

# Additional information relating to the draft risk profile for chlorpyrifos

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## Physico-chemical properties

**Table 1: Physico-chemical properties of chlorpyrifos and its degradation and transformation products**

Detail	Chlorpyrifos	Chlorpyrifos-oxon (CPYO)	3,5,6-Trichloro-2-pyridinol (TCP)	2-Methoxy-3,5,6-trichloro-pyridine (TMP)
Structure				
Property	Value and source	Value and source	Value and source	Value and source
CAS no.	2921-88-2	5598-15-2	6515-38-4	31557-34-3
Molecular weight [g/mol]	350.59	334.52	198.44	212.46
Form	tan, crystalline solid (94 % purity) (EC, 2005)  Colourless to white crystalline solid (ILO & WHO, 2014)	No data	No data	No data
Odour	Mild mercaptan (experimental, 99.6 % purity) (EC, 2005)	No data	No data	No data
Melting point [°C]	41 – 42 (experimental at 97- 99 % purity) (EC, 2005)  42 at 99.9 % purity (Spain, 2017)	83.44 (estimated) (US-EPA, 2012)	82.30 (estimated) (US-EPA, 2012)	58.75 (estimated) (US-EPA, 2012)
Thermal decomposition point [°C] (decomposition before boiling)	170 – 180 Experimental data (EC, 2005; Spain, 2017)	No data	No data	No data

Detail	Chlorpyrifos	Chlorpyrifos-oxon (CPYO)	3,5,6-Trichloro-2-pyridinol (TCP)	2-Methoxy-3,5,6-trichloro-pyridine (TMP)
Vapour pressure [Pa]	<p><math>3.35 \times 10^{-3}</math> 25°C (purity 99.8%) (EC, 2005)</p> <p><math>1.43 \times 10^{-3}</math> 20°C (purity 99.8%) (EC, 2005)</p> <p><math>1.0 \times 10^{-3}</math> Experimental, 25°C (purity 98%) (WHO, 2009)</p> <p><math>2.3 \times 10^{-3}</math> Compiled by Mackay et al. (2014)</p>	<p><math>8.87 \times 10^{-4}</math> (estimated) (US-EPA, 2012)</p>	<p>0.138 (estimated) (US-EPA, 2012)</p> <p><math>3.57 \times 10^{-3}</math> at 25°C</p> <p><math>1.79 \times 10^{-3}</math> at 20°C (purity 99.6%) (Spain, 2017)</p>	<p>1.43 (estimated) (US-EPA, 2012)</p> <p>1.27 at 25°C</p> <p>0.9 at 20°C (purity 100%) (Spain, 2017)</p>
Water solubility [mg/L]	<p>1.05 at 20°C, in unbuffered solution, no pH dependency reported (EC, 2005)</p> <p>0.39 at 19.5°C, pH not cited (98 % purity) (WHO, 2009)</p> <p>0.73 Cited by Mackay et al. (2014)</p> <p>0.941 (20°C, pH unknown, guideline EEC Method A6/OECD 105) Dow, as cited in WHO (2009)</p> <p>0.588 (20°C, pH not stated, guideline OECD 105 flask method) Makhteshim, as cited in WHO (2009)</p>	<p>25.97 (25°C, estimated from log KOW) (US-EPA, 2012)</p> <p>2623.4 (25°C, estimated from fragments) (US-EPA, 2012)</p>	<p>80.85 (25°C, estimated from log KOW) (US-EPA, 2012)</p> <p>125.09 (25°C, estimated from fragments) (US-EPA, 2012)</p>	<p>60.36 (25°C, estimated from log KOW) (US-EPA, 2012)</p> <p>750.88 (25°C, estimated from fragments) (US-EPA, 2012)</p>

Detail	Chlorpyrifos	Chlorpyrifos-oxon (CPYO)	3,5,6-Trichloro-2-pyridinol (TCP)	2-Methoxy-3,5,6-trichloro-pyridine (TMP)
Henry's Law constant [Pa m <sup>3</sup> /mol]	1.09 (25°C) Cited by Mackay et al. (2014)  0.478, estimated (EC, 2005)  1.11 Cited by Mackay et al. (2014)	$5.53 \times 10^{-4}$ (25°C, QSAR estimated) (US EPA 2012)  $1.142 \times 10^{-2}$ (estimated from estimated vapour pressure and estimated water solubility) (US EPA 2012)	$1.91 \times 10^{-3}$ (25°C, QSAR estimated) (US EPA 2012)  $3.370 \times 10^{-1}$ (estimated from estimated vapour pressure and estimated water solubility) (US EPA 2012)	9.89 (25°C, QSAR estimated) (US EPA 2012)  5.021 (estimated from estimated vapour pressure and estimated water solubility) (US EPA 2012)
n-octanol/water partition coefficient (log KOW)	4.7 at 20°C, neutral pH, (EC 2005)  5.0 at 24.5°C (purity 98%), (WHO 2009)  4.96 - 5.11 at 20°C (Gebremariam et al., 2012)  5.2 - 5.267 at 25°C (Gebremariam et al., 2012)	2.89 (estimated) (US EPA 2012)	3.21 (experimental) (US EPA 2012)	No data
n-octanol/air partition coefficient (log KOA)	8.882 (estimated) (US EPA 2012)  8.34 Cited by Mackay et al. (2014)	9.541 (estimated) (US EPA 2012)	9.324 (estimated) (US EPA 2012)	5.669 (estimated) (US EPA 2012)
air/water partition coefficient (log KAW)	-3.922 Experimental database (US EPA 2012)  -3.35 Cited by Mackay et al. (2014)	-6.651 (estimated) (US EPA 2012)	-6.114 (estimated) (US EPA 2012)	-2.399 (estimated) (US EPA 2012)

Detail	Chlorpyrifos	Chlorpyrifos-oxon (CPYO)	3,5,6-Trichloro-2-pyridinol (TCP)	2-Methoxy-3,5,6-trichloro-pyridine (TMP)
Soil organic carbon/water partition coefficient (log KOC)	3.4 – 4.5 (mean: 3.9) (EC 2005)	2.597 (estimated) (US EPA 2012)	2.942 (estimated) (US EPA 2012)	2.640 (estimated) (US EPA 2012)
	3.7 Experimental database (US EPA 2012)	2.618 (estimated) (US EPA 2012)	3.188 (estimated) (US EPA 2012)	3.111 (estimated) (US EPA 2012)
	3.93 cited by Mackay et al. (2014)		2.173 (PPDB 2020)	

## Transformation products

1. Transformation products of chlorpyrifos are 3,5,6-trichloro-2-pyridinol (TCP), chlorpyrifos-oxon, des-ethyl chlorpyrifos, 3,6-dichloro-2-pyridinol (3,6-DCP) and 2,3,5-trichloro-6-methoxypyridine (TMP). For information on chemical identity and physico-chemical properties please see table 1 of the INF-document.
2. TCP is the main degradation product of chlorpyrifos (Spain, 2017). It results from hydrolysis and photolysis of chlorpyrifos (Shemer et al., 2005), via degradation of chlorpyrifos-methyl (Racke, 1993) and triclopyr (US-EPA, 1998) and the metabolization of chlorpyrifos-oxon (Sultatos & Murphy, 1983). The estimated atmospheric half-life for TCP is 60.5 days (Spain, 2017a), which indicates potential for long range transport. The Half-lives in soil show moderate to high persistence with a DT50 of up to 150 days in European assessments (Spain, 2017a) and 360 days in US-EPA assessments (US-EPA, 1998). Acute toxicity of TCP is considered lower than that of the parent compound with an 96h LC50 value of 12.6 mg/L in rainbow trout and 48h LC50 of 10.4 mg/L for *Daphnia magna* (Spain, 2017a), although *Daphnia carinata* is the susceptible species with an 48h LC50 value of  $0.20 \pm 0.08$  µg/L (Cáceres et al., 2007). Chronic toxicity testing produced 21d NOEC of 0.029 mg/L for reproduction in *Daphnia magna* and a NOEC of 0.0808 mg/L for reduction of length and weight in rainbow trout early life stages (Spain, 2017a). TCP has a log KOW of 3.21 and an estimated log KOA of 9.32 (see table 1 INF-document). These values trigger the screening criteria for bioaccumulation assessment in air-breathing organisms set by ECHA (ECHA, 2017). However, no data on TCP bioaccumulation via inhalation could be identified. Aquatic bioaccumulation has been evaluated in two studies, in which BCF have been below 22 for fish, macroinvertebrates and algae (Hedlund (1973) and Lu and Metcalf (1975) as described in Racke (1993)). More data on bioaccumulation is needed to conclude on the fulfilment of the Annex D criteria for TCP.
3. Of the transformation products only chlorpyrifos-oxon is considered more toxic than the parent compound (Spain, 2017). The metabolization of chlorpyrifos to chlorpyrifos-oxon increases toxicity as the oxon exhibits a higher degree of acetylcholinesterase (AChE) inhibition (Timchalk, 2001). For more details on this pathway, please view the human health chapter of the INF-document. With a half-life of 11 hours (Muñoz et al., 2012) chlorpyrifos-oxon is more stable in air than chlorpyrifos. In other compartments it is considered less stable with half-lives of up to 30 days in soil (Mackay et al., 2014) and 40 days in water (Tunink (2010) in Mackay et al. (2014)). Based on these half-lives chlorpyrifos-oxon does not meet the Annex D criteria for persistence and is therefore not a POP candidate.

