Additional information relating to the draft risk profile for chlorpyrifos

Table of content

Physico-chemical properties	2
Transformation products	5
Persistence	6
Abiotic degradation	6
Water: Direct and indirect photochemical degradation	6
Soil photolysis	6
Rate of degradation in water	7
Rate of degradation in soil	8
Rate of degradation in soil: termite control application rates	11
Rate of degradation in soil: field studies	12
Rate of degradation in water-sediment studies	13
Other evidence of persistence	14
Bioaccumulation	14
Potential for long-range transport – Additional Information	24
Exposure	27
References	28

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-
Structure	CI S O O	CI CI O O O O O O O O O O O O O O O O O	CI N OH	pyridine (TMP) CI CI N O
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]	3.35 * 10 ⁻³ 25°C (purity 99.8%) (EC, 2005)	8.87 * 10 ⁻⁴ (estimated) (US-EPA, 2012)	0.138 (estimated) (US-EPA, 2012)	1.43 (estimated) (US-EPA, 2012)
	1.43 * 10 ⁻³ 20°C (purity 99.8%) (EC, 2005)		3.57 *10 ⁻³ at 25°C 1.79 * 10 ⁻³ at 20°C (purity 99.6%) (Spain, 2017)	1.27 at 25°C 0.9 at 20°C (purity 100%) (Spain, 2017)
	1.0 * 10 ⁻³ Experimental, 25°C (purity 98%) (WHO, 2009)		95.0%) (Spain, 2017)	(Spain, 2017)
	2.3 * 10 ⁻³ Compiled by Mackay et al. (2014)			
Water solubility [mg/L]	1.05 at 20°C, in unbuffered solution, no pH dependency reported (EC, 2005)	25.97 (25°C, estimated from log KOW) (US-EPA, 2012)	80.85 (25°C, estimated from log KOW) (US-EPA, 2012)	60.36 (25°C, estimated from log KOW) (US-EPA, 2012)
	0.39 at 19.5°C, pH not cited (98 % purity) (WHO, 2009)	2623.4 (25°C, estimated from fragments) (US-EPA, 2012)	125.09 (25°C, estimated from fragments) (US-EPA, 2012)	750.88 (25°C, estimated from fragments) (US-EPA, 2012)
	0.73 Cited by Mackay et al. (2014)			
	0.941 (20°C, pH unknown, guideline EEC Method A6/OECD 105) Dow, as cited in WHO (2009)			
	0.588 (20°C, pH not stated, guideline OECD 105 flask method) Makhteshim, as cited in WHO (2009)			

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 m³/mol]	1.09 (25°C) Cited by Mackay et al. (2014)	5.53 * 10 ⁻⁴ (25°C, QSAR estimated) (US EPA 2012)	1.91 * 10 ⁻³ (25°C, QSAR estimated) (US EPA 2012)	9.89 (25°C, QSAR estimated) (US EPA 2012)
,	0.478, estimated (EC, 2005) 1.11 Cited by Mackay et al. (2014)	1.142 * 10 ⁻² (estimated from estimated vapour pressure and estimated water solubility) (US EPA 2012)	3.370 * 10 ⁻¹ (estimated from estimated vapour pressure and estimated water solubility) (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)	2.89 (estimated) (US EPA 2012)	3.21 (experimental) (US EPA 2012)	No data
	4.96 - 5.11 at 20°C (Gebremariam et al., 2012) 5.2 - 5.267 at 25°C (Gebremariam			
n-octanol/air	et al., 2012) 8.882 (estimated) (US EPA 2012)	9.541 (estimated) (US EPA 2012)	9.324 (estimated) (US EPA	5.669 (estimated) (US EPA
partition coefficient (log KOA)	8.34 Cited by Mackay et al. (2014)		2012)	2012)
air/water partition coefficient (log KAW)	-3.922 Experimental database (US EPA 2012)	-6.651 (estimated) (US EPA 2012)	-6.114 (estimated) (US EPA 2012)	-2.399 (estimated) (US EPA 2012)
, 	-3.35 Cited by Mackay et al. (2014)			

Detail	Chlorpyrifos	Chlorpyrifos-oxon (CPYO)	3,5,6-Trichloro-2-pyridinol (TCP)	2-Methoxy-3,5,6-trichloro-
				pyridine (TMP)
Soil organic	3.4 – 4.5 (mean: 3.9) (EC 2005)	2.597 (estimated) (US EPA 2012)	2.942 (estimated) (US EPA	2.640 (estimated) (US EPA
carbon/water			2012)	2012)
partition coefficient	3.7Experimental database (US EPA	2.618 (estimated) (US EPA 2012)		
(log KOC)	2012)		3.188 (estimated) (US EPA	3.111 (estimated) (US EPA
			2012)	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 ± 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	рН	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 ₅₀ (d)	Method of calculatio n	DT50 normalise d to 12°C¹	χ2- error	r²	Applicat ion (μg/L)	Temper ature (°C)	pН	Salinity (%)	Oxygen content (%)	Total organic Carbon (mg/L)	Refere nce	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	
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		of DT50 values	
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	High losses due to volatilisation,	
	Pond, sterile	2.92	FOMC	7.2 d	-	0.9783	100.0	21.5 ± 0.2 °C.	8.08	-/-	9.70	10.64	, 2013	, = = =	underestimation of DT50 values
	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	
Borth Sands, Ceredigion, Wales	Coastal	35 d	SFO	35 d	-	0.883	40	12°C	7.83	36	114	812.9		of DT50 values	
> 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 st order	-/-			<water solubility of cpy</water 	25°C					Schimm el, 1983	High losses due to volatilisation (63% of applied cpy in air traps), underestimation of DT 50	
range		<2 – 75 d		6.8 – 124.4											

¹ 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 ₅₀ (d)	Method of Calculatio n	DT50 normalised to 12°C ²	X2- erro r	R ²	Application (ppm)	Tempera ture (°C)	Soil moisture	Ph	Organi c 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	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,	
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	2001a	
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	25ºC	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	25ºC	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	25ºC	75% 1/3 Bar	6.6	0.29		

