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1 Overview

This source category provides a 'catch all' for the agricultural sector. All emissions that cannot be placed under one of the three other chapters (3.B, 3.D and 3.F) will be put in this source category. Thus, this may potentially be a very extensive sector covering lots of different activities not covered by other source categories. Currently, this chapter considers the emission of carbon species resulting from the application of pesticides and the emission of ammonia (NH₃) resulting from the NH₃ treatment of straw.

1.1 Pesticides

Pesticide emissions originate mainly from their use in the agricultural and forest sectors. Other emission sources (e.g. the manufacturing of pesticides or emission of imported products) are not included in this chapter. In the former EMEP/EEA Guidebook 2013, the following pesticides were included: aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene (HCB), mirex, toxaphene, pentachlorophenol and lindane. The use of these pesticides as pure substances listed in the Aarhus Protocol on Persistent Organic Pollutants (POPs) and the Stockholm Convention has already been prohibited by most of the parties who have ratified the Protocol. In accordance with the POP Protocol art. 3, para 8, and art. 9, para. 1 (b) only substances (PAHs, Dioxins/furans, HCB and PCBs) listed in Annex III shall be reported.

Since the early 1990s, HCB has no longer been used as a pure substance. However, it can be present as an impurity or as a by-product in certain pesticides or certain chemicals. Some of these pesticides e.g. chlorothalonil (fungicide) and picloram (herbicide) are still in use and their application is approved until 2017 or longer (see e.g. EU Pesticide database). In 2014, more than 75 % of the total pesticide sales (396 kt) in the EU 28 were fungicide and herbicide (see Eurostat database, pesticide sales). Worldwide more than 24 Mio tones of fungicides and herbicides were used (see FAOSTAT database pesticides use, 2017). For this reason, pesticide applications are still a source of HCB emissions. A detailed description of the calculation of HCB emissions appears to be necessary and is provided in the Annex of this chapter.

1.2 NH₃ emissions of ammonia treated straw

Straw is treated with NH3 to increase its value as a feed for ruminant livestock. The NH3 increases the digestibility and non-protein N content of the straw. After NH3 treatment, the value of the straw as a feed is still relatively low compared to other feedstuffs, so there is little incentive to its use unless the price differential is substantial. The NH3 treatment of straw has been banned in some countries, but is still practiced in others. The exact extent of the practice is currently unknown.

2 Description of sources

2.1 Process description

2.1.1 Pesticides

In the past, several projects and articles reported investigations of the fate and the environmental pathways of pesticides and in particular HCB emissions (e.g. Beall, 1976, Bailey, 2001, Pacyna et al., 2003, Barber et al., 2005a). Emissions arise following the application of pesticides either from volatilization of pesticides deposited to leaf or soil prior to uptake by the crop or soil, or from 'spray drift', the movement of fine droplets of pesticide spray away from the target application zone to

areas downwind. For the calculation of emissions, only primary emissions of active input (e.g. evaporation during application, evaporation from the plant and soil surface after application) have to be taken into account. Further emission paths are neglected, due to the persistence and the high sorption behaviour of the respective pesticide or HCB on the organic soil substance.

2.1.2 Ammonia- treated straw

The commonest method of treatment is to enclose straw bales in plastic and then inject anhydrous NH₃ into the bales. The treated straw is then left for a number of weeks, to allow the chemical reaction between the NH₃ and straw to proceed. The plastic is removed several days before the straw is to be fed to the livestock, to allow excess NH₃ to dissipate. The emission of NH₃ depends on the NH₃ application rate and the extent to which the NH₃ combines chemically with the straw. The latter depends on the gas tightness of the plastic wrapping, the ambient temperature and the length of the maturation process. An application rate of 30–35g (kg DM) ⁻¹ NH₃ is commonly used and a maturation time of four to six weeks is allowed, dependent on ambient temperature. The main source of information concerning this process is Sundstøl and Coxworth (1984).

2.2 Emissions

2.2.1 Pesticides

In general, pesticides are characterized by their chemical structure and the property of semi-volatility. The latter property determines the emission behaviour. A Dutch study (MJPG, 1995) estimated that on average, 25 % of all pesticide used is emitted to the air. Historically, a range of pesticides were of interest. However, the use of the most dangerous pesticides has been prohibited by international agreement (see 2.3.1 below). The only emissions related to pesticide use that shall be currently reported are those of HCB, which is present as a contaminant. According to the Pesticide Leaching Model (PELMO 3.31; Ferrari et al., 2005), all the HCB present as a contaminant will be volatilised.

