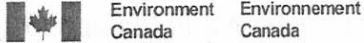


Convention on Long-range Transboundary Air Pollution
Executive Body, 27th session
14 – 18 December 2009
Informal document No. 7

Additional information on Trifluralin submitted by Canada



Chemicals Management Division
351 St. Joseph Blvd.
PVM – 18th Floor
Gatineau, QC
K1A 0H3

December 2, 2009

Catherine Masson
Secretary to the Executive Body for the Convention on Long-range Transboundary Air Pollution
United Nations Economic Commission for Europe (UNECE)
Palais des Nations, Office 346
CH-1211 Geneva 10 SWITZERLAND
Tel: + 41 22 917 23 56
Fax: + 41 22 917 01 07
Email: catherine.masson@unece.org

Re: Submission of additional information for the continued review of Trifluralin under the Protocol on Persistent Organic Pollutants.

Dear Ms. Masson,

As mentioned at the 45th Session of the Working Group on Strategies and Review, Canada is pleased to submit the following additional information on Trifluralin for consideration by the Task Force on POPs.

Sincerely,

Original signed by:
Margaret Kenny
Director General, Chemicals Management Division
Environment Canada



Government
of Canada

Gouvernement
du Canada

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

December 2009

PURPOSE:

At the 45th Session of the Working Group on Strategies and Review, held in Geneva, 31 August – 4 September, 2009, the Government of Canada indicated that it had additional information it was willing to submit on Trifluralin which was not included in the original dossier. Consensus was reached at the meeting to continue the review of trifluralin, taking into consideration new information.

In response, the Government of Canada has drafted this paper for consideration by the Task Force on POPs. The paper highlights potential considerations for the evaluation of the POPs criteria on criteria 1(d) bioaccumulation and on criteria 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. Annex A of this document presents and discusses the additional information that was not included in the original dossier.

1 (D) BIOACCUMULATION:

- i) Evidence that the BCF or BAF for the substance is greater than 5,000 or the log K_{OW} is greater than 5; or**
- ii) Alternatively, if the bio-accumulative potential is significantly lower than (i) above, other factors, such as the high toxicity of the substance, that make it of concern within the scope of the protocol.**

The review of the initial dossier resulted in the following conclusion with respect to criteria 1 (d).

All four reviewers, based on the indicative numerical values ($BCF > 5000$ and $\log K_{OW} = 5.27$), concluded that trifluralin satisfies the LRTAP guidance for bioaccumulation. One reviewer noted that the bioaccumulation data lack clarity since it was difficult to check the validity of the data and that the dossier would gain by adding data from the open literature.

For Consideration

The following additional information should also be considered in the interpretation of 1 (d). A table of additional bioconcentration and bioaccumulation information is presented in Annex A.

The reported and reviewed laboratory BCF and BAF values ranged from 276-4730 in algae, 20 - 870 in snails, 30 - 92 in daphnia, to 8893-8870 in various fish species. It is noted that there is considerable variability in BCF values between studies, within studies and within species suggesting that the evidence for bioaccumulation is conflicting. While some studies suggest that trifluralin exceeds the numeric criteria for bioaccumulation, many of these studies also show that trifluralin is readily depurated (Graper and Rainey, 1988; Spacie and Hamelink, 1979).

There are also a number of field based studies which have determined bioaccumulation and have been reviewed. Reported BAF values for zooplankton range from 255- 4200, for oysters 23- 1168 and for a variety of fish species from 1800 – 6000. We note that for the highest reported BCF and BAF values for fish in the field there are concerns regarding the determinations of values. The BCF value reported by Graper and Rainey (1988) is 5674, however this type of study may not adequately represent bioaccumulation dynamics in the natural environment where it is expected that trifluralin may be primarily adsorbed to sediment. In the case of the BAF value of 6000 from Spacie and Hamelink (1979), the study was conducted downstream of a manufacturing plant, which might not be typical of exposure conditions (i.e. constant high level) compared with concentration and timing of exposure resulting from agriculture uses (lower concentrations, pulsed exposures) or in remote areas (exposures likely via sediment). The study reports BAFs of 6000 for minnows prior to the implementation of treatment for the plant effluent and 5100 in the post treatment period. The authors noted that for larger species, the determined BAFs (e.g. sauger 5800, shorthead redhorse 2800 and golden redhorse 1800) were transitional and not reflective of steady state conditions because the fish body burdens (concentrations) were not yet at equilibrium and that the reported values represented a point in time. While the authors suggest the minnows were near equilibrium because of their smaller size, we note that reported laboratory BCF values of ~ 3200 suggest that even for minnows, equilibrium might not have been reached. Additionally, it is noted that the determination of body burdens in whole fish was

based on sampling of lipid deposits from the larger fish which were subsequently used to estimate whole body burdens. This would not be acceptable by today's standards.

The potential for a substance to bioaccumulate can be expressed in terms of the bioconcentration factor (BCF), the bioaccumulation factor (BAF) or the octanol-water partition coefficient (K_{OW}). BCF and BAF are environmentally more relevant than K_{OW} because they take into account the response of the organisms, and factors such as metabolism, steric effects at the gill/water interface, etc. From a scientific perspective, field derived BAFs could be considered more realistic than laboratory data (e.g., BCFs) and chemical properties ($\log K_{OW}$) as they consider all possible routes of exposure in the environment (uptake directly from the medium and from the diet). Laboratory derived BCF values typically only examine the partitioning between water and organism. While K_{OW} and BCF values are relevant indicators of the potential for bioaccumulation, determination of BAFs, biomagnification factors and the examination of field data will indicate if a chemical moves through a food web. A further discussion of food web bioaccumulation is explored in Arnot and Gobas (2003).

For trifluralin, although some BCF values indicate that there is a potential for bioconcentration, there is no evidence of appreciable levels of trifluralin measured in biota in the field under typical exposure conditions despite evidence of long range transport and the high volume of use in North America and other regions for the past 40 years. There are several possible explanations for the apparent lack of evidence of bioaccumulation in the field.

Trifluralin is readily eliminated in fish and other organisms. Elimination in fish was observed in many of the studies reporting high BCFs when fish exposed continuously to trifluralin were placed in clean water (Graper and Rainey, 1998; Spacie and Hamelink, 1979; Schultz and Hayton, 1993). Reported depuration half-lives for these studies were 4.7 days in bluegill sunfish (Graper and Rainey, 1988), 22-31 days in sauger, 17-57 days in shorthead redhorse, 23 days in golden redhorse and 3 days in fathead minnows (laboratory study) (Spacie and Hamelink, 1979) and between 2-12 days in rainbow trout (Schultz and Hayton, 1993). Reinbold and Metcalfe (1974) showed that trifluralin is metabolised via processes governed by mixed function oxygenase system (MFO) in green sunfish. BCF values were only greater than 5000 when the MFO metabolism pathway was inhibited.

The metabolism profile seen in fish is consistent with the metabolism profile observed in various terrestrial species. This is addressed in section 2.4.1 of the Trifluralin dossier (UN ECE, 2007) and in regulatory reviews (Health Canada, 2008; EPA RED, 1996). The EPA and subsequent Canadian regulatory assessments include extensive metabolism information. In poultry and ruminant metabolism studies, it was concluded that there is no reasonable expectation of finite residues of trifluralin in animal commodities (including meat, milk, poultry and eggs) (Health Canada, 2008; EPA RED, 1996). In studies conducted on rats, trifluralin was shown not to be readily absorbed from the gastrointestinal tract after oral intake. Of the trifluralin that was absorbed, essentially all of it was completely metabolised and eliminated within 3 days after oral administration (EPA RED, 1996). Bioaccumulation was not reported and the elimination half-life in the rat has been estimated to be 16-18 hours (EU DAR, 2005). Available data in the trifluralin dossier indicated that the metabolic pathway in rats and dogs are virtually identical

(Trifluralin Risk Profile, 2007 and EU DAR, 2005). An elimination half-life of 65 hours has been reported in monkeys given a single dose of 2 mg/kg intravenously (Poettenger et al, 1995 as reported in the EU DAR, 2005). Although no robust data on the toxicokinetics of trifluralin in humans have been reported, the Trifluralin Dossier (UN ECE 2007) indicated “*that there is no evidence of bioaccumulation of trifluralin and it does not appear to have been detected in human adipose tissue, breast milk or in blood samples from the general population.*” This is despite evidence of long range transport and the high volume of use in North America and other parts of the world for over 40 years.

Another factor which could influence the bioaccumulation of trifluralin are the chemical dynamics in the environment. The available data indicate that trifluralin is strongly adsorbed to sediments and there is uncertainty whether trifluralin is readily available for bioaccumulation. Under field conditions, trifluralin is not expected to be readily available for uptake by aquatic organisms. The high K_{OC} values ($K_{OC} = 6414-13414$) indicate that trifluralin adsorbs strongly to soil. When entering the aquatic environment, trifluralin migrates quickly from water and adsorbs strongly to sediment thereby reducing the availability for uptake. Toxicity endpoints and bioconcentration factors are significantly lower in systems including sediment-bound residues versus those systems with continual influx of trifluralin residues in the water column. There is evidence in published studies (e.g. Yockim et al. 1980) that toxicity and bioconcentration factors are lower when exposure occurs under realistic conditions in the presence of sediment in a static system versus when fish are exposed to an artificial system where there is a continuous input of trifluralin through the water phase only. Further, it should be noted that the OECD recently convened an expert panel to examine the re-design of the OECD Test Guideline 305 for fish bioconcentration and are proposing to modify this guideline to accommodate exposures from the diet.

The available data and physical/chemical properties of trifluralin lead to the conclusion in the dossier that: *Despite a relatively short atmospheric half-life of 21-74 minutes, trifluralin was observed in air at three Arctic monitoring stations, Tagish, Alert and Dunai at concentrations up to 2.92; 0.64 and 0.13 pg/m³, respectively. The half-life calculations are based solely on photochemical degradation and indicate that trifluralin should not reach the Arctic at measurable quantities even though relatively large amounts ($>5 \times 10^6$ kg) are applied annually to crops in western Canada and the USA. Current results indicate that other pathways such as transport on dry particulate or aerosol might be the primary mode of transport for trifluralin.* Significant transport via particulate material as a source is supported by data reported in Welch et al. 1991 (see Annex A). Given the known adsorption of trifluralin to organic particulate matter, this is not surprising. Given the results of Yokim et al 1980, transport via particulates has likely altered the overall dynamics of this chemical, including bioaccumulation

The lack of field evidence of accumulation in aquatic organisms is further supported by measurements of trifluralin in arctic air, seawater and freshwater sediment (Canadian Arctic Contaminants Program, 2006), however, its abiotic presence has not translated into appreciable residues being measured in biota despite over 40 years of use. In the case of known POPs (e.g. toxaphene, chlordane, PCBs), there is usually some consistency in chemicals being reported in

multiple media in remote areas (e.g. air, water, sediment and accumulation in biota). This is not the case for trifluralin.

Evenset et al. (2004) monitored several pesticides, persistent organic pollutants in high arctic lakes on an island in the Barents Seas. High levels of various compounds considered to be POP's were reported in biota. Trifluralin was reported at concentrations at the limit of detection in zooplankton or sediment-dwelling organisms and was detected in fish at concentrations just slightly above, or at the level of detection, in 50% of the fish sampled. Similarly, Muir et al. (2006) detected several currently used pesticides, including trifluralin, in remote lakes in Ontario but trifluralin was only found in one lake of the three sampled, but not on every sample day. The US EPA conducted a National Lake Fish Study (2000-2003) across the US including "significant agricultural areas" where "trifluralin is used extensively". The summary shows a low detection frequency in fish tissues (10, 3, 0.9 and 0.7% detection frequency in 2000, 2001, 2002, 2003, respectively). Only one predatory fish was found to contain trifluralin.

At this point it is not clear if trifluralin is in fact not widely present in biota from remote areas or if results are an artefact of monitoring programs not reporting non-detects from samples analyzed for a range of chemical contaminants.

While there is 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. There appears to be a lack of field evidence for bioaccumulation in areas of use or in remote areas potentially contaminated through long-range transport mechanisms.

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 review of the initial dossier, resulted in the following conclusion with respect to criteria 2 (b).

All four reviewers concluded that the available data show that trifluralin is highly persistent in soil, highly bioaccumulative, toxic to aquatic organisms, and has carcinogenic potential. One reviewer, while acknowledging the detection of trifluralin in Arctic air (remote from the areas of use), noted that it has not been detected in biota or in humans in the Arctic or other remote regions. The reviewer further stated that the data, therefore, do not allow a conclusion as to whether the measured levels in remote regions, resulting from long-range transboundary atmospheric transport, would lead to significant human and/or environmental effects.

When considered individually, and based on the information and data available in the original dossier, it is clear that toxicity and persistence criteria and long range transport to remote

locations are met. As discussed earlier in this document, there is some debate as to whether the criteria for bioaccumulation are actually met. With respect to criteria 2b, from a scientific perspective, it is not clear from the information presented in the original dossier how the conclusion was reached. At least one reviewer could not reach a conclusion that the criteria was met.

Criteria 2(b) allows the integration of information on hazard and exposure in evaluating the potential for the substance to have significant adverse human health and/or environmental effects as a result of its long-range transboundary atmospheric transport. Lines of evidence could include, among others, the comparison of toxicity and ecotoxicity data with detected or predicted levels of the chemical resulting or anticipated from its long-range environmental transport, evidence of effects on human health or the environment in remote areas, trends in environmental concentrations, or potential for increases in exposure given persistence and bioaccumulation properties and current and possible future regional/global production or use.

Notwithstanding the new information and discussion of the bioconcentration criteria, the following additional information and discussion of the likelihood of significant adverse human health and/or environmental effects considers the information provided in the original dossier and additional data and information which has come to light since.

Consideration of Exposure

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

There appear to be limited data on potential exposure concentrations to biota and humans for trifluralin in remote locations such as the Arctic. 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 (e.g. Evenset et al. 2004), 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)).

While reports of detections in biota are scarce, there are a reasonable number of scientifically credible reports of trifluralin in air, precipitation and snow/ice in both areas of use and remote areas. While it is possible that in remote locations, trifluralin may not have been an analyte in samples of biota, it may also be possible that trifluralin is either not present or present at very low concentrations, generally below limits detection and that these non-detects are an artefact of how data is reported. (Note: Trifluralin has been included as an analyte in Canadian Arctic Monitoring programs; however, as there were no detections, results have not been reported (pers. com., Derek Muir)).

Based on the existing data, it does appear that there is transport to remote areas, likely primarily via adsorption to particles. However, once in a remote location, it seems unlikely that such

adsorbed material is readily bioavailable (see discussion in 1(d)). The original dossier notes “*It should be emphasized that the strong tendency of trifluralin to adsorb to soil, sediment and suspended matter significantly reduces toxicity risks in the water phase because trifluralin will hardly be present there. On the other hand, trifluralin stays present in the sediment and probably adsorbed to suspended matter. Desorption from sediment to water appears to be low.*”

As noted earlier in the discussion of criteria 1(d), when entering the aquatic environment, trifluralin migrates quickly from water and adsorbs strongly to sediment thereby reducing the availability for uptake. Toxicity endpoints are significantly higher (i.e. less toxic) and bioconcentration factors are significantly lower in systems including sediment bound residues versus those systems with continual influx of trifluralin residues in the water column. This, coupled with the known high rate of elimination, suggests that the lack of trifluralin (both detections and low concentrations) in biota are likely related to chemical dynamics and exposure metrics.