## Persistence

### Abiotic degradation

**Table 2: Dependency on pH for abiotic degradation (hydrolysis) of chlorpyrifos**

Reference	pH	Temperature	Half-lives
McCall (1986)	pH 5	25°C	73 d
McCall (1986)	pH 7	25°C	72 d
McCall (1986)	pH 9	25°C	16 d
Meikle and Youngson (1978)	pH 4.7	25°C	62.7 d
Meikle and Youngson (1978)	pH 6.9	25°C	35.3 d
Meikle and Youngson (1978)	pH 8.1	25°C	23.1 d

### Water: Direct and indirect photochemical degradation

4. The studies by Kralj et al. (2007) and Hossain et al. (2013) do not fulfil the OECD 116 test guideline and are thus not suitable to establish a reliable rate of photodegradation.

### Soil photolysis

5. In the study by Yackovich et al. (1985), the degradation of chlorpyrifos also did not differ significantly in light or dark. Since the study was not conducted according to current guidelines and a mercury lamp was used as the irradiation source, the study is only considered as additional information. Walia et al. (1988) irradiated chlorpyrifos under different photochemical conditions and showed that chlorpyrifos gives various photoproducts mainly by oxidative desulfuration, dehalogenation and hydrolytic processes under laboratory conditions. The study is also considered as additional information.

## Rate of degradation in water

**Table 3: Rate of degradation in water, laboratory studies**

Water source	Water	Half-life or DT <sub>50</sub> (d)	Method of calculation	DT50 normalised to 12°C <sup>1</sup>	χ <sup>2</sup> -error	r <sup>2</sup>	Application (µg/L)	Temperature (°C)	pH	Salinity (%)	Oxygen content (%)	Total organic Carbon (mg/L)	Reference	Remarks
Fröschweiher pond, Möhlin AG/Switzerland	pond	46 d	SFO	124.4 d	5.84	0.8851	12.1	22.5°C	7.89	-/-	7.62	13.60	Gassen, 2015	High losses due to volatilisation, underestimation of DT50 values
Fröschweiher pond, Möhlin AG/Switzerland	pond	21 d	SFO	56.8 d	7.51	0.9468	126	22.5°C	7.89	-/-	7.62	13.60		
Biederthal, France	Pond	2.78	FOMC	6.8 d	-	0.9804	100.0	21.5 ± 0.2 °C.	8.08	-/-	9.70	10.64	Caviezel, 2015	High losses due to volatilisation, underestimation of DT50 values
	Pond, sterile	2.92	FOMC	7.2 d	-	0.9783	100.0	21.5 ± 0.2 °C.	8.08	-/-	9.70	10.64		
	Pond	2.98	FOMC	7.3 d	-	0.9510	10.0	21.5 ± 0.2 °C.	8.08	-/-	9.70	10.64		
Ynys Tachwedd, nr Borth, Ceredigion, Wales	Estuarine	45 d	SFO	59.8 d	-	0.935	40	15 °C	7.79	17	110	589.5	Swales, 2003	High losses due to volatilisation, underestimation of DT50 values
Borth Sands, Ceredigion, Wales	Coastal	35 d	SFO	35 d	-	0.883	40	12°C	7.83	36	114	812.9		
> 5 miles off shore from Plymouth, Devon, England	Open Sea water	75 d	SFO	51.3 d	-	0.850	40	8°C	8.06	38	112	645.3		
Range Point, Santa Rosa Island, Escambia County, Florida, USA	Sea water	<2 d	1 <sup>st</sup> order	-/-			<water solubility of cpy	25°C					Schimmel, 1983	High losses due to volatilisation (63% of applied cpy in air traps), underestimation of DT 50
<b>range</b>		<2 – 75 d		6.8 – 124.4										

<sup>1</sup> Temperature normalised using the Arrhenius equation

# Rate of degradation in soil

**Table 4: Rate of degradation in soil, laboratory studies**

Soil source	Soil texture	Half-life or DT <sub>50</sub> (d)	Method of Calculation	DT50 normalised to 12°C <sup>2</sup>	X2-error	R <sup>2</sup>	Application (ppm)	Temperature (°C)	Soil moisture	Ph	Organic Carbon (%)	Reference	Remarks
Boone County, Missouri, USA	Silt Loam	21.43 9.55 (fast phase) 60.70 (slow phase)	DFOP	45.7 d 20.4 d (fast phase) 129.6 d (slow phase)	4.49	-	1.5 µg/g = 1000 g a.i./ha	20±2°C	50% MWHC	5.2/4.7 <sup>+</sup>	1.6	Clark, 2013	
Raymondville, Texas, USA	Sandy Clay Loam	5.964	SFO	12.7 d	10.39	-	1.5 µg/g = 1000 g a.i./ha	20 ± 2	50% MWHC	8.0/7.6	0.65		
MSL-PF, North Dakota, USA	Sandy Loam	9.6	FOMC	20.5 d	2.622	-	1.5 µg/g = 1000 g a.i./ha	20 ± 2	50% MWHC	6.4/6.2	1.7		
Tehama County, California, USA	Clay Loam	36.87 5.3 (fast phase) 49.19 (slow phase)	DFOP	78.7 d 11.3 d (fast phase) 105.0 d (slow phase)	1.174	-	1.5 µg/g = 1000 g a.i./ha	20 ± 2	50% MWHC	6.7/6.4	1.3		
Marcham, UK	Sandy clay loam	22.25	FOMC	47.5 d	2.48	-	1.28 mg/kg = 960 g as	20±2°C	40% MWHC	7.7/8.3	1.7	De Vette and Schoonmade, 2001a	
Charentilly, France	Silty clay loam	94.1	SFO	200.9 d	3.59	-	1.28 mg/kg = 960 g as	20±2°C	40% MWHC	6.1/8.0	1.0		
Cuckney, UK	Sand	110.3	SFO	235.4 d	3.974	-	1.28 mg/kg = 960 g as	20±2°C	40% MWHC	6.0/6.8	1.2		
Thessaloniki, Greece	Sandy silt loam	56.59	FOMC	120.8 d	2.505	-	1.28 mg/kg = 960 g as	20±2°C	40% MWHC	7.9/8.2	0.8		
Commerce, Miss.	Loam	11	Not reported	37.7 d	-	-	6.7 ppm, 7.6 kg/ha	25°C	75% 1/3 Bar	7.4	0.68	Bidlack, H.D., 1979	
Barnes, N.D	Loam	22	Not reported	75.4 d	-	-	6.7 ppm, 7.6 kg/ha	25°C	75% 1/3 Bar	7.1	3.60		
Norfolk, VA	Loamy sand	102	Not reported	349.7 d	-	-	6.7 ppm, 7.6 kg/ha	25°C	75% 1/3 Bar	6.6	0.29		

