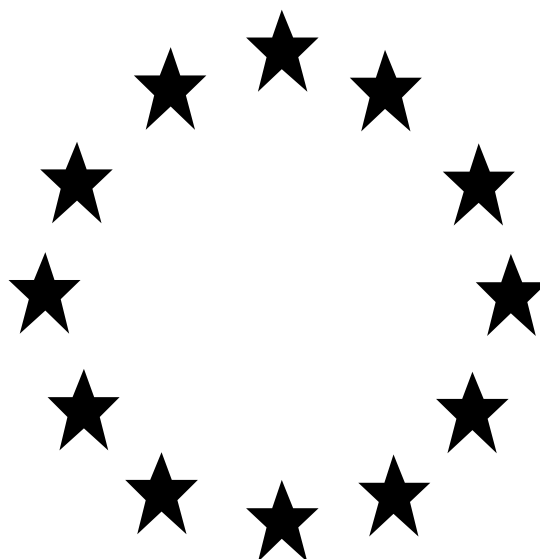




Additional Report to the DAR

- public version -

**Risk assessment provided by the rapporteur Member State
Italy for the existing active substance**

CHLOROPICRIN

**upon resubmission in the framework of the accelerated procedure in
accordance with Commission Regulation (EC) No 33/2008**

**Volume 3
Annex B8**

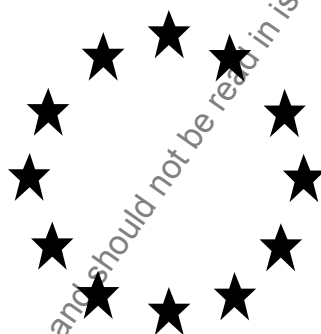
March 2010

Ministry of Health

Rome

Italy

**Addendum to Draft Assessment Report
regarding resubmission of Chloropicrin**



Chloropicrin

Volume 3

Annex B.8: Environmental fate and behaviour

March 2010

B.8 ENVIROMENTAL FATE AND BEHAVIOUR

B.8.1 Route and rate of degradation in soil (IIA 7.1.1, IIIA 9.1.1)

Aerobic degradation studies

Please refer to the DAR from 2006.

Anaerobic degradation studies

Please refer to the DAR from 2006.

Soil photolysis

Please refer to the DAR from 2006.

Field studies

Please refer to the DAR from 2006.

Summary of route and rate of degradation in soil

In general the laboratory degradation studies diverged from EU and SETAC guidance documents but the Völkel, W. 2004 study, which was conducted under aerobic conditions, at 40% moisture holding capacity and at 20°C using four European soils. The DT₅₀ values of [14C]Chloropicrin ranged from approximately 4 to 27 days depending on soil types. DT₉₀ values of 13-89 days were also obtained. One of the 4 soils was further tested at 10°C and DT₅₀ and DT₉₀ values of 10 and 33 days were obtained, respectively. Kinetics of degradation of Chloropicrin showed linear relationships ($0.92 < r^2 < 0.98$). Still, duplicate samplings appear inadequate for soils II (3 time points) and IV (2 time points). No data on recoveries and LOD-LOQ were provided.

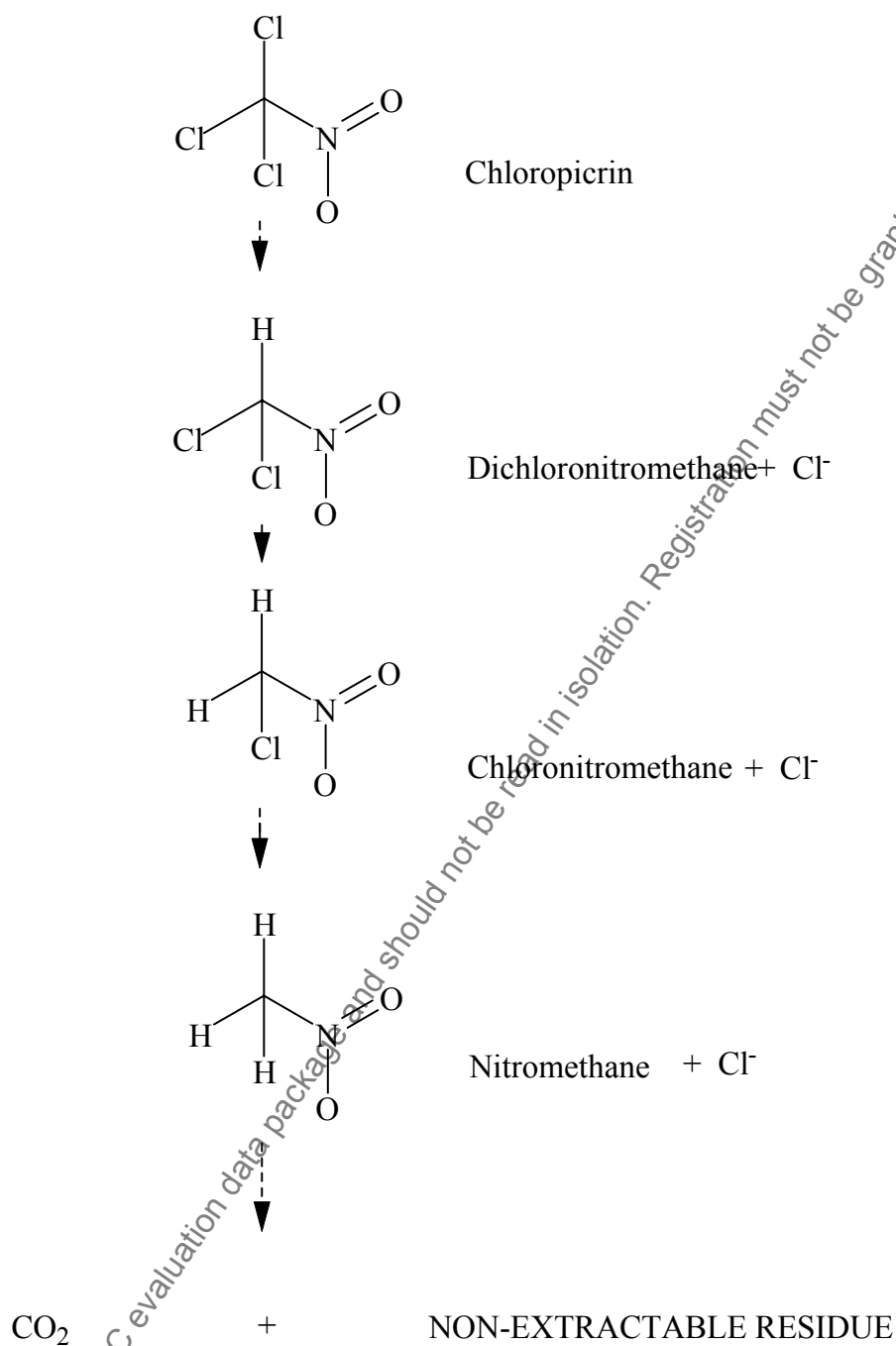
A laboratory degradation study on Chloropicrin, which was conducted in aerobic conditions, at 75% field capacity, 25°C and using a sandy loam soil collected in Ohio, showed a DT₅₀ value of 1 h. Another study, conducted under similar aerobic conditions (75% field capacity, 25°C) but using a sandy loam soil collected in California, showed that the degradation of Chloropicrin proceeds through the formation of Dichloronitromethane, chloronitromethane, and nitromethane and finally to carbon dioxide, with a DT₅₀ value for the parent compound of 4.5 days. The carbon dioxide was the main metabolite (75% after 24 days).

In three separate laboratory sub-experiments, conducted under anaerobic conditions using the Ohio soil was used, DT₅₀ values of Chloropicrin ranged from 6 to 20 hours and nine unidentified degradates and inorganic chloride were detected. The California soil was also used to conduct another anaerobic soil degradation study where <1% of the applied Chloropicrin was detected in soil after 1 d and metabolites chloromethane (trace amounts after 4 hours) and nitromethane were detected (3% after 5 d). These 2 metabolites reached percentages higher than 10 in the water fraction. By the study endpoint, about one third of the applied radioactivity had been incorporated into soil components indicating that significant mineralization occurred even under anaerobic conditions. Nevertheless, the quantitative yield of CO₂ was not reported.

The soil photolysis of Chloropicrin was not investigated as the agricultural practices surrounding the use of Chloropicrin make it unlikely that it will be deposited on the soil surface.

A field dissipation study was conducted using two soils found at two separate test sites within California. Chloropicrin was applied to the test sites at exaggerated rates, and the dissipation was followed by sampling the soil air space at various soil depths. Individual DT_{50} values were calculated for each soil depth in each soil and ranged from 0.48 to 4.95 days (clay loam soil), and from 0.75 to 5.63 days (sand soil). There was a general trend toward increasing DT_{50} values with increasing soil depth. Data indicated a downward movement of Chloropicrin during the study, which was found up to 1.2 m depth which was more pronounced in the sand soil. After 8 days, Chloropicrin concentration was slightly higher than the background level of 2.92 mg/kg in the clay loam soil and was 6 times higher than the background in the sand soil.