The potential decreased bioavailability, metabolism or elimination by a range of organisms and apparent lack of contamination in food webs (including marine mammals and humans) is consistent with statements in the Trifluralin Dossier (UN ECE 2007) “*that there is no evidence of bioaccumulation of trifluralin and it does not appear to have been detected in human adipose tissue, breast milk or in blood samples from the general population.*” This is interpreted as being true both for the general population in areas of use and for those living in remote areas.

Consideration of Effects

Unlike exposure data, there is a considerable amount of information on the toxicity of trifluralin to a variety of organisms. In general, the information is well summarised in the original dossier and in available regulatory risk assessment documents.

Consideration of Risk

In the case of trifluralin, there does not currently appear to be compelling evidence that exposure concentrations have been in the past or are currently at or near levels of concern. Further information supplied to regulatory authorities indicates a general downward trend in use of trifluralin over the past 8 years in North America, suggesting limited potential for increased contamination in the future.

It has been argued for other chemicals that bioaccumulation and food web contamination will lead to increased concentrations in biota over time in remote locations, eventually resulting in the exceedence of threshold concentrations necessary for effects to occur, and this justifies taking action in a protective fashion. In the case of trifluralin, available data and knowledge suggests that while it may bioconcentrate in some organisms under laboratory conditions, that bioaccumulation might occur under some atypical exposure scenarios (e.g. downstream of untreated effluent from a manufacturing plant), it does not appear to occur in areas of use nor in remote areas. Without significant potential for exposure or for accumulation, it is unlikely that significant adverse human health and/or environmental effects as a result of its long-range transboundary atmospheric transport can be present in remote areas.

While it is acknowledged that there is very limited data available on concentrations in biota, unlike other POPs, there does not seem to be widespread detections in biota from remote areas like the arctic despite over 40 years of relatively high use in circumpolar nations. At this point, it is not clear if trifluralin is in fact not widely present in biota from remote areas or if results are 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 in areas of use. (EPA RED, 1999, HC PRVD2008-22 and HC RVD2009-09). These areas would have much higher exposure concentrations than would remote areas such as the arctic.

Conclusion for 2(b)

Considering this information, we suggest that sufficient information and knowledge exists to conclude that use of trifluralin would not lead to significant adverse human health and/or environmental effects as a result of its long-range transboundary atmospheric transport.

It is acknowledged that additional data on concentrations in various biota and media from remote locations would aid in supporting this conclusion.

REFERENCES:

A full list of references is contained in Annex A.

Annex A:

Review of Studies Relating to Bioaccumulation and Long-range Transport

Table of Contents

| | |
|---|----|
| List of Tables | 11 |
| Bioconcentration and Bioaccumulation of Trifluralin..... | 12 |
| Introduction..... | 12 |
| Bioconcentration Factors Determined for Biota in Laboratory Studies | 17 |
| Bioaccumulation Factors Obtained from the Field..... | 36 |
| Summary of Bioaccumulation of Trifluralin | 43 |
| Evidence of Local and Long Range Transport | 45 |
| Concentrations of Trifluralin in Air and Precipitation in Rural and Urban Canada..... | 45 |
| Concentrations of Trifluralin in Remote Locations..... | 56 |
| Summary of Local and Long-Range Transport of Trifluralin | 62 |
| References..... | 65 |

List of Tables

| | |
|---|----|
| Table 1. Summary of Laboratory BCF and BAFs Studies for Trifluralin | 13 |
| Table 2. Summary of BAFs Determined In Biota In Field..... | 15 |
| Table 3. BAFs observed in static soil incorporated and renewal uptake experiments from data provided in tables in Yockim et al. (1980). | 24 |
| Table 4. Concentrations of trifluralin in surviving adult sheepshead minnows (<i>Cyprinodon variegatus</i>) exposed for 166 days. Average tissue residues are whole-body, wet-weight. Duplicate analyses of a pooled sample from each treatment were performed. | 28 |
| Table 5. Concentrations of Trifluralin in Surviving 28-day old juvenile sheepshead minnows (<i>Cyprinodon variegatus</i>). The fish hatched from embryos produced during the first spawning period (days 113-122). Mean (and standard deviation) tissue residues are whole-body, wet-weight. Duplicate analyses of each pooled sample from duplicate aquaria A and B were performed. | 28 |
| Table 6. Description of the sampling sites and periods for the 2003 Canadian air sampling campaign | 47 |
| Table 7. Description of the sampling sites and periods for the 2004 Canadian air sampling campaign..... | 48 |
| Table 8. Concentrations of trifluralin (pg/m ³) in air samples collected under the prairie study during the spring and summer of 2003 ^a | 51 |
| Table 9. Concentrations of trifluralin in air (pg/m ³) samples collected at Bratt's Lake, SK in 2004 (1-m sampler)..... | 51 |
| Table 10. Comparison of Monthly Trifluralin Concentrations (pg/m ³) in air samples collected in 2003 and 2004 at Bratt's Lake..... | 51 |
| Table 11. Concentrations of Trifluralin in Air (pg/m ³)and precipitation (ng/L) samples collected at Abbotsford, BC in 2004..... | 51 |
| Table 12. Concentrations of Trifluralin in Air (pg/m ³) and precipitation (ng/L) samples collected at Egbert, ON in 2004..... | 52 |
| Table 13. Concentrations of Trifluralin in Air (pg/m ³) and precipitation (ng/L) samples collected at Vineland, ON in 2004..... | 52 |
| Table 14. Concentrations of Trifluralin in Air (pg/m ³) and precipitation (ng/L) samples collected at St. Anicet, QC in 2004..... | 52 |
| Table 15. Concentrations of Trifluralin in Air (pg/m ³) and precipitation (ng/L) samples collected at Baie St. Francois, QC in 2004..... | 52 |
| Table 16. Concentrations of Trifluralin in Air (pg/m ³) and precipitation (ng/L) samples collected at Kensington, PEI in 2004 | 53 |
| Table 17. Comparison of trifluralin concentrations in air samples collected in 2003 and 2004 under CANCUP. Monthly average results (pg/m ³). | 53 |
| Table 18. Concentrations of trifluralin in air in Alberta, 1999 to 2000 (Kumar 2001). | 55 |
| Table 19. Concentrations of trifluralin (pg/m ³)detected in air in northern Canada (from http://www.ainc-inac.gc.ca/ncp/pub/phy/occtre8_e.html)..... | 57 |
| Table 20. Summary of Evidence of National and Long-Range Transport of Trifluralin | 62 |

Bioconcentration and Bioaccumulation of Trifluralin

Introduction

A comprehensive search was conducted to determine the availability of studies on the bioconcentration or bioaccumulation of trifluralin. The studies were reviewed with the intent to determine how valid the data was and took into consideration the methodology for both experimental and analytical processes. This entailed the determination of whether a study was conducted using acceptable protocols, or if not, were scientifically sound experimental procedures followed (eg., controls, blanks etc), if the trifluralin used was radio labelled, the purity of the trifluralin, the number of sample dates, if the system could be determined to be at equilibrium, if the residues measured were identified to be parent trifluralin or were transformation products, or indeed if measured concentrations were used to calculate BCF/BAFs. Table 1 summarizes the BCF and BAF data obtained from studies conducted in the laboratory. The EU Dossier (2007) on trifluralin reviewed or used four studies in their analysis (first four rows in Table 1). There were an additional 11 studies available that determined BCFs/BAFs in the laboratory (Table 1) and another five studies that detected trifluralin in biota in the field (Table 2). Not all the field studies were able to calculate a BAF because of low concentrations or low frequency of detection.

Table 1. Summary of Laboratory BCF and BAFs Studies for Trifluralin

| Organism | BCF/BAF | Comments | Included in EU Dossier (2007) | Reference |
|----------------------|---|---|-------------------------------|--|
| Bluegill Sunfish | BCF: 5674 whole fish | Depuration half-life was 4.7 d 86-88% depurated in 14 d BCFs based on total ¹⁴ C residues | Yes | U.S. EPA R.E.D. 1996 (Graper and Rainey 1988) |
| Bluegill sunfish | BAF: 1087 to 1838 | Details were obtained from EU DAR (2003) BAFs reported from a sediment-spiked system | Yes | Francis and Cocke 1985 |
| Bluegill Sunfish | BCF: 1580 | Details were obtained from EU DAR (2003), BCFs calculated from ¹⁴ C residues | Yes | Sleight 1973 (cited in EU DAR 2003) |
| Fathead Minnow | BCF: 1750- 8870 | Details were obtained from EU DAR (2003) BCFs were inversely related to the exposure concentration, method of analysis of fish was not specified in EU DAR (2003) | Yes | Meyerhoff and Gunnoe 1992 (cited in EU DAR 2003) |
| Rainbow trout | BCF: 2280 | Half-life: 2-12 days | No | Schultz and Hayton 1993 |
| Western mosquitofish | BAFs: Day 30 100 µg/L Static Soil: 70 Renewal: 3810 | Continuous input via water resulted in much higher BAFs compared to static soil exposure Soil incorporated input resulted in fewer toxic effects compared to water renewal exposure Steady state in water occurred on approximately day 15. Values reported in this table were measured after steady-state was reached. | No | Yockim et al. 1980 |
| Ramshorn snail | BAFs: Day 30 100 µg/L Static Soil: 20 Renewal: 870 | | | |
| Daphnia | BAF: Day 30 100 µg/L Static Soil: 30 | | | |
| Green Algae | BAF: Day 30 100 µg/L Static Soil: | | | |

| | | | | |
|-------------------|---|--|----|---------------------------|
| | 220 Renewal: 4730 | | | |
| Algae | BAF: 276 | BAFs were based on ¹⁴ C BAFs in fish decreased with increased light conditions. Soil was spiked with trifluralin prior to adding to the test system. | No | Kearny et al. 1977 |
| Snails | BAF: 400 | | | |
| Daphnids | BAF: 92 | | | |
| Mosquito Fish | BAF: 33 (33, 100, 455 in full sun, subdued light and dark treatments, respectively) | | | |
| Sheepshead Minnow | BCFs: 1458-4792 (n=5), 7093, 11538 | High variability at lower test concentrations where higher BCFs were measured. Small sample size. No depuration phase. | No | Parish et al 1978 |
| Topmouth Gudgeon | BCF: 3142 | Continuous exposure Exposure concentration was not reported Equilibrium may or may not have been reached | No | Kanazawa 1981 |
| Green sunfish | BCFs: Trifluralin alone: 1.14 Trifluralin + Piperonyl butoxide: 118 | Addition of piperonyl butoxide (MFO inhibitor) increased accumulation of trifluralin, indicates that trifluralin is likely metabolized by MFO system in green sunfish. | No | Reinbold and Metcalf 1976 |
| Fathead Minnow | BCF: 889, 961, 1333 | Accumulation was directly proportional to the level of exposure Accumulation was essentially linear over the range of concentrations tested | No | Macek et al. 1976 |
| Pouch Snail | BAF: 17700, 153000 | Route of exposure affected the BCFs, BCFs were determined on a single analysis of concentrations in water and biota at termination of study, system was not at equilibrium | No | Sanborn 1974 |
| Mosquito Fish | BAF: 930, 4200 | | | |
| Fathead minnow | BCF: 3261 | An accelerated or kinetic accumulation test 50% Depuration: 3 days | No | Spacie 1975 |
| Mosquitofish | BCF: 1294 | Predicted from solubility correlation as in | | Calculated by |

| | | | | |
|---------------|-------------------------|--|--|---|
| | | Lu et al. 1974 | | Spacie and Hamelink 1979. |
| Rainbow trout | BCF: 1030 (muscle only) | Predicted from partition correlation as in Branson et al. 1975 | | Calculated by Spacie and Hamelink 1979. |

¹ **Font** indicates the value is above the threshold of 5000

Table 2. Summary of BAFs Determined In Biota In Field

| Organism | BAF | Comments | Included in EU Dossier (2007) | Reference |
|--------------------|-------------------------|---|-------------------------------|--------------------------|
| Sauger | 5800¹ | 50% clearance rate: 22-31 d fish were not removed from contaminated water. BAF was based on lipid analysis. Authors state that they do not consider large fish at equilibrium with the system. | No | Spacie and Hamelink 1979 |
| Shorthead Redhorse | 2800 | 50% clearance rate: 17-57 days fish were not removed from contaminated water. BAF was based on lipid analysis. Authors state that they do not consider large fish at equilibrium with the system. | | |
| Golden Redhorse | 1800 | 50% clearance rate: 23 days fish were not removed from contaminated water. BAF was based on lipid analysis. Authors state that they do not consider large fish at equilibrium with the system. | | |
| Minnow sp. | 5100 - 6000 | BAF was based on whole fish. | | |
| Oysters | 23-1167 (n= 33) | Based on range of concentrations in oysters and mean concentration in water (calculated by Canada). | No | Lehotay et al. 1998 |

| | | | | |
|-----------------------|----------------|---|----|---------------------|
| | | Trifluralin accumulated in oyster tissue soon after expected agriculture application periods and then depurated “fairly rapidly”, suggesting that trifluralin may be metabolised and/or excreted by oysters. | | |
| Zooplankton | 255, 4200 | Environment Canada data | No | Muir 2006 |
| Non-specific fish sp. | Not determined | 10, 3, 0.9 and 0.7% detection frequency in 2000, 2001, 2002, 2003, respectively Concentrations <10 µg/kg to 36 µg/kg. Only one predatory fish was found to contain trifluralin (11.3 µg/kg). Suggests low frequency of presence in areas of use. | No | U.S. EPA 2008 |
| Zooplankton | Not determined | <0.006 ng/g ww – concentrations below limits of detection | No | Evenset et al. 2004 |
| Chironomids | Not determined | <0.075 ng/g ww – concentrations below limits of detection | No | |
| Arctic Char | | Concentrations <0.008 to 0.03 ng/g ww 5 of 10 fish had reportable concentrations of trifluralin | | |

¹ **Font** indicates the value is above the threshold of 5000

Bioconcentration Factors Determined for Biota in Laboratory Studies

The EU Dossier (2007) on trifluralin reported BCF values of 5674 and 1580 in bluegill sunfish and a BCF of 8870 in the fathead minnow. The reference for these studies is EUTTF (2002).

The OSPAR Commission (2005) also references EUTTF (2002) for the following BCFs: 5674, 1580 and 1087-1838 in bluegill sunfish and 1750-8870 in the fathead minnow and includes a calculated BCF value of 2280 determined from log P_{ow} correlations according to Meylan et al. (1999). Reviews of these BAF/BCFs and the studies they were derived from follow below.

Graper, L.K. and Rainey, D.P. (1988): Laboratory Studies of ^{14}C Trifluralin Accumulation in Bluegill Sunfish. Dow AgroSciences, unpublished report No. ABC-0372 & ABC-0376, 8 June 1988.

Details of study obtained from:

EU DAR. 2003. Draft Assessment Report-Public Version. Initial Risk Assessment provided by the rapporteur Member State Greece for the existing active substance Trifluralin. Volume 3, Annex B, B.9. 164 pp.

and

the U.S. EPA. 1996. Reregistration Eligibility Decision (RED) Trifluralin. United States Office of Prevention, Pesticides EPA Environmental Protection And Toxic Substances April 1996 Agency (7508W)738-R-95-040. 240 pp. PMRA 1346403.