<sup>2</sup> Temperature normalised using the Arrhenius equation



Soil source	Soil texture	Half-life or DT <sub>50</sub> (d)	Method of Calculation	DT50 normalised to 12°C <sup>2</sup>	X2-error	R <sup>2</sup>	Application (ppm)	Temperature (°C)	Soil moisture	Ph	Organic Carbon (%)	Reference	Remarks
Miami, IND	Silt loam	24	Not reported	82.3 d	-	-	6.7 ppm, 7.6 kg/ha	25°C	75% 1/3 Bar	6.6	1.12		Soils were stored for longer than the recommended 3 months with no measurement of microbial activity
Catlin, ILL	Silty clay loam	34	Not reported	116.6 d	-	-	6.7 ppm, 7.6 kg/ha	25°C	75% 1/3 Bar	6.1	2.01		
German 2.3, Germany	Sandy loam	141	Not reported	483.4 d	-	-	6.7 ppm, 7.6 kg/ha	25°C	75% 1/3 Bar	5.4	1.01		
Stockton, Calif	Clay	107	Not reported	366.9 d	-	-	6.7 ppm, 7.6 kg/ha	25°C	75% 1/3 Bar	5.9	1.15		
Sultan, Washington USA	Silt loam	25 weeks = 175 d	Not reported	232.6 d	-	-	18 mg	15°C	20%	6.3	3.1	Getzin, 1981	
		13 weeks = 91 d	Not reported	312.0 d	-	-		25°C					
		6 weeks = 42 d	Not reported	371.5 d	-	-		35°C					
Chehalis, Washington USA	Clay loam	4 weeks = 28 d	Not reported	96.0 d	-	-	18 mg	25°C	30%	5.7	7.0		
Semongok	clayey red yellow podzolic	77.0	1st order	264.0			5 µg/g	25°C	33%	4.8	2.2	Chai, 2013	Degradation of chlorpyrifos is slowest in the absence of soil microbial activity and at low soil temperatures . Degradation of chlorpyrifos is slower for water logged soils, acidic soils, soils with high
		84.5	1st order	289.7			<b>25 µg/g</b>	25°C	33%	4.8	2.2		
Semongok, moisture dependence	clayey red yellow podzolic	120	1st order	411.4			5 µg/g	25°C	<b>air-dry soil</b>	4.8	2.2		
		77.0	1st order	264.0			5 µg/g	25°C	<b>field moisture content</b>	4.8	2.2		
		124	1st order	425.1			5 µg/g	25°C	<b>Wet (61 - 68%)</b>	4.8	2.2		
Semongok, temperature dependence	clayey red yellow podzolic	224	1st order	297.7			5 µg/g	15°C	33%	4.8	2.2		
		77.0	1st order	264.0			5 µg/g	25°C	33%	4.8	2.2		
		37.5	1st order	331.7			5 µg/g	35°C	33%	4.8	2.2		
Tarat	alluvial	53.3	1st order	182.7			5 µg/g	25°C	32%	5.6	1.8		

Soil source	Soil texture	Half-life or DT <sub>50</sub> (d)	Method of Calculation	DT50 normalised to 12°C <sup>2</sup>	X2-error	R <sup>2</sup>	Application (ppm)	Temperature (°C)	Soil moisture	Ph	Organic Carbon (%)	Reference	Remarks
		76.2	1st order	261.3			25 µg/g	25°C	32%	5.6	1.8		clay, soils at low temperatures and at high application rates. The study was not performed in accordance with the OECD 307 TG, but does provide supporting evidence of abiotic and biotic degradation pathways of chlorpyrifos in soil, however 50% degradation was not achieved in the test.
Tarat, moisture dependence	alluvial	49.5	1st order	169.7			5 µg/g	25°C	air-dry soil	5.6	1.8		
		53.3	1st order	182.7			5 µg/g	25°C	field moisture content (32%)	5.6	1.8		
		63	1st order	216.0			5 µg/g	25°C	Wet (61 - 68%)	5.6	1.8		
Tarat, temperature dependence	alluvial	83.5	1st order	111.0			5 µg/g	15°C	32%	5.6	1.8		
		53.3	1st order	182.7			5 µg/g	25°C	32%	5.6	1.8		
		36.5	1st order	322.9			5 µg/g	35°C	32%	5.6	1.8		
Balai Ringin	Red Yellow Podzolic soil	69.3	1st order	237.6			5 µg/g	25°C	22%	5.6	1.4		
		120	1st order	411.4			25 µg/g	25°C	22%	5.6	1.4		
Balai Ringin, moisture dependence	Red Yellow Podzolic soil	84.5	1st order	289.7			5 µg/g	25°C	air-dry soil	5.6	1.4		
		69.3	1st order	237.6			5 µg/g	25°C	field moisture content (22%)	5.6	1.4		
		63	1st order	216.0			5 µg/g	25°C	Wet (61 - 68%)	5.6	1.4		
Balai Ringin, temperature dependence	Red Yellow Podzolic soil	193	1st order	256.5			5 µg/g	15°C	22%	5.6	1.4		
		69.3	1st order	237.6			5 µg/g	25°C	22%	5.6	1.4		
		23.1	1st order	204.3			5 µg/g	35°C	22%	5.6	1.4		
Nadia District, West Bengal, India	Gangetic alluvial soil	20.1 23.2 36.7	1st order 1st order 1st order				0.1 kg a.i. ha <sup>-1</sup> 10 kg a.i. ha <sup>-1</sup> 100 kg a.i. ha <sup>-1</sup>	28°C	50 % MWHC	7.5	0.49	Sardar & Kole 2005	No air traps.
range		6 - 224		12.7 - 483.4									

## Rate of degradation in soil: termite control application rates

**Table 5: Rate of degradation in soil, termite control application rates**

Soil source	Soil texture	Half-life DT <sub>50</sub> (d)	or	Method of calculation	Application (ppm)	Temperature (°C)	Soil moisture	pH	Organic Carbon (%)	Reference
Tampa, Florida	sand	205.5		Not given	100 ppm	25°C	75% FC	6.40	0.66	Racke 1993, Murray 2001
Tampa, Florida	sand	1575.5		Not given	1000 ppm	25°C	75% FC	6.40	0.66	
Hawaii	Sandy loam	335.2		Not given	1000 ppm	25°C	75% FC	5.70	5.70	
Phoenix, Arizona	Sandy loam	229.8		Not given	1000 ppm	25°C	75% FC	8.30	0.88	
Medina, Texas	Clay loam	115.7		Not given	1000 ppm	25°C	75% FC	8.00	1.20	
St. Petersburg, Florida	sand	213.8		Not given	1000 ppm	25°C	75% FC	7.50	1.92	
Seaford Rise, Australia	Red brown earth	462		Not given	1000 mg/kg	25°C	60% MWHC	7.1	1.2	Baskaran, 1999
Bedding material	Quarry sand	330		Not given	1000 mg/kg	25°C	60% MWHC	9.2	0.1	
Bedding material	Reidmix/sand-dolomite	315		Not given	1000 mg/kg	25°C	60% MWHC	9.6	0.2	

## Rate of degradation in soil: field studies

**Table 6: Rate of degradation in soil, field studies**

Soil source	Soil texture	Half-life or Dist <sub>50</sub> (d)	Method of calculation	Application (kg a.i./ha)	Depth	Soil moisture	pH	Organic Carbon (%)	Reference
Geneseo (Illinois), cropped soil	Silt loam	88.89	SFO	3.36 kg a.i./ha	0-15 cm	45.89 %w/w	5.9	1.6	Fontaine, D.D et al. (1987)
Midland (Michigan), cropped soil	Sandy Loam	30.04	SFO	3.36 kg a.i./ha	0-15 cm	23.10 %w/w	7.7	1.3	
Davis (California), cropped soil	Loam	29.18	SFO	3.36 kg a.i./ha	0-15 cm	42.04 %w/w	7.9	0.75	
Tranent, Scotland, bare soil	Sandy clay loam	7.86 d	SFO	0.960 kg a.i./ha	0-10, 10-20 cm	Not reported	6.7	1.9	Old, J. (2002a)
Charentilly/ Tours, France, bare soil	Clay loam	11 d		0.960 kg a.i./ha	0-10, 10-20 cm	Not reported	7.1	1.1	Old, J. (2002b)
Valtothori/ Thessaloniki, Greece, bare soil	Sandy silt loam	9.022 2.24 (fast) 61.67 (slow)	DFOP	0.960 kg a.i./ha	0-10, 10-20 cm	Not reported	8.0	0.9	Old, J. (2002c)
Tivenys/ Tarragona, Spain, bare soil	Clay loam	0.323 0.09 (fast) 5.42 (slow)	DFOP	0.960 kg a.i./ha	0-10, 10-20 cm	Not reported	8.2	1.4	Old, J. (2002d)
India	Black soil	2.79 d 2.93 d 2.86 d 2.82 d	Not reported	500 g a.i ha 750 g a.i ha 1000 g a.i ha 1500 g a.i ha	Not reported	Not reported	Not reported	Not reported	Vijyalakshmi and Ramesh (1996)
Jaipur, semi-arid India	Loamy sand	12.3 d	Not reported	5 g ai kg <sup>-1</sup> seed and 800 g ai ha <sup>-1</sup> on day 14	0-15 cm	13 % WHC	8.2	0.3	Menon et al, 2004
Delhi, semi-arid India	Sandy loam	16.4 d	Not reported	5 g ai kg <sup>-1</sup> seed and 800 g ai ha <sup>-1</sup> on day 40	0-15 cm	24 % WHC	7.7	1.02	
Range		3 – 89 d							

