

**EMEP CONTRIBUTION TO THE PREPARATORY WORK FOR THE REVIEW
OF THE CLRTAP PROTOCOL ON POPS**

NEW SUBSTANCES:

**Model assessment of potential for long-range transboundary
atmospheric transport and persistence of Trifluralin**

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INTRODUCTION

Trifluralin is a selective pre-sowing or pre-emergence herbicide used for the control of annual grasses and certain broadleaf weeds. Trifluralin has been formulated as emulsifiable concentrates, granules and liquids. It prevents weed growth by inhibiting root development through the interruption of mitosis. This substance may be hazardous to the environment; special attention should be given to aquatic organisms, honey bees.

Trifluralin was first registered in the United States in 1963 and used historically in the agriculture in the Southern United States [Kannan *et al.*, 2003]. Within the EU, Trifluralin is applied in a number of countries according to the review prepared for OSPAR Commission, [Trifluralin. Hazardous Substances Series, 2005]. Total applications of the substance amounts to 3000 tons per year. About a half of total applications is attributed to France. Trifluralin and trifluralin-bearing products are still used in many countries.

Trifluralin as a potential candidate for the inclusion into the Protocol on POPs to the Convention was addressed by the Ad Hoc Expert Group on POPs [Lerche *et al.*, 2002].

A Dossier Trifluralin risk profile prepared by the national expert [Trifluralin Risk Profile, 2007] testifies that its characteristics meet the criteria outlined in the Executive Body Decision 1998/2 and it may be a candidate for the inclusion into the CLRTAP Protocol on POPs. Additional information on the evaluation of this product in accordance with the two criteria: potential for long-range transboundary atmospheric transport (LRTP) and persistence can be provided by the model assessment.

For the evaluation of LRTP and persistence of Trifluralin, MSCE-POP multicompartiment hemispheric transport model is used. Detailed information on the structure of the model and parameterisation of the media processes can be found in the EMEP/MSCE reports [see Gusev *et al.*, 2005 and citations therein] and in the Internet (<http://www.msceast.org>).

To estimate LRTP and persistence for Trifluralin, the model calculation of its atmospheric transport from a conventional point emission source located in Europe is made for one-year period. Information on physical-chemical properties and degradation rates of this pollutants used for modelling is presented in Annex B.

Presented information is divided into four parts.

1. To evaluate **LRTP** of trifluralin, two numerical characteristics are calculated. The first one is residence time in the atmosphere (**Half-life in air** ($T_{1/2}^{air}$)) obtained with allowance of all processes removing the considered pollutant from the atmosphere. The second is **Transport Distance (TD)** that is the distance from the source at which annual mean atmospheric concentration of a chemical in question drops 1000 times compared with the concentration near the source. Additional information on this criterion for Trifluralin is provided by the spatial distribution of air pollution caused by the considered conventional emission source.

2. **Persistence** in the environment is evaluated by **Half-life in the environment** ($T_{1/2}^{env}$) estimated for trifluralin on the basis of the model simulation of its atmospheric transport taking into account deposition processes, degradation and exchange of the pollutant between main environmental media.

3. The values of TD and $T_{1/2}^{env}$, calculated by the model depend on model characteristics (such as resolution, spatial coverage, etc.). To exclude model peculiarities in evaluating LRTP and persistence

of trifluralin with the help of the model dependent TD and $T_{1/2}^{env}$, a comparison of their numerical values against those obtained for an adequately studied “**benchmark substance**” is presented.

4. In **conclusion**, the calculated numerical characteristics of LRTP and persistence of trifluralin are given in relation to the indicative criteria outlined in the Executive Body Decision 1998/2.

Since measurement data in remote regions are mentioned among the criteria for recognizing a substance as a POP, a short review of existing data on levels of trifluralin measured in environmental samples is presented in Annex A to the report. Annex B includes the summary of trifluralin physical-chemical properties used for modelling.

1. LONG-RANGE TRANSPORT POTENTIAL

According to the Executive Body Decision 1998/2 the LRTP criterion for the evaluation of new substances as potential candidates for the inclusion into the Protocol on POPs is characterized by indicative numerical values of their vapour pressure and atmospheric half-life.

The half-life of “new substances” in the atmosphere can be estimated with the help of modelling as residence time in the atmosphere (*Half-life in air_{calc}* ($T_{1/2}^{air}$)) obtained on the basis of simulation of their atmospheric transport taking into account not only degradation process in this medium but also all other removal processes, which in turn are affected by other environmental processes, e. g. gas/particle partitioning. Advantages of modelling approach are contained in possibility to distinguish the most important processes affecting LRTP of a particular considered pollutant in the atmosphere. Additional information on LRTP based also on the model calculations of atmospheric transport is provided by the spatial distribution of air pollution. The latter allows to estimating *Transport Distance* (TD), characterising LRTP of “new substances” as the distance from the source at which annual mean atmospheric concentration drops 1000 times compared with the concentration near the source.

This Section contains the main results on evaluation of LRTP criterion for trifluralin with the help of above-mentioned characteristics obtained on the basis of the hemispheric MSCE-POP model calculations.

1.1. Residence time in the atmosphere

To estimate the residence time of trifluralin in the atmosphere, the model calculation of environmental transport of trifluralin with allowance of such processes as degradation in the atmosphere, partitioning between particulate and gaseous phases, dry and wet deposition of particles and gaseous exchange with various types of underlying surface is carried out. Emissions of trifluralin to the atmosphere are assumed to be 1 tonne per year from a conventional point emission source located in Europe (5°E; 47.5°N). On the basis of model simulations contributions of different atmospheric processes to the removal of trifluralin from the atmosphere is estimated (see Fig.1 a).