The bioconcentration of ^{14}C trifluralin was studied in the bluegill sunfish (*Lepomis macrochirus*) for 28 days of exposure and 14 days depuration. Water samples were taken daily from test and control aquaria throughout the uptake and depuration phases. Four fish were removed for radiochemical analyses from treated and control tanks at four hours, 1, 3, 7, 14, 21 and 28 days during uptake and at 1, 3, 7, 10 and 14 days depuration. At day 21 and 28, 65 fish were removed from the treated tank for transformation product characterization. The mean measured concentration of trifluralin in treated water during exposure was 0.0059 ± 0.0005 mg/L (^{14}C

equivalents). Mean trifluralin uptake in fish tissues reached 90% of steady state concentrations in 14-16 days. On days 21 and 28 of uptake phase 84 -88% of total radioactive residues was identified as trifluralin. However, according to the U.S. EPA (1996) accumulation and depuration in fish could not be fully assessed because radioactive residues in the fish tissues were not completely characterized.

Trifluralin residues accumulated in bluegill sunfish with maximum mean bioconcentration factors of 2041x, 9586x, and 5674x for edible, nonedible, and whole fish tissues, respectively. A depuration half-life of 4.7 days was found in this laboratory study and a DT₉₀ of 15 days was reported. Radioactivity attributed to a total of 10 transformation products at a maximum of 0.804 µg/g was not identified; up to 1.273 µg/g was described only as polar radioactivity. Also, up to 1.8% of the total radioactivity in the aqueous phase of the tissue extracts was not characterized (U.S. EPA 1996).

Francis, P.C. and Cocke, P.J. 1985. Bioavailability of sediment-sorbed trifluralin to bluegill under laboratory conditions. Unpublished. Details of study obtained from EU DAR (2003).

The bioavailability of sorbed trifluralin was determined in bluegill sunfish (*L. macrochirus*) exposed to sediment treated with trifluralin. The study terminated after eight days and was conducted under static conditions with occasional agitation.

Sediment was collected from a pond and air-dried, ground and treated with trifluralin. Six to eight bluegill were placed in 1000L tanks containing 800L conditioned well water. After 30-60 min the spiked sediments were mixed into the tanks at four different suspended sediment levels.

Tanks were stirred every two to four hours for the duration of the 8-d exposure. Trifluralin was determined via GC-ECD.

Trifluralin levels in fish increased with suspended sediment load and sediment trifluralin concentration. Estimated uptake and depuration rate constants were used to calculate steady-state BCFs of 1087-1838.

The EU DAR (2003) states that “this study...did not follow the standard guideline but was designed to investigate the bioavailability of sediment-sorbed test material. It is therefore included in order to provide supplementary information only.”

Sleight, B.H. III (1973) Exposure of fish to ¹⁴C trifluralin: accumulation, distribution and elimination of ¹⁴C residues. Unpublished. Details of study obtained from EU DAR (2003).

The accumulation and distribution of ¹⁴C trifluralin residues in bluegill sunfish (*L. macrochirus*) were studied in a 35 day uptake/14 day depuration study under flow-through conditions. 100 bluegill were placed into 30L tanks exposed to nominal concentrations of 20 µg/L. Other tanks served as controls. No details on photoperiod, volume of test substance or initial starting weight of fish were provided (EU DAR 2003). Samples of water and five fish were taken from each tank prior to exposure and after 1, 3, 7, 10, 14, 21, 28 and 35 days of exposure and fish were sampled on days 1, 3, 7, 10, and 14 during the depuration phase. Distribution of all trifluralin residues in edible and non-edible tissue was determined via LSC. Polar and non-polar residues were evaluated using hexane or methanol extraction (no other information was provided according to the EU DAR (2003)).

The mean measured concentrations of trifluralin in water was 7.87 µg/L (no other exposure condition data were provided (EU DAR 2003). ¹⁴C trifluralin residues in fish reached a

maximum at day 7-10 with mean measured concentrations of 11.7 ± 0.38 mg/kg. The value was said to be “ca. 1580-fold greater than that measured in water” (EU DAR 2003). Measured residues in fish declined to a mean of 7.57 ± 0.53 mg/kg during the remaining days of exposure. Approximately 92% of the total ^{14}C residues were eliminated from edible tissues during the first 7-d of depuration.

There did not appear to be any results presented on the identification of the residues as they were only described as ^{14}C so would include any transformation products.

The EU DAR (2003) cite major deviations of the study as only one test concentration employed, limited data on test conditions and was “included in order to provide supplementary data only”.

It is also important to note that the study only followed ^{14}C residues so did not separate between parent compound and transformation products.

Meyerhoff, R.D. and Gunnoe, M.D. 1992. The toxicity of trifluralin to fathead minnow (*Pimephales promelas*) in a 35-day vertebral lesion study. Unpublished. Details of study obtained from EU DAR (2003).

The bioconcentration of trifluralin in the fathead minnow (*P. promelas*) was determined following exposure for 35-days in a chronic toxicity study under flow-through conditions. Four replicate groups of 30 fathead minnows were exposed for 35 days to nominal concentrations of 0.6, 1.9, 5.6, 16.7 and 50 $\mu\text{g/L}$ trifluralin. Test solutions were delivered via a proportional diluter system using stock solution that was prepared each day. Fish were exposed to 18 L of treated or control water. All physical test conditions were reported. Concentrations of trifluralin in water were taken on days 9, 13, 16, 20, 23, 30 and 35. Identification of trifluralin in water was accomplished via GC-ECD on days 6 and 27.

Exposure concentrations were reported to be 32-100% of nominal which the authors suggested was a result of adsorption to the glass of the diluter apparatus. Bioconcentration factors in the

range of 1750-8870 were calculated on trifluralin levels in fish tissue after a 35-d exposure period (1750 in fish exposed to 30 µg/L, measured and 8870 when exposed to 0.3 µg/L, measured concentration). It was unclear from the EU DAR (2003) how residues were determined in the fish. Fish in the control tanks had detectable levels of trifluralin (limit of detection 0.02 mg/g) that were below the limit of quantitation (0.05 mg/kg). The authors suggested it was due to the residues in the diluter.

The EU DAR (2003) cite major deviations such as single time point measurement of concentrations in fish, no depuration phase and is “included (in the DAR) to provide supplementary data only”.

Schultz, I.R. and W.L. Hayton. 1993. Toxicokinetics of trifluralin in rainbow trout. *Aquat. Toxicol.* 26:287-306

Trout (*Oncorhynchus mykiss*) weighing 60-100 g were exposed to [¹⁴C]-trifluralin via the water, and larger trout (283-1339 g) received [¹⁴C]-trifluralin intravascularly. Rainbow trout were acclimated for at least 2 months at 12°C in 500-L fiberglass aquaria. Individual trout were exposed in 50-L glass aquaria containing 2 ng/mL (2 µg/L) in the dark to prevent photolytic transformation and sampled up to 96-h.

When water samples were collected, a known amount of unlabeled trifluralin dissolved in acetone (cold spike) was immediately added and mixed thoroughly. Fish carcasses were thawed, minced, and homogenized. During homogenization, a 1-g aliquot of homogenate was removed and the cold spike was added. The 1-g homogenate was added to 1 ml tissue solubilizer and shaken for 1 d; 100 µL concentrated acetic acid and 15 ml scintillation cocktail were then added and radioactivity determined by scintillation counting. After homogenization, 150 ml acetone

was added; this mixture was shaken vigorously for several minutes and centrifuged. The supernatant was then decanted into a 250-ml round bottom flask and the acetone evaporated under vacuum. The remaining aqueous liquid was added to a 500-ml separatory funnel and extracted three times with 50 ml methylene chloride. The methylene chloride extracts were pooled in a 50-ml round bottom flask with 20 g of anhydrous sodium sulfate and stored in the dark for 24 h. The methylene chloride was then decanted into a 250-ml round bottom flask and evaporated under vacuum. The residue was dissolved in 3 ml toluene. Water samples underwent a similar extraction procedure except that acetone was not added, and the samples were extracted three times with 15 ml methylene chloride. Plasma samples were cold spiked and extracted three times with an equal volume of toluene. In some cases, a viscous emulsion layer formed that contained most of the trifluralin. To break the emulsion the sample was stored at -20°C until frozen and then immediately centrifuged at 1000 x g for 5-10 min.

The toluene extracts were spotted on TLC plates and developed in carbon tetrachloride. The trifluralin bands were removed and eluted with 500 µL toluene. An aliquot was removed and diluted up to 100-fold in preparation for analysis by GC; the remaining toluene was added to scintillation cocktail and counted. GC-ECD analysis was performed.

Results

In water exposed trout trifluralin was rapidly absorbed with maxima in the blood occurring between 4-8 hours and then slowly declining. The authors state that trifluralin concentrations in the body of the trout continued to rise up to 96-h exposure, however, there appeared to be an obvious leveling off between 48 and 96 hours according to the figures contained in the paper. The experimentally derived BCF was 2280. The half-life varied between 2 and 12 d.

Yockim, R.S., A.R. Isensee, and E.A. Walker. 1980. Behavior of Trifluralin in Aquatic Model Ecosystems. Bull. Environ. Contam. Toxicol. 24(1):134-141

This study was designed to evaluate uptake via two different exposure systems:

1. A recirculating static model ecosystem. Trifluralin was introduced into the ecosystem by incorporating it with soil at field application rates. The treated soil was placed into a large chamber of the ecosystem tanks and then flooded with 16 L of water. Unlabelled and [^{14}C]-trifluralin concentrations were 1, 10 and 100 mg/kg. After flooding the soil, ca. 100 daphnids (*Daphnia magna*), 24 snails (*Helisoma sp.*) and 1 g of algae (*Oedogonium cardiacum*) was added along with 24 mosquito fish (*Gambusia affinis*) contained within a separate small chamber.
2. A continuous dosing system was designed to mimic the direct effects of trifluralin application to the ecosystem. Trifluralin was continuously injected directly into the model ecosystem at concentrations of 1, 10 and 100 $\mu\text{g/L}$ and snails, algae and mosquito fish added as for study 1 above.

Biota were sampled at 1, 3, 7, 15 and 30 days after treatment. Water samples were extracted concentrated and analyzed by LSC. Snails, fish and daphnids were homogenized in methanol and analyzed via LSC of the homogenate. Algae was combusted followed by LSC. TLC was used to determine identity of the ^{14}C . BAFs were determined based on the assumption that all the ^{14}C was trifluralin, therefore, included transformation products of trifluralin.

Results

In both experiments there was a great deal of variability in the concentrations of trifluralin accumulated by biota, especially in the lower exposure concentrations (1 and 10 mg/kg (Exp. 1) or 1 and 10 $\mu\text{g/L}$ (Exp. 2) systems. In experiment 1 the coefficient of variation (CV) ranged

from 71-150%, 30-126% (4 of 5 sample days ranged from 81 -126%) and 13-29% in the 1, 10 and 100 mg/kg, treatments, respectively. In experiment 2 the CVs ranged from 83-133%, 11-120% (with 4 of 5 sample days ranging from 37 -120%) and 14-33% in the 1, 10 and 100 µg/L treatments, respectively.

In the first experiment, the amount of trifluralin available for accumulation by biota depended on the rate of desorption from the soil. The BAFs after 30 days in the 100 ppm treatment were: daphnia, 30; snails, 20; fish, 70; and algae, 220. No toxic effects were detected in this experiment with any of the biota. BAFs in the 1 and 10 mg/kg treatments ranged from 300-5750 (n=1>5000), 140-1000, 110-1250 and 210-1000 in the fish, snails, daphnia and algae, respectively (Table 3) (BAFs taken from tables in Yockim et al. 1980, text of paper shows different numbers).

In the second experiment, where a continuous dose of trifluralin was introduced into the ecosystem, the BAF values on day 30 were fish, 3810; snails, 870; and algae, 4730 in the 100 µg/L treatment. There were several toxic effects observed in fish and algae. BAFs in the 1 and 10 µg/L treatments ranged from 1800-11000 (n= 4>5000), 130-2000 and 1000-23640 (n=2>5000) in the fish, snails and algae, respectively (Table 3) (BAFs taken from tables in Yockim et al. 1980, text of paper shows different numbers).

Table 3. BAFs observed in static soil incorporated and renewal uptake experiments from data provided in tables in Yockim et al. (1980).

| Biota | Treatment Level and Sample Days | Static Soil Incorporated | Renewal Study |
|---|--|--------------------------|-------------------------|
| <i>Gambusia affinis</i> Western mosquitofish | 1 and 10 mg/kg trts, Sample Days: 1-15 100 mg/kg trt, Sample Day 1-30 | 300-5750 70-1150 | 1800-11000 1190-4050 |
| <i>Helisoma sp.</i> Ramshorn snail | 1 and 10 mg/kg trts, Sample Days: 1-15 100 mg/kg trt, Sample Day 1-30 | 140-1000 20-150 | 130-2000 270-1590 |
| <i>Daphnia magna</i> Water flea | 1 and 10 mg/kg trts, Sample Days: 1-15 100 mg/kg trt, Sample Day 1-30 | 110-1250 30-630 | Not performed |

| | | | |
|--|--|----------------------|------------------------|
| <i>Oedogonium cardiacum</i> Green algae | 1 and 10 mg/kg trts, Sample Days: 1-15 100 mg/kg trt, Sample Day 1-30 | 210-1000 160-1030 | 1000-23640 280-4730 |
|--|--|----------------------|------------------------|

Conclusions

Concentrations of trifluralin in biota from the lower treatments of the static soil-incorporated ecosystems (1 and 10 mg/kg) were extremely variable and the one BAF value >5000 had a coefficient of variation (CV) of 98%. In addition, larger BAFs were determined in biota prior to equilibrium in the systems. Therefore, the BAFs reported for the highest treatment concentration are considered and not the lower treatments where outliers would be disproportionately influencing the calculations. The same factors appeared to influence the BAFs calculated for the flow-through renewal ecosystem. The BAFs >5000 had CVs of 69, 91, 120, 133 and 210%. Only one BAF>5000 (5710 in fish) had a CV of 14% indicating much tighter data, however, this value was determined on day 7 when concentrations of trifluralin were still increasing in the system (a steady state appeared to be reached on day 15).

The differences between the two systems were probably related to the decreased availability of soil-incorporated trifluralin due to adsorption in the first experiment and the availability of trifluralin in the water when added to the system by continuous input in the second experiment. A very important difference between the two systems was the toxic effects of trifluralin on the algae and fish during the second experiment. It was the author's contention that the risks of trifluralin in the aquatic ecosystem are greatest when there was a continuous input of trifluralin. With an occasional soil-incorporated input, the transformation processes would minimize the risk. BAFs were also much lower in the static soil-incorporated systems and this would appear to be a much better mimic of the entry method for trifluralin than a continual input.

Kearney, P.C., A.R. Isensee and A. Kontson. 1977. Distribution and degradation of dinitroaniline herbicides in an aquatic ecosystem. Pest. Biochem. Physiol. 7:242-248. PMRA 1240476.