2.3 Controls

2.3.1 Pesticides

Control of this source is effectively to cease the activity, and use of the substances listed has been banned in many countries, albeit with some exceptions. In the beginning of the 1990s, pesticides were regulated mainly at the level of individual Member State countries.

In Northern America, pesticides have been carefully regulated since the early beginning of the 1990s. In the United States, the Federal Insecticide, Fungicide, and Rodenticide Act was implemented in 1996. In Canada pesticides are managed through a pesticide act (a pest management program and pest control products act, PCPA) since 2002.

With the development of a regulatory framework within the EU, Directive 91/414/EEC, strict rules for the authorisation of pesticides were defined, to harmonise the process of risk assessment and pesticide approvals across the EU. In Annex I active substances are listed for the use in pesticides.

In 2011, Regulation (EC) No 1107/2009 entered into force, replacing Directive 91/414/EEC. The EU sets rules for the sustainable use of pesticides to reduce the risks and impacts of pesticide use (Directive 2009/128/EC).

Today, pesticides are only sold in the EU to professional pesticide users, distributors and advisors, all of whom receive proper training in handling these substances, and the application equipment has to be inspected to ensure efficient use (e.g. controlling spray drift or droplet size). Aerial spraying is prohibited or has to be avoided.

FAO reports about sustainable pest and pesticide management give advice concerning risk management and safe pesticide handling worldwide.

2.3.2 Ammonia-treated straw

The treatment of straw is normally conducted on the farm, using relatively simple technology. The control methods available are likewise simple and consist of ensuring that the straw has an adequate moisture content, the NH₃ application rate is appropriate, the NH₃ is well distributed in the stack and the stack is gas tight. See Sundstøl and Coxworth (1984) for further details of the technologies involved.

3 Methods

3.1 Choice of method

Only Tier 1 methods are available.

3.2 Tier 1 default approach

3.2.1 Pesticides

3.2.1.1 Algorithm

The emission of HCB is estimated by summing the product of the amount of each pesticide applied and the concentration of HCB in that pesticide (i.e. its impurity factor):

```
E_{pest} = \sum (m_{pest\_i} \cdot IF_i) where:

E_{pest} = \text{total emission of HCB (in mg a}^{-1}, \text{ unit conversion reported in kg)},
m_{pest,i} = \text{mass of individual pesticide } i \text{ applied (kg a}^{-1}),
IFi = \text{impurity factor of HCB in the } i \text{th pesticide (mg kg}^{-1})
```

3.2.1.2 Impurity

Impurities derived from the manufacturing process and/or product storage are present in all pesticide active ingredients. Impurities can have an adverse impact on human health, the environment or both. Maximum impurity standards (here used as an impurity factor, IF) are listed for specific active constituents. One of the listed substances is HCB. Before pesticide regulations were implemented, HCB impurity levels in many active substances were quite high but producers were obliged to reduce the impurity levels dramatically. Today, the amounts of impurities are clearly below the legally defined impurity levels but national standards for HCB impurity can differ between countries and depend on the year of implementation.

Sources of impurity data:

- Ask the national focal point,
- Ask the pesticide producers (e.g. Syngenta, Dupont, Dow AgroScience, Bayer, BASF etc.),
- Chemical analysis of pesticide products.

3.2.1.3 Activity data

Annual sales of the respective active substance are used to infer the amount that is applied, using the assumption that all pesticides sold to farmers, ranchers, foresters, etc. are applied during that year. Most countries which have a strict pesticide regulation of pesticide use, with a public authority responsible for approving them.

In the European Union competent authorities and contact points of each Member State shall collect and report the data necessary for the specification of the characteristics to the Commission (Eurostat) (regulation 1185/2009, article 3). Thus, the national focal point in the Member State should have information on domestic sales. It is good practice to average data records over three years (current year and two most recent) if emissions are not computed on an annual basis for reporting purposes.