According to the model assessment, removal from the atmosphere is mainly attributed to degradation (about 90% of total removal) and dry deposition over land (about 8% of total removal) processes. The character of the presented balance is governed not only by the physical-chemical properties of the considered substance (degradation rate constants, subcooled liquid vapour pressure values and Henry’s law constants) but also by the type of underlying surfaces under preferable transport pathways and some meteorological parameters.

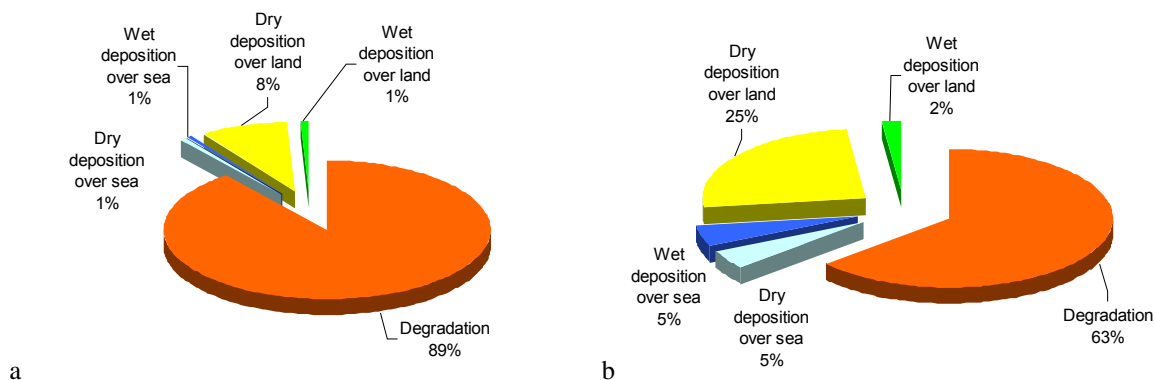


Fig. 1. Calculated balance of trifluralin removal from the atmosphere: (a) – annual, (b) – in January

It should be noted that the balance is essentially changed from month to month. For example, in January the contribution of degradation in the removal from the atmosphere amounts to 63% of the overall removal whereas the contribution of dry deposition enlarges to about $\frac{1}{4}$ from the overall removal. This may be conditioned by different temperature regimes, differences in gas/particle partitioning and types of underlying surface along main paths of the pollutant transport.

The value of residence time in the atmosphere (Half-life in air_{calc} ($T_{1/2}^{air}$)) for trifluralin calculated on the basis of annual balance occurs to be of about **1.8 days**. However, residence time in the atmosphere can vary from 0.1 to 10 days in different months due to geographical conditions along pollutant's pathways within a typical temperature range for Europe. The plot of residence times in the atmosphere in particular months is presented in Fig. 2. Here the value of half-life calculated on the annual basis is shown by the green line.

Since trifluralin is an herbicide, seasonal variations of the half-life are essential for the assessment of its long-range transport. We recall that, for comparability of the results with other substances, model calculations were performed for the emission source acting through the whole year with constant power. For emission source with strong seasonal variations characteristic of trifluralin application as a herbicide, half-life in the atmosphere can be different since for its calculation time and place of its applications will be essential.

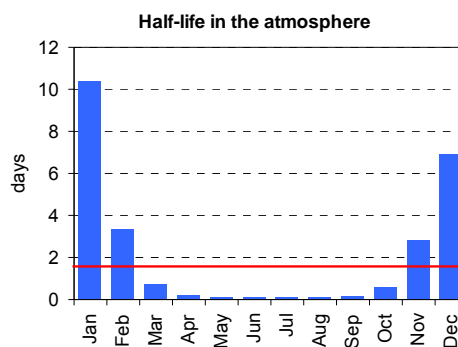


Fig. 2. Residence times of trifluralin in the atmosphere for particular months. Green line shows annual average of $T_{1/2}^{air}$.

1.2. Spatial distribution of pollution from conventional emission source

Additional information on LRTP of trifluralin is provided by the spatial distribution of its air pollution obtained on the basis of simulation of its atmospheric transport from the considered conventional point source. In Fig 3 annual mean air concentration fields of trifluralin in the Northern Hemisphere and EMEP domain are given. For convenience, air concentrations are presented in the relative units i.e. as ratios of the concentration calculated in the particular point to the concentration near a source.

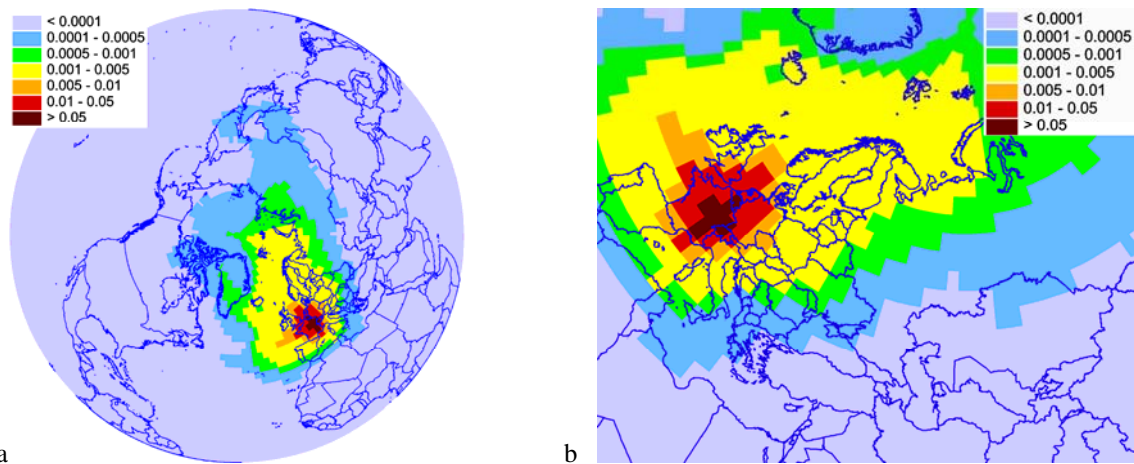


Fig. 3. Spatial distribution of trifluralin concentrations (annual means) in the above-ground air in the Northern Hemisphere (a) and in the EMEP domain (b), relative units