Methods

Matapeake loam soil was treated with 0.1 mg of trifluralin and 1 μCi of ^{14}C -trifluralin, via 10 mL of benzene carrier, evaporating the solvent and mixing the soil thoroughly. The spiked soil was then added to 4-L aquaria filled with “standard reference water”. The treated soil was placed in the bottom of the aquaria and about 100 *Daphnia magna* eight snails (*Helisoma* sp.) and a few strands of algae (*Oedogonium cardiacum*) and 10 mL of old aquaria water which contained various diatoms, protozoa and rotifers added to each aquarium. Duplicate water samples were taken at 3 to 4-day intervals and assayed for ^{14}C using LSC. After 20 days, samples of daphnids were removed for analysis and two mosquito fish (*Gambusia affinis*) were added. All remaining biota were removed 3 days later. Aquaria were maintained at 22°C.

Fish were also exposed to trifluralin in aquaria that were exposed to sunlight, subdued light and dark conditions.

Tissues were homogenized in methanol and analysed by LSC. TLC analysis of water and certain tissues was performed. Concentrations were based on ^{14}C and not on parent compound

Results

BCFs were 276, 400, 92 and 33 in algae, snails (not flushed prior to analysis), daphnids and fish, respectively. BCFs in fish exposed to different light conditions were 33, 100, and 455 in the sunlight, subdued light and dark treatments, respectively.

Conclusions

Because the biota samples were not characterized using methods capable of determining the amount of parent compound present the actual amounts of trifluralin (as parent compound) present in the samples is unknown. However, it is likely that the BCFs are over-estimated because trifluralin would have transformed to some degree during the study.

Parrish, P.R., E.E. Dyar, J.M. Enos, and W.G. Wilson. 1978. Chronic Toxicity of Chlordane, Trifluralin, and Pentachlorophenol to Sheepshead Minnows (*Cyprinodon variegatus*). EPA-600/3-78-010, U.S.EPA, Gulf Breeze, FL. 53 pp. (U.S.NTIS PB-278269)

The bioconcentration of trifluralin was determined in sheepshead minnows (*Cyprinodon variegates*) during a reproductive toxicity test over two generations of continuous exposure in seawater. The temperature was maintained at $30 \pm 1^\circ\text{C}$ by heating the incoming seawater. Fish eggs were fertilized and hatched in the laboratory. Embryos were placed in an incubator cup and were suspended in the test aquaria. The population was reduced to twenty fish (28 days old) per aquarium. Fish were then separating into at least two spawning groups (two males and three females) for 10 days. Eggs were removed, collected and placed in incubator cups in the aquaria as described for the previous generation. Fish were collected for residue analysis as adults alive at the end of the respective exposure; juveniles alive at the end of the 28-day growth period; and eggs and embryos randomly collected during the spawning periods.

Weighed groups of whole fish were homogenized and analysed.

Trifluralin was accumulated by parental fish during the 166-day exposure and by 28-day old F₁ juveniles. Reported bioconcentration factors (based on measured concentrations) for parental fish ranged form 4,500x – 11,500x (Table 4) and bioconcentration factors for juveniles ranged from 1,500X-11,500X (Table 5). No eggs/embryos were analysed.

Table 4. Concentrations of trifluralin in surviving adult sheepshead minnows (*Cyprinodon variegatus*) exposed for 166 days. Average tissue residues are whole-body, wet-weight. Duplicate analyses of a pooled sample from each treatment were performed.

| Measured Concentration | | | |
|------------------------|---------------|----------------------|-------------------|
| Water (µg/l) | Tissue (µg/g) | Concentration Factor | Comment |
| Control | 0.5 | - | - |
| Solvent Control | 2.6 | - | - |
| 1.3 | 15 | 11,538 | - |
| 4.8 | 34 | 7,093 | - |
| 9.6 | 46 | 4,792 | Only one analysis |
| 17.7 | 79 | 4,463 | Only one analysis |

Table 5. Concentrations of Trifluralin in Surviving 28-day old juvenile sheepshead minnows (*Cyprinodon variegatus*). The fish hatched from embryos produced during the first spawning period (days 113-122). Mean (and standard deviation) tissue residues are whole-body, wet-weight. Duplicate analyses of each pooled sample from duplicate aquaria A and B were performed.

| Measured Concentration | | | |
|------------------------|---------------|----------------------|-------------------|
| Water (µg/l) | Tissue (µg/g) | Concentration Factor | Comment |
| Control | 0.9 ± 0.3 | - | Four analyses |
| Solvent Control | 16 ± 11 | - | Four analyses |
| 1.3 | 15 ± 14 | 11,538 | Four analyses |
| 4.8 | 14 ± 7 | 2,917 | Four analyses |
| 9.6 | 14 ± 4 | 1,458 | Four analyses |
| 17.7 | 75 | 4,237 | Only one analysis |

The results of this study indicate that there is a potential for trifluralin to bioconcentrate and it should be noted that the BCF values reported in the two lowest concentrations exceeded 5000. Other factors to consider when looking at this data include that the highest BCF values are reported only in the lowest concentrations tested and are not consistent with the BCF values reported in the higher concentration groups. The standard deviation reported was 93% for the lowest concentration in Table 5. It is noted tissue concentrations for juveniles are similar in the

solvent controls (which appear to be contaminated) and in the three lowest concentrations, suggesting exposures were not well controlled or samples were mislabeled/mixed during analyses. This suggests that resulting BCF values may not be accurate. This study examined continuous water-borne exposure of trifluralin only and did not examine depuration and metabolism and the same BCF value is reported for both the parent and juvenile fish in the 1.3 µg/l concentration. This is suspicious given the variability expected between samples even in the same treatment group. However, this value cannot be confirmed as the raw data is not available. The results of this study although indicative of bioconcentration should be used with great caution as there appears to be high variability in measured concentrations and anomalous results across concentrations. The contamination of controls is particularly troubling.

Kanazawa, J. 1981. Measurement of the bioconcentration factors of pesticides by freshwater fish and their correlation with physicochemical properties or acute toxicities. Pestic. Sci. 12(4):417-424. PMRA 1821933.

Bioconcentration factors for trifluralin in topmouth gudgeon (*Pseudorasbora parva*) were measured under continuous flow conditions in the laboratory. This was conducted in conjunction with the determinations for 14 other pesticides.

The water used was tap water, purified by passing through a water cleaner which included an active carbon filter. The pH was 6.8 and the total alkalinity of the water was 32 mg/L (calculated as CaCO₃). A constant flow micropump was used to obtain a continuous flow of test chemical solution. A glass aquarium tank (45 x 24 x 30 cm) containing 20L of water was used for the experiment. Technical grade trifluralin was used and a fresh stock solution (2.0 mg/ml) was prepared in acetone on the day of testing. Aqueous solutions of pesticide, containing 0.5-2.0 mg/L were prepared by diluting a stock solution with dechlorinated water; these aqueous

solutions were diluted continuously with 100 times their volume of clean water and poured into the aquarium tank. The concentration of test pesticide in the aquarium water was thereby maintained at 5-20 pg/L throughout the experiment. The flow rate of water was adjusted to about 300 ml/min and the temperature was maintained at $20 \pm 2^\circ\text{C}$. Aquarium water was aerated continuously during the experiment.

Test fish were collected from the Inari River in Ibaraki Prefecture; they were 4-8 cm in length and weighed between 2 and 5 g. The fish were acclimatised in the same aquarium tank for about a month before the experiment. After 15-20 fish had been placed in the aquarium tank and reared for 14 days, they were transferred into clean flow water and reared for a further 30 days.

Commercial day food was given once a day throughout the experiment.

At the fixed sampling time, two fish were taken, washed with running water and weighed. After adding anhydrous sodium sulphate and acetonitrile, the fish were blended in an Omni-mixer for 3 min and filtered through a 0.5-cm layer of Celite-545 on a glass filter. The filtrate was concentrated below 50°C under vacuum. The residue was dissolved in hexane, transferred to a 100-ml separating funnel, and extracted with acetonitrile. The acetonitrile extracts were combined, concentrated, and the product dissolved in hexane and then eluted through activated Florisil. The eluant was concentrated under vacuum, dissolved in acetone and analysed using GLC-ECD.

For the determination of pesticides in water, 500-ml samples of water were mixed with 100 ml of 4% sodium chloride and extracted with dichloromethane. The extracts were combined and concentrated under vacuum. The residue was dissolved in hexane or acetone, and examined by GLC-ECD. Recoveries of the pesticides from fortified fish were $>75\%$ at the 0.1-2 mg/kg level;

from tap water recovery was >88 % at the 10-100 pg/L level.

Results

There were no specific results supplied for trifluralin concentrations in fish or water as the study also determined BCFs for 14 other pesticides. Therefore, there is no real data to review.

According to the authors, pesticides with higher BCFs like trifluralin showed a steady increase in concentrations in fish with equilibrium resulting between 7 to 14 days. There is no way to determine if this was the case for trifluralin with the results included in the paper.

The BCF determined for the topmouth gudgeon was 3142.

Reinbold, K.A. and R.L. Metcalf. 1976. Effects of the synergist piperonyl butoxide on metabolism of pesticides in green sunfish. *Pest. Biochem. Phys.* 6:401-412

Piperonyl butoxide (PB) inhibits the action of MFO enzymes which catalyze oxidation reactions, converting lipid-soluble compounds into more water-soluble compounds which can be excreted by an organism rather than it being stored in the lipid tissue. This study determined the effect of PB on the degradation pathways and rates of trifluralin (as well as two other pesticides).

Results

Green sunfish (*Lepomis cyanellus*) were reared from parents collected in a farm pond. Fish were gradually acclimatized to laboratory temperature and transferred to tap water over a period of five days. The fish were then held in the lab for two weeks before the study began. ¹⁴C-trifluralin was used in the study and was determined in water via LSC. Extracts were also used for TLC and preparation of autoradiographs. Three fish were sampled on each sample day and pooled for homogenizing. After extracting an aliquot was removed for LSC and also analyzed by TLC.

Parent equivalent in water were 0.0042 ppm and 0.0013 in the trifluralin and trifluralin + PB treatments, respectively on day 16. Trifluralin in sunfish was eliminated more rapidly when applied to the water alone compared to the trifluralin with PB. With trifluralin alone the sunfish contained only 0.005 ppm compared to 0.225 in the presence of PB after 16 days of exposure. Calculating BCFs from these data it is apparent that the sunfish had BCFs of 1.1 and 118 in the trifluralin and trifluralin +PB treatments, respectively.

In the PB treated systems there was a decrease in the amounts of NHC_3H_7 (transformation product of trifluralin) in the fish exposed to PB compared to the trifluralin alone treatment. It was clear that the trifluralin + PB treatment accumulation was increased 45 times and shows that the MFO system in green sunfish was able to metabolize trifluralin.

Macek, K.J., M.A. Lindberg, S. Sauter, K.S. Buxton, and P.A. Costa. 1976. Toxicity of Four Pesticides to Water Fleas and Fathead Minnows. EPA-600/3-76-099

Water fleas (*D. magna*) and fathead minnows (*P. promelas*) were chronically exposed to various concentrations of acrolein, heptachlor, endosulfan and trifluralin in separate flowing water systems. Exposures were through two complete life cycles for *Daphnia* and through at least one complete life cycle for fathead minnows.

In the trifluralin study, 26 day old fish were exposed to concentrations of 16.5, 8.2, 5.1, 1.9, and 1.5 $\mu\text{g/L}$ for 425 days via by proportional diluters.

Details on the Fathead Minnow Chronic Toxicity Study:

In each test, forty fish were randomly distributed to each test chamber. Cumulative mortality and total length of live fish were determined after 30 and 60 days. After 60 days exposure, the

fathead minnows were fed *ad libitum* twice daily with a commercially prepared trout starter food which was supplemented with daphnids and brine shrimp nauplii.

Five spawning sites of halved, 3 inch transite drain tiles had been placed in each tank when fish were released from growth chambers after 60 days. The tiles were placed concave surface down at locations that minimized the chance of encounters by separate egg guarding males. When spawning began, eggs were removed and counted. Fifty eggs from each spawn were oscillated in their corresponding test water by means of an egg cup and a rocker arm apparatus. Dead eggs were removed and counted each day until hatching was completed. Percent hatch was based on the number of live fry from 50 eggs.

Forty fry from the earliest two spawns in each tank with at least 80% live hatch were placed in the respective growth chambers. Cumulative mortality and total length of live fish were determined at 30 and 60 days photographically. Fry from all other spawns were discarded unless a growth chamber was later made available by termination of 60 day old fry.

Parental fish were sacrificed after all spawning had ceased for one week. Total length, weight, sex and gonadal condition was determined for each fish and three samples of eviscerated fish per concentration were retained for residue analysis in the test with trifluralin.

Residue Analysis and BCF Calculation:

Water samples were extracted with methylene chloride and fish tissues were ground and extracted with hexane-acetonitrile. Trifluralin residues was analysed from by GC-ECD. At study termination (425 days), three samples of pooled eviscerated carcasses of terminated adult fathead minnows in each concentration of trifluralin with surviving adults were analysed to determine residues in the fish. Results of these analyses indicate that the amount of trifluralin residue accumulated is approximately 1000X the concentration in water, is directly proportional

to the level of exposure, and that this response is essentially linear over the range of concentrations tested. The BCF values were 961, 1333 and 889 in the 5.1, 1.9 and 1.5 µg/L concentrations.

Sanborn, J.R.. 1974. The Fate of Select Pesticides in the Aquatic Environment. EPA-660/3-74-025

The behaviour of several pesticides including trifluralin was studied in a model ecosystem using a sand-water interface. The interface consisted of sterilized white quartz sand and standard reference water. Sorghum was grown in the sand and then the leaves were treated with radiolabeled trifluralin. After the sorghum was treated, saltmarsh caterpillar larvae were added to eat the treated plant and to disperse the chemical into the test ecosystem. The water contained several freshwater organisms: snails, water fleas and green filamentous algae. After 27 days, mosquito larvae were added and three days later a mosquito fish was added to the final segment of the system. At the end of 33 days the entire system was taken apart and the organisms and water were analysed.

A second similar system was also studied using soybean which is less sensitive to trifluralin and a direct application method to sand to mimic the application of trifluralin to the field. Since trifluralin was not applied to the leaves in this system, caterpillars were not introduced into the system. The results from both systems were compared.

The author stated that data for the water portion of the model ecosystem support the role of the caterpillar in spreading the trifluralin and metabolites in the system as the total radioactivity in the water at the end of the experiment was about 6.4x greater in the sorghum-treated ecosystem as compared with the sand-treated system. Apparently, trifluralin was adsorbed onto the sand

and therefore does not dissolve in the water. In contrast to the approximately 6-fold difference in total radioactivity in the water of the sorghum-treated system, the amount of parent trifluralin in the water was only 1.5x greater in the sorghum treatment than in the sand treatment.

The bioconcentration factors calculated for each treatment were different. The BCF values reported for trifluralin in the sand study were 4,200 and 153,000 in the fish and the snail respectively. Corresponding values in the sorghum study were 930 and 17,700.

The authors speculated that the lower BCF values in the sorghum were due to the phototransformation of trifluralin on the leaves in addition to the presence of the caterpillars which degraded trifluralin. The author suggested that the snail was not capable of degrading trifluralin.

The validity of the calculated BCF values is questionable. Trifluralin only made up 0.7% and 2.7% of the total radioactivity in the water at test termination in the sorghum and sand study, respectively. Since the BCF values were calculated based on a single analysis of trifluralin concentrations in the water and biota at test termination and water concentrations were continuing to decrease over time as evidenced by the presence of metabolites in both water and biota, it is expected that the BCF estimates are artificially high. There was also no evidence that the test system had reached equilibrium prior to the study termination and the calculation of the BCF values.