Manufacturers usually report the quantities of pesticides sold and should give the amounts of pure active substance, not the amount of technical active substance. If the active substance exists in form of a variant (e.g. ester or salt), the reported amount should refer to the basic active substance, not to the variant. The amounts are generally stated in units of mass (kg), not in units of volume. In the case of liquid formulations, it should be noted that the content of active substance is usually specified in g/L. Therefore, calculations should consider the density. Two cases have to be distinguished:

a) Basic quantity is the product volume:

```
Example: product volume = 650 L, content of active substance = 480 g/L,
```

density = $1,20 \text{ g/cm}^3$;

then:

```
product mass (kg) = product volume * density = 650 * 1,20 = 780 kg
```

mass of active substance (kg) = product volume * (content of active substance/ 1000) = $650 \times (480/1000) = 312 \text{ kg}$.

b) Basic quantity is the product mass:

```
Example: product mass = 780 kg, content of active substance = 480 g/L,
```

```
density = 1,20 \text{ g/cm}^3;
```

then:

product mass (kg) has to be filled in directly without conversion = 780 kg

mass of active substance (kg) = (product mass / density) * (content of active substance / 1000) = (780 / 1.20) * (480 / 1000) = 312 kg

1. Consumption is known for individual pesticides

The most reliable data are obtained when pesticide consumption is known.

2. Totals emissions

The total emission of a specific pesticide can be calculated by using the respective formula (see chapter 3.2.1.1).

3.2.2 Ammonia-treated straw

3.2.2.1 Algorithm

The emission is estimated from the amount of NH₃ applied and an EF as:

```
E_{straw} = m \cdot EF_{straw}
```

where:

 E_{straw} = total emission of NH₃ (in t a⁻¹),

m = mass of NH_3 used (t a^{-1}),

 $EF_{straw} = EF \text{ for NH}_3 \text{ treated straw (t t}^1).$

3.2.2.2 Default emission factors

No published measurements of the emission of NH₃ from the NH₃ treatment of straw are available. However, Sundstøl and Coxworth (1984) specify that 30–35 g (kg DM straw)⁻¹ NH₃ is commonly used, equivalent to 25–28 g (kg DM straw)⁻¹ NH₃–N. Based on Table 7.5, p 228 in Sundstøl and Coxworth (1984), this results in an increase of the N content from about 3 g (kg DM)⁻¹ to about 15 g (kg DM)⁻¹. This means that about 46 % of the NH₃ is retained in the straw and 54 % is lost the atmosphere. It is assumed here that the nitrogen is lost as NH₃, so the value of E_{straw} is 0.54.

3.3 Tier 2 technology-specific approach

No Tier 2 methodology is available for pesticides or NH₃ treated straw. For emissions of HCB, no Tier 2 methodology is necessary.

3.4 Tier 3 emission modelling and use of facility data

No Tier 3 methodology is available for pesticides or NH₃ treated straw.

4 Data quality

4.1 Completeness

For the estimation of HCB emissions and NH3 emissions from NH₃-treatment of straw the requirements of the respective GB chapter 6 (Inventory management, improvement and QA QC, 2016) has to be taken into account.

4.2 Avoiding double counting with other sectors

Double counting is not expected for pesticide emissions.

For emissions from NH3 treatment of straw, it is important to note that anhydrous NH3 is also used in agriculture as a fertiliser. Care therefore needs to be taken to distinguish between these two agricultural uses when obtaining activity data.

4.3 Verification

There are no direct methods to evaluate total inventory estimates of pesticide emissions, and verification is dependent on field studies of emissions from example situations.

The technology used to treat straw with NH₃ means that measurements of NH₃ emission are quite feasible. However, there have been no measurements made.

4.4 Developing a consistent time series and recalculation

With the statistic of pesticide sales (see different EU regulations) time series can be defined for estimating HCB emissions.

The prospect of developing a trend of emissions from the NH3 treatment of straw is also limited, due to lack of information on the activity.

4.5 Uncertainty assessment

4.5.1 Emission & Impurity factor uncertainties

An independent systematic survey on HCB contamination in plant protection products was not carried out. However, samples of individual plant protection products containing the active substances chlorothalonil and picloram were taken to test them for HCB contamination. No general uncertainty for all products can be calculated on the basis of these incremental samples. However, manufacturers have an interest in ensuring that the contamination levels are below the limit values, otherwise they would lose their statutory approval. For this reason an uncertainty between 15% and 30% is estimated, based on the laboratory data.