With a conventional source of emissions located in Europe and acting uniformly throughout the year, the area of air concentration of trifluralin, which is 1000 times lower than the concentration near the source, is located over almost all Europe including Mediterranean Sea and reaching middle-Atlantic and considerable part of the Arctic. Considering the influence of the emission source on the EMEP domain in more detail (see Fig.3b) shows that the most intensive air pollution by trifluralin is characteristic of territories of France and its neighboring countries - Switzerland and Belgium. The area with concentrations 100 times less than that near the source spreads also over some regions of the UK and Italy.

As it was already mentioned, residence times of trifluralin are strongly seasonally dependent with considerable decrease in warm months. This leads to essential differences between spatial distribution of the pollution from the point source in different months. For example, spatial distributions of trifluralin concentrations in January and March (the month with enhances volumes of application) are presented in Fig. 4 a and b.

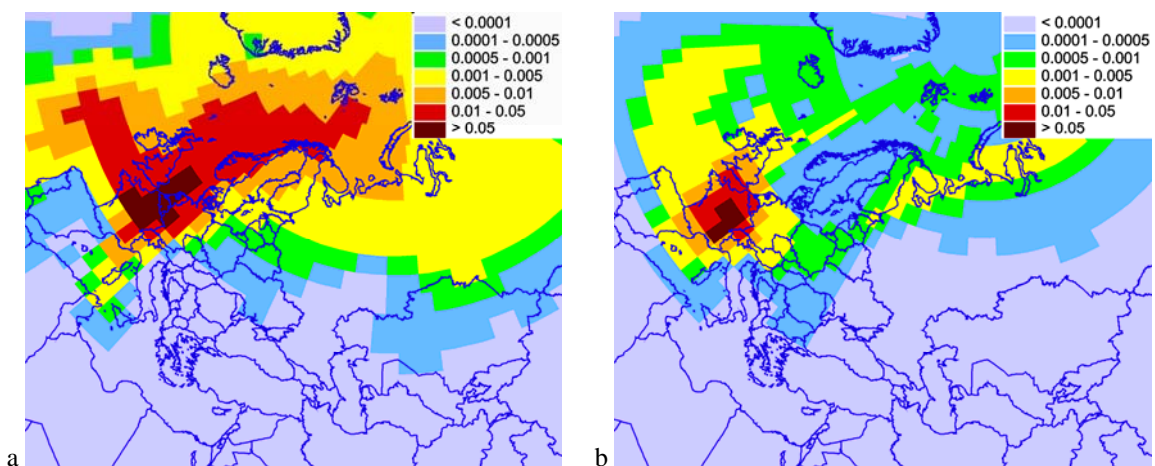


Fig. 4. Spatial distribution of trifluralin concentrations in the above-ground air in the EMEP domain in January (a) and March (b)

Calculations show that trifluralin is more widely spread over the EMEP domain in January than in March. It is important for considerations of trifluralin since it is mainly used as a herbicide.

1.3. Transport Distance

At present several model approaches to evaluation of LRTP of a pollutant by means of different numerical characteristics have been developed and introduced in [Scheringer and Berg, 1994; Scheringer, 1996; Bennett et al., 1998; van Pul et al., 1998; Wania, 1998; Rodan et al., 1999; Beyer et al., 2000; Beyer et al., 2001; Beyer and Matthies, 2001; Leip and Lammel, 2004, etc]. For example such characteristics are spatial range, spatial scale, transport distance, characteristic travel distance, travelling distance, and so on. In this assessment in addition to the residence time of trifluralin in the atmosphere, another characteristic demonstrating LRTP of the considered substance is provided by the model estimate of its *Transport Distance (TD)*. Numerical values of *TD* are defined with the help of Eq. 1 as the average distance from the source at which annual mean atmospheric concentration of a chemical in question drops 1000 times compared with the concentration near the source (as an example see Fig.5):

$$TD_{0.001} = \sqrt{\frac{S_{0.001}}{\pi}} \quad (1)$$

where $S_{0.001}$ is the area covered by air concentrations dropped less than 1000 times.

It should be noted that such an approach is similar to that suggested in [Rodan et al., 1999].

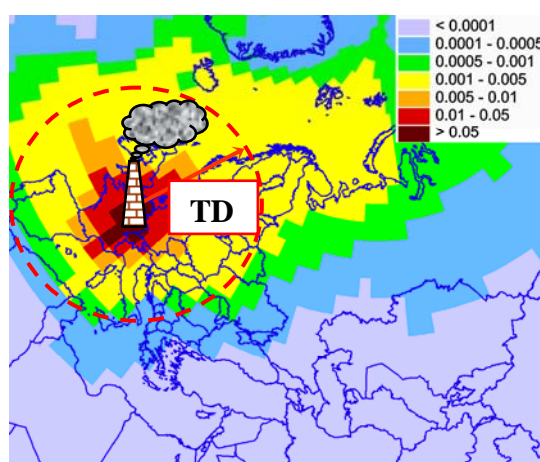


Fig. 5. Definition of the transport distance

The value of *TD* depends on all of the processes removing the pollutant from the atmosphere such as deposition to the underlying surface (land, sea) and atmospheric degradation. The calculated value of *TD* for trifluralin together with the half-life in the atmosphere is presented in Table 1.