Figure 8.1-1: Proposed metabolic pathway for Chloropicrin in soil



Assessment of route and rate of degradation in soil

The routes of both aerobic and anaerobic degradation of Chloropicrin in several soil types have been determined. Nevertheless, only one aerobic degradation study was conducted following SETAC guidelines, nevertheless metabolites were not assessed. In this study, the effect of temperature on Chloropicrin degradation rate has been tested in one soil (silt loam).

Table 8.1-1: Determination of an average aerobic half-life of chloropicrin under normalised soil moisture (pF 2) and temperature (20 °C) conditions according to FOCUS (2000)

Soil texture	DT ₅₀ [d]	Soil moisture during study θ_{act} [% (w/w)]	Soil moisture at field capacity θ_{ref} [% (w/w)]	Soil moisture corr. factor $f_{soil\ moisture}$	Incubation temperature [°C]	Normalised half-lives [d]
Silt loam	3.9	24.2	26	0.95	20 °C	3.7
Sandy loam	26.9	14.1	19	0.8	20 °C	21.8
Loam	6.1	16.8	25	0.76	20 °C	4.6
Silty clay loam	9.8	19.7	30	0.74	20 °C	7.3
Arithmetic mean for chloropicrin						9.4

Table 8.1-2: DT₇₅ and DT₉₀ of chloropicrin

Soil	Soil I (Silt loam) 20°C	Soil II (Sandy loam) 20°C	Soil III (Loam) 20°C	Soil IV (Silty clay loam) 20°C	Soil I (Silt loam) 10°C
DT-75 (days)	7.8	53.8	12.1	19.6	19.6
DT-90 (days)	13.0	89.3	20.2	32.6	32.6

The highest DT50 value observed was 26.9 days from a sandy loam soil. The sandy loam soil used in this study has a much lower microbial biomass (marginally over the recommended 1% criteria of the total organic carbon content of the soil) as compared to the other soils tested, which would account for an uncharacteristically high DT50 value. A more realistic half-life value of 9.4 days has been used for environmental risk assessment (the use of the average is justified in FOCUS 2000, 2002).

Two other laboratory studies, which were not conducted under SETAC guidelines, demonstrated the formation of several degradation products at percentages <5 or in trace amounts (nitromethane, chloronitromethane, Dichloronitromethane, chloroform). Higher percentages for CO₂ (75% after 24 days) were observed.

In anaerobic degradation studies conducted in one soil, Chloropicrin was transformed into inorganic chloride and nine other unidentified degradates with DT50lab values ranging from 6 to 20 hours. In another anaerobic study, <1% of the applied Chloropicrin was detected in soil

after 1 d and the metabolites chloromethane (trace amounts after 4 hours) and nitromethane (3% after 5 d) were detected. CO₂ formation was not quantitatively defined.

Photodegradation in soil has not been investigated as agricultural practices make it unlikely that Chloropicrin will be deposited on the soil surface.

Results from a field dissipation study, conducted at an exaggerated application rate in California, indicates a rapid degradation of Chloropicrin whose DT50 ranged from 0.48 to 4.95 days in a clay loam soil, and from 0.75 to 5.63 days in a sand soil.

B.8.2 Adsorption, desorption and mobility in soil (IIA 7.1.2, 7.1.3, IIIA 9.1.2)

Adsorption and desorption

Please refer to the DAR from 2006 for the original study by Skinner W 1996

Penketh, S. Chloropicrin Adsorption/Desorption on Five Soils. Huntingdon Life Sciences unpublished report number SXC0001. Owner: European Chloropicrin Group. 2008. (IIA 7.4.1/02)

GLP: Yes

In response to comments made in the original DAR reporting table with regards to the acceptability of the Koc data derived by Skinner (1996) an adsorption/desorption study to determine the mobility of Chloropicrin was carried out. The study was conducted to investigate the adsorption/desorption characteristics of Chloropicrin on five soils using the batch equilibrium method. The study was carried out in accordance with OECD guideline number 106.

The test soils represented a range of textural classes, with pH values (in 0.01 M CaCl₂) between 4.3 and 7.2 and an organic carbon content ranging from 0.5 to 3.9%. Five soils were tested (Arrow, Bromsgrove, Elmtown, Evesham and Warsop). Preliminary experiments were conducted to ascertain an appropriate soil-to-solution ratio and adsorption and desorption equilibrium times. Adsorption to the surface of the glass tubes was also investigated. The stability of Chloropicrin under the test conditions was demonstrated in Warsop soil.

The experiment was conducted using sterile soil for Evesham soil only. 20 g soil samples were made up to 20 mL with 0.01 M CaCl₂ solutions containing Chloropicrin at nominal concentrations of 5.0, 1.0, 0.25, 0.1 and 0.05 mg/L (soil-to-solution ratio of 1:1 (w/v) after pre-equilibration. The solutions were equilibrated for 2 hours (Evesham soil) or 24 hours (all other soils), centrifuged, the supernatant was then removed and the solutions were radioassayed. For the desorption phase, the solutions removed were replaced with an identical volume of fresh solution and these solutions were then equilibrated and treated as previously. Radioactivity in the CaCl₂ solutions was determined by LSC. Samples of the highest test substance concentration for each soil were pooled and analysed by HPLC, and such samples remaining from the adsorption and desorption phases were extracted twice with acetonitrile and acetonitrile/water (1:1, v/v) by shaking, where required. Soil/solutions were centrifuged and the supernatant analysed by HPLC. Soil residue remaining after extraction was air-dried, combusted and radioassayed. Adsorption coefficients were estimated from the distribution of radioactivity between the soils and CaCl₂ solutions. A summary of the results is provided in Table B 8.2-1.

Table B.8.2-1 Adsorption and desorption characteristics of ^{14}C -Chloropicrin

Soil	Organic carbon %	Adsorption				Desorption			
		$K_{\text{ads F}}$	$K_{\text{ads Fom}}$	$K_{\text{ads Foc}}$	1/n	$K_{\text{des F}}$	$K_{\text{des Fom}}$	$K_{\text{des Foc}}$	1/n
Arrow	1.9	1.15	34.8	60.5	0.68	nc	-	-	-
Bromsgrove	1.2	0.414	19.7	34.5	1.00	1.04	49.5	86.2	0.88
Elmton	3.9	Nc	-	-	-	nc	-	-	-
Evesham	1.8	0.448	14.5	24.9	0.88	1.12	36.1	62.2	0.89
Warsop	0.5	0.609	67.7	122	1.08	1.28	142	256	0.97

$K_{\text{ads F}}$ Freundlich adsorption distribution coefficient

$K_{\text{ads Foc}}$ Coefficient of adsorption per unit organic carbon

$K_{\text{ads Fom}}$ Coefficient of adsorption per unit organic matter

$K_{\text{des F}}$ Freundlich desorption distribution coefficient

$K_{\text{des Foc}}$ Coefficient of desorption per unit organic carbon

$K_{\text{des Fom}}$ Coefficient of desorption per unit organic matter

1/n Slope of the Freundlich desorption isotherm

nc Not calculable due to degradation of test substance

Analysis of the soil extracts and aqueous supernatants confirmed the stability of Chloropicrin over the period of the study. Mass balance recoveries were in the range 51.8% to 96.0% applied radioactivity.

The Freundlich adsorption coefficients (K_F) for adsorption were in the range 0.414 – 1.15, showing Chloropicrin was not well adsorbed to the test soils. Adsorption coefficients corrected for organic carbon content (K_{oc}) were in the range 24.9 – 122. The desorption coefficients (K_F) were in the range 1.04 – 1.28, indicating a degree of irreversibility to the adsorption of Chloropicrin.

Conclusion:

The study was carried out according to OECD guidelines. The adsorption and desorption behaviour of Chloropicrin has been studied in five soils. Freundlich adsorption coefficients ($K_{\text{ads Foc}}$) were calculated in four of the soils and were in the range 0.414 - 1.15. Adsorption coefficients corrected for organic carbon content (K_{Foc}) were in the range 24.9 – 122 (mean value 60.5 l/kg with 1/n of 0.91), indicating low affinity of Chloropicrin for soil. Using the McCall scale to assess potential mobility (based on $K_{\text{ads Foc}}$), Chloropicrin is classified as having a 'very high' to 'high' potential for mobility in soil. There was no correlation between soil pH and the degree of adsorption.

The study is deemed acceptable.

A K_{oc} value of 24.9 has been estimated for the metabolite Dichloronitromethane (DCNM) using EPTWIN (Posthumus *et. al.* 2005). According to the McCall classification scheme this value indicates high potential for mobility in soil.

Column leaching

The study above (Skinner W., 1996) provides column leaching data. Percentages found in leachates from the four soil columns were: Chloropicrin 8.2-59.6%; Dichloronitromethane 0.8-22.4%; dichloromethylhydroxylamine 0.2-20.7%; nitromethane 1.2-2.5% The metabolite

dichloromethylhydroxylamine was detected in leachates only. Furthermore an aged column leaching study was carried out to OECD guidelines. Please see below.

Aged column leaching

Sheplar, K. Aged Leaching of [¹⁴C]Chloropicrin in Representative Agricultural Soil. PTRL West Inc. unpublished report number 51645W-1. Owner: European Chloropicrin Group. 2009. (IIA 7.4.3/02)

GLP: Yes

In response to comments made in the original DAR reporting table with regards to the need for a study investigating the aged column leaching behaviour of Chloropicrin in soil and the formation of metabolites, a study was carried out in accordance with U.S EPA Pesticide Assessment Guidelines Subdivision N, Chemistry: Environmental Fate Series 163-1 and OECD Guideline 312.

