



Government  
of Canada

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du Canada

**ADDITIONAL INFORMATION AND CONSIDERATIONS  
FOR THE REVIEW OF TRIFLURALIN UNDER THE  
UNECE LRTAP PROTOCOL ON POPS**

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## **Introduction**

In the 2009 submission from the Government of Canada the following was provided related to the 2b criteria:

1. while there was some evidence to suggest trifluralin may bioconcentrate and that some BCFs may exceed the numeric criteria value, factors related to environmental releases, environmental behaviour, and metabolism indicate lower potential for accumulation.
2. there is a lack of field evidence for bioaccumulation in areas of use or in remote areas potentially contaminated through long-range transport mechanisms.
3. information exists to indicate that use of trifluralin would not lead to significant adverse human health and/or environmental effects as a result of its long-range trans-boundary atmospheric transport.
4. and additional data on concentrations in various biota and media from remote locations would aid in supporting these conclusions.

Through this addendum, Canada is providing further information and additional references showing where trifluralin was included as an analyte in monitoring studies in various media including biota, but was below detection limits and therefore not reported. Most of the information gathered for this purpose has only recently been published or was only recently reviewed. Previously published additional information has also been provided for areas of use, where the potential for trifluralin exposure to biota and in abiotic compartments is much greater. The latter information was not provided in Canada's previous submission as the focus generally related to this protocol is on remote areas. The information is relevant as it shows consistency,

in the general low frequency of detections and when detected low concentrations, with results from remote areas.

The information in this addendum provides additional studies where trifluralin was looked for routinely but was rarely detected in biota, sampled from remote areas. In samples from the arctic trifluralin was below detection limits in all samples of lichen, fish, marine mammals, plankton, and amphipods. In areas close to where trifluralin is used it was detectable in zooplankton but not in all samples.

New information within this document confirms that trifluralin is in fact not widely present in biota from remote areas, nor in areas of use. The perceived lack of information on trifluralin in biota is an artefact of monitoring programs not reporting non-detects from samples analyzed for a range of chemical contaminants.

A comparison of thresholds for effects and environmental concentrations for aquatic biota is provided in the addendum using the concentrations of trifluralin detected in water from locations near areas of use. It is unlikely that trifluralin will cause acute or chronic effects. This was also the case when the potential for effects was examined for small terrestrial mammals exposed to trifluralin via inhalation. It is further noted that while based on chemical properties there appears to be a potential for bioconcentration/bioaccumulation, despite the potential even when use peaked several years ago, it has not resulted in any field evidence of significant bioaccumulation. Residues in biota are rarely found to be greater than detection limits.

In the case of known POPs (e.g. toxaphene, chlordane, PCBs), there is some consistency in that chemicals being reported in air, water and sediment are reported as also being found in biota from remote areas. This is not the case for trifluralin.

Despite use for over 40 years, and a number of international monitoring programs for chemicals in the Arctic over the past 20 years, it is only recently that detections in biota have been reported, and these were at relatively low levels, in a limited number of samples. Similarly, it is noted that in areas of use, such as Canada and the US, again while there are detections in air, precipitation and water, reported frequencies of detections in biota are generally low (e.g. EPA National Lake Fish Study (2000-2003)).

The evidence shows past and currently measured levels of trifluralin are not at or near levels of concern. In addition, information provided at the May 2010 Task Force meeting by the chemical manufacturer, indicates a downward trend in use of trifluralin over the past 8 years in North America and worldwide in general, suggesting limited potential for increased contamination in the future. This is in part explained by shifts in agronomic practices to more no-till systems which use products which are applied early post-emergent rather than products such as trifluralin which are applied pre-emergent.

There is a concern that chemicals meeting criteria of bioconcentration will contaminate food webs and lead to increased concentrations in biota over time eventually resulting in the exceedence of threshold concentrations leading to adverse effects. Therefore, taking action in a protective fashion is warranted. In the case of trifluralin, available information suggests that while it may bioconcentrate in some organisms under controlled laboratory conditions and under some atypical exposure scenarios (e.g. downstream of untreated effluent from a manufacturing plant), it does not bioaccumulate in areas of use nor in remote areas. It should be noted that even at its peak usage, detections were rare.