² Temperature normalised using the Arrhenius equation

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

Soil source	Soil texture	Half-life or DT₅₀ (d)	Method of Calculatio n	DT50 normalised to 12°C ²	X2- erro r	R ²	Application (ppm)	Tempera ture (°C)	Soil moisture	Ph	Organi c Carbon (%)	Reference	Remarks
		76.2	1st order	261.3			25 μg/g	25°C	32%	5.6	1.8		clay, soils at
		49.5	1st order	169.7			5 μg/g	25°C	air-dry soil	5.6	1.8		low temperatures
Tarat, moisture dependence	alluvial	53.3	1st order	182.7			5 μg/g	25°C	field moisture content (32%)	5.6	1.8		and at high application rates. The study was not
		63	1st order	216.0			5 μg/g	25°C	Wet (61 - 68%)	5.6	1.8		performed in accordance with the
Tarat,		83.5	1st order	111.0			5 μg/g	15°C	32%	5.6	1.8		OECD 307 TG,
temperature	alluvial	53.3	1st order	182.7			5 μg/g	25°C	32%	5.6	1.8		but does
dependence		36.5	1st order	322.9			5 μg/g	35°C	32%	5.6	1.8		provide supporting
	Red	69.3	1st order	237.6			5 μg/g	25°C	22%	5.6	1.4		evidence of
Balai Ringin	Yellow Podzolic soil	120	1st order	411.4			25 μg/g	25°C	22%	5.6	1.4		abiotoc and biotic degradation
		84.5	1st order	289.7			5 μg/g	25°C	air-dry soil	5.6	1.4		pathways of chlorpyrifos
Balai Ringin, moisture dependence	Red Yellow Podzolic soil	69.3	1st order	237.6			5 μg/g	25°C	field moisture content (22%)	5.6	1.4		in soil, however 50% degradation was not
	3011	63	1st order	216.0			5 μg/g	25°C	Wet (61 - 68%)	5.6	1.4		achieved in the test.
Balai Ringin,	Red	193	1st order	256.5			5 μg/g	15°C	22%	5.6	1.4		
temperature	Yellow Podzolic	69.3	1st order	237.6			5 μg/g	25°C	22%	5.6	1.4		
dependence	soil	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 ⁻¹ 10 kg a.i. ha ⁻¹ 100 kg a.i. ha ⁻¹	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 or DT ₅₀ (d)	Method of calculation	Application (ppm)	Temperature (°C)	Soil moisture	рН	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 Ioam	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/sa nd- 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 ₅₀ (d)	Method of calculation	Application (kg a.i/ha)	Depth	Soil moisture	рН	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)
Valtohori/ 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 reporte d	Not reported	Vijyalakshmi and Ramesh (1996)
Jaipur, semi-arid India	Loamy sand	12.3 d	Not reported	5 g ai kg ⁻¹ seed and 800 g ai ha ⁻¹ 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 ⁻¹ seed and 800 g ai ha ⁻¹ 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	Sedi ment textu re	Half-life or DegT₅o total system (d)	DT50 total system normalised to 12°C ³	DisT50 water (d)	DisT50 sedimen t (d)	Applicati on (ppm)	Temperat ure (water) (°C)	pH sedime nt	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	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									

³ 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 m g/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 (Ambystoma mexicanum)	BCF	3632	mL/g	decrease in chlorpyrifos concentration by 50% during exposure; behavioural effects		
	Fish						
Hansen et al. (1986)	gulf toadfish (Opsanus beta)	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 (Poecilia reticula)	BCF	1847	mL/g	fish not fed during two week experiment; chlorpyrifos concentration decreased by 90%
Mulla et al. (1973)	channel catfish (<i>Ictalurus</i> punctatus)	BCF	4677	mL/g	extreme fluctuations in temperature and O2 concentration; fish analysed without gut
Mulla et al. (1973)	black crappie (<i>Pomoxis</i> nigromaculatus)	BCF	3333	mL/g	extreme fluctuations in temperature and O2 concentration; fish analysed without gut
Mulla et al. (1973)	largemouth bass (Micropterus salmoides)	BCF	1333	mL/g	extreme fluctuations in temperature and O2 concentration; fish analysed without gut
Mulla et al. (1973)	bluegill (Lepomis microchirus)	BCF	1200	mL/g	extreme fluctuations in temperature and O2 concentration; fish analysed without gut
Jarvinen et al. (1983)	fathead minnow (Pimephales promelas)	BCF	1673 ± 423	mL/g	toxic effects
Deneer (1993)	guppy (Poecilia reticulata)	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 (Lepomis microchirus)	BCF	600	mL/g	toxic effects; high fluctuation in chlorpyrifos concentration; Lorsban 4C used
J. Eaton et al. (1985)	fathead minnow (Pimephales promelas)	BCF	1150	mL/g	toxic effects; high fluctuation in chlorpyrifos concentration; Lorsban 4C used
Goodman, Hansen, Cripe, et al. (1985)	california grunion (Leuresthes tenuis)	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 (Cyprinodon variegatus)	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)	Menidia beryllina	BCF	440	mL/g	steady state not reached; mortality in higher concentrations
Goodman, Hansen, Middaugh, et al. (1985)	Menidia peninsulae	BCF	580	mL/g	steady state not reached; mortality in higher concentrations; negative effect of solvent
Macek et al. (1972)	bluegills (Lepomis microchirus)	BCF	2304	mL/g	extreme fluctuations in temperature and O2 concentration; behavioural effects
Macek et al. (1972)	largemouth bass (Micropterus salmoides)	BCF	1440	mL/g	extreme fluctuations in temperature and O2 concentration; behavioural effects
Deneer (1994)	three-spined stickleback (Gasterosteus aculeatus)	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 (Cyprinus carpio)	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 (Carassius auratus)	BCF	763	mL/g	steady state not reached
Tsuda et al. (1997)	white cloud mountain minnow (Tanichthys albonubes)	BCF	745	mL/g	steady state not reached
report no ES-928 (J42) in Spain (2017)	rainbow trout (Onchorhynchus mykiss)	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)	Mytilus galloprovincialis	BCF	400 ± 119	mL/g	concentration of test substance within 25% fluctuation
Thacker et al. (1992)	eastern oyster (<i>Crassostrea</i> virginica)	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</i> virginica)	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)	Asellus aquaticus	BCF	1715	mL/g	Mesocosm experiment with time dependant significantly reduced survival
A. Jantunen et al. (2008)	Lumbriculus variegatus	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 (Pistia stratiotes)	BCF	3000	mL/g	BCF calculated based on daily measurements
Lal et al. (1987)	Blue-Green Algae Anabaena sp.	BCF	678	mL/g	concentration of test substance not maintained, no calculations reported
Lal et al. (1987)	Aulosira fertilissima	BCF	397	mL/g	concentration of test substance not maintained, no calculations reported
	monitoring data				
Landers et al. (2008)	white fir (Abies concolor)	chlorpyrifos concentration	first year not detected, second year 19.7	ng/g lipid weight	
Landers et al. (2008)	lodgepole pine (Pinus contorta)	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)	Pinus ponderosa	BCF _m	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 (Enhydra lutris ssp.)	concentration in blood serum	maximum 342.6	ng/g lipid weight	
Stansley et al. (2010)	river otters (Lontra canadensis)	concentration in liver tissue	maximum 6.91	ng/g wet weight	
Adrogué et al. (2019)	blackbrowed albatross (Thalassarche melanophris)	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 (Daption capense)	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	BCFv	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 _{liver} :caribou _{liver}	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)	Homo sapiens	concentration in breast milk	urban mean 40.5; agricultural mean 139	pg/g milk	
Bedi et al. (2013)	Homo sapiens	concentration in breast milk	median 1664.2	ng/g lipid weight	
Sanghi et al. (2003)	Homo sapiens	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	species	endpoint type	endpoint value	unit	Publicly available
number					
GHE-T-281 (J061)	Eel (Anguilla anguilla)	BCF	400	mL/g	no
GS 1318 (J41)	mosquito fish (Gambusia sp.)	BCF	65 - 472	mL/g	no
DECO-ES-2377 (J66)	Eastern oyster (Crassostrea virginica)	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 μ g/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 μ g/L and 100 μ g/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 μ g/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 μ g/L.
- 9. Asselus aquaticus was exposed to chorpyrifos in the form of Drusban 4E. The nominal concentration of active substance were 0.7 and 5 μ g/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 + 4% and 82 + 5% from water. The limits of detection were 0.001 μ g/L in water and 200 η g/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 μ g/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 μ g/L. Effects included mortality, reduced size, retarded development and behavioural effects such as hyperactivity and hyperventilation. Mortality was significantly increased at the concentration 150 μ g/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 μ g/L and 0.1 μ g/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 μ g/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 μ g/L decreased to below 1 μ g/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 ± 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 μ g/L reduction of growth, deformities and later significant mortality occurred. Growth reduction was also observed for 1.21 μ g/L, later in the test. Sexual maturation and reproduction were reduced in all exposure groups at concentrations as low as 0.12 μ g/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 μ g/L chlorpyrifos. The experiment lasted 24 days, 20 days of exposure and four days for depuration. The uptake constant was calculated as 7000 ± 2000 L/kg/d, the depuration constant as 0.40 ± 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 μ g/L and 35 μ g/L chlorpyrifos, resulted in a BCF of 116. A four-day pulse exposure with water concentration between 4.9 μ g/L and 3.6 μ g/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 to 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 solved 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 μ 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 ± 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 μ g/L chlorpyrifos (Alharbi et al., 2017). The LOD for chlorpyrifos was 0.19 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 ng/g dry weight, while the maximum level of chlorpyrifos oxon was about 110 ng/g dry weight at the same location4. 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 BCFm5 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 ± 1.0 mg/kg. All measured values significantly exceeded the maximum residue level of 0.01 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.