## Rate of degradation in water-sediment studies

Table 7: Rate of degradation in water-sediment studies, laboratory studies

Sediment source	Sediment texture	Half-life or DegT <sub>50</sub> total system (d)	DT50 total system normalised to 12°C <sup>3</sup>	DisT50 water (d)	DisT50 sediment (d)	Application (ppm)	Temperature (water) (°C)	pH sediment	pH water	Organic Carbon (%) sediment	Organic Carbon (%) water	Reference
Brown Carrick Sediment	Sandy loam	22 d	-/-	3 d		960 g a.i./ha	Not given	5.2	7.4	2.5	0.0016	Reeves, G.L. and Mackie, J.A., 1993
Auchingilsie Sediment	Clay loam	51 d	-/-	6 d		960 g a.i./ha	Not given	6.3	6.7	3.2	0.00172	
Range Point, Santa Rosa Island, Escambia County, Florida, USA	Salt marsh	24 d		Not given	Not given	< water solubility	25°C	Not given	Not given	48%	Not given	Schimmel, 1983
Pond sediment	Silty Clay Loam	30.5	104.6	Not given	Not given		25°C	7.7	8.1	3.1	Not given	Kennard, 1996
Calwich Abbey Lake, Staffordshire, UK	Silt loam	30.67 (SFO)	65.5	3.075 (SFO)	3.007 (HS)	0.54 mg a.i./L	20 ± 2°C	7.5	7.71	5.8	Not given	Kang, 2015, kinetics calculated by Abu, A., 2015d
Swiss Lake, Chatsworth, Derbyshire, UK	Sand	58.25 (SFO)	124.3	5.063 (SFO)	34.49 (SFO)	0.54 mg a.i./L	20 ± 2°C	7.0	7.84	0.7	Not given	
range		22 – 58.25 d	65.5 – 124.3 d									

<sup>3</sup> Temperature normalised using the Arrhenius equation

1. The Australian government review (APVMA 2000) refers to pond studies that give a half-life in sediment of 200 days, but no further details or reference were given.
2. A shake-flask screening test with chlorpyrifos was performed by Walker (1984). The test was designed to rapidly evaluate the relative degradation rates under diverse regimes of, e.g., salinity, pH, and microbial biomass. The experimental design for the screening test covered four treatments. For chlorpyrifos, the half-lives ( $n = 2$ ) were 18 and 25 d in active sediment, 17 and 39 d in sterile sediment, 16 and 27 d in active water, and 24 and 29 d in sterile water, respectively. The experiments with sterilized samples showed mostly longer half-lives which may be interpreted as degradation of chlorpyrifos being increased in the presence of micro-organisms (biodegradation).
3. Budd et al. (2011) studied the fate of chlorpyrifos in a ditch and a constructed wetland in California (USA). The DT50 for chlorpyrifos in the ditch sediment under anaerobic (flooded) conditions was 144 d and in the constructed wetland sediment 44 d. Under aerobic conditions the DT50 was 58 d in the ditch. Due to low concentrations it was not determined for the constructed wetland. The test set-up is not comparable to laboratory studies conducted according to OECD TG 308, as the studies in aerobic sediment were conducted in situ, with changing environmental conditions, the water samples are not directly associated with the sediment samples and losses due to volatilisation are not accounted for.

## Other evidence of persistence

4. According to a 10-year water quality assessment study performed by the United States Geological Survey, chlorpyrifos was the most heavily used and frequently detected insecticide; it was found at concentrations exceeding an aquatic-life benchmark of 0.04 mg/L for water in 37% samples collected from water bodies with diverse land-use settings throughout the USA (Gilliom et al., 2006). Chlorpyrifos was detected frequently in both urban and rural streams and major rivers in the USA, but less frequently in groundwater samples (Kolpin et al., 2000).

## Bioaccumulation

**Table 8: Bioaccumulation studies assessed for evaluation of chlorpyrifos**

Publication	Species	Endpoint type	Endpoint value	Unit	Comments
amphibia					
Robles-Mendoza et al. (2011)	axolotl ( <i>Ambystoma mexicanum</i> )	BCF	3632	mL/g	decrease in chlorpyrifos concentration by 50% during exposure; behavioural effects
Fish					
Hansen et al. (1986)	gulf toadfish ( <i>Opsanus beta</i> )	BCF	5100	mL/g	toxic effects; increased mortality at 150 µg/L for which the BCF of >5000 was reported

Publication	Species	Endpoint type	Endpoint value	Unit	Comments
Welling and Vries (1992)	guppies ( <i>Poecilia reticula</i> )	BCF	1847	mL/g	fish not fed during two week experiment; chlorpyrifos concentration decreased by 90%
Mulla et al. (1973)	channel catfish ( <i>Ictalurus punctatus</i> )	BCF	4677	mL/g	extreme fluctuations in temperature and O2 concentration; fish analysed without gut
Mulla et al. (1973)	black crappie ( <i>Pomoxis nigromaculatus</i> )	BCF	3333	mL/g	extreme fluctuations in temperature and O2 concentration; fish analysed without gut
Mulla et al. (1973)	largemouth bass ( <i>Micropterus salmoides</i> )	BCF	1333	mL/g	extreme fluctuations in temperature and O2 concentration; fish analysed without gut
Mulla et al. (1973)	bluegill ( <i>Lepomis microchirus</i> )	BCF	1200	mL/g	extreme fluctuations in temperature and O2 concentration; fish analysed without gut
Jarvinen et al. (1983)	fathead minnow ( <i>Pimephales promelas</i> )	BCF	1673 ± 423	mL/g	toxic effects
Deneer (1993)	guppy ( <i>Poecilia reticulata</i> )	BCF	1580	mL/g	BCF calculated in Gisey et al. 2014
Thomas and Mansingh (2002)	red hybrid tilapia ( <i>Oreochromis</i> sp.)	BCF	116 (semi static exposure); 3313 (pulse exposure)	mL/g	high fluctuation of chlorpyrifos; steady state not reached; Dursban 25 C used
J. Eaton et al. (1985)	bluegills ( <i>Lepomis microchirus</i> )	BCF	600	mL/g	toxic effects; high fluctuation in chlorpyrifos concentration; Lorsban 4C used
J. Eaton et al. (1985)	fathead minnow ( <i>Pimephales promelas</i> )	BCF	1150	mL/g	toxic effects; high fluctuation in chlorpyrifos concentration; Lorsban 4C used
Goodman, Hansen, Cripe, et al. (1985)	california grunion ( <i>Leuresthes tenuis</i> )	BCF	1000	mL/g	significant mortality and toxic effects; control fish contaminated with chlorpyrifos