Given the information has been collected so far, unlike other POPs, there is not widespread detections in biota from remote areas like the arctic despite over 40 years of relatively high use in circumpolar nations. New information within this document confirms that trifluralin is in fact not widely present in biota from remote areas. The lack of information on trifluralin in biota is an artefact of monitoring programs not reporting non-detects from samples analyzed for a range of chemical contaminants.

It is further noted that regulatory risk assessments in Canada and the US have concluded that risks resulting from the use of trifluralin continue to be acceptable for humans and the environment. (EPA RED,1999, HC PRVD2008-22 and HC RVD2009-09). The effects assessment in these references were based on areas of use which would have much higher exposure concentrations than would remote areas such as the arctic.

## **1.0 Additional data on Environmental Concentrations of Trifluralin**

### **2 (B) WHETHER SUFFICIENT INFORMATION EXISTS TO SUGGEST THAT THE SUBSTANCE IS LIKELY TO HAVE SIGNIFICANT ADVERSE HUMAN HEALTH AND/OR ENVIRONMENTAL EFFECTS AS A RESULT OF ITS LONG-RANGE TRANSBOUNDARY ATMOSPHERIC TRANSPORT.**

The following information is provided as indicative of potential exposure concentrations to trifluralin for non-target biota including humans. As there are no specific studies on adverse health or environmental effects resulting from long-range transport, a suitable surrogate is the use of the traditional risk assessment framework to compare potential exposure levels with threshold concentrations for effects. This section outlines additional information on concentrations in various media.

Landers et al., (2008) sampled various media from July 2005 to July 2006 at three Alaskan parks. Trifluralin levels were below detection limits in the Arctic Alaskan parks (Noatak National Preserve, Gates of the Arctic National Park Preserve) in air, snow, lichen, sediment and fish. Detection limits were 0.7 pg/L, 0.001 ng/g dw, 0.1 ng/g lipid, 1.7 ng/g dw and 7.2 pg/g ww in snow, air, lichen, sediment and fish, respectively. It is clear that detection limits were quite low and no trifluralin was detected in the Arctic Alaskan parks. Sampling and analytical methods are acceptable.

Bossi et al. (2008) reported trifluralin in air at a range of <LOD ( LOD not provided) to 1.95 pg/m<sup>3</sup> in Nuuk, West Greenland in 2004-2005. The annual average concentration of trifluralin in Nuuk was 0.09± 0.19 pg/m<sup>3</sup>. The average over both years was 0.16 ± 0.42 pg/m<sup>3</sup>. Trifluralin was only detected in samples collected in winter and autumn and in 6 of 23 samples. The

detection limit for trifluralin was not provided, however, the authors stated that the detection limits for “OCs were between 0.08 and 2.57 pg/m<sup>3</sup>”. Sampling and analytical methods are acceptable.

Muir et al. (2007) analyzed large volume water samples from Lake Hazen in northern Ellesmere Island and from Char Lake on Cornwallis Island, collected in 2005 and 2006. Trifluralin was detected in all samples at low pg/L concentrations. No specific results were provided in Muir et al. (2007). Sampling and analytical methods were not described in this short report.

Water samples collected from Lake Hazen and the river flowing into Lake Hazen had approximately 0.09 and 0.3 pg/L of trifluralin (Environment Canada Report to Parks Canada (2005), respectively. Concentrations in inflow waters were higher than lake concentrations due to dry deposition onto glaciers that fed the river as well as from aerosol particle deposition.

Kurt-Karakus et al. (2011) determined concentrations of trifluralin in water, air and precipitation from 10 remote inland lakes in Ontario, Canada in 2003, 2004 and 2005. They found concentrations of trifluralin in water ranging from <0.0009 to 0.11 ng/L with a frequency of detection of 26%. In precipitation concentrations ranged from <0.0018 to 4.8 ng/L with a detection frequency of 67%. In air, trifluralin concentrations ranged from <0.0009 to 11.1 ng/m<sup>3</sup> with a detection frequency of 91%. Concentrations of trifluralin in zooplankton ranged from <0.0018 to 0.002 ng/g wet wt. BAFs on a wet wt basis ranged from 230 to 2200. Sampling and analytical methods are acceptable.