⁴ The concentration values were estimated from a diagram of the cited publication.

⁵ In this study the BCF_m 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
	fog condensate		5 ng/L	blanks analysed as field
Chernyak et al. (1996)	sea water	1993	max. 65 pg/L	samples, no chlorpyrifos
	melting ice		max. 170 pg/L	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
Hermanson et al. (2003)	ice core	1972 – 1990	max. 16.2 ng/L	corrected
				Method detection limit
Duggiralla et al. (2010)	ico coro	1971 – 2005	max. 808 pg/cm²/year	(MDL, defined as mean blank
Ruggirello et al. (2010)	ice core	1971 – 2005	max. 808 pg/cm ⁻ /year	value + 3 x SD of blank
				values)
Muir et al. (2004)	lake water	1998 – 2001	mean 0.27 ng/L	MDL
				On average concentrations
				found in blanks were 3% of
	snow	2003		the concentration in
Landers et al. (2008)			0.010 - 0.030 ng/L	snowpacks and the
Landers et al. (2008)			0.010 - 0.030 fig/L	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 ³	no information
Pućko et al. (2015)	air	2008	$3.1 \pm 1.9 \text{ pg/m}^3$	no information
Pućko et al. (2015)	sea water	2008	31 ± 19 pg/L	no information
Hung et al 2013 Hung et al.	air	2006 - 2009	<mdl 6.8="" m³<="" pg="" td="" –=""><td>MDL</td></mdl>	MDL
in Balmer et al. (2019)	dil	2006 - 2009	<101DL - 6.8 pg/111	IVIDL
Zhong et al. (2012)	air	2010	1 - 146 pg/m ³	MDL
Zhong et al. (2012)	sea water	2010	0.1 - 111 pg/L	MDL
Pućko et al. (2017)	snow	2012	mean ± SD, 4.8 ± 1.3 pg/L	MDL
Pućko et al. (2017)	melt pond water	2012	mean ± SD, 14.4 ± 2.5 pg/L	MDL
Pućko et al. (2017)	saa watar	2012	mean ± SD, 14.1 ± 6.0 pg/L	MDI
	sea water	2012	(0m), 10.5 ± 1.7 pg/L (5m)	MDL
Pućko et al. (2017)	air	2012	mean \pm SD, 0.10 \pm 0.04 pg/m ³	MDL

Publication	Medium	Time frame	Concentration	Handling of blanks
L. M. Jantunen et al. (2015)	air	2007, 2008, 2010, 2011 and 2013	mean ± SD, 1.1 ± 1.3 pg/m ³	No chlorpyrifos measured in blanks, instrumental detection limits 0.02 pg/m ³ and 0.1 pg/L
L. M. Jantunen et al. (2015)	water	2007, 2008, 2010, 2011 and 2013	mean ± SD, 13 ± 12 pg/L	No chlorpyrifos measured in blanks, instrumental detection limits 0.02 pg/m ³ 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 ³	MDL
Boström (2020)	air	2009 - 2018	median concentrations of 0.002 ng/m ³	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.

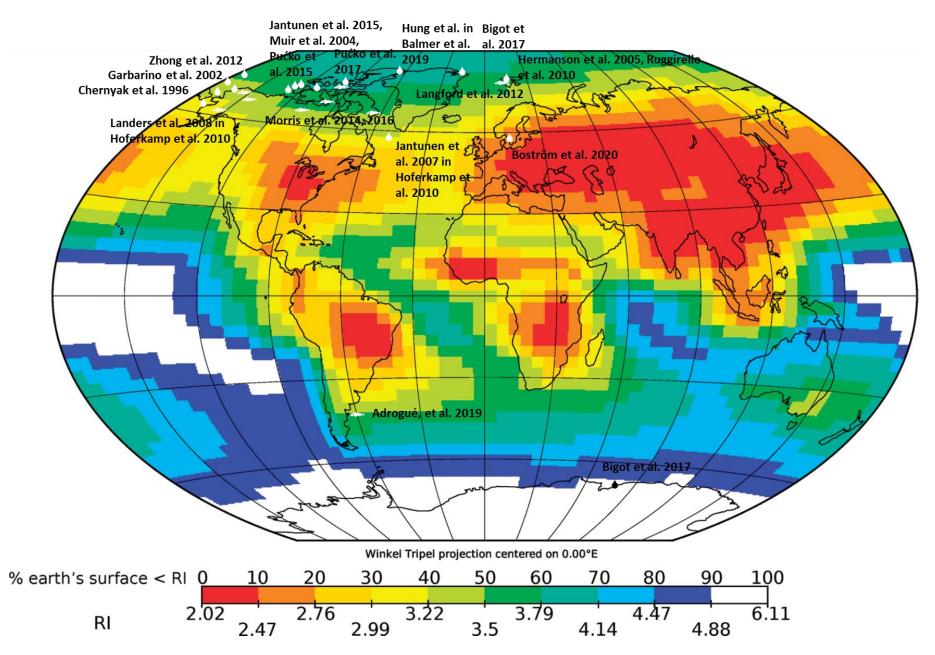


Figure 1: Map of chlorpyrifos findings in remote areas modified after von Waldow et al. 2010; fish symbols indicate finding in biota, drop symbol indicate abiotic findings