Publication	Species	Endpoint type	Endpoint value	Unit	Comments
Cripe et al. (1986)	sheepshead minnows ( <i>Cyprinodon variegatus</i> )	BCF	1830	mL/g	mortality in high concentrations; different feeding regiments tested; BCF increased with CPY concentration and higher feeding rates
Goodman, Hansen, Middaugh, et al. (1985)	<i>Menidia beryllina</i>	BCF	440	mL/g	steady state not reached; mortality in higher concentrations
Goodman, Hansen, Middaugh, et al. (1985)	<i>Menidia peninsulae</i>	BCF	580	mL/g	steady state not reached; mortality in higher concentrations; negative effect of solvent
Macek et al. (1972)	bluegills ( <i>Lepomis microchirus</i> )	BCF	2304	mL/g	extreme fluctuations in temperature and O2 concentration; behavioural effects
Macek et al. (1972)	largemouth bass ( <i>Micropterus salmoides</i> )	BCF	1440	mL/g	extreme fluctuations in temperature and O2 concentration; behavioural effects
Deneer (1994)	three-spined stickleback ( <i>Gasterosteus aculeatus</i> )	BCF	21140 (lipid-based) 1057 (5% lipid)	mL/g	decrease of elimination rate upon increasing exposure concentrations => BCF will increase with increasing exposure concentrations
Tsuda et al. (1992)	carp ( <i>Cyprinus carpio</i> )	BCF	410 ± 100	mL/g	steady state not reached
Tsuda et al. (1997)	guppies ( <i>Poecilia reticulata</i> )	BCF	1506 (female guppy), 2305 (male guppy)	mL/g	steady state not reached
Tsuda et al. (1997)	medaka ( <i>Oryzias latipes</i> )	BCF	1561	mL/g	steady state not reached
Tsuda et al. (1997)	goldfish ( <i>Carassius auratus</i> )	BCF	763	mL/g	steady state not reached
Tsuda et al. (1997)	white cloud mountain minnow ( <i>Tanichthys albonubes</i> )	BCF	745	mL/g	steady state not reached
report no ES-928 (J42) in Spain (2017)	rainbow trout ( <i>Onchorhynchus mykiss</i> )	BCF	1374 ± 321	mL/g	not normalized for lipid or growth
El-Amrani et al. (2012)	zebrafish ( <i>Danio rerio</i> )	BCF	5011	mL/g	not normalized for lipid; eleuthero embryos with 11 - 20% lipid content
Alharbi et al. (2017)	medaka ( <i>Oryzias latipes</i> )	BCF	2691	mL/g	not normalized for lipid; eleuthero embryos with 11 - 20% lipid content



Publication	Species	Endpoint type	Endpoint value	Unit	Comments
macroinvertebrates					
Serrano et al. (1997)	<i>Mytilus galloprovincialis</i>	BCF	400 ± 119	mL/g	concentration of test substance within 25% fluctuation
Thacker et al. (1992)	eastern oyster ( <i>Crassostrea virginica</i> )	BCF	950 (whole oysters); 1600 (tissue fraction)	mL/g	significant dip in CPY by day 21 (56%); chlorpyrifos concentration low in shell liquor
Woodburn et al. (2003)	eastern oyster ( <i>Crassostrea virginica</i> )	BCF	565 (whole oyster); 1400 (oyster tissue)	mL/g	chlorpyrifos concentration low in shell liquor
Rubach et al. (2010)	15 macroinvertebrate species	BCF	100 - 13930	mL/g	C14 labelling of chlorpyrifos at the di-ethyl-phosphorothiol branch
Montañés et al. (1995)	<i>Asellus aquaticus</i>	BCF	1715	mL/g	Mesocosm experiment with time dependant significantly reduced survival
A. Jantunen et al. (2008)	<i>Lumbriculus variegatus</i>	BSAF	Range of 6 to 99		
plants					
Prasertsup and Ariyakanon (2011)	duckweed ( <i>Lemna minor</i> )	BCF	5700	mL/g	BCF calculated based on daily measurements
Prasertsup and Ariyakanon (2011)	water lettuce ( <i>Pistia stratiotes</i> )	BCF	3000	mL/g	BCF calculated based on daily measurements
Lal et al. (1987)	Blue-Green Algae <i>Anabaena</i> sp.	BCF	678	mL/g	concentration of test substance not maintained, no calculations reported
Lal et al. (1987)	<i>Aulosira fertilissima</i>	BCF	397	mL/g	concentration of test substance not maintained, no calculations reported
monitoring data					
Landers et al. (2008)	white fir ( <i>Abies concolor</i> )	chlorpyrifos concentration	first year not detected, second year 19.7	ng/g lipid weight	
Landers et al. (2008)	lodgepole pine ( <i>Pinus contorta</i> )	chlorpyrifos concentration	first year 11.6 , second year 20.5	ng/g lipid weight	

Publication	Species	Endpoint type	Endpoint value	Unit	Comments
Aston and Seiber (1997)	<i>Pinus ponderosa</i>	BCF <sub>m</sub>	9800	mass: mass ratio	combined from wax cuticle and cell
Kurt-Karakus et al. (2011)	zooplankton	BAF	up to 117000		possible adsorption
Jessup et al. (2010)	sea otters ( <i>Enhydra lutris</i> ssp.)	concentration in blood serum	maximum 342.6	ng/g lipid weight	
Stansley et al. (2010)	river otters ( <i>Lontra canadensis</i> )	concentration in liver tissue	maximum 6.91	ng/g wet weight	
Adrogué et al. (2019)	blackbrowed albatross ( <i>Thalassarche melanophris</i> )	concentration in feathers	58.64 ± 27.31 (male); 49.56 ± 18.45 (female)	ng/g	feathers washed with deionized water before analysis
Adrogué et al. (2019)	cape petrels ( <i>Daption capense</i> )	concentration in feathers	84.88 ± 50.57 (male); 75.98 ± 47.97 (female)	ng/g	feathers washed with deionized water before analysis
Morris et al. (2014)	mushrooms, lichen and green plants	BCF <sub>v</sub>	8.0 - 8.7	mass: mass ratio	recovery rate of chlorpyrifos from biota samples 52 ±17%
Morris et al. (2014)	caribou:vegetation	BMF	1.6 ± 0.31 (spring); 1.4 ± 0.43 (summer; 2.1 ± 0.64 (fall/winter)		recovery rate of chlorpyrifos from biota samples 52 ±17%
Morris et al. (2014)	wolf:caribou	BMF	0.078 ± 0.019		recovery rate of chlorpyrifos from biota samples 52 ±17%
Morris et al. (2014)	wolf <sub>liver</sub> :caribou <sub>liver</sub>	BMF	1.7 ± 0.52		recovery rate of chlorpyrifos from biota samples 52 ±17%
Morris et al. (2014)	green plants	TMF	0.61 (0.47 - 0.79)	pg/g lipid weight	recovery rate of chlorpyrifos from biota samples 52 ±17%
Morris et al. (2016)	plankton	BAF	7 943 282 ± 5 011 872	mL/g	recovery rate of chlorpyrifos from biota samples 52 ±17%

Publication	Species	Endpoint type	Endpoint value	Unit	Comments
Morris et al. (2016)	polar bear fat: seal blubber	BMF	1.3 ± 0.22 and 0.90 ± 0.27		recovery rate of chlorpyrifos from biota samples 52 ±17%; concentration in seal blubber not reported; detection in seal blubber below 20%
Morris et al. (2016)	seal blubber	TMF	0.27, 0.57 and 0.18		recovery rate of chlorpyrifos from biota samples 52 ±17%; concentration in seal blubber not reported; detection in seal blubber below 20%
Singh et al. (2008)	chicken	mean concentration in blood	80	ppb	
Singh et al. (2008)	goat	mean concentration in blood	70	ppb	
Singh et al. (2008)	man	mean concentration in blood	40	ppb	
Shaker and Elsharkawy (2015)	buffalo	concentration in raw milk	1.870 – 3.514	mg/kg	
Weldon et al. (2011)	<i>Homo sapiens</i>	concentration in breast milk	urban mean 40.5; agricultural mean 139	pg/g milk	
Bedi et al. (2013)	<i>Homo sapiens</i>	concentration in breast milk	median 1664.2	ng/g lipid weight	
Sanghi et al. (2003)	<i>Homo sapiens</i>	concentration in breast milk	mean value 0.230 ± 0.024	mg/kg	