Table 1. Characteristics of LRTP (*Half-life in air_{calc}* and *Transport Distance*) calculated for trifluralin

Substance	$T_{1/2}^{air}$, days	<i>TD</i> , km
Trifluralin	1.8	2190

Seasonal variability of the atmospheric half-lives for trifluralin leads to the variability of *TD*. Fig. 6 shows the values of *TD* for particular month in the year. The green line shows annual value of *TD*.

It can be noticed that the annual value of TD is considerably higher than the average of TD s over the year. This is conditioned by the fact that annual averages of concentrations at large distances from the source are formed mainly by contributions of the winter months when monthly TD s are comparably high. So, it can be expected that TD calculated for a source with non-uniform emissions with main applications in warmer months (which is characteristic for trifluralin application as a herbicide) can be considerably lower than calculated above since the contribution of the transport in cold months will be much lower than for a permanently acting source.

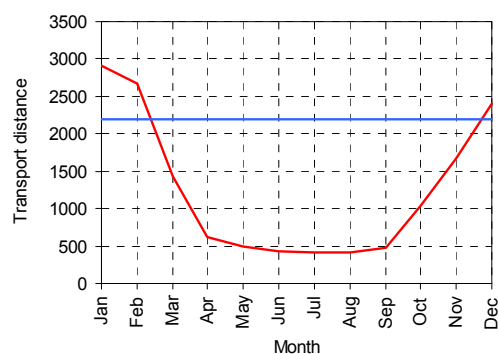


Fig. 6. Transport distance of trifluralin in the atmosphere for particular months. Blue line shows annual value of TD .

2. PERSISTENCE IN THE ENVIRONMENT

The behaviour of a substance in the environment to a large extent is determined by its persistence not only in the atmosphere but also in other environmental media. Its redistribution between the air and soil, seawater, sediment, vegetation etc is important for its ability to be accumulated in the food chain. In this process the main characteristic is its half-life in the media under consideration.

In compliance with the Executive Body Decision 1998/2 the persistence of “new substances” in terms of their possible inclusion into the Protocol on POPs is demonstrated by indicative numerical values of their half-life in water, which should be greater than two months, or half-life in soil, which should be greater than six months, or half-life in sediments, which should be greater than six months also. In addition to these parameters characterizing the persistence for particular media, multimedia model calculations allow estimating complementary characteristic of persistence in the whole environment - overall residence time or overall environmental persistence [Scheringer, 1996; Webster et al., 1998; Gouin et al., 2000, Klasmeier et al., 2006 etc]. In this assessment such characteristic as *Half-life in the environment* ($T_{1/2}^{env}$) is estimated for the considered pollutant on the basis of the model calculations of its atmospheric transport taking into account deposition processes, degradation and gaseous exchange between main environmental media.

The model assessment of persistence in the environment for trifluralin is demonstrated by the numerical value of $T_{1/2}^{env}$ calculated with the help of Eq.2 as an inverse value of weighted mean of degradation rate constants k_j in the environmental media (atmosphere, soil, seawater, vegetation, sediments) with weights being the fractions f_j of a pollutant accumulated in j -th medium:

$$T_{1/2}^{env} = \ln 2 / \sum k_i \cdot f_i \quad (2)$$

Here fractions f_i are evaluated on the basis of the model calculations.

Thus, the value of *Half-life in the environment* is affected by the distribution of the total environmental content of trifluralin between main environmental media (air, soil, water, sediment and vegetation) and the values of its half-life in each particular medium due to degradation process.

The distribution of trifluralin total content in the environment between main environmental media (annual media balance) and relative fractions of the pollutant degraded in each media during a year (annual degradation balance) were obtained on the basis of model simulations for one-year period. It should be noted that seawater includes pollutant content in sediments, and only degradation in forest litter is considered as degradation in vegetation. The model assessment of average media content of trifluralin in the environmental media in comparison with its annual degradation balance is shown in Fig.7.

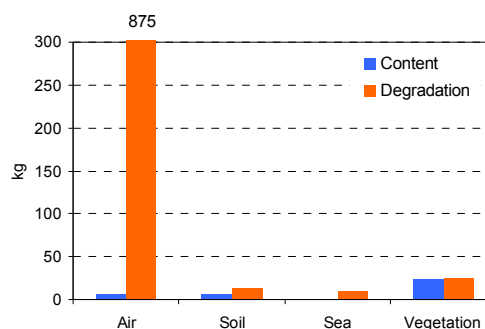


Fig. 7. Annual degradation and average content in the environmental media for trifluralin

By the end of a year 1 tonne of trifluralin emitted to the atmosphere has degraded in all the media by about 92%. From this amount about 95% of emissions degraded in the atmosphere and about 5% – in the other media. The bulk fraction of the pollutant remaining in the environment (about 70%) to the end of the year was accumulated in the terrestrial environment (soil and vegetation). Thus, model calculations allow demonstrating the re-distribution of trifluralin between main environmental media defining among them the media capable to accumulate the most part of the considered pollutant as well as those characterized by the most intensive degradation of the substance.

To evaluate the ability of the considered pollutant to be persistent in the environment, the value of **Half-life in the environment** was estimated on the basis of calculated media balance along with the values of half-lives in the corresponding environmental compartments in accordance to formula (2). Obtained estimates of $T_{1/2}^{env}$ are presented in Table 2.

Table 2. Characteristics of Persistence (Half-life in environment) and half-life of trifluralin in different environmental media used for modelling of atmospheric transport

Substance	$T_{1/2}^{env}$		Half-life, days		
	days	months	air	water	soil
Trifluralin	9.7	≈ 0.32	2	0.2	55

The obtained value of $T_{1/2}^{env}$ shows that persistence of trifluralin in the environment can be characterised as low.

