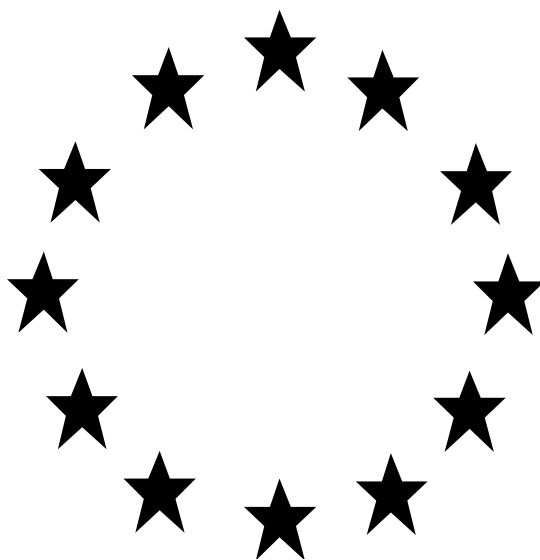




Draft Assessment Report (DAR)

- public version -

**Initial risk assessment provided by the rapporteur Member State
Portugal for the existing active substance**

CALCIUM CARBIDE

**of the fourth stage of the review programme
referred to in Article 8(2) of Council Directive 91/414/EEC**

Volume 3, Annex B, part 5, B.9

August 2008

B.9 Ecotoxicology data and assessment of risks for non-target species

B.9.1 Effects on birds

B.9.1.1 Acute Oral Toxicity

No study available.

B.9.1.2 Avian dietary toxicity (5day)

No study available.

B.9.1.3 Subchronic and reproductive toxicity

No study available.

B.9.1.4 Supervised cage or field trials

No study available.

B.9.1.5 Acceptance of bait, granules or treated seeds by birds (palatability test)

No study available.

B.9.1.6 Effects of secondary poisoning

No study available.

B.9.1.7 Summary of effects on birds

No data submitted.

B.9.1.8 Exposure and Risk Assessment to Birds

PRONTOX Wuhlmausgas or calcium carbide technical is a repellent containing 80% w/w calcium carbide and minor quantities (0.025-0.05% w/w) of calcium phosphide. It is applied in granular form for the control of voles (*Arvicola terrestris*) and moles (*Talpa europaea*). The useful recommended mode of application is at rate of 10g PRONTOX Wuhlmausgas/ tunnel (voles) and at rate of 20g PRONTOX Wuhlmausgas/burrow (moles). The application rate ranges between 2.5-10kg product/ha. The product is intended to be applied once only. After application burrows and tunnels should be covered. Between two or four days after treatment inspection of the rodent holes or burrows must be done.

Calcium carbide placed in tunnels and burrows in contact with soil moisture breaks down rapidly to produce the gas acetylene, solid calcium hydroxide and minor quantities of gas phosphine. Phosphine is produced by calcium phosphide, one impurity of technical calcium carbide. Phosphine is known as a powerful respiratory poison, since it is highly toxic by inhalation even at low concentrations, used as rodenticide and insecticide. Moreover phosphine is the substance responsible for the repellent action by its characteristic garlic-like smell. For that reason the emissions of phosphine underground can not be ignored and risks to birds should be addressed. The remaining degradation products from the reaction of calcium carbide with soil moisture are of negligible toxicity to birds as they are inactive and inert compounds.

Since PRONTOX Wuhlmausgas is to be applied underground in burrows and tunnels, the risk of direct exposure (e.g. ingestion of granules) by birds should be negligible. Birds can be exposed to the product by ingestion of contaminated food. Regarding herbivorous birds, the risk should be negligible, contamination of plants from use of PRONTOX Wuhlmausgas is not expected. However, risks to insectivorous birds or birds eating earthworms can not be excluded, since soil insects and earthworms can be part of a bird's diet.

As mentioned before phosphine may represent an issue for terrestrial organisms since it is very toxic. In absence of any available information or study, it will be assumed that calcium phosphide is highly toxic as well as phosphine gas and that soil organisms will be directly exposed to this substance, without any degradation.