**Table 9 Bioaccumulation studies not used for assessment but used in Spain 2017**

in summary as report number	species	endpoint type	endpoint value	unit	Publicly available
GHE-T-281 (J061)	Eel ( <i>Anguilla anguilla</i> )	BCF	400	mL/g	no
GS 1318 (J41)	mosquito fish ( <i>Gambusia</i> sp.)	BCF	65 - 472	mL/g	no
DECO-ES-2377 (J66)	Eastern oyster ( <i>Crassostrea virginica</i> )	BCF	430	mL/g	no

## Details of bioaccumulation studies not listed in the dossier:

5. According to a review by (Giesy et al., 2014) relevant and reliable BCF values for aquatic plants range from 72 to 5700.
6. The highest BCF value of 5700 was measured for duckweed (*Lemna minor*) (Prasertsup & Ariyakanon, 2011). In a seven-day static experiment plants were exposed to a nominal concentration of 100 µg/L chlorpyrifos. Samples of plants and water were taken daily and analysed for chlorpyrifos content by gas chromatography at recovery rates of  $98 \pm 2\%$ . With the same experimental set up, a BCF of 3000 was calculated for water lettuce (*Pistia stratiotes*). This study is considered unreliable as the chlorpyrifos concentration declined by more than 30% over the time of the experiment.
7. Rubach et al. (2010) conducted exposure experiments of 15 invertebrate species with C14 labelled chlorpyrifos. This resulted in highest BCF value for the diptera *Culex pipens* of 13 930. This value should be evaluated with caution as the C14 label was placed at the di-ethyl-phosphorothiol branch of the chlorpyrifos molecule. Accordingly radioactivity measured was not limited to chlorpyrifos but included phosphorylated proteins Mackay et al. (2014) and could result in an overestimated BCF.
8. The BCF for the axolotl (*Ambystoma mexicanum*) was determined in a 48 h static test (Robles-Mendoza et al., 2011). The nominal concentrations were 50 µg/L and 100 µg/L. Ten animals per concentration were tested. Chemical analysis of water and tissue samples were conducted with gas chromatography with a recovery rate of  $>95\%$ . Water samples were taken to determine chlorpyrifos concentration at 0 h, 24 h and 48 h. Chlorpyrifos concentration had declined up to 50% at the end of the experiment. The calculated BCF was 3632 at 100 µg/L. This value has some level of uncertainty as chlorpyrifos level were not stable. Additionally, toxicity test showed significant acetylcholinesterase inhibition, reduced motor activity and reduced hunting at 50 µg/L.
9. *Asselus aquaticus* was exposed to chlorpyrifos in the form of Drusban 4E. The nominal concentration of active substance were 0.7 and 5 µg/L (Montañés et al., 1995). Exposure took place in nature-like mesocosms, 40 m long ditches lined with water-tight, non-toxic PVC and a 0.25 m sediment layer and filled with water drawn from a underground well. Polythene spheres were used to hold 10 animal each. 120 animals per concentration were exposed this way. 50 animals were used as controls in a ditch without chlorpyrifos. Water samples were taken at 15 min and at 1, 2, 4, 7, 14 and 29 days after application. On days 1, 2, 3, 4, 6, 8, 13, 17 and 23 animals were sampled by harvesting one or two spheres. The recovery rate from biota was  $54 \pm 4\%$  and  $82 \pm 5\%$  from water. The limits of detection were 0.001 µg/L in water and 200 ng/g lipid weight (lw) for *Asselus aquaticus*. The concentration of chlorpyrifos was not stable and declined continuously over the course of the experiment with a decline above 25% in the first three days. Survival was significantly reduced in the course of the experiment, the authors noted that this may be due to predation or toxicity of chlorpyrifos. An average lipid content of  $0.69 \pm 0.26\%$  was observed. Kinetic BCF were calculated for days two to seventeen. On average the BCF was 1715.
10. An extensive review on bioaccumulation was conducted by Giesy et al. (2014) with BCFs ranging from 0.6 to 6760 in fish. The highest valid study as assessed by the authors was Hansen et al 1986 with a BCF of 5100 for the gulf toad fish.
11. Hansen et al. (1986) conducted a 49-day early life stage toxicity test with the marine gulf toadfish (*Opsanus beta*). Embryos were exposed to chlorpyrifos concentrations ranging from 1.2 to 150 µg/L in a flow through system. The authors reported a range of BCFs from 100 to 5100. The results of this study must be interpreted with caution as toxic effects occurred at all concentrations higher than 3.7 µg/L. Effects included mortality, reduced size, retarded development and behavioural effects such as hyperactivity and hyperventilation. Mortality was significantly increased at the concentration 150 µg/L which produced the BCF of 5100.
12. In a 28-day field experiment, artificial ponds were dosed with a mosquito larvicide application of granular chlorpyrifos resulting in mean water concentrations between 0.6 µg/L and 0.1 µg/L, exposing four fish species (Mulla et al., 1973). Concentrations in the water declined as concentrations in the upper sediment layer increased to a maximum of 180 µg/kg. Sediment associated species such as channel catfish (*Ictalurus punctatus*) and black crappie (*Pomoxis nigromaculatus*) accumulated mean maximum residues of 0.8 mg/kg and 0.6 mg/kg, resulting in BCFs of 4667 and 3333 respectively. Free swimming species such as largemouth

bass (*Micropterus salmoides*) and bluegill (*Lepomis microchirus*) accumulated 0.2 mg/kg and 0.1 mg/kg, resulting in BCF of 1333 and 1200. This study may underestimate chlorpyrifos bioaccumulation, as the viscera was removed from fish before analysis. Results should be interpreted with caution as chlorpyrifos concentrations varied above the 20% mark throughout the experiment.

13. A BCF of 1700 for juvenile guppies (*Poecilia reticula*) was reported in a 14-day static exposure with chlorpyrifos (Welling & Vries, 1992). This study is considered unsuitable for BCF calculation as the nominal concentration of 10 µg/L decreased to below 1 µg/L by day 9. Furthermore, fish were not fed during the experiment.
14. Jarvinen et al. (1983) exposed fathead minnows (*Pimephales promelas*) to chlorpyrifos in a 200-day full life cycle experiment under flow through conditions. A BCF of  $1673 \pm 423$  for first generation minnows at 60 days was calculated. Steady state was assumed. Effects occurred proportional to acetylcholinesterase inhibition. At the highest concentration of 2.68 µg/L reduction of growth, deformities and later significant mortality occurred. Growth reduction was also observed for 1.21 µg/L, later in the test. Sexual maturation and reproduction were reduced in all exposure groups at concentrations as low as 0.12 µg/L. In the second generation, deformities occurred more frequently and at lower water concentrations. Based on the toxic effects, the BCF should be interpreted with caution.
15. Deneer (1993) calculated uptake and elimination constants for the guppy (*Poecilia reticulata*) under flow through conditions of 2 µg/L chlorpyrifos. The experiment lasted 24 days, 20 days of exposure and four days for depuration. The uptake constant was calculated as  $7000 \pm 2000$  L/kg/d, the depuration constant as  $0.40 \pm 0.11$  L/kg/d. The BCF was calculated in (Giesy et al. 2014) as 1580. Steady state was not reached and chlorpyrifos concentration showed a high fluctuation.
16. Thomas and Mansingh (2002) conducted two experiments exposing red hybrid tilapia (*Oreochromis* sp.) to the commercial product Dursban 25 C with 25% chlorpyrifos active ingredient. A three-day semi-static exposure, with the water concentration fluctuating between 48 µg/L and 35 µg/L chlorpyrifos, resulted in a BCF of 116. A four-day pulse exposure with water concentration between 4.9 µg/L and 3.6 µg/L resulted in a BCF of 3313. This study must be interpreted with caution, as steady state was not reached and the concentration of chlorpyrifos fluctuated highly. Moreover, Dursban 25 C contains other ingredients that can have effects on fish.
17. Artificial streams were exposed to Lorsban 4E with 40,7% active ingredient chlorpyrifos in a 100-day experiment (J. Eaton et al., 1985). One stream was continuously dosed, the other was subjected to pulse exposure every two weeks. Water concentration in the continuously dosed stream varied between 0.12 µg/L and 0.83 µg/L during the 100 days and also spatially between the sections of the stream up to 0.17 µg/L. The pulsed stream reached maximum concentrations of up to 7 µg/L directly after pulse events. Both streams received the equivalent amount of chlorpyrifos during the experiment. Bluegills (*Lepomis microchirus*) and fathead minnows (*Pimephales promelas*) were exposed. For fathead minnows deformities occurred in the pulse experiment only, reproductive losses and decreased body weight of second generation fish occurred in both streams. For bluegills behavioural effects occurred. Both fathead minnows and bluegills showed acetylcholinesterase inhibition. For fatheaded minnow a tissue BCF of 760 was calculated and a lipid BCF of 23000. Normalised to 5% lipid content the BCF is 1150. For bluegill a tissue BCF of 100 was calculated and a lipid BCF of 12000, which gives a BCF of 600 when normalised to 5% lipid content. These values should be interpreted with caution as Lorsban was used instead of pure chlorpyrifos, in addition chlorpyrifos concentrations were not constant and toxic effects occurred. Additionally, the authors did not specify which tissue was analysed nor give the lipid content of the fish.
18. In a 30-day early life stage toxicity test, the california grunion (*Leuresthes tenuis*) was exposed to 0.14 µg/L chlorpyrifos under flow through conditions (Goodman, Hansen, Cripe, et al., 1985). A BCF of 1000 was determined. This result should be interpreted with caution, as chlorpyrifos residue was also found in fish sampled from the seawater and solvent control.
19. A BCF of 1830 was determined for sheepshead minnows (*Cyprinodon variegatus*) in a 28-day early life stage toxicity test under flow through conditions (Cripe et al., 1986). The effect of different feeding ratios and chlorpyrifos concentrations were examined. Fish were exposed to 10 different concentrations ranging from 0.6 µg/L to 52 µg/L and three different feeding regiments. BCF increased with increasing chlorpyrifos