3. COMPARISON WITH BENCHMARK SUBSTANCE

Since the numerical values of $T_{1/2}^{air}$ and $T_{1/2}^{env}$ of particular chemicals are model dependent, one of the possible ways to diminish uncertainties in evaluating new substances proposed by Scheringer [1997] and Beyrer *et al.* [2000] and discussed at the OECD/UNEP Workshop on the Use of Multimedia Models for the Estimation of Environmental Persistence and Long-Range Transport (Ottawa, Canada, 2001) was to use a “benchmark” approach. This approach suggests that model results on LRTP and persistence are used to compare the pollutants under study with some adequately studied “benchmark substance” with known values of the considered parameters.

This procedure enables assessment of “new substance”, by considering their ranking in terms of persistence or LRTP among the well-known benchmark chemicals. Examples of chemical ranking and

classification approach are described by *Matthies et al.* [1999], *Beyer et al.* [2000] and *Bennett et al.* [2001]. Benchmark approach may also be applicable when the desired outcome is the screening of a large set of existing chemicals, to establish priority classes of substances for further assessment or action [ENV/JM/MONO(2004)5, 2004].

The comparison of calculated characteristics of LRTP and persistence for trifluralin against those obtained for a benchmark pollutant is presented in this subsection. Benzo[a]pyrene (B[a]P) is used as a benchmark substance in this assessment. Characteristics of its behaviour in the environment are well studied and clearly meet UN ECE criteria. It is already included in the Protocol on POPs and is considered as pollutant of regional concern. Model calculations were performed for one-year period and a conventional point emission source with one and the same location in Europe and one and the same emissions intensity.

The comparison of the transport distances and half-lives in the environment for trifluralin and B[a]P are shown in Fig. 8 a and b.

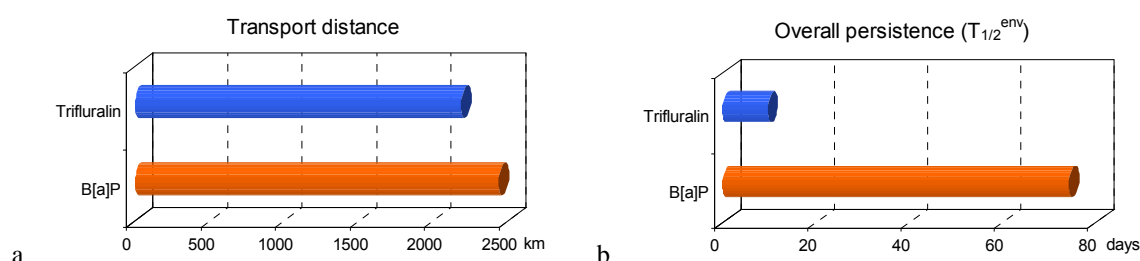


Fig. 8. Transport distance and Half-life in the environment calculated for trifluralin and B[a]P

According to the model calculations of TD , LRTP for trifluralin is approximately the same as for that of B[a]P. The ranking of trifluralin and B[a]P with respect to $T_{1/2}^{env}$ shows that trifluralin is considerably less persistent than B[a]P.

4. CONCLUDING REMARKS

The results of evaluation of trifluralin LRTP and persistence by MSCE-POP model along with its physical-chemical properties are given in Table 3 in relation to the LRTP and persistence criteria outlined in the Executive Body Decision 1998/2.

The results of the model assessment demonstrate the considerable long-range atmospheric transport potential and low persistence of trifluralin in the environment.

The value of residence time in the atmosphere calculated by MSCE-POP model is about 1.8 days, which is slightly lower than the threshold given in POP criteria (2 days). However, in some months half-life in the atmosphere can be essentially higher (up to 10 days). Thus, according to the results of the present investigation, trifluralin meets the LRTP criteria for POPs. Model calculations show weak persistence of the trifluralin in the environment. But it should be taken into account that half-life in soil for this substance varies from 4 to 356 days. So it can be expected that the persistence of trifluralin can be essentially higher under different environmental conditions.

Table 3. Comparison of properties of trifluralin and criteria of **Executive Body Decision 1998/2** based on published data and with additions of MSCE-POP model outputs

Criterion	Criterion values	Meets the criterion (Yes/No)	Characteristics of trifluralin	Remarks
Potential for Long-range Transboundary Atmospheric transport				
Vapour pressure, Pa	< 1000	Yes	0.0061 – 0.0095	<i>Trifluralin Risk Profile</i> , 2007
			0.0029 – 0.0137	<i>Mackay et al.</i> , 2006
Half-life in air, days	> 2	Yes	0.02 – 0.13	<i>Mackay et al.</i> , 2006
			0.96 – 3.6	<i>HSDB database</i>
Half-life in air (calc), days		Yes	1.8	$T_{1/2}^{air}$ calculated by MSCE-POP
Persistence				
Half-life in water, months	> 2	No	1 – 2 days	<i>Trifluralin Risk Profile</i> , 2007
			13 days	IUPAC FOOT PRINT, Pesticides Properties Database
			0.4 days - > 1 Year	PRVD 2008-22
Half-life in soil, months	> 6	No	23 – 356 days	PRVD 2008-22
			4 – 322	<i>Mackay et al.</i> , 2006
Half-life in the environment	-	-	0.3 months (9.7 days)	$T_{1/2}^{env}$ calculated by MSCE-POP
Bioaccumulation				
Log K_{ow}	> 5	Yes	3.97 – 5.34	<i>Mackay et al.</i> , 2006

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<http://extoxnet.orst.edu/pips/triflura.htm>.
- ICSC: 0205; IPCS (International Programme on Chemical Safety):
www.ilo.org/public/english/protection/safework/cis/products/icsc/.../_icsc02/icsc0205.htm -

- IUPAC FOOT PRINT, Pesticides Properties Database: <http://sitem.herts.ac.uk/aeru/iupac/667.htm>.
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LEVELS OF TRIFLURALIN MEASURED IN ENVIRONMENTAL SAMPLES

The available data on the environmental concentrations of trifluralin are presented below.