The guidelines state that the test should not be applied to chemicals which are highly volatile from soil and water and thus do not remain in soil and/or leachate under the experimental conditions. As such some modifications to the guidelines were undertaken to ensure the validity of the results. To minimise the effect of the volatility of Chloropicrin, the soil columns were contained in a sealed outer glass column with a constant airflow through a series of volatile traps during the aging and leaching periods to ensure that the test substance remained in the leachate.

The leaching behaviour of Chloropicrin was examined after ageing of its residues in soil for 8 days. Columns were prepared, injected with Chloropicrin and immediately covered with a Virtually Impermeable Film (VIF) tarp. Leachate fractions of approximately 100 mL were collected from each column. Each soil section was extracted with acetonitrile and the post-extracted residues were combusted and radioassayed.

Bromsgrove loamy sand soil was used for this study. Teflon ® columns (~ 48 cm long, 2" internal diameter) were used in this study. Teflon was chosen as it was demonstrated to be non-reactive with Chloropicrin. Normally, a column would be filled to a depth of 28 cm, however, since Chloropicrin is injected 20 cm below the surface, the depth of the columns was increased to 48 cm. Due to the volatility of Chloropicrin, the soil was immediately covered with a Virtually Impermeable Film (VIF) tarp to retain Chloropicrin. Duplicate columns were treated with [¹⁴C]Chloropicrin and aged for 8 days. Microbial viability of the soil was demonstrated prior to dosing. The columns were treated with 90 mg of test substance. This corresponded to the maximum use rate of 448 kg a.s./hectare based on the soil column surface. Due to the volatility of Chloropicrin, the soil columns were contained in a sealed outer glass column with a constant airflow through a series of volatile traps during the ageing and leaching periods.

Following the ageing period, the outer container was opened briefly while the tarp was removed then resealed. The columns were leached with 694 mL of 0.01M CaCl₂ aqueous solution with continuous trapping of volatiles from the top and bottom of the columns. The recommended volume (equal to 200 mm) is approximately 405 mL for a column radius of 2.54 cm. However, this volume was adjusted by multiplying by a factor to compensate for the 20 cm difference in height between this column and the normal guideline column height (factor = 48/28 = 1.7).

Leachate fractions of approximately 100 mL each were collected until the flow from the column stopped. Aliquots of each fraction were taken for radioassay using liquid scintillation

counting (LSC). After the leachate flow had ceased, each soil column was frozen then cut into sections. The top 18 cm of soil (above the treatment zone) was taken for the first column section and the remaining soil column was divided into one 4 cm section at the dose level (18-22 cm) and four 6.5 cm sections (22-28.5, 28.5-35, 35-41.5, 41.5-48). Each section was extracted with acetonitrile (200 mL x 2). The post-extracted residues (PES) were combusted and radioassayed. Radiocarbon recoveries were calculated based on the sum of the leachates, soil extracts, post extracted soil (PES) and volatile traps. Preliminary tests to evaluate the trapping efficiency of the apparatus were performed.

Selected soil leachates, segment extracts and methanol volatile trap solutions were analyzed by high performance liquid chromatography (HPLC). HPLC peak assignments were verified by gas chromatography in tandem with mass spectroscopy (GC/MS).

Expressed as percent of radiocarbon recovered, the distribution of radiocarbon was similar for both columns with the leachates containing 62.2 and 53.4%, the soil extracts 8.6 and 7.1%, the PES 23.4 and 26.3% and the volatile traps 5.7 and 13.1% for columns A and B, respectively.

Chloropicrin represented the largest component in the soil columns and leachates, averaging 33.3% of the recovered radiocarbon in Column A and 28.2% in column B. Dichloronitromethane (DCNM), the largest observed degradate in the study represented 20.4% of the recovered radiocarbon in column A and 21.3% in column B. Chloronitromethane and at least two other minor peaks were detected by HPLC, but these three combined peaks did not exceed 9.4% of available radiocarbon.

The distribution coefficients (K_d) for Chloropicrin and Dichloronitromethane were calculated by determining the volume of leachate necessary to remove 50% of the compound. The results of the K_d calculations for Chloropicrin and Dichloronitromethane are presented in Table B.8.2-2.

Table B.8.2-2 Calculation of K_d Values for Chloropicrin and Dichloronitromethane Following the Aged Leaching of [^{14}C]Chloropicrin in a Loamy Sand

Soil	Volume leachate (mL)	% of compound in leachate	Volume required to leach 50%	Weight soil (g)	Wet/dry ratio	Dry wt soil (g)	K_d (mL/g)
Chloropicrin Column A	683.3	95.2	358.9	1130.6	1.079	1047.8	0.343
Chloropicrin Column B	705.1	85.1	414.3	1067.5	1.079	989.3	0.419
Average							0.381
DCNM Column A	683.3	99.5	343.4	1130.6	1.079	1047.8	0.328
DCNM Column B	705.1	89.7	393.0	1067.5	1.079	989.3	0.397
Average							0.363

A K_{OC} value, relating the volume required to leach 50% of the compound to the organic carbon content of the soil was also calculated for both compounds. The average K_{OC} was calculated to be 31.65 and 30.14 for Chloropicrin and Dichloronitromethane, respectively.

Conclusion:

The study was carried out to OECD guidelines. The average K_d values for Chloropicrin and Dichloronitromethane based on the leachate volumes necessary for 50% elution from the columns were calculated to be 0.381 and 0.363, respectively.

The major breakdown product of Chloropicrin was found to be Dichloronitromethane with a formation fraction of 20.4% of the recovered radiocarbon in column A and 21.3% in column B (mean value of 21%). The proposed degradation pathway inferred by the study reports supports that presented in Figure B.8.1-1.

Radiocarbon recoveries were 139.7 % and 94.7% for columns A and B, respectively based on the applied radiocarbon. This discrepancy in recoveries was the result of a spill during the application of column A that affected the amount of radiocarbon applied to the column and also the amount recovered. Since most of the dose was comprised of unlabeled Chloropicrin, the spill did not significantly affect the concentration of Chloropicrin in the columns. The validity and integrity of the study results were not considered to be significantly affected by the difference in radioactivity between the two columns. The study is acceptable.

Lysimeter and field leaching studies

Data from the study "Quantitative Characterisation of [^{14}C] Residues Present in Soil, Strawberries, Green Beans and Red Beets Grown Under Actual Field Conditions Following Treatment of Soil with [^{14}C] Chloropicrin", Lawrence, J. L., 1990, demonstrate that Chloropicrin is readily converted to CO_2 in soil. The study is not available.

Summary of adsorption, desorption and mobility in soil

The approach used for the definition of Chloropicrin adsorption, desorption and mobility in soil is according to recommended OECD guidelines. An adsorption/desorption study was carried out in five soils. Freundlich adsorption coefficients ($K_{\text{ads, Foc}}$) were calculated in four of the soils and were in the range 0.414 - 1.15. Adsorption coefficients corrected for organic carbon content (K_{Foc}) were in the range 24.9 – 122 (mean value of 60.5 l/kg with 1/n value of 0.91), indicating low affinity of Chloropicrin for soil. Using the McCall scale to assess potential mobility (based on $K_{\text{ads, Foc}}$), Chloropicrin is classified as having a 'very high' to 'high' potential for mobility in soil.

An aged column leaching study using was carried out in order to determine the breakdown products of Chloropicrin in soil and to derive K_d values. Some modifications of the guidelines were required due to the volatility of Chloropicrin and its application method. The major breakdown product of Chloropicrin in soil was found to be Dichloronitromethane. The average K_d values for Chloropicrin and Dichloronitromethane based on the leachate volumes necessary for 50% elution from the columns were calculated to be 0.381 and 0.363, respectively. K_{oc} of 30.14 l/kg has been calculated for DCNM from the K_d value of 0.363.

On the basis of the above mentioned results Chloropicrin and its metabolites have some leaching potential when saturated soils are subjected to extreme rainfall events. This potential is investigated in section B.8.5 below.

Assessment of adsorption, desorption and mobility in soil

In response to comments in the original DAR reporting table adsorption/desorption and aged column leaching studies have been carried out. Data on the mobility of Chloropicrin and its major metabolite Dichloronitromethane in soil has been derived. Generally both substances have demonstrated “high” potential for mobility in soil. Literature data supports some of these results, particularly for Chloropicrin.

B.8.3 Predicted environmental concentrations in soil (PEC_{soil}) (IIIA 9.1)

Moltmann, J.F. Predicted Environmental Concentrations in Soil (PEC_{soil}) and Ground Water (PEC_{gw}) for Chloropicrin and its Major Metabolite Dichloronitromethane (DCNM) in Preparation of the Planting of Tomatoes. ECT Oekotoxikologie GmbH report number P8054-01-09. Unpublished. Owner: European Chloropicrin Group. 2009. (IIIA 9.4/01)

Chloropicrin is intended for use as a pre-emergence soil fumigant for the preventive control of soil borne fungi before the planting of crops. The recommended maximum application rate for Chloropicrin is 448 kg/ha (equivalent to 272 l/ha). One application per season is proposed. Chloropicrin is proposed for use as a soil fumigant that is applied by soil injection methods to a depth of 20 cm. The treated area is then covered with tarp to reduce Chloropicrin losses to the atmosphere.