concentrations and increasing amount of feed. These results should be interpreted with caution as significant mortality occurred in higher concentrations.

20. Different silverside species were exposed to chlorpyrifos in a 28-day early life stage toxicity test under flow through conditions (Goodman, Hansen, Middaugh, et al., 1985). For *Menidia beryllina* a BCF of 440 was determined. For *Menidia peninsulae* a BCF of 580 was reported. BCFs increased with higher chlorpyrifos concentrations. Results should be interpreted with caution as mortality occurred in higher concentrations for both fish species and *M. peninsulae* survival was negatively affected by the solvent used.
21. Macek et al. (1972) described the uptake of chlorpyrifos in bluegills (*Lepomis microchirus*) and largemouth bass (*Micropterus salmoides*) during a 63-day field study with chlorpyrifos applied at mosquito larvicide rates to small ponds. Two applications were performed on day one and day 35. The maximum BCF for bluegill was 2304 on day seven and 1440 BCF for largemouth bass on day three. Water temperatures could rise up to 31 °C as the experiment was conducted during summer months. This influenced the dissolved oxygen, which could drop below 50%. Behavioural effects were noted shortly after each application. Results should be interpreted with caution as the variation of chlorpyrifos concentrations exceeded the 20% window.
22. For the three-spined stickleback (*Gasterosteus aculeatus*) a BCF of 1057 was derived from a 30-day laboratory experiment (Deneer, 1994). Fish were exposed to chlorpyrifos at  $0.19 \pm 0.03 \mu\text{g/L}$  for 21 days under flow through conditions, depuration lasted 9 days. Insufficient information is reported on BCF calculation, therefore the BCF value should be interpreted with caution.
23. Tsuda et al. (1992) exposed carp (*Cyprinus carpio*) to  $0.49 \pm 0.11 \mu\text{g/L}$  chlorpyrifos during a 14-day flow through experiment. A BCF of  $410 \pm 100$  was calculated on day 14. Although steady state was not reached, the BCF was calculated as it would be under steady state conditions. The same reason for caution applies to the study from Tsuda et al. (1997) with the same experimental set up, where a BCF of 2406 was calculated for male guppies (*Poecilia reticulata*), a BCF of 1464 calculated for female guppies, 1561 for medaka (*Oryzias latipes*), 763 for goldfish (*Carassius auratus*) and 745 for white cloud mountain minnow (*Tanichthys albonubes*).
24. An experiment following the same setup was conducted for medaka (*Oryzias latipes*) at  $10 \mu\text{g/L}$  chlorpyrifos (Alharbi et al., 2017). The LOD for chlorpyrifos was  $0.19 \text{ ng/g}$ . Steady state was not reached, therefore the kinetic BCF was calculated at 2187. In a separate experiment instead of exposure medium, processed water from surface level mining, containing chlorpyrifos, was used. This resulted in a kinetic BCF of 8912.
25. Chlorpyrifos and its transformation product chlorpyrifos oxon were detected in needles of potted ponderosa pines at three sites in California in 1994 (Aston & Seiber, 1997). Needle compartments were analysed separately and included a wash for polar and non polar adsorbed substances, the waxy cuticle and the remainder needle. Values for chlorpyrifos residue in each compartment were combined to calculate total burden per sample. Two sites were sampled, one was located at the edge of the Central Valley (114 m altitude), while the others were situated at higher altitudes in the Sequoia National Park (533 and 1920 m, resp.). The detection frequency was significantly higher at the site in the Central Valley than those at the other two locations. The maximum level of chlorpyrifos in pine needles, which was found at the site in the Central Valley, amounted to ca.  $129 \text{ ng/g}$  dry weight, while the maximum level of chlorpyrifos oxon was about  $110 \text{ ng/g}$  dry weight at the same location<sup>4</sup>. Assuming that the needles of the potted pines, located at the site in the Central Valley, were in equilibrium with the compound in the surrounding air after 10 weeks of exposure, the vegetation: air BCF<sub>m</sub> was estimated as 9800.
26. Shaker and Elsharkawy (2015) detected chlorpyrifos in raw buffalo milk samples offered for sale in the Egyptian city of Assiut in 2013. The compound was found in 33 % of the samples. The average concentration was  $3.01 \pm 1.0 \text{ mg/kg}$ . All measured values significantly exceeded the maximum residue level of  $0.01 \text{ mg/kg}$  set by the European Commission (EC, 2008) for chlorpyrifos. Contaminated feed, grass or corn silage, and direct application on dairy cattle were assumed as the main sources of the chlorpyrifos residues in milk.

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<sup>4</sup> The concentration values were estimated from a diagram of the cited publication.

<sup>5</sup> In this study the BCF<sub>m</sub> was defined as the mass : mass ratio of the concentration of a chemical in vegetation tissues to its concentration in air.

## Potential for long-range transport – Additional Information

Publication	Medium	Time frame	Concentration	Handling of blanks
Chernyak et al. (1996)	fog condensate sea water melting ice	1993	5 ng/L max. 65 pg/L max. 170 pg/L	blanks analysed as field samples, no chlorpyrifos detected
Garbarino et al. (2002)	snow	1995/96	70 – 80 ng/L	no information
Hermanson et al. (2005)	ice core	1972 – 1990	max. 16.2 ng/L	concentrations blank corrected
Ruggirello et al. (2010)	ice core	1971 – 2005	max. 808 pg/cm <sup>2</sup> /year	Method detection limit (MDL, defined as mean blank value + 3 x SD of blank values)
Muir et al. (2004)	lake water	1998 – 2001	mean 0.27 ng/L	MDL
Landers et al. (2008)	snow	2003	0.010 - 0.030 ng/L	On average concentrations found in blanks were 3% of the concentration in snowpacks and the concentration in blanks was subtracted from concentrations found in snow samples.
L. M. Jantunen et al. (2007)	air	2007	0.36 to 30.4 pg/m <sup>3</sup>	no information
Pučko et al. (2015)	air	2008	3.1 ± 1.9 pg/m <sup>3</sup>	no information
Pučko et al. (2015)	sea water	2008	31 ± 19 pg/L	no information
Hung et al 2013 Hung et al. in Balmer et al. (2019)	air	2006 - 2009	<MDL – 6.8 pg/m <sup>3</sup>	MDL
Zhong et al. (2012)	air	2010	1 - 146 pg/m <sup>3</sup>	MDL
Zhong et al. (2012)	sea water	2010	0.1 - 111 pg/L	MDL
Pučko et al. (2017)	snow	2012	mean ± SD, 4.8 ± 1.3 pg/L	MDL
Pučko et al. (2017)	melt pond water	2012	mean ± SD, 14.4 ± 2.5 pg/L	MDL
Pučko et al. (2017)	sea water	2012	mean ± SD, 14.1 ± 6.0 pg/L (0m), 10.5 ± 1.7 pg/L (5m)	MDL
Pučko et al. (2017)	air	2012	mean ± SD, 0.10 ± 0.04 pg/m <sup>3</sup>	MDL