The mass balance approach used to estimate the emission factor for NH₃ treated straw is considered robust, although there is no direct evidence that the nitrogen lost is emitted as NH₃ (rather than nitrous oxide, nitric oxide or dinitrogen gasses). No systematic survey of treatment practices has been conducted. However, operators have an economic incentive to optimise the process, so it is considered that the uncertainty in the emission factor is 15-25 %.

4.5.2 Activity data uncertainties

Where pesticide sales data are available on Member State level two sources of uncertainty exist for pesticides /HCB emissions:

- 1) uncertainties in the amount of pesticides applied to the seeds or plants;
- 2) uncertainties in the net amount.

Activity data uncertainties will depend on the accuracy of sales, and/or usage data. Usage and sales data are likely to have the least uncertainty. Inventory compilers may use a conservative approach and assume that pesticides or HCB are purchased for application (application on seeds or plants).

Since the emission of NH₃ from NH₃-treated straw has only recently been included as a source, there is at present no basis for assessing the uncertainty of the activity data.

4.6 Inventory quality assurance/quality control QA/QC

The quality of emission estimates of pesticide use will vary considerably from country to country, depending largely on the quality of the information regarding the types and amounts of pesticides used.

4.7 Gridding

Considering the potential for pesticides to have local effects on ecology, emission estimates should be disaggregated on the basis of land use data as much as possible.

5 References

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

Barber, J. L., A. J. Sweetman, and K. C. Jones (2005a). "Hexachlorobenzene - Sources, environmental fate and risk characterisation." Euro Chlor, pp 115, (www.eurochlor.org), accessed 23 July 2019.

Beall, M. (1976). "Persistence of aerially applied hexachlorobenzene on grass and soil." Journal of Environmental Quality 5(4): 367-369.

Council Directive 91/414/EEC of 15 July 1991 concerning the placing of plant protection products on the market, (1991).

Commission Directive 2009/128/EC of the European Parliament and of the council of 21 October 2009 establishing a framework for Community action to achieve the sustainable use of pesticides DIRECTIVE 2009/128/EC C.F.R. (2009), (https://ec.europa.eu/food/plant/pesticides/sustainable use pesticides en), accessed 23 July 2019.

EU Pesticides database (2017), (http://ec.europa.eu/food/plant/pesticides/eu-pesticidesdatabase/public/?event=activesubstance.selection&language=EN), accessed 23 July 2019.

Eurostat database, pesticide sales (2017): (http://ec.europa.eu/eurostat/web/products-datasets/product?code=aei fm salpest09), accessed 23 July 2019.

FAOSTAT database pesticides use (2017): (http://www.fao.org/faostat/en/#data/RP), accessed 23 July 2019.

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

MJPG-Emissie-evaluatie 1995. Achtergronddocument Commissie van deskundigen Emissie-Evaluatie MJP-G, IKC, Ede.

Pacyna, J. M., K. Breivik, J. Münch and J. Fudala (2003). "European atmospheric emissions of selected persistent organic pollutants, 1970–1995." Atmospheric Environment 37: 119-131.

REGULATION (EC) No 1107/2009 of the European Parliament and of the Council of 21 October 2009 concerning the placing of plant protection products on the market and repealing Council Directives 79/117/EEC and 91/414/EEC Regulation (EC) No 1107/2009 C.F.R. (2009).

REGULATION (EC) No 1185/2009 of the European Parliament and of the Council of 25 November 2009 concerning statistics on pesticides (Text with EEA relevance) Regulation (EC) No 1185/2009 C.F.R. (2009).

Sundstøl, F. and Coxworth, E.M. (1984). Ammonia treatment In: Straw and other fibrous by-products as feed. Sundstøl, F. and Owen, E. (eds.). Developments in Animal and Veterinary Sciences 14, Elsevier, pp. 196–247, Amsterdam.

6 Point of enquiry

Enquiries concerning this chapter should be directed to the relevant leader(s) of the Task Force on Emission Inventories and Projection's expert panel on Agriculture and Nature. Please refer to the TFEIP website (www.tfeip-secretariat.org/) for the contact details of the current expert panel leaders.





7 Annex

7.1 Overview

According art. 3, para 8, and art. 9, para. 1 (b) of the POP Protocol only substances which are listed in Annex III shall be reported. This chapter considers a more detailed description about the HCB emissions resulting from the application of pesticides.