The maximum concentration of calcium phosphide in soil, as result of application of 10 kg PRONTOX Wuhlmausgas/ha, is 0.0066 mg/kg soil. Assuming that an earthworm with a body weight of 100 mg incorporates 30% of its body weight as contaminated soil with calcium phosphide, it is possible to estimate that an earthworm incorporates 0.002 mg calcium phosphide/kg soil. Moreover, it will be assumed that all incorporated substance will remain in earthworm's body as residue (0.002mg/kg food). Regarding a large insectivorous bird (eg. Crow) with a maximum daily food intake of 0.107 kg food/day it is possible to estimate a level of 0.0002 mg calcium phosphide as the highest possible daily food intake for earthworm eating birds (Sanco/4145/2000¹).

Following the same approach, after an application of 10 kg/ha of the product (with 0.05% w/w of calcium phosphide) soil insects can be exposed to 0.005 kg calcium phosphide/ha. The estimated RUD acute for insects is eleven. Considering the food intake rate for an insectivorous bird (eg. Wren with 10g body weight) of 1.03g fresh material/bw day, it is possible to estimate a daily dose (ETE) of 0.056 mg calcium phosphide/kg bw to insectivorous birds. (Sanco/4145/2000¹).

So, the values estimated for of calcium phosphide daily food intake for an insectivorous bird or earthworm eating birds can be considered residual. In addition, regarding that the substance that might cause adverse effects to soil organisms is phosphine gas and that in soil this substance is adsorbed and degraded to phosphates, the concentration that soil organisms can be exposed should be much lower than the considered in the estimate, so, the risk to birds can be considered negligible.

B.9.2 Effects on aquatic organisms (fish, aquatic invertebrates, algae)

B.9.2.1 Acute Toxicity of the active substance and metabolites, degradation or reaction products to fish

Acute fish toxicity test Rainbow trout – *Oncorhynchus mykiss* according to OECD Guideline 203 (1992)

Kleiner, R. (1999)

Guidelines and GLP:

The study was conducted according to OECD guideline 203 (1992). Principles of GLP were complied with.

¹ Guidance Document on Risk Assessment for Birds and Mammals Under Council Directive 91/414/EEC. European commission Helat & Consumer Protection Directorate-General. SANCO/4145/2000. September 2002-final.

Material and methods:

In the pre test, groups of 3 juveniles (5.0 ± 1 cm) of rainbow trout (*Oncorhynchus mykiss*) were exposed to calcium carbide, under static conditions at $16.0 - 16.5^\circ\text{C}$ and LOD of 16:8, at nominal concentrations of 5, 10, 50, 100 and 150 mg/l calcium carbide technical. The main test was conducted under the same test conditions, with one group of 10 juveniles of rainbow trout at concentration of 50 mg/l of calcium carbide. The batch number is not available in study report.

Fish were observed for number of dead and behaviour anomalies, per vessel, after 3h, 6h, 24h, 48h, 72h and 96 hours.

The determination of the median lethal concentration value (LC_{50}) was carried out by non-linear interpolations (Easy Assay Critical Values, Ver. 3.0, 1998 by Rate) between 50.0 and 100.0 mg/l of calcium carbide. The NOEC and LOEC were considered regarding the absence or not of symptoms, respectively.

In contact with water calcium carbide (CaC_2) reacts very vigorously and rapidly into calcium hydroxide $\text{Ca}(\text{OH})_2$, occurring an alkaline reaction, with release of acetylene gas (C_2H_2), and phosphine gas (PH_3). The determination of test concentrations was conducted by AAS method with determination of Ca content in water.

Findings:

In the pre-test the median lethal concentration (LC_{50}) of calcium carbide, after 96 hours was $70.7 \text{ CaC}_2/\text{mg/l}$. Regarding the symptoms observed after 3 and 6 hours of the test a LOEC of 50 mg/l could be considered. In the absence of mortality and symptoms the NOEC was 10 mg/l could be established. At concentration of 100 mg CaC_2/l 100% mortality was registered after 3 hours, highlighting the acute effect of the product, in this case, due to the high instability of the product in water, the effects should represent the toxicity of calcium hydroxide ($\text{Ca}(\text{OH})_2$).

Table 9-1 - Rainbow trout survival 3, 6, 24, 48, 72 and 96 hours after application, registered in the preliminary test.