The study lacks the necessary scientific rigour and although indicative of potential bioaccumulation, is not suitable for determination of BCF values for use in a regulatory context. The results of the spiked sand experiment suggest that exposure route (water vs. sediment) affects bioconcentration factors of trifluralin.

Bioaccumulation Factors Obtained from the Field

Spacie, A. and J.L. Hamelink. 1979. Dynamics of trifluralin accumulation in river fishes. *Env. Sci. Technol.* 13:817-822. PMRA 1152024.

Methods

The paper describes the accumulation of trifluralin in a natural fish population from the Wabash River, Indiana upstream and downstream of a chemical plant manufacturing trifluralin. Surface river water was collected in 4-L amber glass bottles and stored at 10°C. Fish were captured using nets or via electroshocking. Whole fish were dissected and frozen and most residue analyses were performed on adipose tissue from the viscera. Whole fish and cross-sections were also analyzed on some samples.

River water samples were pooled depending on the concentrations expected. Three litre water samples were extracted with 200 mL of hexane and then the hexane was decanted through anhydrous Na₂SO₄. Hexane fractions were combined and concentrated via rotoevaporation to approximately 10 mL and passed through deactivated florisil, adjusted to volume and analyzed by GLC-ECD. Trifluralin was confirmed by GLC-MS. Recovery of spiked water was 83±7%. Reported concentrations were corrected for daily blanks and extraction efficiency.

Adipose tissue from fish (200-300 mg) was ground with 10-15 g of anhydrous Na₂SO₄, transferred to a glass funnel and eluted with 30-40 mL of hexane. The hexane extract was analyzed by GLC as above. Whole fish, muscle and viscera samples were ground with dry ice, then dried with anhydrous Na₂SO₄ and extracted as above with hexane. Recovery was “essentially” 100% and precision for the tissue extraction was ±5%. Lipid was determined via freon extraction under subdued light to prevent loss of trifluralin.

Rates of trifluralin uptake and depuration were also determined in the laboratory using fathead minnows exposed in tanks at 20 µg/L reagent grade trifluralin at 19.5 to 21.5°C. The solution was not refreshed during the uptake phase of the study. Six fish were removed at 5, 10, 20 and 40 h for analysis. At 40 h the spiked solution was removed and the tank filled with clean water and refreshed at a rate of 1L/min. Trifluralin residues were analyzed as above.

Clearance rates in fish from the Wabash River were determined by comparing concentrations of trifluralin in fish prior to, and 2 to 8 weeks after carbon treatment of the effluent was initiated at the manufacturing plant.

Results

Residue levels in fish fat were similar for all species regardless of size, sex or feeding habits.

Wet wt. trifluralin burdens in whole fish were calculated from the lipid based concentrations.

This would not be acceptable by today's standards.

Fish bioconcentration factors (on a wet wt. basis) estimated from field data where trifluralin was present downstream of a manufacturing plant were: sauger (*Stizostedion canadense*), 5,800; shorthead redhorse (*Moxostoma macrolepidolum*), 2800; and golden redhorse (*M. erthrurum*), 1,800. An experimental value of 6000 for fathead minnows (*Pimephales promelas*) was determined (Spacie and Hamelink 1979). These BCF values suggest the potential for bioconcentration in aquatic organisms is high.

Calculated clearance rates from fish captured prior to the initiation of carbon filtration of the effluent compared to those captured 2 to 8 weeks after carbon filtration showed that half-lives ranged from 22-31 days in sauger, 17-57 days in shorthead redhorse, 23 days in golden redhorse and 3 days in fathead minnows (laboratory study). Clearance rates in the fathead minnow laboratory study were likely faster compared to the other fish species because the fathead

minnows were placed into unspiked water, whereas, the other fish species may have been still exposed to trifluralin in the river water even though the carbon filtration system at the manufacturing plant decreased trifluralin in the effluent by 99.7%.

The authors calculated the K value for the fish within the Wabash River which is defined as a BCF at an unsteady state, i.e., the fish from the Wabash River had not reached an equilibrium point with the water (trifluralin concentrations in fish were still decreasing). K values for sauger, shorthead redhorse, golden redhorse and minnows were 87000, 95000, 27000 and 5100, respectively. They remarked that the K value for minnows was very similar to the BCF for minnows (6000 vs. 5100, respectively) and suggested that the smaller minnows were able to reach equilibrium faster than the larger fish thus, the K values represent a temporary condition and are not an estimate of the BCF. This is important in other studies as residue data of larger fish can lead to an overestimate of the BCF if concentrations in the exposure media are still decreasing.

The field portion of the study also examined residues at two trophic levels. Nine saugers were found to contain undigested whole fish (minnows) in their stomachs. The median residue content of the whole minnows was 10.78 mg/kg. The sauger which had eaten them contained a median of 6.37 mg/kg body weight. There was no significant difference between the two groups, suggesting biomagnification does not occur with trifluralin.

Spacie and Hamelink (1979) provided four other BCFs for fathead minnow (3261 and 1060), mosquitofish (1294) and rainbow trout (1030). These were derived from a laboratory based exposure and were determined based on ratio of kinetic rate constants, determined in a chronic exposure test (the fathead minnow values), or were predicted from a solubility correlation (mosquitofish) or partition correlation (rainbow trout).

Conclusions

The study was completed in 1975 and considered fish populations that were exposed to trifluralin via effluent from a manufacturing plant. Although this does provide information on the potential BCF or BAFs in natural fish populations this is unlikely to mimic conditions where trifluralin is registered for use as an agricultural pesticide. In addition, the clearance rates calculated for the fish from the river are over-estimated because the fish remaining in the receiving waters of the effluent from the manufacturing plant did not have sufficient time to equilibrate their body burdens in the short time between introduction of the treatment and subsequent sampling (even though trifluralin concentrations in water were reduced 99.7% via carbon filtration).

The similarity of the predicted BCFS from correlations to the results observed in the Wabash River demonstrated to the authors that existing partition correlations were adequate predictors of BCFs for the purpose of chemical hazard evaluation.

Residues measured in a predatory fish and residues in the undigested minnows in their stomachs were found not to be significantly different (i.e., no difference in levels of trifluralin between two trophic levels).

It should also be noted that the authors calculated wet wt. body burdens from the lipid based concentrations which would also increase the error in body burdens in fish.

Lehotay, S.J., J.A. Harman-Fetcho and L.L. McConnell. 1998. Agricultural pesticide residues in oysters and water from two Chesapeake Bay tributaries. Mar. Pollut. Bull. 37: 32-44. PMRA 1415182.

Two tributaries of Chesapeake Bay, Maryland were selected for this preliminary study to determine pesticide residues in oyster tissues as part of the Mussel Watch Project. The Patuxent River runs through agriculture, urban and suburban areas and the Choptank River runs through

mainly agriculture and rural land before emptying into Chesapeake Bay. Both tributaries have oyster bars at approximately 5.5 m depth. Oyster (*Crassostrea virginica*) and water samples were collected on monthly, biweekly or weekly intervals from February to November 1997 with increased sampling effort taking place when pesticide concentrations were expected to be highest in the water.

Oyster samples were collected by dredging and 10-12 adult oysters larger than 3.5 inches were scrubbed, rinsed with water and shucked. Each oyster sample was fortified with deuterated phenanthrene solution, homogenized and stored at -20°C until analyzed. Water samples were taken from a depth of 3.7 m over the area where the oysters were collected and stored in 18 L stainless steel canisters.

Solid-phase extraction (SPE) with polymer-based ENV+ cartridges was used for extraction of water samples, and the results reported by the authors were for the dissolved phase only. Oysters were blended with acetonitrile and a series of SPE cartridges were used for clean-up. Samples of water and oysters were analyzed by GC with ion-trap mass spectrometry detection.

Results

Trifluralin was detected in oysters at concentrations ranging from 0.007 to 0.35 ng/g wet weight in two different river systems. The Patuxent River oysters had concentrations averaging 0.073 ± 0.070 ng/g wet weight (n=20) and the Choptank River oysters had concentrations averaging 0.15 ± 0.12 ng/g wet weight (n= 13). Maximum concentrations were observed in June and early July which corresponds to both increased lipid content in oysters as well as trifluralin application timing. Trifluralin accumulated in oyster tissue soon after expected agriculture application periods and then depurated “fairly rapidly” in the oysters, suggesting that trifluralin may be metabolized and/or excreted by oysters (Lehotay et al. 1998). Concentrations of

trifluralin in water were very similar between the two sites at 0.30 ± 0.12 ng/L and 0.30 ± 0.18 ng/L in the Patuxent and Choptank Rivers, respectively.

Results and Conclusions

Using the mean water concentrations supplied by the authors and the range of concentrations of trifluralin in oysters, the BCFs ranged from 23.3 to 1167 in both river systems. This provides a rough estimate of the BCFs observed in oysters in this marine system, however, it should be noted that water concentrations at specific sampling times may have been much lower than the mean values used to determine the BCF. But using the mean water concentrations may be more indicative of the exposure time required to accumulate trifluralin in the oysters.

Muir, D.C.G. 2006. Unpublished Data, based on: Spatial/Temporal trends of current use pesticides in surface waters and precipitation in Ontario, -2003-2005. Environment Canada Pesticide Science Fund (PSF) project summary report. PMRA #1403269

Muir (2006) sampled zooplankton from three lakes located in southwestern and north/central Ontario in 2003 and 2004. One of three lakes contained measurable concentrations of trifluralin in the zooplankton. Calculated bioaccumulation factors (BAFs) for trifluralin in the zooplankton samples ranged from 255 to 4200 on a wet weight basis and 152,700 to 1,575,000 in zooplankton on a lipid weight basis. Muir (Dr. Derek Muir, Environment Canada, personal communication, March 14, 2007) states that confidence levels in the lipid based BAFs may be over or underestimated by at least 10,000 due to errors measuring the small percentages of lipid contained in the zooplankton.

U.S. EPA 2008 -The National Study of Chemical Residues in Lake Fish Tissue.

<http://www.epa.gov/waterscience/fish/study/>. Validated 20 August 2008.

The U.S. EPA conducted a four year monitoring study to determine pesticide concentrations in predator and bottom dwelling fish from various locations across the contiguous U.S.A.

Sampling was apparently done across the US including “significant agricultural areas” where “trifluralin is used extensively”. The summary provided shows low detection frequency of trifluralin in fish tissues (10%, 3%, 0.9% and 0.7% in 2000, 2001, 2002, 2003, respectively) and a maximum concentration of 36 µg/kg. The limit of detection was 10 µg/kg. Only one predatory fish was found to contain trifluralin (11.3 µg/kg).

Evenset, A., G. N. Christensen, T. Skotvold, E. Fjeld, M. Schlabach, E. Wartena and D. Gregor. 2004. A Comparison of Organic Contaminants in two High Arctic Lake Ecosystems, Bjørnøya (Bear Island), Norway. *Sci Total Environ.* 318: 125-141. PMRA # 1656267.

Methods

Trifluralin (along with other potential POPs) was determined in two high Arctic lakes, Ellasjøen and Øyangen on Bjørnøya (Bear Island), Norway. Sediment, plankton, benthic animals and Arctic char were sampled from both lakes. Trifluralin was quantified using HRGC combined with LSMS-NICI .

Results

Concentrations of trifluralin were below detection limits (<0.006 ng/g ww) in zooplankton from Lake Ellasjøen. It is unclear whether trifluralin was detected in chironomids (“The concentration pattern (*of all chemicals*) in chironomid samples mirrored the pattern observed in zooplankton...”). However, Anita Evenset (personal communication, Akvaplan-niva, Polar

Environmental Centre, Tromsø N-9296, Norway, August 18, 2009 and October 30, 2009) provided data showing that concentrations of trifluralin in chironomids was <0.075 ng/g ww, i.e., below the detection limit in chironomids from Lake Øyangen. There was also no specific data provided in Evenset et al. (2004) on concentrations of trifluralin in arctic char, however A. Evenset, (pers. com. Oct 30, 2009) provided data showing that trifluralin was detected in three of 6 fish and two of 4 fish in Arctic char from Ellasjøen and Øyangen lakes, respectively. According to A. Evenset (pers. comm.. Oct 30, 2009), they only analysed a “few fish” from each lake for trifluralin). The concentrations ranged from 0.02 to 0.03 ng/g ww in Ellasjøen and ranged from 0.01 to 0.02 ng/g ww in Øyangen. Three other fish had concentrations of trifluralin below level of quantitation (<0.012 , <0.008 and <0.03 ng/g ww) from Ellasjøen. Two other fish from Øyangen also had concentrations of trifluralin below level of quantitation (<0.012 and <0.01 ng/g ww).

Conclusions

Although it is impossible to calculate bioaccumulation factors for arctic char from the data provided it is apparent that trifluralin was never detected in zooplankton and chironomids and was detected in arctic char in approximately 50% of the samples from these remote lakes at concentrations just slightly above the levels of detection.

Summary of Bioaccumulation of Trifluralin

In total there are 23 reported BAF/BCFs from laboratory studies (not including multiple BAF/BCFs from different treatments within a single report) that determined the bioaccumulation and or bioconcentration of trifluralin in various biota (Table 1). Of those 23 reported BAF/BCFs

one BCF/BAF was reported to be >5000 in each of the following: Bluegill sunfish (1 of 3), fathead minnow (1 of 5), Sheepshead minnow (1 of 1) and Pouch snail (1 of 1).

In studies that determined BAF/BCFs in the field, one of five studies found a BAF >5000 (sauger, Table 2). Two other studies did not calculate BAFs but found that trifluralin concentrations were rarely detected or never detected.

Evidence of Local and Long Range Transport

Concentrations of Trifluralin in Air and Precipitation in Rural and Urban Canada

Waite, D.T., P. Bailey, J.F. Sproull, D.V. Quiring, S.F. Chau, J. Bailey and A.J. Cessna. 2005. Atmospheric concentrations and dry and wet deposits of some herbicides currently used on the Canadian Prairies. Chemosphere 58: 693-703. PMRA 1346404

Waite et. al. (2005) conducted high volume air sampling in the Canadian Prairies in 2002, in order to characterize the atmospheric concentration of 10 currently used herbicides, including trifluralin. In the 2002 sampling, trifluralin was detected in 38% of the samples analysed. Mean and maximum concentrations were 0.15 and 0.81 ng/m³, respectively. No apparent concentration pattern was observed during the sampling period, with concentrations fluctuating throughout the sampling period. Highest concentrations of trifluralin were consistently measured in the 30 m elevation samples compared to the 1 m and 10 m samples which the authors suggested was due to atmospheric transport from other application regions rather than local application sources (Waite et al. 2005).

In their study, Waite et al (2005), estimated the atmospheric loadings of the herbicides in the Canadian Prairies at an elevation of 30 m. For purpose of loading estimates, a hemi-ellipsoid of radii 300 km and 700 km was assumed with a 1 km height (Volume = $\frac{2}{3} \times \pi \times 200 \times 700 \times 1 = 439\,879 \text{ km}^3$). The east-west transect encompassed by this area spans the agricultural region of the Canadian prairies from Winnipeg to Calgary and the north-south transect from Waskesiu to the United States border. The average atmospheric loading for each pesticide was calculated by averaging the atmospheric concentration (1-m height) for Regina, Hafford and Waskesiu sites and average concentrations (1-, 10- and 30-m heights) at Bratt's Lake. The number, representing the average atmospheric concentration along the sampling transect, was multiplied by the

volume of the hemi-ellipsoid. The calculated atmospheric loading of trifluralin for 2002 was 75 kg during the week of the maximum detected concentration. The hemi-ellipsoid shape provides a conservative estimate of atmospheric loading compared with a box model that would assume a 1-km height rectangular shape.