Air concentrations

Most data on trifluralin content in the atmosphere presented in Table A1 characterize contamination levels in Canada. Almost all of them are taken from Canadian Atmospheric Network for Currently Used Pesticides (CANCUP) being the first comprehensive, nationwide air surveillance study of pesticides in Canada. Highest levels were detected in the beginning of 80th in Melfort, Saskatchewan. More recent investigations show reduction of trifluralin concentrations. Namely, in 2002 maximum concentrations were observed in Abbotsford, British Columbia, and their difference with contamination levels of 80th were of order of magnitude.

It is known that trifluralin was first applied in America from the middle of 60th. Most widely it was used in South states (in the Mississippi delta) for cultivation of cotton and rice. By the data from [Coupe *et al.*, 1998], in 1995 about 200 tonnes of trifluralin were used in these regions. Geographical distribution of trifluralin and other pesticides were determined in air over the Mississippi River from New Orleans, La, to St. Paul, MN is presented in [Majewski *et al.*, 1998]. Obtained results show not only differences in trifluralin concentrations in Mississippi waters but also independence of trifluralin concentration levels from application volumes of the considered region.

US Geological Survey included trifluralin as one of the pesticides analyzed for in a 2-year –long study of airborne pesticides in the Sacramento area in 1996 – 1997 [Majewski and Baston, 2002], as well as in a 10-day study of airborne pesticides near the Mississippi River in early June 1994 [Majewski *et al.*, 1998].

Measurements of trifluralin concentrations in the European air are given in [Sanusi *et al.*, 2000] and [Scheyer *et al.*, 2007]. Investigations of atmospheric contamination by trifluralin in the Alsace region, France, with 10 year interval indicate reduction of its atmospheric concentrations, see Table A1.

It is hard to make reliable conclusions on typical trifluralin levels for Europe and North America with the help of the data of Table A1. The only exception is the Canadian territory where air sampling were performed at many locations during several years. Additional information can be obtained from the results of investigations if atmospheric contamination by pesticides with the help of passive samplers. The result of this experiment show 10 times differences in trifluralin concentrations. Maximum contamination was detected not only in the air in Toronto (large town in the Ontario region) but also at Egbert (IADN master station). For instance, levels of trifluralin are highest during May 2003 at Egbert, and the air mass moving away from Egbert in May 2003 indicates the potential for a strong source-receptor relationship between agricultural regions in south-western Ontario and southern regions of Lake Ontario, whereas poor source-receptor relationships are apparent between the source regions and northern Ontario.

Table A1. Levels of trifluralin in air

Sampling location	Sampling data/period	Trifluralin, concentrations, ng/m ³	References	Remarks	
Canada					
Toronto	May-October 2003	0.030	<i>Gouin et al.</i> , 2008	urban	
Downsview		0.030		rural	
Egbert, Ontario		0.050		forested	passive sampler
Trent Univercity		0.003			
Haliburton forest		0.001			
Sprucedale		0.001			
Loxton Lake		ND			
Fraserdale		ND			
Regina, Saskatchewan	April-November 1981	<1	<i>Grover et al.</i> , 1988	Here and below the results obtained by high-volume samplers are given	
	May-September 1989	<0.5 – 3.0	<i>Waite et al.</i> , 2004	Site located approximately 5 km south of the city of Regina	
		0.2 – 2.3		Site located approximately 10,5 km south of the city of Regina	
	May-September 1990	0.1 - 1.45		Site located approximately 5 km south of the city of Regina	
Melfort, Saskatchewan	May-November 1982	<10-63		<i>Grover et al.</i> , 1988	
Agriculture and Agri-Food Canada Research Station, Saskatchewan	May-July 2002	ND – 0.03	<i>Waite et al.</i> , 2005	Prairie region immediately south of the city Regina	
Bratts's Lake, Saskatchewan	May-July 2002	ND – 0.57	<i>Waite et al.</i> , 2005	Rural and intensive agricultural area (cereals) with few trees. Prairie region approximately 35 km southwest of the city Regina, 150 km north of the United States border	
	May-August 2003	<u>ND – 0.81</u> 0.17	<i>Yao et al.</i> , 2006		
	May-August 2004	<u>ND – 0.91</u> 0.27	supplementary information for <i>Yao et al.</i> , 2008		
	May-July 2005	<u>0.91 – 2.57</u> 0.27			
Hafford, Saskatchewan	May-July 2002	ND – 0.34	<i>Waite et al.</i> , 2005	Agricultural area (cereals, oilseeds) with trees. Unseeded fields located adjacent to the site. Approximately 300 km north of Regina, in a mixed aspen parkland	
	May-August 2003	<u>ND – 0.73</u> 0.07	<i>Yao et al.</i> , 2006		
Waskesieu, Saskatchewan	May-July, 2002	ND	<i>Waite et al.</i> , 2005	In a Prince Albert National Park, densely treed. Approximately 500 km north of Regina, within the Boreal Forest and approximately 50 km north of farm land.	
	May-August 2003	<u>ND – 0.025</u> 0.005	<i>Yao et al.</i> , 2006		
Abbosford, British Columbia	May-August, 2003	0.006	<i>Yao et al.</i> , 2006	Fraser Valley, pig and chicken farms and berry crops	
	April-June 2004	<u>ND – 0.117</u> 0.064	supplementary information for <i>Yao et al.</i> , 2008		
	May 2005	<u>ND – 2.22</u> 1.22			
Egbert, Ontario	July – August 2003	0.091	<i>Yao et al.</i> , 2006	Rural and suburban area, surrounded by fields and mixed forest	
	May-July 2004	<u>ND – 0.53</u> 0.24	supplementary information for <i>Yao et al.</i> , 2008		
	May-July 2005	<u>0.30 – 4.39</u> 1.26			
Vineland, Ontario	May-July 2004	<u>ND – 0.66</u> 0.24	supplementary information for <i>Yao et al.</i> , 2008	Intensive agricultural area (fruit, vegetable, wine)	
	June-August 2005	<u>0.04 – 2.16</u> 0.65			
Downsview, Ontario	June-August 2005	<u>0.20– 0.43</u> 0.34	supplementary information for <i>Yao et al.</i> , 2008	Residential and industrial area	