PECs in soil were calculated according to the Draft Working Document (EU DG Agriculture, VI B II.1, Document No. 7193/VI/99 rev.0 of 09.08.1999) and the FOCUS Document on Soil Persistence Models (FOCUS 1996). Soil PECs are not calculated specifically for certain crops or regions in the EU, and are based only on application rate and plant interception, and, for off-crop soils, on drift rate – which is not of concern for Chloropicrin because of the application by injection and tarping. In an aged column leaching study (Sheplar, 2009) Dichloronitromethane was found to be a soil metabolite of Chloropicrin with a formation fraction of approximately 20%. As such Dichloronitromethane concentrations in soil were also calculated.

Actual PECs over time PECs(t) and Time Weighted Average TWAC(t) concentrations of Chloropicrin and DCNM have been calculated. PEC_{soil} values for Chloropicrin and DCNM were calculated according to the GAP. Soil concentrations are given as mg/kg of dry soil starting at the day of application and are shown in Table B8.3.1..

Table B 8.3-1: PEC_{soil} values (actual after application and time-weighted average) for Chloropicrin and DCNM in-crop (no crop interception; distribution to 20 cm); application rate 448 kg a.s./ha, DT₅₀ 2.9/9.4 days (biphasic)

In crop Time [d]	Chloropicrin		DCNM	
	PEC soil actual [mg a.s./kg dw]	TWA conc. [mg a.s./kg dw]	PEC soil actual [mg met./kg dw]	TWA conc. [mg met./kg dw]
Initial	149.3	-	44.1 ^a	-
1	117.6	132.8	34.7	39.2
2	92.6	118.7	27.3	35.0
4	57.4	96.2	16.9	28.4
7	28.0	72.5	8.3	21.4
14	16.7	56.3	4.9	16.7

In crop Time [d]	Chloropicrin		DCNM	
	PEC soil actual [mg a.s./kg dw]	TWA conc. [mg a.s./kg dw]	PEC soil actual [mg met./kg dw]	TWA conc. [mg met./kg dw]
28	6.0	36.6	1.8	10.9
50	1.2	21.8	0.35	6.5
100	0.029	10.5	0.009	3.1

^{a)} DCNM PEC_{soil} calculations start at the maximum of 132.2 kg/ha four days after application

RMS comment: PECs calculations are not acceptable and have been updated with the following input data for chloropicrin and its metabolite.

Table B 8.3-2: Input parameters

Parameters	Chloropicrin	DCNM
Molecular weight	164.4	130
DT₅₀ (aerobic) soil 20°C	9.4 days (mean value)	9.4 days (mean value)
Formation fraction		21%
Application rate	448 kg/ha	74.4 kg/ha
Interception	0	0

Italy disagrees with the Notifier's assumption regardless the fact that there will be a temperature gradient from the top of soil downwards. The effects of solarization on the rate of loss are evident under particular climatic conditions (Serrano et al. 2010; Gopal et al. 2000), moreover a specific field study, in the application conditions, could be useful to predict the soil temperature after the tarping period.

PECs in soil were calculated according to the Draft Working Document (EU DG Agriculture, VI B II.1, Document No. 7193/VI/99 rev.0 of 09.08.1999) and the FOCUS Document on Soil Persistence Models (FOCUS 1996). PEC calculations have been updated with the input data in table above.

Table B 8.3-3: PEC_{soil} values (actual after application and time-weighted average) for Chloropicrin and DCNM in-crop (no crop interception; distribution to 20 cm); application rate 448 kg a.s./ha, DT₅₀ 9.4 days

In crop Time [d]	Chloropicrin		DCNM	
	PEC soil actual [mg a.s./kg dw]	TWA conc. [mg a.s./kg dw]	PEC soil actual [mg met./kg dw]	TWA conc. [mg met./kg dw]
Initial	149.3	-	24.8 ^a	-
1	138.7	144.0	23.0	23.9
2	128.9	138.8	21.4	23.0
4	111.2	129.3	18.5	21.5
7	89.1	116.6	14.8	19.4
14	53.2	93.1	8.8	15.5
21	31.7	75.9	5.3	12.6
28	18.9	63.2	3.1	10.5
50	3.7	39.5	0.6	6.6
100	0.1	20.2	0.02	3.4

a) DCNM PEC_{soil} calculations start at the maximum of 74.4 kg/ha four days after application

B.8.4 Fate and behaviour in water (IIA 7.2.1, IIIA 9.2)

Hydrolytic degradation

Please refer to the DAR from 2006.

Photolytic degradation

Please refer to the DAR from 2006.

Ready biodegradability study

Please refer to the DAR from 2006.

Water/sediment studies

No further study has been performed to investigate the degradation of Chloropicrin or its metabolites in the saturated zone.

During Chloropicrin treatment of soil the soil area is tarped with plastic covers to prevent escape to the atmosphere by volatilisation. Tarping reduces exposure of treated soil to possible rainfall that might cause soil runoff (physical transport of product or soil particles, to which the product can be adsorbed) into water streams or ponds.

In addition, according to the Draft OECD Guideline 308, a water sediment study should not be carried out on chemicals that are highly volatile from water (e.g. fumigants, organic solvents) and thus cannot be kept in water/or sediment under the experimental conditions. As

this would apply for Chloropicrin it is proposed that this study is therefore not relevant to Chloropicrin. Furthermore the feasibility of carrying out a study to investigate the behavior of Chloropicrin in a water/sediment system was investigated by Huntingdon Life Sciences. Given the particular properties of Chloropicrin including its volatility and its extremely rapid dissipation in water it was concluded that such a study would be technically very difficult to undertake.

Summary of Fate and Behavior in water

A hydrolysis study showed that Chloropicrin was stable to hydrolysis at pH 5, 7, and 9. In an aqueous photolysis study conducted using sterile pH 7 buffer and artificial sunlight, the photolytic half-life was 1.3 days. When this value was corrected to reflect the natural light flux as measured at the testing laboratory, the DT₅₀ was adjusted upward to 5 days. In aqueous solution, Chloropicrin degraded in light to CO₂ (and HCO₃⁻), chloride, nitrate, and nitrite ions. In a separate study, Chloropicrin's quantum yield was determined to be 0.5699.

In a biodegradability study, Chloropicrin was not readily biodegradable (starting dose decrease <60% after 28 d).

Still, it did not inhibit degradation of the reference material sodium benzoate, and was classified as 'inherently biodegradable'.

Chloropicrin is a volatile compound with a high Henry constant and it is unlikely to reach the surface water and saturated zone, thus no water/sediment data were developed, or required.

Assessment of fate and behavior in water

The hydrolysis of Chloropicrin was investigated over the environmentally relevant pH range. Chloropicrin was found to be stable at pH 4, pH 7 and pH 9. These results indicate that hydrolysis will not be an important route in the degradation of Chloropicrin. Aqueous photolysis was investigated using an artificial light source (e.g. xenon arc). Under the conditions of the experiment, Chloropicrin was found to degrade with a DT₅₀ value of 1.3 days, a value that corresponds to 5 days in natural sunlight. Carbon dioxide (and HCO₃⁻), chloride, nitrate, and nitrite ions were the observed photolysis products. In a separate experiment, the quantum yield was determined which will allow photolysis rates to be calculated for various seasons and latitudes if required. The relatively short half-life of 5 days indicates that photolytic degradation of Chloropicrin would be an important route of degradation in the unlikely event that Chloropicrin were found in surface water.

Degradation of Chloropicrin in sediment/water systems was not investigated as the high volatility of Chloropicrin makes it unlikely that it will reach the saturated zone. Technical difficulties also mean that the feasibility of such a study is questionable.

Dichloronitromethane (CHCl₂NO₂) was identified as a soil metabolite of Chloropicrin in an aged column leaching study. This metabolite was found at levels of 21% of the parent compound. As such it has triggered further consideration as a potentially relevant soil metabolite, as determined by the European Commission Guidance Document on the Assessment of the Relevance of Metabolites in Groundwater for Substances Regulated under Council Directive 91/414/EEC.

The accepted breakdown pathway of Chloropicrin in many environmental and animal systems is sequential dechlorination from Chloropicrin → Dichloronitromethane → Chloronitromethane → Nitromethane → CO₂. This breakdown pathway is discussed further later in this document. Dichloronitromethane has been identified in several studies as a

chlorination by-product in drinking water and has been shown to be a common breakdown product in soils.

As required by the European Commission Guidance Document on the Assessment of the Relevance of Metabolites in Groundwater for Substances Regulated under Council Directive 91/414/EC, FOCUS groundwater and surface water modelling simulations have been carried out to model the levels of Dichloronitromethane in the environment as a breakdown product of Chloropicrin.

B.8.5 Predicted environmental concentrations in surface water and ground water (PEC_{sw}, PEC_{gw}) (IIIA 9.2)

Surface water

Moltmann, J.F. Predicted Environmental Concentrations in Surface Water (PEC_{sw}) and Sediment (PEC_{sed}) for Chloropicrin and its Major Metabolite Dichloronitromethane (DCNM) in Preparation of the Planting of Tomatoes. ECT Oekotoxikologie GmbH report number P8054-02-09. Unpublished. Owner: European Chloropicrin Group. 2009. (IIIA 9.7/01)

In response to comments in the DAR reporting table requesting that a new modelling approach be submitted a FOCUS surface water report has been provided for Chloropicrin. The calculations followed the recommendations of the FOCUS Surface Water Scenarios Working Group (FOCUS 2001; final 2003), to determine entry into three types of surface water bodies (pond, ditch, stream).