Calcium carbide (mg/l) nominal	3h	6h	24h	48h	72h	96h
control	3	3	3	3	3	3
5	3	3	3	3	3	3
10	3	3	3	3	3	3
50	3*	3*	3	3	3	3
100	0**	0*	0	0	0	0
150	0**	0	0	0	0	0
LC_{50} (mg/l)	70.7	70.7	70.7	70.7	70.7	70.7
LOEC (mg/l)	50	50	50	50	50	50
NOEC (mg/l)	10	10	10	10	10	10

*: light cauterisation of the anal, pelvic and pectoral fin edge

**: very strong cauterisation of the sclera and anal, pelvic and pectoral fin

In the main test only one concentration was tested, 50 mg CaC_2/l . At this concentration no mortality was registered. After 3 and 6 hours very strong cauterisation of the sclera and anal, pelvic and pectoral fin was observed, those symptoms were registered until the end of the study with a slight reduction compared to the initial observation. After 24 hours until the end of the study the fish looked coloured in comparison to control. In addition, it is important to mention that an alkaline reaction occurred immediately after CaC_2 application in water, with high increase of pH to 10.58, decreasing to normal values (compared with the control) after 24 hours. The pH value of the test solution was not adjusted.

Table 9-2 - Rainbow trout survival 3, 6, 24, 48, 72 and 96 hours after application, registered in the main test including pH values.

Calcium carbide (mg/l) nominal	0h	3h	6h	24h	48h	72h	96h
control		10	10	10	10	10	10
pH values	7.75			8.25	8.89	8.35	8.40
50		10*	*10	10***	10	10	10
pH values	10.58			8.17	8.30	8.28	8.24

*: light cauterisation of the anal, pelvic and pectoral fin edge

***: the fish looked coloured in comparison to control.

Comments: the study was considered of poor reliability. The methodology followed for the main test is not appropriate, since only one concentration was tested, so is not possible to take conclusions on the results. Moreover, due to the low number of fish tested in the preliminary test (only 3) is not possible to accept the estimated values of LC₅₀, LOEC or NOEC.

Regarding both study results it can be assumed that calcium carbide is toxic to fish and an LC₅₀ > 50mg CaC₂/l can be considered. Another information that this study can provide is the high increase of pH at the beginning of the study, as result of the calcium carbide reaction in water. The registered pH of 10.5 can not be ignored neither the influence of that on study results.

B.9.2.2 Chronic toxicity to fish

No study available.

B.9.2.3 Bioaccumulation potential in fish

No study available.

B.9.2.4 Summary of effects on Fish

Although the available data is of very poor quality it can be expected that calcium carbide is toxic to fish based on the observation that mortality occurred above 50 mg/l test concentration.

B.9.2.5 Acute toxicity to aquatic invertebrates

Acute Immobilisation Test *Daphnia-Daphnia magna* according to OECD 202-I Calcium carbide

Kleiner, R. (1999).

Guidelines and GLP:

The study was conducted according to OECD 202, Part I, Guideline (1984). Principles of GLP were complied with.

Material and methods:

Groups of 20 Daphnids (*Daphnia magna*) less than 24 hours old were exposed to calcium carbide technical at concentrations of 0.99, 1.48, 2.22, 3.33, 5.00, 7.50 and 11.25 mg CaC₂/l, under static conditions for up to 48 hours. Daphnids were maintained under 19 -21.5°C and LD cycle of 16:8 hours. Assessment of immobilisation was carried out for 3 times at 3, 24 and 48 hours. Batch number is not available.

The determination of the EC₅₀ was carried out by Probit analysis according to Finney (1971). The NOEC and LOEC values were provided by means of multiple comparison procedure, testing the significance of the differences between each of the treatments compared to the mean values of each group.

Calcium carbide is very unstable in contact with water into Ca(OH)₂, C₂H₂ and PH₃ gas. The determination of test concentrations was conducted by AAS method with determination of Ca content in water.

Findings:

During the test period the dissolved concentration of oxygen decreased from 8.8 to 8.6 after 48 hours for control and all test concentrations. The pH values ranged from 7.88 to 8.16 in the control and from 10.86 to 9.81 from the beginning until the end of the study (for the highest tested concentration). The relation between calcium carbide concentration and pH increase was clear for concentrations bigger than 5 mg/l. Due to the high instability of calcium carbide in water, the concentration of calcium carbide in water was measured by the Ca content. The test concentrations were maintained at more than 80% of the nominal value throughout the study. The pH value of the test solution was not adjusted.

Table 9-3 - pH values registered in control and in test solutions

Calcium carbide (mg/l) (nominal concentration)	0h	48h
Control	7.88	8.16
0.99	8.14	8.15
1.48	8.27	8.15
2.22	8.40	8.21
3.33	8.55	8.28
5.00	8.19	8.39
7.50	9.27	8.46
11.25	10.86	9.81

The concentration which provides 50% of daphnia immobilisation was 4.62 mg/l of calcium carbide, a LOEC of 3.33 mg/l and a NOEC of 2.22 mg/l were estimated. No visible signs of abnormalities of surviving Daphnia were registered during the exposure period.