Sampling location	Sampling data/period	Trifluralin, concentrations, ng/m ³	References	Remarks
St. Anicet, Quebec	July – August 2003	0.036	<i>Yao et al.</i> , 2006	Rural and agricultural area (corn, pasture land)
	April-June 2004	<u>ND – 0.37</u> 0.12	supplementary information for <i>Yao et al.</i> , 2008	
	June 2005	<u>ND – 0.51</u> 0.21		Rural location surround by farms and included within the Quebec corn crop belt
	June 2005	0.23	<i>Sadiki and Poissant</i> , 2008	
Bay St. Francois, Quebec	July – August 2003	0.038	<i>Yao et al.</i> , 2006	Wetland covered with mixed vegetation and the nearest field is located more than 5 km, then the Bay St. Francois represents a receptor site. Located at about 160 km northeast from St. Anicet
	April-June 2004	<u>0.06 – 0.48</u> 0.26	supplementary information for <i>Yao et al.</i> , 2008	
	June 2005	<u>0.74 – 2.59</u> 1.05		
	June 2005	1.21	<i>Sadiki and Poissant</i> , 2008	
Kensington, Prince Edward Island	July – August 2003	0.011	<i>Yao et al.</i> , 2006	Heart of potato growing country
	June – September 2004	<u>ND – 0.060</u> 0.017	supplementary information for <i>Yao et al.</i> , 2008	
	August-September 2005	ND		
USA				
New Orlean, Luisiana	June 1994	0.75	<i>Majewski et al.</i> , 1998	Geographical distribution of trifluralin and other pesticides were determined in air over the Mississippi River from New Orleans, La, to St. Paul, MN
Greenville, Mississippi		80		
Memphis, Tennessee		78		
Cairo, Illinois		67		
St. Luis, Missouri		2.8		
Sacramento, California	January1996-December 1997	<u>0.09 – 14.58</u> 2.88	<i>Majewski and Baston</i> , 2002	Franklin Field Airport, wind direction - south
		<u>0.10 – 19.50</u> 2.53		Franklin Field Airport, wind direction - north
		<u>0.08 – 10.28</u> 2.29		Sacramento Metropolitan Area, wind direction - south
		<u>0.17 – 43.01</u> 3.63		Sacramento Metropolitan Area, wind direction - north
		<u>0.02 – 19.18</u> 4.78		Sacramento International Airport, wind direction - south
		<u>0.13 – 12.87</u> 2.49		Sacramento International Airport, wind direction - north
Hasting, Florida	December 2006	<u>ND – 376</u> 84	<i>Air Monitoring in Hastings, Florida, Technical Report</i> , 2007	Experiment Area - an agricultural area adjacent to fields near South Woods Elementary School in Hastings, Florida
	October - December 2007	<u>ND – 136</u> 29	<i>Air Monitoring in Hastings, Florida, Technical Report</i> , 2008	
France				
Aubure	April-May 1993	6.79	<i>Sanusi et al.</i> , 2000	Remote. Sampling site was situated 50 km west of Colmar on a summit of the Vosges Mountains at Aubure at an altitude of 1100 m above sea level.
	June- July 1994	1.96		
Colmar	April-May 1993	4.81		Rural. Sampling site was situated in the meteorological station of the experimental I.N.R.A. farm located 5 km south – east of Colmar town centre
	July 1994	1.26		

Sampling location	Sampling data/period	Trifluralin, concentrations, ng/m ³	References	Remarks
Strasbourg	June- July 1994	2.03	<i>Scheyer et al., 2007</i>	Urban. Samples were collected on the roof top of the A.S.P.A. (Association pour la Surveillance de la Pollution Atmospherique en Alsace') building situated near historical centre of Strasbourg
	March – May 2002	<u>ND – 0.179</u> 0.05		
Strasbourg, Geisposheim Gamsheim	March – May 2003	<u>ND – 0.182</u> 0.09		Geipolsheim is closer to corn crops than Gamsheim, the Gamsheim site experiences have stronger winds which might have a stronger dilution effect

The potential of trifluralin long-range transport is confirmed by monitoring data from remote Arctic regions (see Table A2). The trifluralin concentrations presented in Table A2 differ from concentrations in continental regions as much as 1000 times and higher.