Drainage

Contamination of surface water is possible through drainage. The adsorption and desorption behaviour of Chloropicrin has been studied in five soils (Penketh S, 2008). Freundlich adsorption coefficients ($K_{ads, Foc}$) were calculated in four of the soils and were in the range 0.414 - 1.15. Adsorption coefficients corrected for organic carbon content (K_{Foc}) were in the range 24.9 - 122, indicating the low affinity of Chloropicrin for adsorption to soil. Using the McCall scale to assess a chemical's potential mobility (based on $K_{ads, Foc}$), Chloropicrin is classified as having a 'very high' to 'high' potential for mobility in soil.

Degradation of Dichloronitromethane (DCNM)

There are no studies available for direct degradation of the metabolite DCNM. However, since the mechanism of dechlorination is the same as for the parent compound, the same half-lives were assumed for the metabolite as for the parent (i.e. water 5 days; sediment 1 day; soil 1 day).

Plant interception was not assumed in the modelling since Chloropicrin is applied by injection into the soil at -20 cm. Although Chloropicrin is expected to distribute within the soil because of its high volatility, it is not expected that significant amounts of Chloropicrin will be present at the surface of the soil and the compound is therefore not expected to be available for runoff. Any residual Chloropicrin on the surface of the soil is expected to rapidly volatilize, and so would not be available for runoff events.

The label recommendation for removal of tarpaulin is 8 days; this is representative of practices occurring through the general use of the product. Therefore, PEC_{sw} concentrations were calculated for 8 days after application, as this represents the time when the tarp would typically be removed under normal field conditions.

A summary of the input parameters used in the FOCUS surfacewater modeling is given in Table B.8.5-1. Maximum PEC_{sw} and PEC_{sed} for Chloropicrin and DCNM for each scenario at FOCUS Step 3 are given in Tables B.8.5-2 and B.8.5-3, respectively. As many surface water scenarios as possible are presented in order to give a wide indication of the behaviour of Chloropicrin in various environmental conditions and soil types. Overall, the highest PEC_{sw} estimates from the ten scenarios are likely to represent at least a 90th percentile worst-case for surface water exposure in the EU.

Table B.8.5-1: Surface water modelling input parameters.

Input Parameter	Unit	Chloropicrin	DCNM	FOCUS Default
Molar Mass	g/mol	164.38	129.93	-
Saturated Vapor Pressure	Pa	26.7 (21°C)	466.6 (25°C)	-
Water Solubility	mg/L	10,000 (25°C)	17,000 (25°C)	-
Molar Enthalpy of Dissolution	Kj/mol	-	-	27
Koc	L/kg	60.5	39.3	-
Freundlich Exponent 1/n	-	0.9	0.9	1
Application Rate	kg/ha	448	-	-
Application Type	-	Soil Injection	Metabolite	-
Formation Rate	%	-	21	-
Q₁₀ Factor	-	-	-	2.58
20°C Aerobic DT₅₀	Days	9.4	9.4	-

Table B.8.5-2: Maximum $PEC_{\text{surface water}}$ and PEC_{sediment} of Chloropicrin from soil injection for different scenarios at FOCUS Step 3

Scenario		1 st application date	$PEC_{\text{sw, max}}$ [$\mu\text{g a.s./L}$]	$PEC_{\text{sed, max}}$ [$\mu\text{g a.s./kg}$]
D3 Vredepeel	ditch	4 th April	0.0	0.0
D4 Skousbo	pond	18 th April	0.000095	0.000087
D4 Skousbo	stream	18 th April	0.000413	0.000354
D5 La Jaillière	pond	7 th March	0.0	0.0
D5 La Jaillière	stream	7 th March	0.0	0.0
D6 Thiva	ditch	9 th April	0.00893	0.00481
R1 Weiherbach	pond	26 th April	0.0	0.0
R1 Weiherbach	stream	26 th April	0.0	0.0
R2 Porto	stream	22 nd April	0.0	0.0
R3 Bologna	stream	4 th April	0.0	0.0
R4 Roujan	stream	8 th April	0.0	0.0

Due to the proposed method of application (soil injection) neither spray drift nor run-off contribute to the PECs. The main entry route for Chloropicrin to water bodies is via drainage.

Table B.8.5-3: Maximum $PEC_{\text{surface water}}$ and PEC_{sediment} of DCNM from soil injection of Chloropicrin in different scenarios at FOCUS Step 3

Scenario		1 st application date	$PEC_{\text{sw, max}}$ [$\mu\text{g/L}$]	$PEC_{\text{sed, max}}$ [$\mu\text{g/kg dw}$]
D3 Vredepeel	ditch	4 th April	0.0	0.0
D4 Skousbo	pond	18 th April	0.000085	0.000064
D4 Skousbo	stream	18 th April	0.000617	0.000420
D5 La Jaillière	pond	7 th March	0.0	0.0
D5 La Jaillière	stream	7 th March	0.0	0.0
D6 Thiva	ditch	9 th April	0.00413	0.00188
R1 Weiherbach	pond	26 th April	0.0	0.0
R1 Weiherbach	stream	26 th April	0.0	0.0
R2 Porto	stream	22 nd April	0.0	0.0
R3 Bologna	stream	4 th April	0.0	0.0
R4 Roujan	stream	8 th April	0.0	0.0

Atmospheric deposition

The impact of Chloropicrin in air has been addressed according to the FOCUS Air guidance document, 'European Commission Document SANCO/10553/2006, Rev 2, June 2008. Following this it can be concluded that Chloropicrin is not of concern for long-range transport (LRT) as it's half-life in air is below the trigger value set by FOCUS Air (≤ 2 days). The short range transport (SRT) of Chloropicrin in air was evaluated in a tiered approach; a second tier evaluation was required. At Tier II FOCUS Air recommends that the model EVA 2.0 should be used for measuring potential exposure via deposition of volatilised pesticide residues.

However, according to the FOCUS Air document and following further consultation with a member of the FOCUS Air group, it was confirmed that very volatile substances would not adequately be assessed by the given exposure assessment schemes for SRT.

Therefore, due to the extremely high vapour pressure of Chloropicrin, the model EVA₂ is clearly out of its validity range and any assessment schemes proposed for SRT are inadequate in this regard. Thus, the assessment of dry deposition of Chloropicrin, to surface water is not possible at this time due to the lack of appropriate guidance in this area. In any case, when Chloropicrin is applied to the soil and covered with virtually impermeable film, it is unlikely to be released in significant amounts into the atmosphere. While covered by tarp Chloropicrin is degraded and so, once the tarp is removed, volatilization to the atmosphere is lower. This has been confirmed by the results of a soil emission study (Trevisan, 2009) which charted concentrations following applications of Chloropicrin during and after the tarping period. The Daily Weight Mean (DWM) values were maximum 0.0491 mg/m³ on the day application reaching a DWM maximum of 0.1702 mg/m³ on the day 4.

RMS comment: PECs calculations are not acceptable and have been updated with the following input data for chloropicrin and its metabolite.

Table B.8.5-4: Surface water modelling input parameters.

Input Parameter	Unit	Chloropicrin	DCNM	FOCUS Default
Molar Mass	g/mol	164.4	130.0	-
Saturated Vapor Pressure	Pa	2670 (21°C)	466.6 (25°C)	-
Water Solubility	mg/L	10,000 (25°C)	17,000 (25°C)	-
Molar Enthalpy of Dissolution	Kj/mol	-	-	27
Koc	L/kg	60.5	30.14 ^a	-
Freundlich Exponent 1/n	-	0.9	0.9	1
Application Rate	kg/ha	230.7 ^b	74.4 ^c	-
Application Type	-	Soil Injection	Metabolite	-
Formation Rate	%	-	21	-
Q ₁₀ Factor	-	-	-	2.58
20°C Aerobic DT ₅₀ soil	Days	9.4	9.4	-
20°C Aerobic DT ₅₀ water/sed	Days	5/1	5/1	

^a Koc value is 30.14 l/kg corresponding to Kd = 0.363 from Aged column leaching study

^b In order to simulate the fact that rainfall cannot induce a leaching while soil is covered with a tarp (8 days), application of 230.7 kg/ha has been considered (initial application 448 kg/ha)

$\text{Appl (t day)} = \text{Appl}_{\text{initial}} e^{(-t \times \ln 2 / \text{DT}_{50})}$

^c $\text{Appl (met)} = \text{Appl a.s.} \times 0.21 \times 130/164.4 = 74.4 \text{ kg/ha}$

Italy disagrees with the Notifier's assumption regardless the fact that there will be a temperature gradient from the top of soil downwards. The effects of solarization on the rate of loss are evident under particular climatic conditions (Serrano et al. 2010; Gopal et al. 2000), moreover a specific field study, in the application conditions, could be useful to predict the soil temperature after the tarping period.

Due to the proposed method of application (soil injection) neither spray drift nor run-off contribute to the PECs. The main entry route for Chloropicrin to water bodies is via drainage.

In the following tables have been reported the results for PEC calculations of Chloropicrin.