Table 9-4 - Number of immobilised Daphnia, EC50, NOEC and LOEC after application of calcium carbide

Concentration (mg/l)	3h	24h	48h
Calcium carbide (nominal/measured)	number of immobilised Daphnia		
Control	0	0	0
0.99/1.04	0	0	0
1.48/1.5	0	0	0
2.22/2.18	0	0	1
3.33/3.40	0	0	3*
5.00/5.10	0	3*	9*
7.50/6.01	7*	14*	20*
11.25/7.74	20*	20*	20*
EC50 (mg/l)		6.49/5.64	4.62/4.42
95% confidence interval		5.78...7.18	4.10...5.21
spole		9.89/19.16	6.95/7.82
LOEC (mg/l)		5.0/5.1	3.3/3.4
NOEC (mg/l)		3.3/3.4	2.22/2.18

*: statistically significant, Dunnett-Test, $p < 0.05$

Comments: Due to the high unstability of calcium carbide in water, the effects should represent the toxicity of calcium hydroxide ($\text{Ca}(\text{OH})_2$). An EC_{50} of 4.62 CaC_2 mg/l can be considered. Once again is important to note that the high pH registered might have some influence in the results.

B.9.2.6 Chronic toxicity to aquatic invertebrates

No study available.

B.9.2.7 Summary of Effects on Aquatic Invertebrates

Based on the available data, calcium carbide can be considered as toxic to aquatic invertebrates.

B.9.2.8 Effects on algal growth

Algae Growth Inhibition Test *Scenedesmus subspicatus* according to OECD 2001, Calcium carbide

Kleiner, R.

Guidelines and GLP:

The study was conducted according to OECD 210 Guideline (1984). Principles of GLP were complied with.

Material and methods:

A suspension of 1.7×10^4 cells/ml of green alga, *Scenedesmus subspicatus*, was exposed to calcium carbide at test concentrations of 2.6, 5.6, 12.4, 27.3 and 60 mg/l, under static conditions.

Cultures were maintained under 22°C and illuminated permanently with continuous uniform light with the spectral range of 400-700 nm. Samples were measured at 24, 48 and 72 hours of cell concentration.

The pH values of the test solutions were measured at the start and at the end of the study. The temperature was measured daily.

The EC₅₀ was estimated by evaluation of the growth in the control with inhibition growth rate of each concentration. The NOEC and LOEC values were estimated by means of multiple evaluation procedure for comparing several treatments. The analysis was made by means of the statistical program: "Easy Assay, Algae Growth Inhibition".

Calcium carbide is very unstable in contact with solutions, the product hydrolysed to C₂H₂, Ca(OH)₂ and PH₃. The determination of test concentrations was conducted by AAS method with determination of Ca content in water.

Findings:

At test concentrations up to 5.6 mg/l of technical calcium carbide a statistically significant inhibition of the cell growth (biomass) was registered regarding the control after 48 and 72 hours. At the test concentration 2.6 mg/l no statistically significant inhibition of cell growth was determined after 72 hours. An E_bC₅₀ (72h) of 12.4 mg/l (equivalent to 5.03 mg/l C₂H₂) and a NOEC (72h) of 2.6 mg CaC₂/l was established.

Table 9-5 - Percentage inhibition of the cell growth (biomass) at each test substance concentration correlated with the control (Dunnett-test; $\alpha = 0.05$)

Calcium carbide nominal concentration (mg/l)	Inhibition of cell growth (IA) %		
	0-24h	24-48h	48-72h
Control	0	0	0
2.6	16.7*	19.5*	8.5
5.6	36.3*	49.9*	33.1*
12.4	70.6*	56.5*	45.4*
27.3	85.3*	77.8*	64.5*
60.0	124.5*	105.7*	97.5*
E _b C ₅₀			12.4
E _b C ₁₀			2.7
NOEC			2.6

*: significant difference to control ($p \leq 0.05$)

At test concentrations up to 12.4 mg CaC₂/l a significant inhibition of the growth rate with respect to the control was observed after 72 hours. At test concentrations of 2.6 and 5.6 mg CaC₂/l no significant inhibition of growth rate was determined. An E_rC₅₀ (72h) of 46.5 mg CaC₂/l and a NOEC (72h) of 5.6 mg CaC₂/l calcium carbide was determined.