In the EMEP Guidebook 2005 (chapter BHCB-1) it was pointed out that HCB can be contained as an impurity or as a by-product in pesticides. Some of these are still on the global market and thus HCB can be released unintentionally.

HCB is among the most persistent environmental pollutant because of its chemical stability and resistance to degradation. If released to the atmosphere, HCB exists primarily in the vapor phase and degradation is extremely slow. Furthermore, re-emissions of historic HCB emissions which are sorbed at the soil or sediment surface could occur due to the loop behaviour influenced by meteorological conditions (Barber et al., 2005b).

7.2 Description of sources

7.2.1 HCB-Emissions

Before 1990, HCB was normally used as a pure substance (fungicide) for the treatment of grain seeds (mainly wheat). Bailey (2001) reported HCB emissions around 6.5 t/yr of pesticide application worldwide including the US and Canada for the mid 1990s. Pacyna et al. (2003) estimated HCB emissions for the mid 1990s around 23 t/yr only for Europe. The estimates considered the EU 28 countries, the EFTA countries, Norway, Switzerland and also Russia, Ukraine and Belarus. 80 % (approximately 18.4 t/yr) of the emissions were attributed to the agricultural sector which are three times higher than the estimates of Bailey (2001) and the differing quantity could indicate data gaps in the emission estimates. Van Drooge and Grimalt (2013) reported for the period 2002 until 2009 that the HCB atmospheric concentration level did not show any decrease and remained around 50 pg/m³ on the European continent. This information underlines that still HCB emissions occur in relevant amounts in Europe.

HCB is still present as an impurity in some authorized active ingredients in pesticide products which are used worldwide. The main active substances which contain HCB impurities from the past until today are chlorothalonil and picloram. Further active substances which are known for HCB impurity are: lindane, DCPA (also known as chlorthal-dimethyl), PCP, atrazine, simazine, propazine and PCNB (also known as quintozine).

A first estimate of HCB emissions from pesticide use can be provided by a simple methodology, which considers the mass of individual active substances applied (statistics of pesticide sale) and the regulatory levels.

For pesticides which contain the active substances chlorothalonil and picloram, Table 1 gives an overview of products which are available under different trade names and type of application.

Table 1: Overview of some commercial pesticide products for the fungicide chlorothalonil and herbicide picloram, trade name and application use

Chemical agent	Trade name	Application for			
_	BRAVO 500	Wheat			
_	Sambarin	Wheat			
_	Pugil 75 WG	Wheat			
_	AMISTAR Opti	Wheat, barley und rye			
Chlorothalonil –	Tattoo C	Potatoes			
Chiorothalonii	CREDO	Wheat, barley			
_	Simbo Extra	Winter barley			
		golf course greens, tees, and fairways,			
	Daconil 2787 Extra	ornamental turfgrass and ornamental herbs,			
		shrubs and trees.			
Dialouere	EFFIGO	Rapeseed (winter), maize, round cabbage			
Picloram	Runway	rapeseed (winter)			

7.3 Controls

7.3.1 HCB controls

In the early period of the 1990s, HCB concentrations in active substances were not regulated worldwide and until today the HCB concentrations vary from pesticide to pesticide, the implementing year and from country to country. Limit concentrations of HCB impurity were published by the FAO in Specifications for Agricultural Pesticides (FAO, 2005, 2012 and 2015). The objectives of these specifications for the agricultural use were to promote the manufacture and use of pesticides to meet quality requirements. The proposed HCB concentrations of the FAO were considered in the European regulation Council Directive 91/414/EEC and in other national pesticide regulations.

7.4 Methods

7.4.1 Tier 1 default approach

7.4.1.1 Impurity factor

For the estimation of HCB emissions the HCB concentration (here named impurity factor) in the active substance has to be known. To get an annual average of the HCB concentration for the particular active substance, all major pesticide products that are used in a significant volume should be tested for HCB concentrations and those HCB concentrations should be weighted by their usage volume. In general, the information about the real HCB concentration is confidential and national institutions for pesticide control should have access to it.

The following active substances contained HCB as an impurity:

Atrazine, propazin, simazine, picloram, pentachloronitrobenzene (PCNB), chlorothalonil, dimethyl tetrachloroterephthalate (Dacthal or DCPA), tefluthrin, lindane, pentachlorophenol (PCP) and PCP-Na.