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 $0.00003 - 10~\mu g/L$), 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 $0.0001 - 0.5~\mu g/L$)(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 $0.0004 - 2~\mu g/L$)

References

- Abdelaziz, K. B., El Makawy, A. I., Elsalam, A. Z. E.-A. A., & Darwish, A. M. (2010). Genotoxicity of Chlorpyrifos and the Antimutagenic Role of Lettuce Leaves in Male Mice. *Comunicata Scientiae*, 1(2), 137. doi:10.14295/cs.v1i2.51
- Adrogué, Q. A., Miglioranza, K. S. B., Copello, S., Favero, M., & Seco Pon, J. P. (2019). Pelagic seabirds as biomonitors of persistent organic pollutants in the Southwestern Atlantic. *Marine Pollution Bulletin, 149*, 110516. doi:10.1016/j.marpolbul.2019.110516
- Aldershof, S., Roig, J., & Bakker, F. (2008). Field trial to determine the effects of EF-1315 (75% WG chlorpyrifos formulation) on the nontarget, foliar-dwelling, arthropod fauna of a citrus orchard crop, following one and two applications during spring/summer. Dow AgroSciences. MITOX Consultants, Amsterdam, The Netherlands.
- Alharbi, H. A., Alcorn, J., Al-Mousa, A., Giesy, J. P., & Wiseman, S. B. (2017). Toxicokinetics and toxicodynamics of chlorpyrifos is altered in embryos of Japanese medaka exposed to oil sands process-affected water: evidence for inhibition of P-glycoprotein. *Journal of applied toxicology: JAT, 37*(5), 591–601. doi:10.1002/jat.3397
- Aston, L. S., & Seiber, J. N. (1997). Fate of Summertime Airborne Organophosphate Pesticide Residues in the Sierra Nevada Mountains. *Journal of Environmental Quality*, 26(6), 1483–1492. doi:10.2134/jeq1997.00472425002600060006x
- Atkinson, R., Guicherit, R., Hites, R. A., Palm, W.-U., Seiber, J. N., & Voogt, P. d. (1999). Transformation of pesticides in the atmosphere: a state of the art. *Water, Air, and Soil Pollution, 115*(1/4), 219–243. doi:10.1023/a:1005286313693
- Balmer, J. E., Morris, A. D., Hung, H., Jantunen, L. M., Vorkamp, K., Rigét, F., . . . Muir, D. C. (2019). Levels and trends of current-use pesticides (CUPs) in the arctic: An updated review, 2010–2018. *Emerging Contaminants*, *5*, 70-88.
- Bedi, J. S., Gill, J. P. S., Aulakh, R. S., Kaur, P., Sharma, A., & Pooni, P. A. (2013). Pesticide residues in human breast milk: risk assessment for infants from Punjab, India. *The Science of the total environment, 463-464*, 720–726. doi:10.1016/j.scitotenv.2013.06.066
- Biever, R. C., Giddings, J. M., Kiamos, M., Annunziato, M. F., Meyerhoff, R., & Racke, K. (1994). Effects of chlorpyrifos on aquatic microcosms over a range of off-target spray drift exposure levels.
- Bigot, M., Hawker, D. W., Cropp, R., Muir, D. C., Jensen, B., Bossi, R., & Bengtson Nash, S. M. (2017). Spring melt and the redistribution of organochlorine pesticides in the sea-ice environment: A comparative study between Arctic and Antarctic regions. *Environmental Science & Technology*, *51*(16), 8944-8952.
- Boström, G. (2020). Available data from the Swedish national monitoring program. Uppsala: Swedish University of Agricultural Sciences Retrieved from https://www.slu.se/en/departments/aquatic-sciences-assessment/environment/pesticide monitoring/pesticide data/
- Brazner, J. C., & Kline, E. R. (1990). Effects of chlorpyrifos on the diet arid growth of larval fathead minnows, pimephales promelas, in littoral enclosures. *Canadian Journal of Fisheries and Aquatic Sciences, 47*(6), 1157-1165.
- Brock, T., Van den Bogaert, M., Bos, A., Van Breukelen, S., Reiche, R., Terwoert, J., . . . Roijackers, R. (1992). Fate and effects of the insecticide Dursban® 4E in indoor Elodea-dominated and macrophyte-free freshwater model ecosystems: II. Secondary effects on community structure. *Archives of Environmental Contamination and Toxicology*, 23(4), 391-409.
- Brock, T. C., Arts, G. H., Maltby, L., & Van den Brink, P. J. (2006). Aquatic risks of pesticides, ecological protection goals, and common aims in European Union legislation. *Integrated Environmental Assessment and Management: An International Journal*, 2(4), e20-e46.
- CalEPA. (2018). Final Toxic Air Contaminant Evaluation of Chlorpyrifos Risk Characterization of Spray Drift,
 Dietary, and Aggregate Exposures to Residential Bystanders. Retrieved from
 https://www.cdpr.ca.gov/docs/whs/pdf/chlorpyrifos final tac.pdf
- Casida, J. E., Nomura, D. K., Vose, S. C., & Fujioka, K. (2008). Organophosphate-sensitive lipases modulate brain lysophospholipids, ether lipids and endocannabinoids. *Chemico-Biological Interactions, 175*(1), 355-364. doi:https://doi.org/10.1016/j.cbi.2008.04.008
- CDPR. (2020a). Chlorpyrifos Cancellation. Retrieved from https://www.cdpr.ca.gov/docs/chlorpyrifos/index.htm
 CDPR. (2020b). Chlorpyrifos Cancellation Notices. Retrieved from https://www.cdpr.ca.gov/docs/chlorpyrifos/cancellation_notice.htm
- Chernyak, S. M., Rice, C. P., & McConnell, L. L. (1996). Evidence of currently-used pesticides in air, ice, fog, seawater and surface microlayer in the Bering and Chukchi seas. *Marine Pollution Bulletin, 32*(5), 410–419. doi:10.1016/0025-326x(95)00216-a
- Connors, S. L., Levitt, P., Matthews, S. G., Slotkin, T. A., Johnston, M. V., Kinney, H. C., . . . Zimmerman, A. W. (2008). Fetal Mechanisms in Neurodevelopmental Disorders. *Pediatric Neurology*, *38*(3), 163-176. doi:10.1016/j.pediatrneurol.2007.10.009