Table 9-6 - Percentage inhibition of the growth rate at each test substance concentration correlated with the control (Dunnett-test; $\alpha = 0.05$)

Calcium carbide nominal concentration (mg/l)	Inhibition of growth rate (IA*) %		
	0-24h	24-48h	48-72h
Control	0	0	0
2.6	9.4*	7.7	-1.7
5.6	22.3*	27.5*	2.6*
12.4	53.2*	22.6*	12.4*
27.3	72.6*	43.9*	19.8*
60.0	146.8*	84.7*	65.5*
E _r C50			46.5
E _r C10			12.9
NOEC			5.6

*: significant difference to control ($p \leq 0.05$)

The pH was measured at the start and at the end of the test with algae, according to the OECD Guideline No. 201 the pH value of test solution should normally not derive more than 1 unit during the test. The utmost strong algae growth caused a high CO₂ consumption leading to a deviation of the pH, of the control and tested concentrations, of 2-3 units, even so, no inhibition in cell growth or cell growth rate occurred in the control. The deviation of the pH between the calcium carbide solutions measured after 72 h and at the start resulted from calcium carbide hydrolysis. The test was repeated under the same test conditions to show that the results were repeatable, for assessing the validity of the study.

Table 9-7 - pH values of test solutions measured at start and at the end of the study

Calcium carbide (mg/l) (nominal concentration)	pH value		deviations of pH (0-72h)
	0 h	72 h	
Control	7.99	11.12	3.12
2.6	8.23	11.20	2.97
5.6	9.25	11.29	2.04
12.4	9.60	11.41	1.81
27.3	10.20	11.54	1.34
60.0	10.63	11.54	0.91

Due to the high instability of calcium carbide in water, the concentration of calcium carbide in water was measured by the Ca content. The test concentrations were maintained at more than 80% of the nominal value throughout the study.

The cell concentration in the control cultures increased by a factor of more than 16, within three days (i.e. by a factor of 33.1).

Comments: The pH validity criteria was not fulfilled, the increase of the pH in the control can not be ignored, but no adverse effects on algae were registered. In addition the increase of pH in test solution must be carefully evaluated since in contact with water the technical calcium carbide reacts very vigorously and rapidly into calcium hydroxide, occurring an alkalinity reaction. Despite the poor reliability of the test it can be concluded that calcium carbide is toxic to algae.

B.9.2.9 Summary of Effects on Algal growth

Although the available data is of poor quality it can be expected that calcium carbide is toxic to algae.

B.9.2.10 Effects on sediment dwelling organisms

No study available.

B.9.2.11 Effects on aquatic plants

No study available.

B.9.2.12 Microcosm and mesocosm study

No study available.

B.9.2.13 Residue data in fish

No study available.

B.9.2.14 Supplementary studies of toxicity to fish and aquatic invertebrates

No study available.

B.9.2.15 Exposure and risk assessment for aquatic organisms

The studies conducted with aquatic organisms indicate that calcium carbide technical is toxic to aquatic organisms. However it should be considered that calcium carbide reacts vigorously in water into calcium hydroxide, acetylene and small amounts of phosphine. The alkaline reaction increases water pH, immediately after calcium carbide application, in particular at higher concentrations. The degradation product calcium hydroxide might be responsible for the toxic effects. The other degradation products should not affect the toxicity of calcium carbide technical in water since acetylene is a very volatile substance¹ not classified to the environment, and although the calcium phosphide is classified as very toxic to aquatic organisms² (classified on the basis of the phosphine, very toxic to aquatic organisms but not stable in water) it is present at residual levels in the technical product. Moreover at low levels phosphine may be oxidized to phosphoric acids and phosphates. So the influence of acetylene and phosphine for aquatic toxicity should be considered negligible.

The calcium carbide technical, as well as the product PRONTOX Wuhlmausgas, since product and technical substance are the same, should be classified as Toxic to aquatic organisms. Regarding the intended use of the product the exposure of surface water should be negligible; the aquatic environment should not be at risk.

B.9.3 Effects on other terrestrial vertebrates

No study available.