The dry deposition rate was also determined in this study. Trifluralin deposits fluctuated throughout the sampling period with no obvious pattern, matching the atmospheric concentrations. Of six herbicides where deposition velocities were calculated, trifluralin was determined to be the lowest at 0.26 cm/s. A weak relationship was reported between the dry deposition rate (ng/m²/d) and the atmospheric concentrations for trifluralin ($r^2 =$ approximately 0.36). Waite et al. (2005) attributed the poor fit to the much lower concentrations and deposition rates which increase the intrinsic error within those measurements.

Harner, T. and P. Blanchard. 2006. Canadian Pesticide Air Sampling Campaign, Progress Report, (August, 2006). Environment Canada's Pesticide Science Fund. 72 pp. PMRA 1347826.

The Canadian Pesticide Air Sampling Campaign was initiated in 2003 through funding from Environment Canada (EC) Pesticide Science Fund (PSF) (Harner and Blanchard 2006). This project, which integrates the efforts of collaborators in several regions (Prince Edward Island, Québec, Ontario, Saskatchewan and British Columbia), assessed atmospheric levels of pesticides, especially currently used pesticides in agricultural and background regions across Canada. This 3-year air surveillance program consisted of two subprojects: 1. The Canadian Atmospheric Network for Currently Used Pesticides (CANCUP) (samples from Kensington, PEI, St. Anicet, QC, Baie St. Francois, QC, Egbert, ON, Vineland, ON and Abbotsford, BC and) and 2. An intensive field study in the Canadian Prairies (Prairie Study) (samples from Bratt's Lake, SK, Waskesiu, SK and Hafford, SK). Three sampling campaigns were undertaken

during the spring to summer of 2003 and during the spring to fall of 2004 and 2005. In 2003, the CANCUP sampling did not take place during peak application periods (spring). In 2004, air sampling did take place during the peak application periods and therefore, is more indicative of potential air concentrations during all periods of application and non-application. Samples were collected using high volume and passive air samplers and precipitation and dry/wet deposition collectors. Sample analysis was conducted through several external laboratories. The progress report summarized the results from 2003 and 2004 campaigns. The data for the 2005 samples were not available during the process of this review.

Description of Sampling Sites

Table 6 and Table 7 describe the sampling sites and the sampling periods for 2003 and 2004, respectively.

Table 6. Description of the sampling sites and periods for the 2003 Canadian air sampling campaign

| Sampling site | Latitude | Longitude | Description | Sampling period |
|------------------------------|-----------------|------------------|--|-------------------------|
| Kensington, PEI | 46°25' N | 63°37' W | Heart of potato growing area. | Jul. 22 - Aug. 26, 2003 |
| St. Anicet, QC | 45°07' N | 74°17' W | Rural and agricultural area (corn, pasture land). | Jul. 22 - Aug. 19, 2003 |
| Baie St. Francois, QC | 46°05' N | 72°56' W | Wetland covered with mixed vegetation. Receptor site. | Jul. 22 - Aug. 19, 2003 |
| Egbert, ON | 44°14' N | 79°47' W | Rural and suburban area, surrounded by fields and mixed forest. | Jul. 22 - Aug. 19, 2003 |
| Bratt's Lake, SK | 50°16' N | 104°42' W | Rural and intensive agricultural area (cereals) with few trees. | May 12 - Aug. 13, 2003 |
| Hafford, SK | 52°43' N | 107°21' W | Agricultural area (cereals, oilseeds) with trees. Unseeded fields located adjacent to this site. | May 12 - Aug. 13, 2003 |
| Waskesiu, SK | 53°55' N | 107°21' W | In a national park, densely treed. No crops within 50 km of the site. Receptor site. | May 12 - Aug. 13, 2003 |
| Abbotsford, BC | 49°01' N | 122°20' W | Fraser Valley, pig and chicken farms and berry crops. | Jul. 22 - Aug. 19, 2003 |

Table 7. Description of the sampling sites and periods for the 2004 Canadian air sampling campaign.

| Sampling site | Latitude | Longitude | Description | Sampling period |
|------------------------------|-----------------|------------------|--|-------------------------|
| Kensington, PEI | 46°25' N | 63°37' W | Heart of potato growing area. | Jun. 24 - Sep. 28, 2004 |
| St. Anicet, QC | 45°07' N | 74°17' W | Rural and agricultural area (corn, pasture land). | May 4 - Jun. 29, 2004 |
| Baie St. Francois, QC | 46°05' N | 72°56' W | Wetland covered with mixed vegetation. Receptor site. | May 4 - Jun. 29, 2004 |
| Egbert, ON | 44°14' N | 79°47' W | Rural and suburban area, surrounded by fields and mixed forest. | May 18 – Jul. 13, 2004 |
| Vineland, ON | 43°11' N | 79°24' W | Intensive agricultural area (fruit, vegetables, wine). | May 21 – Jul. 23, 2004 |
| Bratt's Lake, SK | 50°16' N | 104°42' W | Rural and intensive agricultural area (cereals) with few trees. | May 19 – Aug. 4, 2004 |
| Hafford, SK | 52°43' N | 107°21' W | Agricultural area (cereals, oilseeds) with trees. Unseeded fields located adjacent to this site. | May 18 – Aug. 3, 2004 |
| Waskesiu, SK | 53°55' N | 107°21' W | In a national park, densely treed. No crops within 50 km of the site. Receptor site. | May 18 – Aug. 3, 2004 |
| Abbotsford, BC | 49°01' N | 122°20' W | Fraser Valley, pig and chicken farms and berry crops. | Apr. 28 – Jun. 1, 2004 |

In 2003, concentrations of trifluralin in Saskatchewan at Bratt's Lake ranged from ND (4 pg/m³) - 811, ND - 503 and 63.7 to 816 pg/m³ in air samplers positioned 1-, 10- and 30m above the soil surface, respectively (Table 8). Concentrations at Hafford and Waskesiu ranged from ND – 734 pg/m³ and ND-24.8 pg/m³, respectively (Table 8). Trifluralin concentrations in air at Bratt's Lake 1-m sampler ranged from ND-921 pg/m³ in 2004 (Table 9). Monthly average concentrations in 2004 at Bratt's Lake 1-m samplers were slightly higher compared to 2003 (Table 10). The lower concentrations observed in Waskesiu are likely due to the region being in a national park and further away from the intensive agricultural regions of Bratt's Lake and

Hafford. The fact that trifluralin was detected at Waskesiu indicates the potential transport of trifluralin from agricultural regions to non-target zones.

Concentrations of trifluralin in air at Abbotsford, BC ranged from ND to 117 pg/m³ and averaged 59.6 pg/m³ (Table 11) in 2004. Concentrations of trifluralin in air at Egbert, ON ranged from ND to 535 pg/m³ and averaged 241 pg/m³ (Table 12) in 2004. Concentrations of trifluralin in air at Vineland, ON ranged from ND to 660 pg/m³ and averaged 269 pg/m³ (Table 13) in 2004.

Concentrations of trifluralin in air at St. Anicet, QC ranged from ND to 374 pg/m³ and averaged 119 pg/m³ (Table 14) in 2004. Concentrations of trifluralin in air at Baie St. François ranged from 60.3 to 481 pg/m³ and averaged 248 pg/m³ (Table 15) in 2004. Concentrations of trifluralin in air at Kingston, PEI ranged from ND to 60.3 pg/m³ and averaged 16.8 pg/m³ (Table 16) in 2004. Trifluralin concentrations in air were higher in all sites in 2004 compared to 2003, although the increase at Kingston, PEI was not as dramatic as observed in the other CANCUP sampling sites (Table 17). The higher 2004 concentrations were likely associated with an earlier sampling campaign (April vs. late July in 2003) that would have captured pre-emergence applications. Highest monthly average concentrations were observed at Bratt's Lake for both 2003 (170 pg/m³) and 2004 (256 pg/m³) (Table 10) indicating that Saskatchewan is a major trifluralin source region in Canada. An annual usage of 132 tonnes of active ingredient in Saskatchewan was previously estimated by Yao et al. (2006), which is approximately eight times higher than in Ontario (17 tonnes a.i./yr). As observed in Waskesiu, SK, trifluralin was detected in significant quantities in Baie St. François, QC, a non-agricultural region, indicating the atmospheric transport of trifluralin to areas where it is not used.

Concentrations of trifluralin in precipitation were not detectable in Abbotsford, BC (Table 11), Egbert, ON (Table 12), St. Anicet, QC (Table 14), Baie St. François, QC (Table 15) and

Kingston, PEI (Table 16). Concentrations of trifluralin in precipitation at Vineland, ON ranged from 2.1 to 319 ng/L in 2004 (Table 13). Vineland, ON is an intensive agricultural zone, therefore, it is not surprising that trifluralin concentrations were detected in precipitation in this region. However, due to its low water solubility and fast photolysis rate in water (assuming photolysis rate would be equivalent in precipitation as in water) the presence of detectable levels of trifluralin in precipitation indicates that the levels observed at Vineland, ON were likely much higher initially than were reported.

Table 8. Concentrations of trifluralin (pg/m³) in air samples collected under the prairie study during the spring and summer of 2003^a

| | Bratt's Lake, SK | | | Hafford, SK | Waskesiu, SK |
|------------|------------------|-------------------|-------------------|------------------|------------------|
| | Air sample (1-m) | Air sample (10-m) | Air sample (30-m) | Air sample (1-m) | Air sample (1-m) |
| Max | 811 | 503 | 816 | 734 | 24.8 |
| Ave | 170 | 272 | 388 | 70.6 | 5.0 |
| Min | ND | ND | 63.7 | ND | ND |

^a The method detection limit (MDL) based on a sample volume of 2 500 m³ and an extract volume of 1 mL is 4 pg/m³

Table 9. Concentrations of trifluralin in air (pg/m³) samples collected at Bratt's Lake, SK in 2004 (1-m sampler).

| 19/05-26/05 | 26/05-02/06 | 02/06-09/06 | 09/06-16/06 | 16/06-23/06 | 23/06-30/06 | 30/06-07/07 | 07/07-14/07 | 14/07-21/07 | 21/07-28/07 | 28/07-04/08 | Max | Ave | Min |
|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-----|-----|-----|
| 283 | 177 | 164 | ND | 175 | 47.2 | 636 | 105 | 921 | 183 | 130 | 921 | 256 | ND |

Table 10. Comparison of Monthly Trifluralin Concentrations (pg/m³) in air samples collected in 2003 and 2004 at Bratt's Lake

| | 2003 | 2004 |
|------------|------------------|------------------|
| | Air sample (1-m) | Air sample (1-m) |
| Max | 811 | 921 |
| Ave | 170 | 256 |
| Min | ND | ND |

Table 11. Concentrations of Trifluralin in Air (pg/m³) and precipitation (ng/L) samples collected at Abbotsford, BC in 2004

| Air (pg/m-3) | | | | | | | Precipitation (ng/L) |
|--------------|-------------|-------------|-------------|-----|------|-----|----------------------|
| 28/04-05/05 | 05/05-12/05 | 12/05-26/05 | 26/05-01/06 | Max | Ave | Min | 21/04-26/05 |
| 52.4 | 117 | 68.8 | ND | 117 | 59.6 | ND | ND |

Table 12. Concentrations of Trifluralin in Air (pg/m³) and precipitation (ng/L) samples collected at Egbert, ON in 2004

| Air (pg/m ³) | | | | | | | | | | | Precipitation (ng/L) | | |
|--------------------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-----|-----|-----|----------------------|-------------|-----|
| 18/05-25/05 | 25/05-01/06 | 01/06-08/06 | 08/06-15/06 | 15/06-22/06 | 22/06-29/06 | 29/06-06/07 | 06/07-13/07 | Max | Ave | Min | 18/05-15/06 | 15/06-13/07 | Ave |
| 291 | ND | 535 | 501 | 216 | 90.3 | 44.6 | 248 | 535 | 241 | ND | ND | ND | ND |

Table 13. Concentrations of Trifluralin in Air (pg/m³) and precipitation (ng/L) samples collected at Vineland, ON in 2004

| Air (pg/m ³) | | | | | | | | | | | Precipitation (ng/L) | | |
|--------------------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-----|-----|-----|----------------------|-------------|-----|
| 21/05-27/05 | 04/06-11/06 | 11/06-22/06 | 22/06-25/06 | 25/06-02/07 | 02/07-09/07 | 13/07-16/07 | 16/07-23/07 | Max | Ave | Min | 21/05-25/06 | 25/06-23/07 | Ave |
| ND | 165 | 176 | 398 | 660 | 206 | 549 | ND | 660 | 269 | ND | 2.1 | 319 | 161 |

Table 14. Concentrations of Trifluralin in Air (pg/m³) and precipitation (ng/L) samples collected at St. Anicet, QC in 2004

| Air (pg/m ³) | | | | | | | | | | | Precipitation (ng/L) | | |
|--------------------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-----|-----|-----|----------------------|-------------|-----|
| 04/05-11/05 | 11/05-18/05 | 18/05-25/05 | 25/05-01/06 | 01/06-08/06 | 08/06-15/06 | 15/06-22/06 | 22/06-29/06 | Max | Ave | Min | 04/05-01/06 | 01/06-29/06 | Ave |
| 216 | 374 | 314 | 45.9 | ND | ND | ND | ND | 374 | 119 | ND | ND | ND | ND |

Table 15. Concentrations of Trifluralin in Air (pg/m³) and precipitation (ng/L) samples collected at Baie St. Francois, QC in 2004.

| Air (pg/m ³) | | | | | | | | | | | Precipitation (ng/L) | | |
|--------------------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-----|-----|------|----------------------|-------------|-----|
| 04/05-11/05 | 11/05-18/05 | 18/05-25/05 | 25/05-01/06 | 01/06-08/06 | 08/06-15/06 | 15/06-22/06 | 22/06-29/06 | Max | Ave | Min | 04/05-01/06 | 01/06-29/06 | Ave |
| 194 | 481 | 234 | NA | 240 | 177 | 60.3 | 347 | 481 | 248 | 60.3 | ND | ND | ND |

Table 16. Concentrations of Trifluralin in Air (pg/m³) and precipitation (ng/L) samples collected at Kensington, PEI in 2004

| Air (pg/m ³) | | | | | | | | | | | Precipitation (ng/L) | | |
|--------------------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|------|------|-----|----------------------|-------------|-----|
| 24/06-01/07 | 01/07-08/07 | 08/07-15/07 | 15/07-22/07 | 18/08-25/08 | 25/08-01/09 | 14/09-21/09 | 21/09-28/09 | Max | Ave | Min | 06/07-06/08 | 06/08-01/09 | Ave |
| 35.9 | ND | 38.3 | 60.3 | ND | ND | ND | ND | 60.3 | 16.8 | ND | ND | ND | ND |

Table 17. Comparison of trifluralin concentrations in air samples collected in 2003 and 2004 under CANCUP. Monthly average results (pg/m³).

| Abbotsford | | Egbert | | St. Anicet | | Baie St. Francois | | Kensington | |
|-------------|-------------|-------------|-------------|-------------|-------------|-------------------|-------------|-------------|-------------|
| 2003 | 2004 | 2003 | 2004 | 2003 | 2004 | 2003 | 2004 | 2003 | 2004 |
| 22/07-19/08 | 28/04-01/06 | 22/07-19/08 | 18/05-13/07 | 29/07-19/08 | 04/05-29/06 | 29/07-19/08 | 04/05-29/06 | 22/07-26/08 | 24/06-28/09 |
| 6.2 | 59.6 | 91.1 | 241 | 36.0 | 119 | 38.2 | 248 | 11.4 | 16.8 |

Grover, R., L.A. Kerr, K.E. Bowren and S.U. Uhan. 1988. Airborne residues of triallate and trifluralin in Saskatchewan. Bull. Environ. Contam. Toxicol. 40:683-688. PMRA 1415173.