Donald et al. (2007) sampled 15 drinking water reservoirs corresponding with areas of use in Manitoba, Saskatchewan and Alberta in 2003, 2004 and 2005. Water was sampled at a depth of 2 m from the center of the reservoir every two weeks in 2003 from early May to mid August as well as once in October 2003, through the ice in mid-winter (January 2004) and after spring

snowmelt runoff in April 2004 and 2005. Water that had gone through the local treatment plant was also collected in 2004 and 2005, simultaneously with the reservoir samples. Sampling and analytical methods are acceptable. All reservoirs were located within the prairie agricultural region of Canada and were fed primarily from snowmelt runoff or runoff due to heavy precipitation. Trifluralin was detected in 1% of the samples (2 detections of 206) collected from the reservoirs (detection limit 5.15 ng/L). The detections were below the limit of quantification (LOQ), however, Donald et al. (2007) estimated the concentrations to be approximately 1 ng/L. Lower detection frequency in this study compared to Kurt-Karakus et al (2011) is likely due to the difference in detection limits (<0.0009 and 5.15 ng/L in Kurt-Karakus et al. 2011 and Donald et al. 2007, respectively).

Donald and Syrgiannis (1995) collected water, sediment and zooplankton from 19 large southern Saskatchewan lakes. These lakes are within the agricultural zone of Saskatchewan. Detection limits were 5 ng/L, 0.02 ng/g and 1 ng/g for water, sediment and zooplankton, respectively.

Trifluralin was not detected in water, sediment or zooplankton from any of the lakes (sample n = 23). The relatively high detection limits for each matrix compared to studies such as Kurt-Karakus et al. (2011) could account for the lack of detection observed. This itself is simply due to the age of the study and analytical methods available then compared to newer analytical methods employed later.

Ruggirello et al. (2010) collected an ice core from an ice cap in Svalbard, Norway in 2005.

Trifluralin was one of 9 current use pesticides (CUPs) detected in the ice core. The peak concentration of trifluralin was detected in the years 1995-2005 and decreased consistently with depth and age of core. However, in two horizons from the core trifluralin was below detection limits. A peak flux of 2.32 pg/cm<sup>2</sup>/year was determined, with a total burden of 3.6 ng in the years

1953-2005 deposited. The authors defined the maximum accumulation as “small” (other compounds detected had fluxes ranging from 1.05 – 809 pg/cm<sup>2</sup>/year). The lowest input occurs before its registration suggesting some downward movement in the core perhaps due to the seasonal spring melt. The input to the Devon Ice cap (Muir and Zheng 2007) is less than 1% of that found in the Svalbard ice cap. Sampling and analytical methodology are acceptable.

Morris, A, D.C.G. Muir et al. (2011 in prep.) collected seawater, plankton, fish, Greenland shark and marine mammals from three locations in the Canadian Arctic (Barrow Strait, Rae Strait and Cumberland Sound) between 2008 and 2010. They included trifluralin as one of a series of halogenated pesticides analyzed by GC-negative ion mass spectrometry. Trifluralin was not detected in biota (plankton n=19, Fish n=36, sharks n=11 or marine mammals n=34) (Instrument detection limit = 4 pg/g) or in seawater samples at 0.01 pg/L (n=11) (see IDL information in Table 2).

**Table 1. Summary of Evidence of National and Long-Range Transport of Trifluralin**

Environmental Compartment	Concentrations	Location/Comments	Reference
Air Snow	Below detection limit Air: <0.001 ng/g dw Snow: <0.7 pg/L	Arctic Alaskan National Parks (2005-2006)	Landers et al. 2008
Air	Range: <DL – 1.95 pg/m <sup>3</sup> Annual Average: 0.09±0.19 pg/m <sup>3</sup> Detection frequency: 26%	Nuuk, West Greenland (2004-2005)	Bossi et al. 2008
Lake water	“Low pg/L”	Lake Hazen, NU	Muir et al. 2007
Lake water Inflow water	0.09 pg/L 0.3 pg/L	Lake Hazen, NU and inflow stream to Lake Hazen	Environment Canada Report to Parks Canada 2005
Water Precipitation Air	<0.0009 – 0.11 ng/L <0.0018 – 4.8 ng/L <0.0009 – 11.1 ng/m <sup>3</sup>	10 remote inland lakes Ontario	Kurt-Karakus et al. 2011 <sup>1</sup>
Water	<5.15 ng/L 1% of samples had ‘detects’ below method detection limit	Manitoba, Saskatchewan, Alberta (2003, 2004, 2005)	Donald et al. 2007
Water Sediment	Not detected in 23 samples <5 ng/L water <0.02 ng/g sediment	19 Southern Saskatchewan lakes	Donald and Syrgiannis 1995
Ice core	Total Burden: 3.6 ng from 1953-2005 Peak flux: 2.32 pg/cm <sup>2</sup> /year	Svalbard, Norway	Ruggirello et al. 2010
Arctic Ocean water	<0.010 pg/L Seawater (Based on 400 L)	Canadian Arctic	Morris and Muir 2011 in prep