Table B.8.5-5: $PEC_{\text{surfacewater}}$ and PEC_{sediment} of Chloropicrin from soil injection for different scenarios at FOCUS Step 3

Scenario		1 st application date	$PEC_{\text{sw, max}}$ [$\mu\text{g a.s./L}$]	$PEC_{\text{sed, max}}$ [$\mu\text{g a.s./kg}$]
D6 Thiva	ditch	April	6.573	1.410
R2 Porto	stream	April	0.0	0.0
R3 Bologna	stream	April	0.0	0.0
R4 Roujan	stream	April	0.0	0.0

In the tables below are reported the $PEC_{\text{surfacewater}}$, PEC_{sediment} and TWA values of Chloropicrin only for the scenario with PEC values > 0 (D6).

Table B.8.5-6: $PEC_{\text{surfacewater}}$, PEC_{sediment} and TWA values of Chloropicrin (soil injection) for D6 scenario at FOCUS Step 3

Crop	Water-body	Location	Time (days)	Step 3 PEC_{sw} ($\mu\text{g/l}$)	Step 3 TWA ($\mu\text{g/l}$)
Tomatoes	Ditch	D6	0	6.573	-
			1	4.486	6.259
			4	0.471	3.790
			7	0.141	2.345
			14	0.0645	1.129
			21	0.101	0.859
			28	0.101	0.663
			50	0.0439	0.403
			100	0.0497	0.223
Crop	Water-body	Location	Time (days)	Step 3 PEC_{sed} ($\mu\text{g/kg}$)	Step 3 TWA ($\mu\text{g/kg}$)
Tomatoes	Ditch	D6	0	1.410	-
			1	1.147	1.377
			4	0.303	0.045
			7	0.0944	0.731
			14	0.0301	0.397
			21	0.0331	0.278
			28	0.0308	0.216
			50	0.0127	0.131
			100	0.0131	0.0731

In the following tables have been reported the results for PEC calculations of DCNM.

Table B.8.5-7 Maximum $PEC_{\text{surfacewater}}$ and PEC_{sediment} of DCNM from soil injection of Chloropicrin in different scenarios at FOCUS Step 3

Scenario		1 st application date	$PEC_{\text{sw, max}}$ [$\mu\text{g/L}$]	$PEC_{\text{sed, max}}$ [$\mu\text{g/kg dw}$]
D6 Thiva	ditch	April	4.350	0.779

Scenario		1 st application date	PEC _{sw, max} [µg/L]	PEC _{sed, max} [µg/kg dw]
R2 Porto	stream	April	0.0	0.0
R3 Bologna	stream	April	0.0	0.0
R4 Roujan	stream	April	0.0	0.0

In the tables below are reported the PEC_{surfacewater}, PEC_{sediment} and TWA values of the metabolite DCNM only for the scenario with PEC values > 0 (D6).

Table B.8.5-8: PEC_{surfacewater}, PEC_{sediment} and TWA values of DCNM (soil injection) for D6 scenario at FOCUS Step 3

Crop	Water-body	Location	Time (days)	Step 3 PEC _{sw} (µg/l)	Step 3 TWA (µg/l)
Tomatoes	Ditch D6		0	4.350	-
			1	2.900	4.120
			4	0.369	2.453
			7	0.161	1.541
			14	0.083	0.830
			21	0.119	0.601
			28	0.112	0.475
			50	0.060	0.306
			100	0.061	0.181
Crop	Water-body	Location	Time (days)	Step 3 PEC _{sed} (µg/kg)	Step 3 TWA (µg/kg)
Tomatoes	Ditch D6		0	0.779	-
			1	0.639	0.760
			4	0.183	0.575
			7	0.072	0.407
			14	0.027	0.229
			21	0.032	0.164
			28	0.029	0.130
			50	0.014	0.083
			100	0.013	0.048

Groundwater

Moltmann, J.F. Predicted Environmental Concentrations in Soil (PEC_{soil}) and Ground Water (PEC_{gw}) for Chloropicrin and its Major Metabolite Dichloronitromethane (DCNM) in Preparation of the Planting of Tomatoes. ECT Oekotoxikologie GmbH report number P8054-01-09. Unpublished. Owner: European Chloropicrin Group. 2009. (IIA 9.4/01)

In response to comments in the DAR reporting table requesting that a new modelling approach be submitted, a FOCUS groundwater report has been provided for Chloropicrin and its metabolite Dichloronitromethane (DCNM). The FOCUS groundwater scenarios are described in SANCO Document 321/2000 rev. 2 (FOCUS 2000). Simulations were conducted for all nine

groundwater scenarios and as recommended by the “Opinion of the Scientific Panel on Plant Health, Plant Protection Products and their Residues on a request of EFSA related to FOCUS groundwater models [The EFSA Journal (2004)93, 1-20]”, calculations for PEARL and PELMO were presented.

In order to simulate the fact that rainfall cannot induce leaching while the soil is covered with a tarp, application was split in the groundwater models. When the tarp is removed, the soil is exposed to rainfall events. Once rainfall or irrigation occurs, the soil becomes saturated with water which facilitates leaching of Chloropicrin and its metabolite DCNM to ground water. Both substances possess a low adsorptivity. Temporary saturated conditions very much resemble the situation in the experiment by Hatton et al. (1995), from which a half-life of 1 day for Chloropicrin and DCNM was derived under flooded conditions.

The PEC_{gw} calculations were based on an initial application of 448 kg a.s./ha and a period under tarp of 7 days after application (35 °C; $DT_{50,aerob}$ 2.9 days) resulting in a level of Chloropicrin equivalent to 66.2 kg a.s./ha at day 8, when the tarp is removed, and thereafter a soil temperature of 20°C and a $DT_{50,flooded}$ of 1 day. The same half-lives were applied for metabolite DCNM. In the case of the scenario Porto (no irrigation), it was assumed that the soil remains aerobic and a DT_{50} of 9.4 d was applied after removal of the tarp on day 8. A summary of the input parameters used in the PEARL and PELMO groundwater models is presented in table B8.5-4

Table B.8.5-9: Surface water modelling input parameters.

Input Parameter	Unit	Chloropicrin	DCNM	FOCUS Default
Molar Mass	g/mol	164.38	129.93	-
Saturated Vapor Pressure	Pa	26.7 (21°C)	466.6 (25°C)	-
Water Solubility	mg/L	10,000 (25°C)	17,000 (25°C)	-
Molar Enthalpy of Dissolution	Kj/mol	-	-	27
Koc	L/kg	60.5	39.3	-
Freundlich Exponent 1/n	-	0.9	0.9	1
Application Rate	kg/ha	448	-	-
Application Type	-	Soil Injection	Metabolite	-
Formation Rate	%	-	21	-
Q₁₀ Factor	-	-	-	2.58
20°C Aerobic DT₅₀	Days	9.4	9.4	-
20°C Flooded Soil DT₅₀	Days	1	1	-

PEC_{gw} for Chloropicrin and Dichloronitromethane (DCNM) are shown in Table B.8.5-5.

Table B.8.5-10: PEC_{ground water} values for Chloropicrin and DCNM (80th percentile of annual average) calculated with PEARL and PELMO for the tomato scenarios

PEARL	80 th percentile of PEC _{gw} (µg/L)	
Scenario	Chloropicrin	DCNM
Châteaudun	< 0.00001	< 0.00001
Piacenza	0.000003	0.000049
Porto	0.000933 ^a	0.034269 ^a
Sevilla	< 0.00001	< 0.00001
Thiva	< 0.00001	< 0.00001

^a) Values for scenario Porto were derived under aerobic conditions (no irrigation) with a DT₅₀ of 9.4 days.

PELMO	80 th percentile of PEC _{gw} (µg/L)	
Scenario	Chloropicrin	DCNM
Châteaudun	<0.001	<0.001
Piacenza	<0.001	<0.001
Porto	<0.001 ^a	<0.001 ^a
Sevilla	<0.001	<0.001
Thiva	<0.001	<0.001

^a) Values for scenario Porto were derived under aerobic conditions (no irrigation) with a DT₅₀ of 9.4 days

RMS comment: PECs calculations are not acceptable and have been updated with the following input data for chloropicrin and its metabolite (Table B.8.5-11).

Table B.8.5-11: Groundwater modelling input parameters.

Input Parameter	Unit	Chloropicrin	DCNM	FOCUS Default
Molar Mass	g/mol	164.4	130.0	-
Saturated Vapor Pressure	Pa	2670 (21°C)	466.6 (25°C)	-
Water Solubility	mg/L	10,000 (25°C)	17,000 (25°C)	-
Molar Enthalpy of Dissolution	Kj/mol	-	-	27
Koc	L/kg	60.5	30.14 ^a	-
Freundlich Exponent 1/n	-	0.9	0.9	1
Application Rate	kg/ha	230.7 ^b	74.4 ^c	-
Application Type	-	Soil Injection	Metabolite	-
Formation Rate	%	-	21	-
Q₁₀ Factor	-	-	-	2.58
20°C Aerobic DT_{50 soil}	Days	9.4	9.4	-

^a Koc value is 30.14 l/kg corresponding to Kd = 0.363 from Aged column leaching study

^b In order to simulate the fact that rainfall cannot induce a leaching while soil is covered with a tarp (8 days), application of 230.7 kg/ha has been considered (initial application 448 kg/ha)

Appl (t day) = Appl_{initial} e^{*}(- t x ln2/DT₅₀)

^c Appl (met) = Appl a.s. x 0.21 x 130/164.4 = 74.4 kg/ha

Italy disagrees with the Notifier's assumption regardless the fact that there will be a temperature gradient from the top of soil downwards. The effects of solarization on the rate of loss are evident under particular climatic conditions (Serrano et al. 2010; Gopal et al. 2000), moreover a specific field study, in the application conditions, could be useful to predict the soil temperature after the tarping period.