- Costa, L. G., Giordano, G., Cole, T. B., Marsillach, J., & Furlong, C. E. (2013). Paraoxonase 1 (PON1) as a genetic determinant of susceptibility to organophosphate toxicity. *Toxicology*, *307*, 115-122. doi:https://doi.org/10.1016/j.tox.2012.07.011
- Cripe, G. M., Hansen, D. J., Macauley, S. F., & Forester, J. (1986). Effects of Diet Quantity on Sheepshead Minnows. In T. M. Poston & R. Purdy (Eds.), *Aquatic toxicology and environmental fate, ninth volume* (pp. 450-450-411). Philadelphia, Pa.: ASTM.
- Cui, Y., Guo, J., Xu, B., & Chen, Z. (2011). Genotoxicity of chlorpyrifos and cypermethrin to ICR mouse hepatocytes. *Toxicology mechanisms and methods*, *21*(1), 70-74.
- Deneer, J. W. (1993). Uptake and elimination of chlorpyrifos in the guppy at sublethal and lethal aqueous concentrations. *Chemosphere*, 26(9), 1607–1616. doi:10.1016/0045-6535(93)90106-f
- Deneer, J. W. (1994). Bioconcentration of chlorpyrifos by the three-spined stickleback under laboratory and field conditions. *Chemosphere*, *29*(7), 1561–1575. doi:10.1016/0045-6535(94)90286-0
- Eaton, D. L., Daroff, R. B., Autrup, H., Bridges, J., Buffler, P., Costa, L. G., . . . Spencer, P. S. (2008). Review of the Toxicology of Chlorpyrifos With an Emphasis on Human Exposure and Neurodevelopment. *Critical Reviews in Toxicology*, 38(sup2), 1-125. doi:10.1080/10408440802272158
- Eaton, J., Arthur, J., Hermanutz, R., Kiefer, R., Mueller, L., Anderson, R., . . . Pritchard, H. (1985). Biological Effects of Continuous and Intermittent Dosing of Outdoor Experimental Streams with Chlorpyrifos. In R. C. Bahner (Ed.), Aquatic toxicology and hazard assessment (pp. 85-85-34). Philadelphia, Pa.: American Soc. for Testing and Materials.
- EC. (2005). Review report for the active substance chlorpyriphos. SANCO/3059/99 rev. 1.5.
- EC. (2008). Commision Regulation No. 149/2008 of 29 January 2008 amending Regulation (EC) No. 396/2005 of the European Parliament and of the Council by establishing Annexes II, III and IV seeting maximum residue levels for products covered by Annex I. Official Journal(L58/1). Retrieved from https://op.europa.eu/en/publication-detail/-/publication/944dff43-f1fc-4ca9-8a12-3d698bd92b49/language-en
- Commission Implementing Regulation (EU) 2020/18 of 10 January 2020 concerning the non-renewal of the approval of the active substance chlorpyrifos, in accordance with Regulation (EC) No 1107/2009 of the European Parliament and of the Council concerning the placing of plant protection products on the market, and amending the Annex to Commission Implementing Regulation (EU) No 540/2011 (Text with EEA relevance), (2020).
- EFSA-PPRP, their, r., Ockleford, C., Adriaanse, P., Berny, P., Brock, T., . . . Bennekou, S. H. (2017). Investigation into experimental toxicological properties of plant protection products having a potential link to Parkinson's disease and childhood leukaemia. *EFSA Journal*, 15(3), e04691. doi:10.2903/j.efsa.2017.4691
- EFSA. (2019a). Statement on the available outcomes of the human health assessment in the context of the pesticides peer review of the active substance chlorpyrifos-methyl. Retrieved from https://efsa.onlinelibrary.wiley.com/doi/10.2903/j.efsa.2019.5810
- EFSA. (2019b). Statement on the available outcomes of the human healthassessment in the context of the pesticides peer review ofthe active substance chlorpyrifos. Retrieved from https://efsa.onlinelibrary.wiley.com/doi/epdf/10.2903/j.efsa.2019.5809
- El-Amrani, S., Pena-Abaurrea, M., Sanz-Landaluze, J., Ramos, L., Guinea, J., & Cámara, C. (2012).

 Bioconcentration of pesticides in zebrafish eleutheroembryos (Danio rerio). *The Science of the total environment, 425*, 184–190. doi:10.1016/j.scitotenv.2012.02.065
- Flaskos, J. (2012). The developmental neurotoxicity of organophosphorus insecticides: A direct role for the oxon metabolites. *Toxicology Letters*, *209*(1), 86-93. doi:https://doi.org/10.1016/j.toxlet.2011.11.026
- Garbarino, Snyder-Conn, Leiker, & Hoffman. (2002). Contaminants in Arctic Snow Collected over Northwest Alaskan Sea Ice. *Water, Air, and Soil Pollution, 139*(1), 183–214. doi:10.1023/a:1015808008298
- Gebremariam, S. Y., Beutel, M. W., Yonge, D. R., Flury, M., & Harsh, J. B. (2012). Adsorption and desorption of chlorpyrifos to soils and sediments. *Reviews of environmental contamination and toxicology, 215*, 123–175. doi:10.1007/978-1-4614-1463-6 3
- Giddings, J. (1993). Chlorpyrifos (Lorsban 4E): outdoor aquatic microcosm test for environmental fate and ecological effects. *Springborn Laboratories for Dow Chemical, Wareham, MA (unpublished report)*.
- Giddings, J. M., Biever, R. C., & Racke, K. D. (1997). Fate of chlorpyrifos in outdoor pond microcosms and effects on growth and survival of bluegill sunfish. *Environmental Toxicology and Chemistry*, 16(11), 2353-2362.
- Giddings, J. M., Williams, W. M., Solomon, K. R., & Giesy, J. P. (2014). Risks to aquatic organisms from use of chlorpyrifos in the United States. In *Ecological Risk Assessment for Chlorpyrifos in Terrestrial and Aquatic Systems in the United States* (pp. 119-162): Springer, Cham.
- Giesy, J. P., Solomon, K. R., Mackay, D., & Anderson, J. (2014). Evaluation of evidence that the organophosphorus insecticide chlorpyrifos is a potential persistent organic pollutant (POP) or persistent, bioaccumulative, and toxic (PBT). *Environmental Sciences Europe, 26*(1), 359. doi:10.1186/s12302-014-0029-y