Table A2. Levels of trifluralin in Arctic air

Sampling location	Sampling data/period	Trifluralin, concentrations, pg/m ³	References	Remarks
Arctic regions				
Alert	1993	<u>0.03 – 0.32</u> 0.12	<i>Halsall et al., 1998</i>	Canada
	1994	<u>0.08 – 0.64</u> 0.12		
Tagish	1993	<u>0.06 – 0.21</u> 0.005		Canada
	1994	<u>0.04 – 2.92</u> 0.18		
Dunai	1993	<u>0.09 – 0.33</u> 0.18		Russia
Nuuk, West Greenland	2004 - 2005	<u>ND – 1.95</u> 0.16	<i>Bossi et al., 2008</i>	Canada, detected only in samples collected in winter and autumn

Water concentrations

Summary of the water monitoring studies available for trifluralin in Canada are presented in the report Pest Management regulatory Agency Health Canada, [PRVD 2008-22]. Observed concentrations (arithmetical means including non-detects at ½ LOD) range in a very wide range from 0.000002 to 0.061 µg/L.

Contamination of surface waters, subsoil waters and storm runoff were investigated in USA for the period of 10 years under National Water-Quality Assessment (NAWQA) Program. In the framework of the Program 51 major river basins were examined from 1992 to 2001. Trifluralin was also included into the Program. For the whole observation period trifluralin was found in the surface river waters not more than for 15% of the investigated rural regions and about 10% of urban regions. In subsoil waters trifluralin was detected even rarer [*Pesticides in the Nation's Streams and Ground Water, 1992–2001, USGS Circular 1291*]. Unfortunately, neither trifluralin concentrations nor their range are not presented in the report.

Storm runoff to the Tuolumne river (California) was also investigated in the NAWQA Program [Kratzer, 1998]. Trifluralin concentrations in storm runoff from drains in Modesto (agricultural runoff) in 1994 were detected in the range 0.013 – 0.024 µg/L. In samples of urban runoff in the McHenry Storm Drain during February 1995 trifluralin concentrations were somewhat lower and ranged from 0.010 to 0.018 µg/L.

The data on trifluralin measurements in precipitation obtained in the framework of the same program in four rural regions (Maryland, Nebraska, Indiana and California) in 2003 – 2004 show that median observed concentrations were, as a rule, at the detection limit of the analytical method. Maximum value (0.148 µg/L) was detected in Nebraska. Median concentrations through all investigated states were < 0.009 µg/L [Vogel *et al.*, 2008].

Most complete data on trifluralin concentrations in European waters can be found in [*Trifluralin. Hazardous Substances Series*, 2005].

Soil concentrations

The analysis of literature information on trifluralin soil concentrations shows that literature sources were mainly devoted to examination of the behavior of the substance in soils of agricultural lands or of its stability in these soils [Kim and Feagley, 2002; Grover *et al.*, 1997]. The persistence of trifluralin in agricultural soils following application is highly variable, depending on several factor such as depth of incorporation, soil moisture, soil temperature, soil air, and soil organic matter content. Estimated half-life under a variety of agronomic conditions range from 25 to > 200 days, thus categorizing its stability from “moderate” to “persistent”.

Residues of trifluralin in cotton field soils from South Carolina ranged from 3.3 to 574 ng/g dry weight (with mean 115 ng/g), whereas those from Georgia ranged from 1 to 548 ng/g dry weight (with mean 150 ng/g). Concentrations of trifluralin in soils collected from vegetable farms in British Columbia varied from 55 to 310 ng/g dray weight [Kannan *et al.*, 2003]

PHYSICAL-CHEMICAL PROPERTIES OF TRIFLURALIN USED FOR MODELLING

Some parameters needed for modelling of trifluralin atmospheric transport with their temperature dependencies were taken from the literature or from special databases. Physic-chemical properties for which literature data are absent were evaluated by known relations with other constants, see Table B1.

Table B1. Trifluralin parameters used for atmospheric transport modelling

Parameter (base values are given at 10° C)	Numerical value	Source
Henry's law constant for fresh water, Pa·m ³ /mol	6.05	Calculated on the basis of data from <i>Rice et al.</i> , 1997
Temperature coefficient for Henry's law constant, K	3851.3	
Henry's law constant for seawater, Pa·m ³ /mol	8.0	
Temperature coefficient for Henry's law constant, K	2101.3	
Washout ratio	40 000	Estimated by the analogy with other pesticides on the basis of van Pul et al., 1998; <i>Eisenreich et al.</i> , 1981
Vapor pressure over subcooled liquid, Pa	3.16×10^{-3}	Mackay et al., 2006
Temperature coefficient for vapor pressure, K	10530	
Second order degradation rate constant for reaction with OH-radical, cm ³ /sec	2.4×10^{-11}	HSDB database
Degradation in air constant, s ⁻¹	3.89×10^{-6}	Estimated by the MSCE-POP model on the basis of [OH] distribution.
Half-life in air, days	2.1	
First order degradation rate constant for water, sec ⁻¹	4.52×10^{-5}	Estimated *
Half-life in water, days	32.8	
First order degradation rate constant for soil, sec ⁻¹	1.46×10^{-7}	Estimated *
Half-life in soil, days	123	
Molar volume, cm ³ /mol	295.9	Mackay et al., 2006
Octanol/water partitioning coefficient, K _{ow}	1.17×10^5	EXTOXNET ; ICSC: 0205; IPCS (International Programme on Chemical Safety)
Octanol/air partitioning coefficient, K _{oa}	4.57×10^7	Estimated on the basis of the relation between K _{oa} , K _{ow} and K _{aw}
Temperature coefficient for K _{oa} , K	3560	
Molecular diffusion coefficients, m ² /sec:		
for water	4.65×10^{-10}	Calculated with the help of equations from <i>Schwarzenbach et al.</i> , 1993
for air	4.70×10^{-6}	
Partitioning coefficient in the system organic carbon/water, m ³ /kg	48.17	Calculated with the help of relationship between K _{OC} and K _{OW} given in <i>Karickhoff</i> , 1981

* Values of half-life in water and soil for trifluralin were estimated as averages of data found in publications and available in data bases.