PEC_{gw} for Chloropicrin and Dichloronitromethane (DCNM) are shown in Table B.8.5-10.

Table B.8.5-10: PEC_{ground water} values for Chloropicrin and DCNM (80th percentile of annual average) calculated with PEARL and PELMO for the tomato scenarios

PEARL	80 th percentile of PEC _{gw} (µg/L)	
Scenario	Chloropicrin	DCNM
Châteaudun	59.05	74.3
Piacenza	206.5	135.8
Porto	0.24	0.39
Sevilla	42.4	12.9
Thiva	2.45	1.03
PELMO	80 th percentile of PEC _{gw} (µg/L)	
Scenario	Chloropicrin	DCNM
Châteaudun	1.5	153.4
Piacenza	49.1	108.6
Porto	0.27	85.3
Sevilla	13.3	302.2
Thiva	0.78	172.6

Impact on water treatment procedures

Please refer to the DAR from 2006.

Degradation in the saturated zone

Please refer to the DAR from 2006.

B.8.6 Fate and Behaviour in Air (IIA 7.2.2, IIIA 9.3)

Following the release of the FOCUS Air guidance document, additional information / text was included in the resubmission dossier to address the fate and behaviour of Chloropicrin in air. Please also refer to the DAR from 2006.

Following the recent report prepared by the FOCUS Air Group on 'Pesticides in Air: Considerations for Exposure Assessment', a method has been proposed to generate PECs in air and to assess possible exposure from deposition following volatilisation (European Commission Document SANCO/10553/2006 Rev 2, June 2008). In view of this FOCUS Air guidance, an attempt has been made to assess the risk to air quality, via short-range and long-range transport, following application of Chloropicrin to soil.

Short-range transport

Short-range transport (SRT) is defined as being less than 1km from the point of application.

A tiered short-range exposure assessment scheme has been established:

Tier I

Substances that are applied to soil and have a vapour pressure of less than 10^{-4} Pa, need not be considered in the short-range risk assessment. As Chloropicrin exceeds this trigger value (vapour pressure = 2666.447 Pa) a second tier evaluation is required.

Tier II

FOCUS recommends that the model EVA 2.0 should be used for measuring potential exposure via deposition of volatilised pesticide residues. However, according to the FOCUS Air document and following further consultation with a member of the FOCUS Air group, it was confirmed that very volatile substances would not adequately be assessed by the given exposure assessment schemes for SRT. Therefore, due to the extremely high vapour pressure of Chloropicrin, the model EVA is clearly out of its validity range and any assessment schemes proposed for SRT are inadequate in this regard.

Long-range transport

Long-range transport (LRT) is considered as >1000 km from the point of application.

A tiered long-range exposure assessment scheme has been established:

Tier I

FOCUS Air proposes that a LRT (conservative) DT_{50} trigger value in air of ≤ 2 days be used to determine if substances require further evaluation. Both direct and indirect phototransformation in air was evaluated. Indirect photo oxidation was calculated using the Atkinson method (based on the computer modelling program AOP), whilst Carter *et al* (1996) investigated the influence of direct photolysis on the degradation of Chloropicrin in air. The atmospheric half-life (DT_{50}) of Chloropicrin was estimated to be 82 days, as a result of gas-phase reactions between Chloropicrin and photochemically produced atmospheric hydroxyl radicals (O' Carroll, 2005). However, according to Carter *et al*, the more relevant route of degradation of Chloropicrin in air is via direct photolysis by sunlight. The atmospheric half-life of Chloropicrin by direct photolysis, is approximately 18 hours. The intensity and wavelength of the light striking the Chloropicrin molecules can affect the rate of photolysis (Gillis *et al*, 2002). Reported half-lives for the photodegradation of Chloropicrin ranged from 18 hours (Carter *et al*, 1996) to 480 hours/20 days (Moilanen *et al*, 1974). Following a recent review of the Carter and Moilanen studies, it was concluded that the half-life reported by Carter was more accurate (Carter *et al*, 1996). Gillis *et al* estimated a minimum value of the photolytic half-life of Chloropicrin to be 27.5 hours (expressed as total elapsed time). This value takes into account the maximum number of hours of daylight (14.5 hours) on the longest day of the year at moderate latitudes (37°). In any case the main route of degradation for Chloropicrin in air is via photolytic degradation and as both of the possible estimates i.e. 18 and 27.5 hours are below the trigger value set by FOCUS Air (≤ 2 days), it is proposed that Chloropicrin is not of concern for LRT.

Exposure of air to Chloropicrin is not considered likely, as Chloropicrin has been shown to degrade in soils (average half-life in soil is 9.4 days) to CO_2 . Furthermore, in a laboratory experiment to determine the volatilisation of Chloropicrin from soil, its volatilisation was delayed, maximum volatilisation being observed 11 h after fumigant injection (Gan *et al*, 2004). The slow volatilisation of Chloropicrin was apparently a result of its slow movement from the injection point to the soil surface. This slow diffusion of Chloropicrin was attributed

to a number of reasons including the time needed for the applied liquid Chloropicrin to completely vaporise in soil, which has been estimated to be approximately 75 minutes. Covering the soil surface with polyethylene (PE) or a high-barrier film (HB) greatly changed the volatilisation pattern compared to uncovered soil. Current practices include use of virtually impermeable film (VIF) tarping, which further reduces the release of Chloropicrin to the atmosphere. Emission of Chloropicrin from the PE column decreased to a quarter of that from the uncovered column. The HB film was virtually impermeable to Chloropicrin and only 1.2% of the applied mass volatilised from the HB column up to day 9 when the film was purposefully torn. Destruction of the HB film resulted in relatively small increases in volatilisation flux of Chloropicrin. The additional loss of Chloropicrin from the HB column after film rupture was less than 3%.

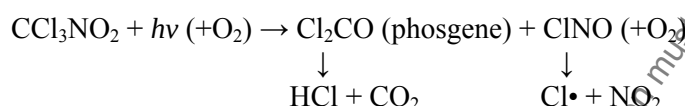
The findings reported in the laboratory study were further confirmed in field and greenhouse studies carried out in Italy (Capri, 2001, 2003). These studies analysed the quantity of Chloropicrin vapour emissions in air during and after treatment, at day 0, 1 and 4 after treatment, at the removal of the tarp edges from soil (day 7), at complete uncovering of the ground (day 8), and finally halfway through the period of aeration prescribed prior to transplanting crops (day 15). The collection times were therefore at days 0, 1, 4, 7, 8 and 15 after treatment. Please note, that on day 7 only the tarp edges were lifted up from the soil where they had been buried 15-20 cm deep at the time of tarp placing. Thus, the soil remained tarped, except the edges, until day 8. In the field study, Chloropicrin was applied *via* soil injection. In the field study, samples were collected by means of vials and pumps which were fixed at mans height (1.5 m) on three poles placed at even distances within the area to be treated and one fourth pole placed outside the treated area as a control. For the collection of the active substance air was sampled with a flow rate of 50 ml/min for 10 hours. Vials and pumps were also fixed on the chest of the three operators in order to have a direct count of the Chloropicrin emissions that the operators might breathe in during the treatment and tarp removal. In the open field study the check points were the same as those in the greenhouse study, however, 3 additional check points at day 0 (treatment) were taken from the three operators, and 1 additional check point at day 8, was taken from the single operator (who removed the tarp from soil). For the operator samples air was sampled with a flow rate of 50 ml/min for 58 or 30 minutes. Only two air samples contained Chloropicrin residues higher than the occupational level of 0.67 mg/m³ allowed in closed factory working places. One of these air samples was collected at treatment time from the tractor driver (residue = 0.552 mg/m³) and the second, also collected during treatment, was from one of the two operators following the injecting equipment (residue = 0.159 mg/m³). The average residue found on the three operators was 0.252 mg/m³. All other air samples, obtained from the equipment fixed to the poles, contained residues lower then the detection limit of the analytical method. The highest levels were found in the samples collected during the treatments whilst in subsequent sampling residue levels were reduced to trace amounts or were not detectable, even when the tarp was removed.

Trevisan (2009) carried out a study to provide data for airborne concentrations of Chloropicrin resulting from field applications *via* soil injection systems. Chloropicrin was applied according to normal application practices at a rate equivalent to 432 kg/ha and then covered with a virtually impermeable film (VIF) for 7 days. Air samplers were installed at three distances (1, 20 and 50 m) from the field margins in the four cardinal directions, and the concentration of chloropicrin in the sampled air was measured continuously for 14 days after the application. Air samples were also taken from the operators who were involved in the chloropicrin application. The highest exposure reported during the application process was 0.474 mg/m³ (tiller operator). Lower concentrations were reported in the air samples of the operators who were involved in opening or cutting of the VIF covering (Day 7) and in the air samples of the operators who were involved in removing the VIF covering (Day 8). In the air samples taken from the field margins continuously after application for 14 days, levels of

Chloropicrin were highest at the 1.5 m height sampling stations situated 1 m away from the treated field margins. The daily weighted mean (DWM) values were a maximum of 0.0491 mg/m³ on the day of application (day 1) reaching a DWM maximum of 0.1702 mg/m³ on day 4. There was a good correlation between the higher values observed to the orientation of the field with respect to the wind direction. After 12 days, there was no Chloropicrin detected in any of the samples.