- Gilliom, R., Barbash, J., Crawford, C., Hamilton, P., Martin, J., Nakagaki, N., . . . Thelin, G. (2006). The quality of our Nation's waters—Pesticides in the Nation's streams and ground water, 1992–2001: US Geological Survey Circular 1291, 172 p., accessed April 1, 2008. In.
- Goodman, L. R., Hansen, D. J., Cripe, G. M., Middaugh, D. P., & Moore, J. C. (1985). A new early life-stage toxicity test using the California grunion (leuresthes tenuis) and results with chlorpyrifos. *Ecotoxicology and Environmental Safety, 10*(1), 12–21. doi:10.1016/0147-6513(85)90003-x
- Goodman, L. R., Hansen, D. J., Middaugh, D. P., Cripe, G. M., & Moore, J. C. (1985). Method for Early Life-Stage Toxicity Tests Using Three Atherinid Fishes and Results with Chlorpyrifos. In R. D. Cardwell (Ed.), *Aquatic toxicology and hazard assessment* (pp. 145-145-110). Philadelphia, Pa.: ASTM.
- Hansen, D. J., Goodman, L. R., Cripe, G. M., & Macauley, S. F. (1986). Early life-stage toxicity test methods for gulf toadfish (Opsanus beta) and results using chlorpyrifos. *Ecotoxicology and Environmental Safety*, 11(1), 15–22. doi:10.1016/0147-6513(86)90025-4
- Hermanson, M. H., Isaksson, E., Teixeira, C., Muir, D. C. G., Compher, K. M., Li, Y. F., . . . Kamiyama, K. (2005). Current-use and legacy pesticide history in the Austfonna Ice Cap, Svalbard, Norway. *Environmental Science & Technology*, 39(21), 8163–8169. doi:10.1021/es051100d
- Hung, H., Kurt-Karakus, P., Ahrens, L., Bidleman, T., Evans, M., Halsall, C., . . . Xiao, H. Chapter 3 Occurrence and Trends in the Physical Environment. In *Canadian Arctic Contaminants Assessment Report on Persistent Organic Pollutants III-2013* (pp. 147-272).
- ILO, & WHO. (2014, 15.4.2020). ICSC 0851 CHLORPYRIFOS: International Chemical Safety Cards. Retrieved from http://www.ilo.org/dyn/icsc/showcard.display?p_version=2&p_card_id=0851
- Jantunen, A., Tuikka, A., Akkanen, J., & Kukkonen, J. (2008). Bioaccumulation of atrazine and chlorpyrifos to Lumbriculus variegatus from lake sediments. *Ecotoxicology and Environmental Safety*, 71(3), 860-868.
- Jantunen, L. M., Wong, F., Bidleman, T. F., & Stern, G. (2007). Occurrence and Levels of Current-Use and Legacy Pesticides in Air: Leg 1 of ArcticNet 2007. *Arctic Net. Collingwood, ONpp*.
- Jantunen, L. M., Wong, F., Gawor, A., Kylin, H., Helm, P. A., Stern, G. A., . . . Bidleman, T. F. (2015). 20 years of air–water gas exchange observations for pesticides in the Western Arctic Ocean. *Environmental Science & Technology*, 49(23), 13844-13852.
- Jarvinen, A. W., Nordling, B. R., & Henry, M. E. (1983). Chronic toxicity of Dursban (Chlorpyrifos) to the fathead minnow (Pimephales promelas) and the resultant acetylcholinesterase inhibition. *Ecotoxicology and Environmental Safety*, 7(4), 423–434. doi:10.1016/0147-6513(83)90008-8
- Jessup, D. A., Johnson, C. K., Estes, J., Carlson-Bremer, D., Jarman, W. M., Reese, S., . . . Ziccardi, M. H. (2010). Persistent organic pollutants in the blood of free-ranging sea otters (Enhydra lutris ssp.) in Alaska and California. *Journal of wildlife diseases*, 46(4), 1214–1233. doi:10.7589/0090-3558-46.4.1214
- Kolpin, D. W., Barbash, J. E., & Gilliom, R. J. (2000). Pesticides in ground water of the United States, 1992–1996. *Groundwater, 38*(6), 858-863.
- Kopjar, N., Žunec, S., Mendaš, G., Micek, V., Kašuba, V., Mikolić, A., . . . Želježić, D. (2018). Evaluation of chlorpyrifos toxicity through a 28-day study: Cholinesterase activity, oxidative stress responses, parent compound/metabolite levels, and primary DNA damage in blood and brain tissue of adult male Wistar rats. *Chem Biol Interact*, *279*, 51-63. doi:10.1016/j.cbi.2017.10.029
- Kurt-Karakus, P. B., Teixeira, C., Small, J., Muir, D., & Bidleman, T. F. (2011). Current-use pesticides in inland lake waters, precipitation, and air from Ontario, Canada. *Environmental Toxicology and Chemistry*, 30(7), 1539–1548. doi:10.1002/etc.545
- Lal, S., Lal, R., & Saxena, D. M. (1987). Bioconcentration and metabolism of DDT, fenitrothion and chlorpyrifos by the blue-green algae Anabaena sp. and Aulosira fertilissima. *Environmental Pollution*, 46(3), 187–196.
- Landers, D. H., Simonich, S. L., Jaffe, D. A., Geiser, L. H., Campbell, D. H., Schwindt, A. R., . . . others. (2008). The fate, transport, and ecological impacts of airborne contaminants in western national parks (USA). Western Airborne Contaminants Assessment Project Final Report. Corvallis.
- López-Mancisidor, P., Carbonell, G., Fernández, C., & Tarazona, J. V. (2008). Ecological impact of repeated applications of chlorpyrifos on zooplankton community in mesocosms under Mediterranean conditions. *Ecotoxicology*, *17*(8), 811-825.
- Lopez-Mancisidor, P., Carbonell, G., Marina, A., Fernandez, C., & Tarazona, J. V. (2008). Zooplankton community responses to chlorpyrifos in mesocosms under Mediterranean conditions. *Ecotoxicology and Environmental Safety, 71*(1), 16-25.
- Lu, C., Liu, X., Liu, C., Wang, J., Li, C., Liu, Q., . . . Shao, J. (2015). Chlorpyrifos Induces MLL Translocations Through Caspase 3-Dependent Genomic Instability and Topoisomerase II Inhibition in Human Fetal Liver Hematopoietic Stem Cells. *Toxicol Sci, 147*(2), 588-606. doi:10.1093/toxsci/kfv153
- Macek, K. J., Walsh, D. F., Hogan, J. W., & Holz, D. D. (1972). Toxicity of the Insecticide Dursban (R) to Fish and Aquatic Invertebrates in Ponds. *Transactions of the American Fisheries Society, 101*(3), 420–427. doi:10.1577/1548-8659(1972)101<420:totidr>2.0.co;2
- Mackay, D., Giesy, J. P., & Solomon, K. R. (2014). Fate in the Environment and Long-Range Atmospheric Transport of the Organophosphorus Insecticide, Chlorpyrifos and Its Oxon. In Solomon, Giesy, & Keith