Grover et al. (1988) sampled air in agricultural zones near Regina, SK in 1981 and Melfort, SK in 1981 and 1982. Concentrations of trifluralin in Regina in 1981 were <1 ng/m³.

Concentrations of trifluralin at Melfort in 1981 ranged from <DL to 15 ng/m³ with the maximum occurring on May 13 and in 1982 were <DL to 63 mg/m³, with the maximum occurring on June 15. Concentrations decreased to <20 ng/m³ after June 15 until October 1 when airborne residues increased in response to the fall application period (maximum concentration in October was 36 ng/m³). The authors concluded that trifluralin concentrations were higher in 1982 due to wetter conditions compared to 1981 which resulted in increased volatilization.

Hill, B.D., K.N. Harker, P. Hasselback, D.J. Inaba, S.D. Byers and J.R. Moyer. 2002. Herbicides in Alberta Rainfall as Affected by Location, Use and Season:1999 to 2000. Water Quality Research Journal of Canada 37(3):515-542. PMRA 1307559.

Hill et. al. (2002) detected trifluralin seven times (2.6% detection) in rainfall samples collected in Alberta in 1999. Due to the low number of detections, no further information was provided on the concentration ranges detected. Trifluralin was not detected in rainfall samples taken in 2000. However, the authors indicated through stability experiments that their collection system was not a reliable indicator of trifluralin in rainfall. They showed that trifluralin was completely lost from the sample bottles in a week. Considering the samples were collected on a rainfall event basis or over a few minor rainfall events or every 14 days maximum, it is surprising that they detected trifluralin at all in their samples.

Kumar, Y. 2001. Pesticides in Ambient Air in Alberta. ISBN 0-7785-1889-4. Report prepared for the Air Research Users Group, Alberta Environment, Edmonton, Alberta. PMRA 1311145.

Kumar (2001) analyzed air samples in Alberta between April 1999 and January 2000. Trifluralin was detected at all sites sampled. Concentrations ranged from <DL to 0.56 ng/m³ at all sites and detection percentages were 94, 35, 88 and 88% in Lethbridge, Lundbreck, Lacombe and Vegreville, respectively (Table 18).

Table 18. Concentrations of trifluralin in air in Alberta, 1999 to 2000 (Kumar 2001).

| Location | Concentration Range (ng/m ³) | % Detection |
|------------|--|-------------|
| Lethbridge | ND - 0.14 | 94 |
| Lundbreck | ND - 0.10 | 35 |
| Lacombe | ND - 0.56 | 88 |
| Vegreville | ND - 0.40 | 88 |

Hoff, R.M., D.C.G. Muir and N.P. Grift. 1992. Annual cycle of polychlorinated biphenyls and organohalogen pesticides in air in southern Ontario. 1. Air concentration data. Environ. Sci. Technol. 26:266-275. PMRA 1415180.

Hoff et al. (1992) also detected trifluralin in air in southern Ontario at Egbert, Ontario from July 1988 to September 1989. Samples were taken approximately every two days up to July 1, 1989 and then every 6 days after this point. Concentrations ranged from <DL to 3400 pg/m³, with a 52% frequency of detection. Annual average concentrations were calculated to be 270 pg/m³. The maximum concentration was found in June which coincided with its use pattern.

Donald, D. B., A. J. Cessna, E. Sverko and N. Glozier. 2007. Pesticides in Surface-Water Supplies in the Northern Great Plains. Environmental Health Perspectives. 115:8: 1183-1191. Canadian Arctic Contaminants Assessment Report II. http://ainc-inac.org/ncp/pub/phy/summ3a_e.html. Verified 20 Aug 2008. PMRA # 1656257.

Pesticide concentrations were determined in drinking water reservoirs and treated water in 15 communities in Manitoba, Saskatchewan and Alberta

Methods

Water samples were collected from water reservoirs near the centre of each reservoir at a depth of 2 m. In 2003, samples were collected every two weeks from early May to mid August and once in October, once in January 2004 and after spring runoff in April 2004 and 2005. Drinking water samples were collected simultaneously with reservoir samples in July 2004 and 2005.

Sample containers were 1-L amber glass bottles and were preserved with 2 mL of concentrated, sulphuric acid. Samples were stored at 4°C in the dark until analysis.

Water was extracted with dichloromethane. The extracts were concentrated and transferred to a test tube and 2mL of *iso*-octane was added. The sample was then evaporated to approximately 1 mL with nitrogen gas. The extracts were then cleaned up on deactivated florisil followed and the eluant concentrated and analyzed via GC-MS.

Results

Trifluralin was rarely detected in the sampled water, with 1% detection rate (2 detections in 163 samples). The maximum concentration was 1.0 ng/L which is below the reporting limit for this herbicide. The detection limit for trifluralin was 5.15 ng/L

Concentrations of Trifluralin in Remote Locations

Chernyak, S.M., C.P. Rice and L.L. McConnell. 1996. Evidence of currently-used pesticides in air, ice, fog, seawater and surface microlayer in the Bering and Chukchi Seas. Mar. Pollut. Bull. 32:410-419. PMRA 1415179.

And

Rice, C.P. and S.M. Chernyak. 1997. Marine arctic fog: an accumulator of currently used pesticides. Chemosphere 35:867-878. PMRA 1415176.

Chernyak et al. (1996) investigated the presence of currently used pesticides including trifluralin in the Bering and Chukchi (north of the Bering Strait) marine ecosystems in the summer of 1993. Seawater, air, marine fog, surface layer (or microlayer), and ice were sampled at various times. Trifluralin was not found above the detection limit in sub-surface seawater (n=9) or melted ice (n=1) or air samples (n=5). In the surface water microlayer, concentrations of trifluralin were 1110-1150 pg/L (n=2). Concentrations of trifluralin in fog condensates ranged from <DL to 25 ng/L (n=7), however, the authors indicate that there is uncertainty in the three detections of 2, 6, and 25 ng/L because the detections were less than twice the detection limits. In a closely related study, Rice and Chernyak (1997) sampled fog water (droplets >8 µm diameter), fog vapour (<8 µm in diameter) and particulates found in fog in the Bering and Chukchi Seas using a “dichotomous air sampler”. This sampler was designed to collect all fog droplets greater than 8 µm in diameter separately from fog droplets <8 µm in diameter and particulates. Rice and Chernyak (1997) did not detect trifluralin in fog water (>8 µm), however, they did detect trifluralin in the vapour phase (<8 µm) at 5 pg/m³ and in particulates at 0.4 pg/m³.

National Contaminants Program (http://www.ainc-inac.gc.ca/ncp/pub/phy/occtre8_e.html)

Concentrations of trifluralin have been detected in air in northern Canada during the National Contaminants Program (1993-1997) (http://www.ainc-inac.gc.ca/ncp/pub/phy/occtre8_e.html). Concentrations in air from Alert, Tagish and Dunai ranged from 0.03 to 2.92 pg/m³ (Table 19).

Table 19. Concentrations of trifluralin (pg/m³) detected in air in northern Canada (from http://www.ainc-inac.gc.ca/ncp/pub/phy/occtre8_e.html)

| Location | Mean | Minimum | Maximum |
|----------|------|---------|---------|
| Alert | 0.12 | 0.03 | 0.64 |
| Tagish | 0.16 | 0.04 | 2.92 |

Skov, H., R. Bossi, P. Wåhlin, J. Vikelsøe, J. Christensen, A.H. Egeløv, N.Z. Heidam, B. Jensen, H.P. Ahleson, L. Stausgård, I. Jensen, D. Petersen. 2005. Contaminants in the Atmosphere AMAP- Nuuk, Westgreenland 2002-2004. National Environmental Research Institute, Ministry of the Environment Greenland. NERI Technical Report, No. 547. 48 pp. PMRA 1346401

Trifluralin has also been detected at Nuuk, Greenland (southwest Greenland). Trifluralin was detected in 4 of 13 air samples at concentrations ranging from <DL to 0.60 pg/m³ (Skov et al. 2005). Concentrations are comparable across the Arctic indicating a uniformity of the contamination in the arctic atmosphere (Skov et al. 2005).

Welch, H.E., D.C.G. Muir, B.N. Billeck, W.L. Lockhart, G.J. Brunskill, H.J. Kling, M.P. Olson and R.M. Lemoine. 1991. Brown snow: A long range transport event in the Canadian Arctic. Environ. Sci. Technol. 25:280-286. PMRA 1415178.

Welch et al. (1991) documented the occurrence of a brown snow event near Saqvaquac Nunavut Territory (close to Chesterfield Inlet) in 1988. Brown snow is a euphemism for the transport of soil dust and deposition during a snowfall event. Although these episodes have been observed before in various regions in the Arctic, this was the first known sampling and analysis of the actual brown snow. Concentrations of trifluralin in melted snow and particulates (>1 µm) were 660 pg/L and 2.2 ng/g, respectively. A total concentration in melted snow was determined by summing the concentrations in melted snow and particulates and was calculated to be 764 pg/L. The brown snow event covered at least 20,000 km² with an estimated 4000 tonnes of soil dust depositing on the land and sea of the District of Keewatin. Back trajectory analysis of atmospheric currents, the clay mineral composition and organic composition (via microscopic analysis) of the dust suggested an Asian source for other compounds detected in the brown snow,

however, the presence of trifluralin and a shorter term southern wind flow may indicate that trifluralin was deposited from both Asian and North American sources.

Jantunen, L. M., F. Wong, T. F. Bidleman and G. Stern. Occurrence and Levels of Current-Use and Legacy Pesticides in Air: Leg 1 of ArcticNet 2007. http://www.arcticnet-ulaval.ca/pdf/posters_2007/jantunen_et_al.pdf. Verified 20 Aug 2008. PMRA #1656259.

Trifluralin was detected in all 11 air samples that were taken, at concentrations of 0.2 to 0.91 pg/m³. A full report was not available. This information, although of limited value due to its brevity, confirms that trifluralin is detected in air at remote sites. Concentrations of trifluralin in these sites are comparable to those found in the literature in other remote sites (0.03 to 2.92 pg/m³) and reported in RVD 2009-09.

Muir, D., C. Teixeira, and X. Wang. 2005. Atmospheric Deposition and Bioaccumulation of Current Use Pesticides in Remote Lakes in Ontario, Canada. SETAC abstract. <http://abstracts.co.allenpress.com/pweb/setac2005/document/56956>. Verified 21 Aug 2008. PMRA 1656260

There was very little information on the bioaccumulation or long range transport of trifluralin in this abstract that the registrant provided during the re-evaluation process in Canada.

Su, Y., H. Hung, P. Blanchard, G. W. Patton, R. Kallenborn, A. Konoplev, P. Fellin, H. Li, C. Geen, G. Stern, B. Rosenberg, and L. A. Barrie. 2008. A Circumpolar Perspective of Atmospheric Organochlorine Pesticides (OCPs): Results from six Arctic Monitoring Stations in 2000-2003. *Atmospheric Environment*. 42:4682-4698. PMRA 1656262.

This submission from the registrant provided only the following limited information in regards to the levels of trifluralin detected in air from six arctic sites "...trifluralin (concentrations) were quite low and mostly below MDLs.". There was no data as to what the range of levels were and what sort of detection frequency was observed. The report did not provide any relevant

information on trifluralin.

Muir, D.C.G. and J. Zheng. 2007. Environmental trends monitoring of new chemical contaminants in the Canadian high Arctic via ice and snow cores. In: Synopsis of research conducted under the 2006-2007, Northern Contaminants program, Indian and Northern Affairs Canada.

In 2005 and 2006 snow/ice samples were collected from a snow pit from the Devon Island Ice cap. Duplicate samples were taken horizontally at 25cm or 20 cm intervals to a depth of 4.5 m (2005) and 6.8 m (2006). The samples were pooled according to annual deposition. The samples were screened for 45 current use pesticides using GC-low resolution MS, however, the 2006 samples were analyzed by GC-electron capture detection for a limited number of current use pesticides which did not include trifluralin. Only 12 of 45 current use pesticides were detected from the 2005 snow pit, seven of which were detectable in all “recent horizons”. Trifluralin was among those that were detected in “almost all recent horizons”. Trifluralin was “less than detection limits in surface and near surface layers” of the snow pit. In the 2005 samples the flux of trifluralin was determined to be $0.22 \text{ ng} \cdot \text{m}^2/\text{yr}$ in the horizons determined to be from the years 2000-2001 and was $0.16 \text{ ng} \cdot \text{m}^2/\text{yr}$ in the horizons that were determined to be from the years 2004-2005.

Muir, D.C.G. 2006. Spatial/Temporal trends of current use pesticides in surface waters and precipitation in Ontario, -2003-2005. Environment Canada Pesticide Science Fund (PSF) project summary report. PMRA #1403269

Current use pesticides were analyzed in surface (1-4m) and subsurface (4.5-50 m) waters from three lakes in southwestern Ontario (areas of trifluralin use) and seven lakes in north/central Ontario (remote sites) from May to July in 2003 and 2004 and five lakes (southern and central)

in 2005. Precipitation was also collected at three southern sites and two north/central locations from April to end of August in 2003 and 2004 and at four locations in 2005. Passive air samples were taken from the precipitation sampling sites in 2004 and 2005. Zooplankton samples were also obtained during lake water sampling times.

Trifluralin was detected in >80% of lake water and precipitation samples in the southern sites with lower frequency of detection (data not provided) in the more northerly lakes. In southern, central and northern lakes concentrations of trifluralin were approximately 0.015, 0.0014 and 0.007 ng/L, respectively. Flux of trifluralin in precipitation at Grand Bend (area of use) ranged from less than detection limit to 0.42 $\mu\text{g}/\text{m}^2$ and showed increasing flux from 2003 to 2005. Concentrations of trifluralin in air in the southern (area of use) and central/northern (remote) lakes was approximately 1.2 ng/m^3 and approximately 0.0013 ng/m^3 , respectively. The concentrations were estimated from available figures as no data were provided. There was no report of trifluralin being detected in zooplankton.

It is difficult to make many conclusions from this report as it is an interim report and contains no actual data for trifluralin or any other compound (only figures were provided). However, it can be shown that trifluralin is detected in lake water, precipitation and air in areas of use and also in remote areas albeit at lower concentrations and with a lower detection frequency.

Evenset, A., G. N. Christensen, T. Skotvold, E. Fjeld, M. Schlabach, E. Wartena and D. Gregor. 2004. A Comparison of Organic Contaminants in two High Arctic Lake Ecosystems, Bjørnøya (Bear Island), Norway. Sci Total Environ. 318: 125-141. PMRA # 1656267.