Some of these substances e.g. chlorothalonil (fungicide) and picloram (herbicide) are still in use worldwide and their application is approved until 2017 and later (see e.g. EU pesticide database).

Tefluthrin is used for the treatment of seed in closed storage buildings where air purification systems are in place and thus it is not emission-relevant.

Before pesticide regulations were implemented HCB concentrations in many active substances were quite high. Thus, the amount of HCB impurity depends on the active substance and on the approval year, and varies among countries according to their legislation. Tables 3 and 4 summarize the information on the impurity factors for different regions and their regulation history. The trend of HCB concentrations in pesticide products is declining over time.

Bailey (2001) and Yang (2006) compiled an overview of the HCB concentrations in different pesticides by analyzing producer reports, journals and fact sheets for North America (the United States and Canada) (see Table XX-3).

Table 3: Proposed maximum HCB-concentration in active substances used in North America from 1990 onwards (compiled by Bailey, 2001, and Yang, 2006).

Active Substances	1990-1999	2000-2006	2007 -	Reference (for max. concentration)
	mg/kg	mg/kg	mg/kg	
Atrazine	1	1	1	А
Clopyralid	2.5	2.5	2.5	В
Chlorothalonil	40	5	5	Α
DCPA, Dacthal, Chlorthaldimethyl	1000	40	8,00E-6	A, F
Endosulfan	0.1	0.1	0.1	С
Lindane	50	50	use stopped	D
Propazine	1	1	1	С
Pentachloronitrobenzene (PCNB), Quintozene	500	500	500	А
Picloram	50	8	8	Α
Simazine	1	1	1	С
Pentachlorophenol (PCP)	50	50	50	Е

A: Phenicie, 2003, **B**: Durkin, et al., 2004, **C**: Benazon Environmental. 2000., **D**: Bailey, R. 2001, **E**: Wilkinson, J and et al., 2006. All references listed in Yang, C. (2006), **F**: Material Safety Data Sheet, 2012, **G**: FAO Specifications 2005, 2015, **H**: FAO Specification 2012

For active substances sold in Europe the HCB impurity levels differ a little bit due to the EU regulation and their national implementation (see Table 4). Where no infomation is known about the max. concentration of HCB for the early 1990s, the concentrations for North America are adopted (e.g. Endosulfan and Clopyralid). The use of some presented active substances (e.g. Atrazine, Simazine and Lindane) is since 2005 prohibited and the reregistration is not approved (see EU pesticide database).

In 1998 the impurity HCB concentration in Chlorothalonil was 300 mg/kg (see FAO, 2005). With the Council directive 2005/53/EC Chlorothalonil was added to this list and a maximum concentration of HCB of 0.01 g/kg has been set in the EU. Due to a review by the FAO (FAO, 2005,

p.22) and taking into account results of batch samples testing the impurity the max. concentration was raised again up to 0.04 g/kg (see also 2006/76/EC).

Picloram was added to Annex I with the Commission Directive 2008/69/EC where the HCB impurity has been set to 8 % and minor (see also FAO specification, 2012).

Table 4: Proposed maximum HCB-concentration (impurity factor) in active substances used in Europe from 1990 onwards taken into account the implemented EU regulation.

							Reference		
Active Substances	1990	1995	2000	2005	2010	2015	(for max.	Banned in EU since	EU Directives or Regulations
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg			
Atrazine	2.5	1	1	use stopped	use stopped	use stopped	Α	End 2003	No 2004/248/EC
Clopyralid*	not used in EU	not used in EU	not used in EU	not used in EU	2.5	2.5	В		Reg. (EU) No 2019/168, 06/64/EC, No 540/2011, No 678/2014
Chlorothalonil**	300	300	40	10	40	40	G, I, J		2005/53/EC, Reg. (EU) 2018/1262, Reg. (EU) No 540/2011, Reg. (EU) 2017/1511, Reg. (EU) No 533/2013
DCPA, Dacthal, Chlorthaldimethyl*****	1000	1000	40	40	use stopped	use stopped	A, F	End 2010	2009/715/EC*****
Endosulfan	0.1	0.1	0.1	0.1	use stopped	use stopped	С	End 2005	05/864/EC, No 1107/2009
Lindane***	100	50	50	50	use stopped	use stopped	D	End 2007	No 1107/2009, EC 850/2004, 2000/801/EG
Pentachloronitrobenzene (PCNB), Quintozene	500	500	500	use stopped	use stopped	use stopped	Α	End 2000	No 2000/816/EC
Picloram****	50	50	50	50	50	50	Н		No 540/2011, 2010/39/EU, Reg. (EU) No 2018/1796
Propazine	1	1	1	use stopped	use stopped	use stopped	like Simazine		No 2002/2076
Simazine****	1	1	1	use stopped	use stopped	use stopped	С	End 2004	No 2004/247/EC
Pentachlorophenol (PCP)	50	50	50	use stopped	use stopped	use stopped	E	End 2002	No 2002/2076