Publication	Medium	Time frame	Concentration	Handling of blanks
L. M. Jantunen et al. (2015)	air	2007, 2008, 2010, 2011 and 2013	mean $\pm$ SD, $1.1 \pm 1.3$ pg/m <sup>3</sup>	No chlorpyrifos measured in blanks, instrumental detection limits 0.02 pg/m <sup>3</sup> and 0.1 pg/L
L. M. Jantunen et al. (2015)	water	2007, 2008, 2010, 2011 and 2013	mean $\pm$ SD, $13 \pm 12$ pg/L	No chlorpyrifos measured in blanks, instrumental detection limits 0.02 pg/m <sup>3</sup> and 0.1 pg/L
Bigot et al. (2017)	sea ice Arctic	2015	5.2 – 12.0 pg/L	MDL
Bigot et al. (2017)	sea water Arctic	2015	0.74 – 1.0 pg/L	MDL
Bigot et al. (2017)	snow Arctic	2015	6.2 – 11.5 pg/L	MDL
Bigot et al. (2017)	sea-ice meltwater Antarctic	2015	< MDL - 7.3 pg/L	MDL
Bigot et al. (2017)	Air Antarctica	2015	4.1– 16.8 pg/m <sup>3</sup>	MDL
Boström (2020)	air	2009 - 2018	median concentrations of 0.002 ng/m <sup>3</sup>	no information
Boström (2020)	precipitation	2002 – 2018	max. concentrations between 0.0001 and 0.01015 µg/L	no information

27. Muir et al. (2004) compared their findings of current-use pesticides in remote areas with the predicted atmospheric half-lives and characteristic travel distances (CTDs). Predicted half-lives in air of the most current-use pesticides do not exceed the Stockholm criterion for LRTP. The authors discussed that the discrepancy between modelling data and monitoring findings is due to an overestimation of the atmospheric OH radical concentration applied in the model calculations. Furthermore, precipitation scavenging may be overestimated by LRTP models assuming a high ability of current-use pesticides to dissolve in rain droplets. If the atmosphere is sufficiently cold, cloud water and falling hydrometeors will be frozen and have a much smaller capacity to take up water-soluble organic chemicals. Snow may have a considerably lower scavenging efficiency for the vapours of water-soluble pesticides compared to that of rain. Snow may limit the LRTP of these pesticides much less than rain. The accuracy of degradation rates estimated by AOPWIN was discussed as well. Referring to QSAR forming the basis of AOPWIN, “it is expected that the predictions will be more uncertain the more complex the chemical is (i.e., how many functional groups it contains) and especially if the chemical contains halogen atoms and/or N- or S-atoms.” (Atkinson et al. (1999) as cited in Muir et al. (2004)). This aspect may also be the case for more recent models.
28. The following figure (figure 1) has been taken from von von Waldow et al. (2010) and modified by the drafters of this dossier to present chlorpyrifos findings in remote areas.

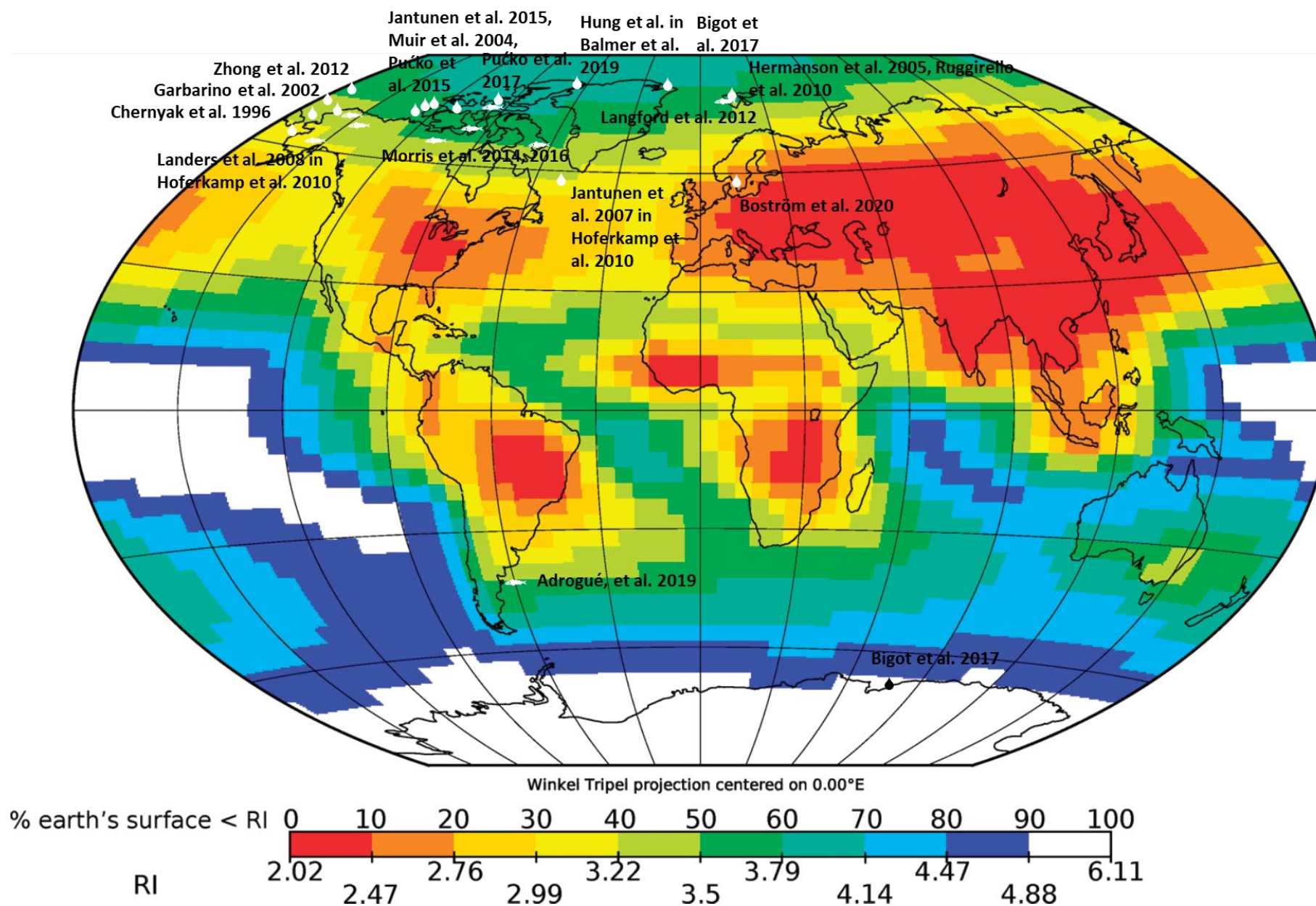


Figure 1: Map of chlorpyrifos findings in remote areas modified after von Waldow et al. 2010; fish symbols indicate finding in biota, drop symbol indicate abiotic findings

## Exposure

29. Chlorpyrifos, which is a priority substance in the Water Framework Directive of the EU (Directive 2000/60/EC), is regularly monitored in surface and groundwater in Europe. Chlorpyrifos was detected in 204 276 river and lake samples (8.6% quantified samples) from 6 002 sites in 23 Member States (UK included) for the period 2006 – 2019 (LOQ is 0.00003 – 10 µg/L), and in 5 439 coastal and transitional surface water samples (4.2% quantified samples) from 364 sites in 9 Member States (UK included) for the period 2008 – 2019 (LOQs is 0.0001 – 0.5 µg/L)(WISE database 2021, European Environment Agency) (. In groundwater, chlorpyrifos was detected in 97 896 samples (5.1% quantified samples) from 10 509 sites in 14 Member States (UK included) for the period 2006 – 2019 (LOQs is 0.0004 – 2 µg/L)

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