Methods

Trifluralin (along with other potential POPs) was determined in two high Arctic lakes, Ellasjøen and Øyangen on Bjørnøya (Bear Island), Norway. Sediment, plankton, benthic animals and Arctic char were sampled from both lakes. Trifluralin was quantified using HRGC combined with LSMS-NICI .

Trifluralin was only detected in surface sediments from Lake Ellasjøen at 0.04 ng/g dry wt.

Summary of Local and Long-Range Transport of Trifluralin

Even though phototransformation of trifluralin is rapid in air ($t_{1/2}$ = 21 min to 16 h), residues have been detected in air, precipitation (rain and snow) and fog in remote areas such as the Canadian Arctic, Greenland and the Bering Sea (Table 20). This long range transport indicates that trifluralin is likely bound to airborne particulates which prevents phototransformation from taking place. The sorbed trifluralin is then dry or wet deposited to the remote areas.

Table 20. Summary of Evidence of National and Long-Range Transport of Trifluralin

| Environmental Compartment | Concentrations | Location/Comments | Reference |
|---------------------------|--|--|---------------------------|
| Canadian Sites | | | |
| Air | mean: 0.15, max: 0.81 ng/m ³ | Canadian Prairies 38% detection frequency | Waite et al. 2005 |
| Air | <4 – 816 pg/m ³ (2003) | Bratt’s Lake, SK, Rural area with intensive agriculture; 1-30 m above soil surface | Harner and Blanchard 2006 |
| Air | <4 – 921 pg/m ³ (2004) | | |
| Air | <4 – 734 pg/m ³ (2003) | Hafford, SK, Agriculture area | |
| | <4 – 24.8 pg/m ³ (2003) | Waskesiu, SK, National park area | |
| Air Precipitation | <4 - 117 pg/m ³ ND | Abbstford, BC, animal and berry crop ag. | |
| Air Precipitation | <4 – 535 pg/m ³ ND | Egbert, ON, Rural and suburban area | |
| Air Precipitation | <4 – 660 pg/m ³ 2.1-319 ng/L | Vineland, ON, intensive ag. area | |

| | | | |
|--|--|---|----------------------------------|
| Air Precipitation | <4 – 374 pg/m ³ ND | St. Anicet, QC, rural and ag. area | |
| Air Precipitation | 60 – 481 pg/m ³ ND | Baie St. François, Wetland area | |
| Air Precipitation | <4 – 60 pg/m ³ ND | Kingston, PEI, ag. area | |
| Air | <1 ng/m ³ | Regina, SK, ag. area | Grover et al. 1988 |
| Air | <ND – 15 ng/m ³ | Melfort, SK, ag. area | |
| Precipitation | 2.6% detection frequency (1999) never detected in 2000 | Alberta, sampling procedure likely resulted in almost complete loss of trifluralin | Hill et al. 2002 |
| Air | <ND – 0.56 ng/m ³ 94% detection frequency 35% detection frequency 88% detection frequency 88% detection frequency | All sites, Alberta Lethbridge, AB Lundbreck, AB Lacombe, AB Vergreville, AB | Kumar 2001 |
| Air | <DL – 3400 pg/m ³ 52% detection frequency | Egbert, ON | Hoff et al. 1992 |
| Lake Water and Precipitation | >80% detection frequency 0.015 ng/L 0.0014 ng/L | Southern Ontario lakes Southern ON lakes Central ON lakes | Muir 2006 |
| Air | 1.2 ng/m ³ | Southern ON | |
| Water | 1% detection frequency | MB, SK, AB | Donald et al. 2007 |
| Remote Locations | | | |
| Subsurface seawater, melted ice, air samples | Not detected | Bering and Chukchi Seas | Chernyak et al. 1996 |
| Surface water microlayer | 1110 – 1150 pg/L | | |
| Fog | <DL – 25 ng/L | | |
| Fog water Fog Vapour Particulates | ND 5 pg/m ³ 0.4 pg/m ³ | | Rice and Chernyak 1997 |
| Air | 0.03 – 2.92 pg/m ³ | Canadian Arctic | National Contaminants Program |
| Air | <DL – 0.60 pg/m ³ 31% detection frequency | Greenland | Skov et al. 2005 |
| Melted Snow Particulates | 660 pg/L 2.2 ng/g | Nunavut Territory | Welch et al. 1991 |
| Air | 0.2 – 0.91 pg/m ³ 100% detection frequency | Northern Newfoundland, Quebec and Hudson Bay | Jantunen et al. 2007 |

| | | | |
|------------------------------|---|--------------------------------|---------------------|
| Air | “mostly below detection limits” | Arctic | Su et al. 2008 |
| Snow | “detected in almost all recent horizons (snow layers)” “less than detection limits in surface and near surface layers” | Devon Island | Muir and Zheng 2007 |
| Lake Water and Precipitation | 0.007 ng/L | Northern ON lakes | Muir 2006 |
| Air | 0.0013 ng/m ³ | Northern ON lakes | |
| Surface Sediment | 0.04 ng/g dry wt. | Bjørnøya (Bear Island), Norway | Evenset et al. 2004 |

References

- Branson, D.R., G.E. Blau, H.C. Alexander and W.B. Neely. 1975. Bioconcentration of 2,2',4,4'-tetrachlorobiphenyl in rainbow trout as measured by an accelerated test. *Trans. Am. Fish. Soc.* 104:785- 792. Cited in Spacie and Hamelink 1979.
- Chernyak, S.M., C.P. Rice and L.L. McConnell. 1996. Evidence of currently-used pesticides in air, ice, fog, seawater and surface microlayer in the Bering and Chukchi Seas. *Mar. Pollut. Bull.* 32:410-419.
- Donald, D. B., A. J. Cessna, E. Sverko and N. Glozier. 2007. Pesticides in Surface-Water Supplies in the Northern Great Plains. *Environmental Health Perspectives.* 115:8: 1183-1191. Canadian Arctic Contaminants Assessment Report II. http://ainc-inac.org/ncp/pub/phy/summ3a_e.html. Verified 20 Aug 2008.
- EU DAR. 2003. Draft Assessment Report-Public Version. Initial Risk Assessment provided by the rapporteur Member State Greece for the existing active substance Trifluralin. Volume 3, Annex B, B.9. 164 pp.
- EU Dossier 2007. Trifluralin Dossier prepared in support of a proposal of trifluralin to be considered as a candidate for inclusion in the Annex I to the Protocol to the 1979 Convention on Long-Range Transboundary Air Pollution on Persistent Organic Pollutants (LRTAP Protocol on POPs) European Commission, DG Environment, Brussels. July 2007. 29 pp.
- EUTTF (European Union Trifluralin Task Force). 2002. EU-Directive 91/414/EEC Annex IIA and IIIA. Summaries of studies on trifluralin and representative formulations (Dossier).
- Evenset, A., G. N. Christensen, T. Skotvold, E. Fjeld, M. Schlabach, E. Wartena and D. Gregor. 2004. A Comparison of Organic Contaminants in two High Arctic Lake Ecosystems, Bjørnøya (Bear Island), Norway. *Sci Total Environ.* 318: 125-141.
- Francis, P.C. and Cocke, P.J. 1985. Bioavailability of Sediment-Sorbed Trifluralin to Bluegill Under Laboratory Conditions. Dow AgroSciences, unpublished report No. F03085, 22 October 1985.
- Grafer, L.K. and Rainey, D.P. 1988. Laboratory Studies of ¹⁴C Trifluralin Accumulation in Bluegill Sunfish. Dow AgroSciences, unpublished report No. ABC-0372 & ABC-0376, 8 June 1988.
- Grover, R., L.A. Kerr, K.E. Bowren and S.U. Uhan. 1988. Airborne residues of triallate and trifluralin in Saskatchewan. *Bull. Environ. Contam. Toxicol.* 40:683-688. PMRA 1415173.

- Harner, T. and P. Blanchard. 2006. Canadian Pesticide Air Sampling Campaign, Progress Report, (August, 2006). Environment Canada's Pesticide Science Fund. 72 pp.
- Hill, B.D., K.N. Harker, P. Hasselback, D.J. Inaba, S.D. Byers and J.R. Moyer. 2002. Herbicides in Alberta Rainfall as Affected by Location, Use and Season:1999 to 2000. Water Quality Research Journal of Canada 37(3):515-542.
- Hoff, R.M., D.C.G. Muir and N.P. Grift. 1992. Annual cycle of polychlorinated biphenyls and organohalogen pesticides in air in southern Ontario. 1. Air concentration data. Environ. Sci. Technol. 26:266-275.
- Jantunen, L. M., F. Wong, T. F. Bidleman and G. Stern. Occurance and Levels of Current-Use and Legacy Pesticides in Air: Leg 1 of ArcticNet 2007. http://www.arcticnet-ulaval.ca/pdf/posters_2007/jantunen_et_al.pdf. Verified 20 Aug 2008.
- Kanazawa, J. 1981. Measurement of the bioconcentration factors of pesticides by freshwater fish and their correlation with physicochemical properties or acute toxicities. Pest. Sci. 12:417-424.
- Kearney, P.C., A.R. Isensee and A. Kontson. 1977. Distribution and degradation of dinitroaniline herbicides in an aquatic ecosystem. Pest. Biochem. Physiol. 7:242-248.
- Kumar, Y. 2001. Pesticides in Ambient Air in Alberta. ISBN 0-7785-1889-4. Report prepared for the Air Research Users Group, Alberta Environment, Edmonton, Alberta.
- Lehotay, S.J., J.A. Harman-Fetcho and L.L. McConnell. 1998. Agricultural pesticide residues in oysters and water from two Chesapeake Bay tributaries. Mar. Pollut. Bull. 37: 32-44.
- Lu, P.Y. 1974. Model aquatic ecosystem studies of the environmental fate and biodegradability of industrial compounds. PhD. Thesis, University of Illinois, Urbane-Champaign, Ill. 138 pp. Cited in Spacie and Hamelink 1979.
- Macek, K.J., M.A. Lindberg, S. Sauter, K.S. Buxton, and P.A. Costa. 1976. Toxicity of Four Pesticides to Water Fleas and Fathead Minnows. EPA-600/3-76-099
- Meylan, W.M., P.H. Howard, R.S. Boethling, S.D. Aronson, H. Printup, S. Gouchie. 1999. Improved method for estimating bioconcentration/bioaccumulation factor from octanol/water partition coefficient. Environ. Toxicol. Chem. 18 (4): 664-672.
- Meyerhoff, R.D. and Gunnoe, M.D. 1992. The toxicity of trifluralin to fathead minnow (*Pimephales promelas*) in a 35-day vertebral lesion study. Unpublished. Cited in EU DAR (2003).

- Muir, D.C.G. 2006. Spatial/Temporal trends of current use pesticides in surface waters and precipitation in Ontario, -2003-2005. Environment Canada Pesticide Science Fund (PSF) project summary report.
- Muir, D.C.G. and J. Zheng. 2007. Environmental trends monitoring of new chemical contaminants in the Canadian high Arctic via ice and snow cores. In: Synopsis of research conducted under the 2006-2007, Northern Contaminants program, Indian and Northern Affairs Canada.
- Muir, D., C. Teixeira, and X. Wang. 2005. Atmospheric Deposition and Bioaccumulation of Current Use Pesticides in Remote Lakes in Ontario, Canada. SETAC abstract. <http://abstracts.co.allenpress.com/pweb/setac2005/document/56956>. Verified 21 Aug 2008.
- OSPAR Commission. 2005. OSPAR Background Document on Trifluralin. The Convention for the Protection of the Marine Environment of the North-East Atlantic (the "OSPAR Convention"). ISBN 1-904426-37-9. Publication Number: 2005/203. 32 pp.
- Parrish, P.R., E.E. Dyar, J.M. Enos, and W.G. Wilson. 1978. Chronic Toxicity of Chlordane, Trifluralin, and Pentachlorophenol to Sheepshead Minnows (*Cyprinodon variegatus*). EPA-600/3-78-010, U.S.EPA, Gulf Breeze, FL. 53 pp. (U.S.NTIS PB-278269)
- Reinbold, K.A. and R.L. Metcalf. 1976. Effects of the Synergist Piperonyl Butoxide on Metabolism of Pesticides in Green Sunfish. *Pest. Biochem. Phys.* 6:401-412
- Rice, C.P. and S.M. Chernyak. 1997. Marine arctic fog: an accumulator of currently used pesticides. *Chemosphere* 35:867-878.
- Sanborn, J.R.. 1974. The Fate of Select Pesticides in the Aquatic Environment. EPA-660/3-74-025
- Schultz, I.R. and W.L. Hayton. 1993. Toxicokinetics of trifluralin in rainbow trout. *Aquat. Toxicol.* 26:287-306
- Skov, H., R. Bossi, P. Wåhlin, J. Vikelsøe, J. Christensen, A.H. Egeløv, N.Z. Heidam, B. Jensen, H.P. Ahleson, L. Stausgård, I. Jensen, D. Petersen. 2005. Contaminants in the Atmosphere AMAP- Nuuk, Westgreenland 2002-2004. National Environmental Research Institute, Ministry of the Environment Greenland. NERI Technical Report, No. 547. 48 pp.
- Sleight, B.H. III 1973. Exposure of fish to ¹⁴C trifluralin: accumulation, distribution and elimination of ¹⁴C residues. Unpublished. Cited in EU DAR 2003.

- Spacie, A. 1975. The bioconcentration of trifluralin from a manufacturing effluent by fish in the Wabash River. PhD. Thesis. Purdue University, Lafayette, Indiana. 136 pp. Cited in Spacie and Hamelink 1979.
- Spacie, A. and J.L. Hamelink. 1979. Dynamics of trifluralin accumulation in river fishes. *Env. Sci. Technol.* 13:817-822.
- Su, Y., H. Hung, P. Blanchard, G. W. Patton, R. Kallenborn, A. Konoplev, P. Fellin, H. Li, C. Geen, G. Stern, B. Rosenberg, and L. A. Barrie. 2008. A Circumpolar Perspective of Atmospheric Organochlorine Pesticides (OCPs): Results from six Arctic Monitoring Stations in 2000-2003. *Atmospheric Environment.* 42:4682-4698.
- U.S. EPA. 1996. Reregistration Eligibility Decision (RED) Trifluralin. United States Office of Prevention, Pesticides EPA Environmental Protection And Toxic Substances April 1996 Agency (7508W)738-R-95-040. 240 pp.
- U.S. EPA. 2008. <http://www.epa.gov/waterscience/fish/study/>
- Waite, D.T., P. Bailey, J.F. Sproull, D.V. Quiring, S.F. Chau, J. Bailey and A.J. Cessna. 2005. Atmospheric concentrations and dry and wet deposits of some herbicides currently used on the Canadian Prairies. *Chemosphere* 58: 693-703.
- Welch, H.E., D.C.G. Muir, B.N. Billeck, W.L. Lockhart, G.J. Brunskill, H.J. Kling, M.P. Olson and R.M. Lemoine. 1991. Brown snow: A long range transport event in the Canadian Arctic. *Environ. Sci. Technol.* 25:280-286.
- Yockim, R.S., A.R. Isensee, and E.A. Walker. 1980. Behavior of Trifluralin in Aquatic Model Ecosystems. *Bull. Environ. Contam. Toxicol.* 24(1):134-141.