- (Eds.), Ecological Risk Assessment for Chlorpyrifos in Terrestrial and Aquatic Systems in North America (pp. 35–76). s.l.: Springer.
- McCall, P. J. (1986). Hydrolysis of chlorpyrifos in dilute aqueous buffer. Dow Chemical USA.
- Mehta, A., Verma, R. S., & Srivastava, N. (2008). Chlorpyrifos-induced DNA damage in rat liver and brain. Environmental and molecular mutagenesis, 49(6), 426-433. doi:10.1002/em.20397
- Meikle, R., & Youngson, C. (1978). The hydrolysis rate of chlorpyrifos, OO-diethylO-(3, 5, 6-trichloro-2-pyridyl) phosphorothioate, and its dimethyl analog, chlorpyrifos-methyl, in dilute aqueous solution. *Archives of Environmental Contamination and Toxicology, 7*(1), 13-22.
- Montañés, J. C., Van Hattum, B., & Deneer, J. (1995). Bioconcentration of chlorpyrifos by the freshwater isopod Asellus aquaticus (L.) in outdoor experimental ditches. *Environmental Pollution*, 88(2), 137-146.
- Morris, A. D., Muir, D. C. G., Solomon, K. R., Letcher, R. J., McKinney, M. A., Fisk, A. T., . . . Duric, M. (2016). Current-use pesticides in seawater and their bioaccumulation in polar bear-ringed seal food chains of the Canadian Arctic. *Environmental Toxicology and Chemistry*, 35(7), 1695–1707. doi:10.1002/etc.3427
- Morris, A. D., Muir, D. C. G., Solomon, K. R., Teixeira, C., Duric, M., & Wang, X. (2014). Trophodynamics of current use pesticides and ecological relationships in the Bathurst region vegetation-caribou-wolf food chain of the Canadian Arctic. *Environmental Toxicology and Chemistry*, 33(9), 1956–1966. doi:10.1002/etc.2634
- Muir, D. C. G., Teixeira, C., & Wania, F. (2004). Empirical and modeling evidence of regional atmospheric transport of current-use pesticides. *Environmental Toxicology and Chemistry*, 23(10), 2421–2432. doi:10.1897/03-457
- Mulla, M. S., Norland, R. L., Westlake, W. E., Dell, B., & St. Amant, J. (1973). Aquatic Midge Larvicides, Their Efficacy and Residues in Water, Soil, and Fish in a Warm-Water Lake1. *Environmental Entomology*, 2(1), 58–65. doi:10.1093/ee/2.1.58
- Nolan, R. J., Rick, D. L., Freshour, N. L., & Saunders, J. H. (1984). Chlorpyrifos: pharmacokinetics in human volunteers. *Toxicol Appl Pharmacol*, 73(1), 8-15. doi:10.1016/0041-008x(84)90046-2
- Prasertsup, P., & Ariyakanon, N. (2011). Removal of chlorpyrifos by water lettuce (Pistia stratiotes L.) and duckweed (Lemna minor L.). *International journal of phytoremediation, 13*(4), 383–395. doi:10.1080/15226514.2010.495145
- Pućko, M., Stern, G. A., Burt, A. E., Jantunen, L. M., Bidleman, T. F., Macdonald, R. W., . . . Rysgaard, S. (2017). Current use pesticide and legacy organochlorine pesticide dynamics at the ocean-sea ice-atmosphere interface in resolute passage, Canadian Arctic, during winter-summer transition. *Science of the Total Environment*, 580, 1460-1469.
- Pućko, M., Stern, G. A., Macdonald, R. W., Jantunen, L. M., Bidleman, T. F., Wong, F., . . . Rysgaard, S. (2015). The delivery of organic contaminants to the Arctic food web: Why sea ice matters. *Science of the Total Environment*, 506, 444-452.
- Reuters. (2020). Corteva to stop making pesticide linked to kids' health problems. Retrieved from https://www.reuters.com/article/us-corteva-agriculture-pesticide/corteva-to-stop-making-pesticide-linked-to-kids-health-problems-idUSKBN20023I
- Robles-Mendoza, C., Zúñiga-Lagunes, S. R., de León-Hill, C. A. P., Hernández-Soto, J., & Vanegas-Pérez, C. (2011). Esterases activity in the axolotl Ambystoma mexicanum exposed to chlorpyrifos and its implication to motor activity. *Aquatic toxicology*, 105(3-4), 728–734.
- Rodríguez-Cortez, V. C., & Menéndez, P. (2020). Genotoxicity of permethrin and clorpyriphos on human stem and progenitor cells at different ontogeny stages: implications in leukaemia development. *EFSA Supporting Publications*, *17*(5), 1866E. doi:10.2903/sp.efsa.2020.EN-1866
- Rubach, M. N., Ashauer, R., Maund, S. J., Baird, D. J., & Van den Brink, P. J. (2010). Toxicokinetic variation in 15 freshwater arthropod species exposed to the insecticide chlorpyrifos. *Environmental Toxicology and Chemistry*, 29(10), 2225–2234.
- Ruggirello, R. M., Hermanson, M. H., Isaksson, E., Teixeira, C., Forsström, S., Muir, D. C. G., . . . Meijer, H. A. J. (2010). Current use and legacy pesticide deposition to ice caps on Svalbard, Norway. *Journal of Geophysical Research*, 115(D18). doi:10.1029/2010jd014005
- Sandhu, M. A., Saeed, A. A., Khilji, M. S., Ahmed, A., Latif, M. S. Z., & Khalid, N. (2013). Genotoxicity evaluation of chlorpyrifos: a gender related approach in regular toxicity testing. *The Journal of toxicological sciences,* 38(2), 237-244. doi:10.2131/jts.38.237
- Sanghi, R., Pillai, M. K. K., Jayalekshmi, T. R., & Nair, A. (2003). Organochlorine and organophosphorus pesticide residues in breast milk from Bhopal, Madhya Pradesh, India. *Human & experimental toxicology, 22*(2), 73–76. doi:10.1191/0960327103ht321oa
- Serrano, López, Hernández, & Peña. (1997). Bioconcentration of Chlorpyrifos, Chlorfenvinphos, and Methidathion in Mytilus galloprovincialis. *Bulletin of environmental contamination and toxicology, 59*(6), 968–975. doi:10.1007/s001289900577