<sup>1</sup> This data was reported previously in Canada’s Position paper

**Table 2. Summary of New Information of Trifluralin in Biota.**

Environmental Compartment	Concentrations	Location/Comments	Reference
Lichen Fish	Below detection limits <0.1 ng/g lipid Lichen <7.2 pg/g ww Fish	Arctic Alaskan National Parks (2005-2006)	Landers et al. 2008
Zooplankton	<0.0018 – 0.002 ng/g ww BAFs: 230-220 wet wt	10 remote inland lakes Ontario	Kurt-Karakus et al. 2011 <sup>1</sup>
Arctic biota	Below detection limits Blubber/fat < 4.34 pg/g ww Inverts (plankton, amphipods) <1.45 pg/g ww whole fish homogenate/liver/algae/muscle <0.868 pg/g ww	Canadian Arctic	Morris and Muir 2011 in prep

## **2.0 Consideration of Potential for Significant Adverse Effects**

### ***2.1 Inhalation Assessment***

Health Canada's re-evaluation of trifluralin included an inhalation risk assessment for rats based on a 4-h LC<sub>50</sub> of 4.66 mg a.i./L and the maximum concentration of trifluralin detected in air monitoring programs in Canada at the time of the risk assessment (3.4 x10<sup>-9</sup> mg a.i./L or 3400 pg/m<sup>3</sup> See Table 3 for calculation methods).

The risk quotient was determined to be 1.7x10<sup>-8</sup>. Based on maximum concentrations monitored in Canada and the 4-h toxicity endpoint of concern (1/10 LC<sub>50</sub> concentration), the level of concern was not exceeded and there is negligible risk to mammals expected (Table 4).

Concentrations of trifluralin detected in Arctic air are <5 pg/m<sup>3</sup>. This is ca. 680 x less than the concentrations used in the inhalation risk assessment. This analysis suggests there is no inhalation risk to mammals in the Arctic. Maximum concentration of trifluralin from new data obtained from Ontario air (Kurt-Karkus et al. 2011) was 11.1 ng/m<sup>3</sup> (11,100 pg/m<sup>3</sup>). Even at the highest measured air concentration which is 3.3 x greater than the air concentration used in the risk assessment it is clear that there is no inhalation risk to mammals even in more southerly locations (Ontario).

<b>Table 3. Estimation of Mammalian toxicity endpoint of concern.</b>		
<b>Value</b>		<b>Explanation/Conversion</b>
<b>rat 4-hour LC50 (mg a.i./L)</b>	>4.66, assumed to be 4.66	most sensitive mammalian inhalation endpoint
<b>rat 4-hour LD50 (mg/kg bw)</b>	524 mg a.i./kg bw	LD50 (mg/kg bw) = [LC50 (mg/L) x inhalation rate (L/min) x exposure duration (min)] ÷ kg bw  rat inhalation rate (in lab) = 0.164 L/min (see below) exposure duration in lab = 4 hours = 240 minutes kg bw rat = 0.35 kg (default value)
<b>rat inhalation rate (L/min)</b>	0.164 L/min (in laboratory; at rest)  0.491 L/min (in field; active)	inhalation rate in L/min = [ 379 (kg bw) <sup>0.80</sup> ] ÷ 1000 kg bw rat = 0.35 kg (default)  inhalation rate for field, multiply by 3
<b>Convert the mammalian toxicity endpoint (in mg/kg bw) to an equivalent air concentration in the field (in mg/L). (i.e. determine the air concentration which will result in a dose (in mg/kg bw) equivalent to the toxicity endpoint of concern). (note: will need to use field inhalation rate for this conversion)</b>		
<b>estimated air concentration (mg/L) resulting in the mammalian 4-hour LD50 dose (air concentration equivalent to an inhalation LC50)</b>	0.76 mg a.i./L for 350 g rat or: 0.2 for sensitive species	Field inhalation X-min LC50 (mg/L) = $\frac{\text{inhalation X-min LD50 (mg/kg bw)} \times \text{BW (kg)}}{\text{Field IR (L/min)} \times \text{ED (min)}}$  Where: LD50 = LD50 <sup>5th percentile(50%)</sup> in the screening level = 0.76/3.8 = 0.2 ED = exposure duration (ED same as laboratory toxicity exposure duration) Field IR is the mammalian FIELD inhalation rate (based on Eqn 4a or 4b). Eqn 4a: Resting mammal IR (mL/min) = 379 (BW in kg) <sup>0.80</sup> And conversion: Field IR = Resting IR x 3 And conversion: L/min = mL/min ÷ 1000
<b>estimated air concentration (mg/L) resulting in the mammalian 4-hour 1/10LD50 dose (air concentration equivalent to 1/10)</b>	0.076 mg a.i./L for a 350 g rat or: 0.02 for sensitive species	1/10 above value