See reference notation under Table 3

**** Authorised in AT, BG, CZ, DE, DK, EE, FI, HR, HU, IE, LT, LU, LV, PL, RO, SE, SK, UK

***** According Article 2(3) of 2004/247/EC some MS (UK, EL, NL, IE, BG, ES) could use Simazine until 2007

****** 2009/715/EC (Commission Decision of 23 September 2009 concerning the non-inclusion of chlorthal-dimethyl in Annex I to Council Directive 91/414/EEC and the withdrawal of authorisations for plant protection products containing that substance)

Source: EU pesticides database

At the time of writing, no new information about the legal regulations in the EECCA states were available.

7.4.2 Default emission factors

Very little published information about the HCB quantities that are emitted during application in practice is available that also takes into account factors such as climate, application procedures, formulations and behaviour over time (Bailey, 2001).

By using the Pesticide Leaching Model (PELMO 3.31) which is also used for the European registration process of pesticides the EF is estimated. The one-dimensional pesticide leaching model has been extended to predict the pesticide volatilisation after agricultural applications under field conditions (Ferrari et al., 2005). However, it is also able to calculate the behaviour of impurities in the products.

^{*} Authorised in most of the EU-MS (see http://ec.europa.eu/food/plant/pesticides/eu-pesticides-database)

^{**} Some European countries use lower IF since 2005 because the HCB impurity concentration in the actives substances is markedly lower than indicated in the regulation, these countries use 10 mg/kg.

^{***} At the beginning of 1990 lower max. HCB concentration was in place in the US. For Europe 100 mg/kg is applied.

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, 2002 and 2017). As a test substance chlorothalonil was used in the simulation for different regions in Europe. A detailed description of the input parameters is available (see model description Klein, 2017). It is assumed that the HCB volatilisation of the impurity in picloram or other HCB containing pesticides is the same. The result of the emission factor is 1 or 100%. In this context, the use of an emission factor is negligible for the calculation of HCB emissions.

7.4.3 Activity data

Annual sales of the respective active substance are used to infer the amount that is applied on crop seed. The national institution which is responsible for regulating the production and use of pesticides should estimate pesticides industry sales and usage annually.

For the European Member States, the EU has a set of regulations of which the regulation (EC) Nr. 1185/2009 (statistics on pesticides) is important for HCB reporting.

To fulfil the obligation of the regualtion (e.g. reporting of pesticides or the active substances, sales and information of the producers) a national institution is in charge. A list of the competent authorities and contact points of each Member State is presented on the webpage of the European Commission (https://ec.europa.eu/food/plant/pesticides/approval active substances/eu rules en).

According to article 3 of Regulation 1185/2009, competent authorities and contact points of each Member State shall collect and report the data necessary for the specification of the characteristics to the European Commission (Eurostat).

Producers usually report the quantities of pesticides sold. From this, the active ingredient quantity is calculated using the pure active substance content of the pesticide. If sales quantities are specified in litres, the active ingredient quantity must be converted by using the density.

7.5 Data quality

7.5.1 Verification

There are no direct methods to evaluate total inventory estimates of pesticide emissions, and verification is dependent on field studies of emissions from example situations. However, van Drooge and Grimalt (2013) reported that emission reports and air concentration measurements indicate that the atmospheric concentrations of the most well studied POP (e.g. HCB) declined between 1990 and 2000 but decreased more slowly during the last decade. Some of the HCB emissions sources are still primary sources which can be observed by the background content in environmental samples (e.g. soil, ice, air) (Barber et al., 2005a and b).

7.6 References used in the Annex

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

Barber, J. L., A. J. Sweetman, and K. C. Jones (2005a). "Hexachlorobenzene - Sources, environmental fate and risk characterisation." Euro Chlor, pp 115, www.eurochlor.org.