- Shaker, E. M., & Elsharkawy, E. E. (2015). Organochlorine and organophosphorus pesticide residues in raw buffalo milk from agroindustrial areas in Assiut, Egypt. *Environmental toxicology and pharmacology, 39*(1), 433–440. doi:10.1016/j.etap.2014.12.005
- Singh, P. B., Singh, V., & Nayak, P. K. (2008). Pesticide residues and reproductive dysfunction in different vertebrates from north India. *Food and chemical toxicology: an international journal published for the British Industrial Biological Research Association*, 46(7), 2533–2539. doi:10.1016/j.fct.2008.04.009
- Slotkin, T. A. (2004). Cholinergic systems in brain development and disruption by neurotoxicants: nicotine, environmental tobacco smoke, organophosphates. *Toxicology and Applied Pharmacology, 198*(2), 132-151. doi:https://doi.org/10.1016/j.taap.2003.06.001
- Smith, J. N., Hinderliter, P. M., Timchalk, C., Bartels, M. J., & Poet, T. S. (2014). A human life-stage physiologically based pharmacokinetic and pharmacodynamic model for chlorpyrifos: Development and validation. *Regulatory Toxicology and Pharmacology, 69*(3), 580-597. doi:https://doi.org/10.1016/j.yrtph.2013.10.005
- Spain. (2017). Renewal Assessment Report (RAR) on the active substance chlorpyrifos prepared by the rapporteur Member State Spain in the framework of Commission Implementing Regulation (EU) No 844/2012. Retrieved from www.efsa.europa.eu
- Spain. (2019). Revised Renewal Assessment Report (RAR) on the active substance chlorpyrifos, volumes relevant for mammalian toxicology, prepared by the rapporteur Member State Spain in the framework of Commission Implementing Regulation (EU) No 844/2012, February 2019. Retrieved from
- Stansley, W., Velinsky, D., & Thomas, R. (2010). Mercury and halogenated organic contaminants in river otters (Lontra canadensis) in New Jersey, USA. *Environmental Toxicology and Chemistry, 29*(10), 2235–2242. doi:10.1002/etc.267
- Thacker, J. D., Strauss, K. A., & Smith, G. J. (1992). *Chlorpyrifos: a bioaccumulation test with eastern oyster.:* unpublished report ES-2526.
- Thomas, C. N., & Mansingh, A. (2002). Bioaccumulation, elimination, and tissue distribution of chlorpyrifos by red hybrid Tilapia in fresh and brackish waters. *Environmental technology*, 23(11), 1313–1323. doi:10.1080/09593332308618324
- Timofeeva, O. A., & Levin, E. D. (2010). Chapter 33 Lasting Behavioral Consequences of Organophosphate Pesticide Exposure During Development. In R. Krieger (Ed.), *Hayes' Handbook of Pesticide Toxicology (Third Edition)* (pp. 837-846). New York: Academic Press.
- Tsuda, T., Aoki, S., Kojima, M., & Fujita, T. (1992). Accumulation and excretion of pesticides used in golf courses by carp (Cyprinus carpio) and willow shiner (Gnathopogon caerulescens). *Comparative biochemistry and physiology: C: Comparative pharmacology and toxicology*.
- Tsuda, T., Kojima, M., Harada, H., Nakajima, A., & Aoki, S. (1997). Relationships of bioconcentration factors of organophosphate pesticides among species of fish. *Comparative biochemistry and physiology: C:*Comparative pharmacology and toxicology, 116(3), 213–218.
- US-EPA. (2012). Estimation Programs Interface Suite™ for Microsoft® Windows (Version v 4.11). Washington, DC, USA: United States Environmental Protection Agency.
- US-EPA. (2016). *Chlorpyrifos Revised Human Health Risk Assessment (2016)*. Retrieved from https://www.regulations.gov/document?D=EPA-HQ-OPP-2015-0653-0454
- Chlorpyrifos; Final Order Denying Objections to March 2017 Petition Denial Order, (2019).
- Usmani KA, C. T., Rose RL, Hodgson E. (2006). Inhibition of the human liver microsomal and human cytochrome P450 1A2 and 3A4 metabolism of estradiol by deployment-related and other chemicals. *Drug Metab Dispos* 34:1606–1614.
- Usmani KA, R. R., Hodgson E. (2003). Inhibition and activation of the human liver microsomal and human cytochrome P450 3A4 metabolism of testosterone by deployment-related chemicals. *Drug Metab Dispos*, 31:384–391.
- van den Brink, P. J., van Donk, E., Gylstra, R., Crum, S. J., & Brock, T. C. (1995). Effects of chronic low concentrations of the pesticides chlorpyrifos and atrazine in indoor freshwater microcosms. *Chemosphere,* 31(5), 3181-3200.
- von Waldow, H., MacLeod, M., Scheringer, M., & Hungerbühler, K. (2010). Quantifying Remoteness from Emission Sources of Persistent Organic Pollutants on a Global Scale. *Environmental Science & Technology, 44*(8), 2791-2796. doi:10.1021/es9030694
- Walia, S., Dureja, P., & Mukerjee, S. K. (1988). New photodegradation products of chlorpyrifos and their detection on glass, soil, and leaf surfaces. *Archives of Environmental Contamination and Toxicology, 17*(2), 183-188. doi:10.1007/BF01056023
- Ward, S., Arthington, A. H., & Pusey, B. J. (1995). The effects of a chronic application of chlorpyrifos on the macroinvertebrate fauna in an outdoor artificial stream system: species responses. *Ecotoxicology and Environmental Safety*, 30(1), 2-23.

- Weldon, R. H., Barr, D. B., Trujillo, C., Bradman, A., Holland, N., & Eskenazi, B. (2011). A pilot study of pesticides and PCBs in the breast milk of women residing in urban and agricultural communities of California. *Journal of environmental monitoring: JEM, 13*(11), 3136–3144. doi:10.1039/c1em10469a
- Welling, W., & Vries, J. W. d. (1992). Bioconcentration kinetics of the organophosphorus insecticide chlorpyrifos in guppies (Poecilia reticulata). *Ecotoxicology and Environmental Safety, 23*(1), 64–75. doi:10.1016/0147-6513(92)90022-u
- WHO. (2009). Specification and Evaluations for Public Health Pesticides, Chlorpyrifos, O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate.
- Wijngaarden, R. P. V., Brock, T. C., & Van Den Brink, P. J. (2005). Threshold levels for effects of insecticides in freshwater ecosystems: a review. *Ecotoxicology*, 14(3), 355.
- Woodburn, K. B., Hansen, S. C., Roth, G. A., & Strauss, K. (2003). The bioconcentration and metabolism of chlorpyrifos by the eastern oyster, Crassostrea virginica. *Environmental Toxicology and Chemistry*, 22(2), 276–284. doi:10.1002/etc.5620220207
- Yackovich, P. J., McCall, P. J., & Miller, J. H. (1985). *Photodegradation of chlorpyrifos on commerce soil surface*. DOW Chemical.
- Zhong, G., Xie, Z., Cai, M., Möller, A., Sturm, R., Tang, J., . . . Ebinghaus, R. (2012). Distribution and air-sea exchange of current-use pesticides (CUPs) from East Asia to the high Arctic Ocean. *Environmental Science & Technology*, 46(1), 259–267. doi:10.1021/es202655k