<b>Table 3. Estimation of Mammalian toxicity endpoint of concern.</b>	
<b>Value</b>	<b>Explanation/Conversion</b>
<b>LC50)</b>	

<b>Table 4. Comparison of the air exposure concentrations with the mammalian toxicity endpoint of concern.</b>			
<b>Exposure Concentration (Section 5.4.3.3)</b>	<b>Mammalian Toxicity Endpoint of concern: LC50 or 1/10 LC50 (air concentration resulting in inhalation dose of LD50 or 1/10 LD50)</b>	<b>Risk Quotient (Exposure/Toxicity) based on LD50 concentration</b>	<b>Risk Quotient (Exposure/Toxicity) based on 1/10LD50 concentration</b>
3.4 ng a.i./m <sup>3</sup> = 3.4 x10 <sup>-9</sup> mg a.i./L	350 g rat: LC50: 0.76 mg a.i./L 1/10LC50: 0.076 mg a.i./L	350 g rat: 4.5 x10 <sup>-9</sup> Sensitive Species: 1.7 x 10 <sup>-8</sup>	350 g rat: 4.5 x 10 <sup>-8</sup> Sensitive Species: 1.7 x 10 <sup>-7</sup>

**2.2 Aquatic Assessment**

For determining potential for adverse environmental effects in remote areas the highest water concentration that has been detected in remote areas was used. The maximum concentration of trifluralin determined in Arctic water was 1.15 ng/L in the subsurface microlayer (Chernyak et al. 1996) which would have a tendency to be more hydrophilic thus sequestering trifluralin in this matrix. In Ontario lakes concentrations of trifluralin were reported to be 0.11 ng/L (Kurt-Karakus et al. 2011).

HC-PMRA conducted a risk assessment for trifluralin using the most sensitive endpoints for each group of biota (freshwater and marine/estuarine invertebrates, fish, plants, algae etc) that was available at the time. For brevity sakes only results for the most sensitive biota will be

reported here. The most sensitive acute toxicity endpoint for aquatic organisms is an LC<sub>50</sub> of 8.4 µg a.i./L for bluegill sunfish (*Lepomis macrochirus*) and for chronic toxicity it was an NOEC of 0.3 µg a.i./L for fathead minnow (*Pimephales promelas*). As seen in Table 5 the LOC is not exceeded and it is clear that concentrations are not close to threshold values for either acute or chronic adverse effects.

<b>Table 5. Calculation of Risk Quotients for aquatic biota using maximum concentrations of trifluralin in water found in monitoring programs of remote areas</b>		
<b>Water Concentration (µg/L)</b>	<b>Bluegill sunfish (<i>Lepomis macrochirus</i>) (0.84 µg a.i./L)<sup>1</sup> Acute Risk Quotient</b>	<b>Fathead minnow (<i>Pimephales promelas</i>) (0.3 µg a.i./L) Chronic Risk Quotient</b>
0.00115 (arctic seawater)	0.001369	0.003833
0.00011 (northern Ontario)	0.000131	0.000367

<sup>1</sup>LC<sub>50</sub> (8.4 µg a.i./L)/10 to account for potential uncertainty

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