Barber, J. L., A. J. Sweetman, D. Van Wijk and K. C. Jones (2005b). "Hexachlorobenzene in the global environment: emissions, levels, distribution, trends and processes." Science of the total environment, 349(1): 1-44.

Beall, M. (1976). "Persistence of aerially applied hexachlorobenzene on grass and soil." Journal of Environmental Quality, 5(4): 367-369.

Benazon Environmental Inc., (2000). HCB Sources, Regulations, and Programs for the Ontario Great Lakes Basin 1988, 1998, and 2000. Draft Report to Toxics Prevention Division. EC-Ontario Region, EC-Ontario Region.

Council Directive 91/414/EEC of 15 July 1991 concerning the placing of plant protection products on the market, (1991).

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).

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).

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).

Regulation (EC) No 1185/2009 of the European Parliament and of the Council of 25 November 2009 concerning statistics on pesticides (Text with EEA relevance) REGULATION (EC) No 1185/2009 C.F.R. (2009).

Durkin, P., Follansbee, M., (2004). Human Health and Ecological Risk Assessment on Clopyralid. USDA Report.

EMEP/CORINAIR Guidebook 2005, chapter BHCB-1, Sources of Hexachlorobenzene Emissions.

EU Pesticides database, 2019, (http://ec.europa.eu/food/plant/pesticides/eu-pesticides-database/public/), accessed 5 July 2019.

FAO, 2005: FAO Specifications and Evaluations for Chlorothalonil, Evaluation report 288/2005, Table 1, pp40.

FAO (2015): FAO Specifications and Evaluations for Chlorothalonil, p 51.

FAO and WHO (2014) The International Code of Conduct on Pesticide Management (http://www.fao.org/fileadmin/templates/agphome/documents/Pests_Pesticides/Code/CODE_2014 Sep ENG.pdf) accessed 5 July 2019.

FAO (2012): FAO Specifications and Evaluations for Picloram, Table 2, p 23.

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

Fiedler, H., M. Hub, S. Willner and O. Hutzinger (1995). "Stoffbericht Hexachlorbenzol (HCB)." Landesanstalt für Umweltschutz Baden-Württemberg, Karlsruhe.

Martin, H., (1972) Pesticide manual. 3rd ed. The British Crop Protection Council, London, p. 183.

Material Safety Data Sheet for Dacthal, AMVAC MSDX No.: 291_9, 2012

Klein, M. (2000): Berechnung zonaler und kompartimentbezogener Halbwertszeiten persistenter organischer Schadstoffe (POPs) in der Umwelt. BUA-Bericht 232. S Hirzel wissenschaftliche Verlagsgesellschaft Stuttgart.

Klein, M. (2017), Calculation of emission factors for impurities in organic pesticides with PELMO. Personel communication, Fraunhofer Institute for Molecularbiology and Applied Ecology (IME), Schmallenberg (Germany).

Material Safety Data Sheet, AMVAC MSDX No.: 291_9, 2012

Pacyna, J. M., K. Breivik, J. Münch and J. Fudala (2003). "European atmospheric emissions of selected persistent organic pollutants, 1970–1995." Atmospheric Environment 37: 119-131.

Phenicie, D. (2003). GLBTS Presentation. BaP/ HCB Workshop. Dec 2003. GLBTS Presentation. BaP/ HCB Workshop.

POP Protocol (1998): Protocol to the 1979 convention on long-range transboundary air pollution on persistent organic polltants.

Rippen, G. (1994), Handbuch Umweltchemikalien, Stoffdaten, Prüfverfahren, Vorschriften, ecomed, Landsberg/Lech, Loseblattsammlung, Redaktioneller Stand 1994.

van Drooge, B. and J. Grimalt (2013). Persistent Organic Pollutants in the European Atmosphere. Urban Air Quality in Europe, Hdb Env Chem. Berlin Heidelberg, Springer Verlag. 26: 75-100.

Wilkinson, J., Estreicher, H. (2006). Penta Task Force. Personal Communication. Feb. 2006.

Yang, C. (2006). Estimating HCB Releases from Pesticide Applications in USA and Canada – All Years, Environmental Canada unpublished, Penta Task Force. Personal Communication. Feb. 2006.