage.

Table V: Recalculation of HCB emisssion from 1990 until the latest reported year, in kg.

Emissions	Unit	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999
HCB_SUB 2022	kg	107.2	138.1	55.7	29.7	26.7	18	26.6	24.2	5.0	45.0
HCB_SUB 2021	kg	107.1	138	55.7	29.7	26.7	18	26.6	24.2	5.0	45.0
Difference	kg	0.1	0.1	0.1	0.04	0.03	0.01	0.02	0.01	0.0	0.0
Difference	%	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.0	0.0	0.0

Emissions	Unit	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009
HCB_SUB 2022	kg	18.6	0.8	1	9.6	1.6	34.3	36.2	29.6	28.8	21
HCB_SUB 2021	kg	18.6	0.8	1	9.6	1.6	11.4	12.1	9.9	9.6	5.3
Difference	kg	0	0	0	0	0	22.9	24.1	19.8	19.2	15.8
Difference	%	0	0	0	0	0	200	200	200	200	300

Emissions	Unit	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019
HCB_SUB 2022	kg	24.8	26	20.7	22.6	40	35.4	45.9	56.8	8.6	9.1
HCB_SUB 2021	kg	6.3	6.7	5.5	5.8	10.2	9.0	11.7	14.4	8.8	8.8
Difference	kg	18.5	19.3	15.2	16.8	29.8	26.4	34.2	42.4	-0.2	0.3
Difference	%	293.9	288.8	277.9	287.3	291.8	292.3	292.6	294.3	-2.2	3.6

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

According to the BVL, no maximum permitted HCB concentrations have ever been legally established for the technical active substances atrazine, simazine, lindane and clopyralid, nor are such limits in place today. Further information on the sales volumes of atrazine, simazine and cloparylide is now available but not included in the current submission. The method will be reviewed accordingly, adjusted and extended for the 2023 submission.

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

[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] BVL 2022, “ Absatz an Pflanzenschutzmitteln in der Bundesrepublik Deutschland Ergebnisse der Meldungen gemäß § 64 Pflanzenschutzgesetz für das Jahr 2017, korrig. Version von Nov 2018, Tab 3.2, https://www.bvl.bund.de/SharedDocs/Downloads/04_Pflanzenschutzmittel/01_meldungen_par_64/meld_par_64_2017.pdf;jsessionid=575C3CE6FEC9CF7B81387944C90C6972.1_cid372?__blob=publicationFile&v=2

[7] 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.

[8] 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.

[9] BVL (2021a) (Bundesamts für Verbraucherschutz und Lebensmittelsicherheit Braunschweig): personal communication of the active substance data, 2021.

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

[11] BVL,(2021b): Berichte über Inlandsabsatz und Export von Pflanzenschutzmitteln, 2021, https://www.bvl.bund.de/DE/Arbeitsbereiche/04_Pflanzenschutzmittel/01_Aufgaben/02_ZulassungPSM/03_PSMInlandsabsatzAusfuhr/psm_PSMInlandsabsatzAusfuhr_node.html

[12] 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

[13] 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

[14] 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/

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

[16] 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).

[17] 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

[18] FAO (2020): FAO (Food and Agriculture Organization of the United Nations) Specifications and Evaluations for Chlorothalonil, http://www.fao.org/agriculture/crops/thematic-sitemap/theme/pests/jmps/ps-new/en/#C

[19] 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).

[20] 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/

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

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

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

[24] cf. BVL; 2019: BVL - Fachmeldungen - Widerruf der Zulassung von Pflanzenschutzmitteln mit dem Wirkstoff Chlorthalonil zum 31. Oktober 2019. (2019, 31. Oktober). Abgerufen am September 2021, von https://www.bvl.bund.de/SharedDocs/Fachmeldungen/04_pflanzenschutzmittel/2019/2019_06_19_Fa_Widerruf_Chlorthalonil.html