Fate of Chloropicrin Metabolites in Air

The following diagram depicts the reactions involved in the degradation of Chloropicrin in air



Chloropicrin is photooxidised to phosgene and a trioxalene intermediate (nitric oxide chloride). The trioxalene intermediate rapidly undergoes photolytic degradation to form chlorine and nitric oxide. The chlorine atoms can then react quickly with other VOCs to create ozone, and in most cases generating OH radicals, which will further react with VOCs to produce ozone (Carter *et al.*, 1996). Nitric oxide may undergo further reactions to form nitrogen dioxide, dinitrogen tetroxide and can also participate in ozone forming reactions. According to Gillis *et al.* (2002), phosgene is considered to be stable in the environment, however it can eventually mineralize to CO₂ and HCl. Most tropospheric phosgene is removed by hydrolysis in cloud water with an average residence time of 70 days.

A computer model (ISCST3), developed by the US EPA for assessment of atmospheric dispersion of pollutants from pollution sources, was used by Gillis *et al* to estimate the downwind concentration of Chloropicrin and its degradation products. Model runs were made with and without the degradation half-life (27.5 hours), holding other input parameters the same. The differences between the two model runs, expressed as a molar ratio (pptv; part per trillion by volume), for various distances downwind from the field are the maximum potential phosgene concentrations. The following input parameters were used: 10 acre field; measured emission rates from a Chloropicrin field flux study fumigated at a maximum practical rate of 350 lbs/acre (395.5 kg/ha); half-life of 27.5 hours; and the standard meteorological conditions used by the California Department of Pesticide Regulation model for determining regulatory buffer zones (Gillis *et al*, 2002). Based on this data, Gillis *et al.* estimated maximum values for the 1-hour, 24-hour and 7-day average potential downwind concentrations of degradates from Chloropicrin photolysis of 263 pptv, 135 pptv and 14 pptv, respectively. Please note that according to TERA (2005b) and Gillis *et al* (2002), these model estimates are based on conservative assumptions i.e. that the wind blew at a constant speed and direction for the entire exposure duration of interest. More realistic fluctuations in wind speed and direction would decrease the exposure adjacent to the field. Based on these results the potential concentration of phosgene in air may be considered to be negligible. Phosgene is not likely to exceed 263 pptv for short durations; this concentration according to TERA (2005a) is a factor of 400 below the 8-hour National Ambient Air Quality Standard (NAAQS) of 0.8 ppm, and a factor of 600 below the 1-hour NAAQS of 0.12 ppm. Based on this analysis, the potential exposure is well below health criteria, and thus is not of concern.

Further to this, the TERA report (2005b) also includes a summary of recently conducted assessments for acute exposure to phosgene by the US EPA. Using data from studies on exposure of phosgene to rats the TERA report derived a value of 10 ppb for a tolerable exposure limit to phosgene. A 1-hour conservative exposure estimate of 263 pptv is 1/40 of

this tolerable exposure value. Thus, no health effects would be expected to occur, following exposure to phosgene in air.

In a document prepared by Toxicology Excellence for Risk Assessment (TERA, 2005a) on the contribution of Chloropicrin to ozone, factors are outlined that must be considered when assessing the potential ozone generation by Chloropicrin. These factors include the absolute and relative concentrations of reactive organic gases (ROGs) and NO_x in the atmosphere, regional weather patterns, the dispersal of Chloropicrin by wind and the amount and timing of Chloropicrin applications. Chloropicrin is photooxidised to phosgene and a trioxalane intermediate. The resulting Cl atom can then react with other volatile organic compounds to create ozone, also creating other OH radicals that react with other VOCs to produce ozone. A basic calculation of the potential contribution of Chloropicrin to ozone generation was carried out in the TERA report. This calculation was based on a worst-case scenario. It was assumed that the ozone impact (i.e., the relative amount of ozone formed per molecule of chloropicrin) is 1.5 times that of other VOC pesticides; a reasonable lower limit on the ozone impact is 0.5. As a worst-case overestimate, as much as 51 % (1.5 x 34 %) of the ozone in the San Joaquin valley results from Chloropicrin. Conservative calculations suggested that although Chloropicrin may contribute to regional ozone levels its use alone, as a soil fumigant, would not appear to result in an exceedance of ozone levels. More refined analyses would likely substantially reduce the estimated Chloropicrin contribution, even compared to a lower estimate.

In a report prepared by Dr. Andrew Craven (2005), an independent consultant, the potential of Chloropicrin to act as an ozone generator is reviewed. This report discusses the fact that Methyl Bromide is being phased out for use as a soil fumigant due to its impact on ozone depletion. However, Chloropicrin is an ozone generator and so it is proposed that the benefits through the use of Chloropicrin far outweigh the negative effects of the use of Methyl Bromide. Only limited areas will be treated with Chloropicrin due to the intensive method of treatment. As a result only limited exposure to the air by Chloropicrin will occur at any time. Although reaction with OH radicals is by far the most common of the atmospheric chemical reactions for the majority of pesticides, Chloropicrin is unusual in that direct photolysis appears to be the only significant loss process in the lower atmosphere. O₃ is also created by urban vehicle exhaust emissions and other industrial discharges but Chloropicrin will be primarily applied in rural areas. The contribution of Chloropicrin to the ozone will take place in the lower atmosphere and not in the widespread upper atmosphere as with Methyl Bromide. O₃ in lower atmosphere is a contributor to photochemical smog pollution normally associated with industrial or domestic atmosphere discharges in urban areas. However, considering the small volumes of Chloropicrin in its use as a soil fumigant only small increases of Chloropicrin in rural areas will occur and should be rapidly dispersed by natural prevailing wind currents, so in rural areas ozone generation will be minor. In addition to this, guidance for assessing the potential of a compound to move in the air over longer distances is under-developed in the EU. As a result calculations and modelling approaches in this area are poorly developed and no agreed regulatory methods currently exist. This tends to lead to grossly overestimated values for air concentrations, based on unrealistic worst-case assumptions.

In conclusion, the levels of Chloropicrin and its metabolites released to the air following its application *via* soil injection, and subsequent soil tarping, are low.

Conclusions on fate and behaviour in air

At the date of the dossier submission by Notifier, no agreed European guidance on determination of predicted environmental concentration in air, PECA, was available. At

present, FOCUS document (Pesticides in Air: Considerations for Exposure Assessment – 2005) is available.

Henry's constant (13,625.1 Pa.m³.mol⁻¹), vapour pressure (2.66 mPa), and molecular weight (164.4), indicate that Chloropicrin 99 will readily volatilise from field into the atmosphere at ambient temperature and pressure.

No data are available for metabolites, but open scientific literature data indicate formation in air of metabolites as phosgene, nitric oxide, chlorine, nitrogen dioxide, dinitrogen tetroxide. Phosgene degrades into CO₂ and hydrogen chloride (HSDB April 2005).

Chloropicrin may have a not negligible effect on tropospheric ozone formation, it has been found to be a relatively reactive compound under simulated atmospheric conditions (Carter et al., 1997).

B.8.7 Definition of the residue (IIA 7.3)

Chloropicrin may be relevant for the atmosphere. This compound and its major metabolite Dichloronitromethane may be relevant for surface water, groundwater and soil.

B.8.8 Reference relied on

Active substance/formulation

Annex point / reference number	Author(s)	Year	Title Source (where different from company) Company, Report No. GLP or GEP status (where relevant) Published or not	Data Protection claimed Y/N	Owner
IIA 7.4.3/02	Shepler, K	2009	Aged Leaching of [¹⁴ C]Chloropicrin in Representative Agricultural Soil. PTRL West Inc. report number 51645W-1. GLP. Unpublished.	Yes	European Chloropicrin Group
IIA 7.4.1/02	Penketh, S.	2008	Chloropicrin Adsorption/Desorption on Five Soils. Huntingdon Life Sciences report number SXC0001. GLP. Unpublished.	Yes	European Chloropicrin Group
IIIA 9.4/01	Moltmann, J.F.	2009	Predicted Environmental Concentrations in Soil (PEC _{soil}) and Ground Water (PEC _{gw}) for Chloropicrin and its Major Metabolite Dichloronitromethane (DCNM) in Preparation of the Planting of Tomatoes. ECT Oekotoxikologie GmbH report number P8054-01-09. Non GLP. Unpublished.	Yes	European Chloropicrin Group
IIIA 9.7/01	Moltmann, J.F.	2009	Predicted Environmental Concentrations in Surface Water (PEC _{sw}) and Sediment (PEC _{sed}) for Chloropicrin and its Major Metabolite Dichloronitromethane (DCNM) in Preparation of the Planting of Tomatoes. ECT Oekotoxikologie GmbH report number P8054-02-09. Non GLP. Unpublished.	Yes	European Chloropicrin Group