¹ European Commission. Summary Record Commission Working Group on the Classification and Labelling of dangerous substances: Environmental Effects. 27-29 September 1995. ECBI/81/95 – Rev.2

² European Commission. Summary Record Meeting of the Commission Working Group on the Classification and Labelling of dangerous substances. Pesticides. ECB Ispra, 17-19 November 1999. ECBI/07/00 Rev.3 29 August 2000.

B.9.3.1 Exposure and risk assessment to terrestrial vertebrates other than birds

Calcium carbide technical is a repellent containing 80% w/w calcium carbide and minor quantities (0.025-0.05% w/w) of calcium phosphide. It is intended to be applied directly underground, in voles tunnels and mole burrows, at application rate of 2.5-10 kg/ha of technical calcium carbide. After application tunnels and burrows should be covered.

Calcium carbide placed in tunnels and burrows in contact with soil moisture breaks down rapidly to produce the gas acetylene, solid calcium hydroxide and minor quantities of gas phosphine. Phosphine is produced by calcium phosphide, one impurity of technical calcium carbide, classified as very toxic and dangerous for the environment. Phosphine is classified as toxic based on acute effects via the inhalation route of exposure, acting as a powerful poison.

Since PRONTOX Wuhlmausgas is applied in a granular form, directly applied underground in burrows and tunnels that should be covered after application, only terrestrial vertebrates that live below soil surface or in burrows (eg. rabbits) can be directly exposed to this gas. In acute inhalation toxicity tests in rats a LC_{50} (4hr) > 14 mg/l for phosphine gas was estimated. In the short term inhalation toxicity test, with repeated exposure (6hours/day, 5 days/week), with rats a NOAEL of 0.007mg/l (EPA, 1999¹) was estimated. In an worst case approach, i.e., assuming the maximum proposed application rate and that all calcium phosphide degrades in phosphine, the maximum concentration of calcium phosphide in soil is 0.0066 mg/kg soil, as result of application of 10 kg PRONTOX Wuhlmausgas/ha. Assuming that the estimated concentration of phosphine in soil is over estimated, the risk of direct exposure of mammals to phosphine concentrations that might cause some adverse effects by inhalation can be considered very low.

Terrestrial vertebrates can be at risk from consumption of contaminated food. Regarding herbivorous mammals, the risk should be negligible. Contamination of plants from use of PRONTOX Wuhlmausgas is not expected. However, risks to insectivorous terrestrial vertebrates can not be excluded, since soil insects and earthworms can be part of a mammal diet.

The approach followed previously on section B.9.1 for birds will be used for the exposure of mammals by food intake estimate. After the application of 10kg of product/ha an earthworm might incorporate 0.002mg calcium phosphide/kg. Regarding a medium insectivorous mammal (eg. hedgehog) with a maximum daily food intake of 0.374 kg food/day it is possible mammals of 0.02 mg calcium phosphide/kg bw. In both cases the level of mammals exposure to calcium phosphide is very low (Sanco/4145/2000²).

So, the values estimated for calcium phosphide daily food intake for an insectivorous mammal or earthworm eating mammal can be considered residual. Regarding that the substance that might cause adverse effects to soil organisms is phosphine gas, the calcium phosphide degradation product, and that the release of phosphine from calcium phosphide is gradual, and that underground this substance is adsorbed and degraded to phosphates, the concentration that soil organisms can be exposed should be much lower than the considered for the estimate of mammal food intake of both insects and earthworms, so, the risk to mammals can be considered negligible.

¹ EPA – United States Environmental Protection Agency, Office of prevention, Pesticides and toxic substances (7505C). Pesticide Fact Sheet, Conditional Registration, Dec. 1999.

² Guidance Document on Risk Assessment for Birds and Mammals Under Council Directive 91/414/EEC. European commission Helat & Consumer Protection Directorate-General. SANCO/4145/2000. September 2002-final.

B.9.4 Effects on bees

B.9.4.1 Acute toxicity to bees

No study available.

B.9.4.2 Bee brood feeding test

No study available.

B.9.4.3 Acute toxicity of the preparations to bees

No study available.

B.9.4.4 Effects on bees of residues on crops

No study available.

B.9.4.5 Cage tests

No study available.

B.9.4.6 Field tests to investigate special effects

No study available. to estimate a concentration of 0.0007 mg calcium phosphide as the highest possible daily food intake for earthworm eating mammals. Soil insects will be exposed to 0.005kg calcium phosphide/ha. Considering food intake rate for insectivorous mammal of 0.51 g fresh material/bw day and RUD of eleven it is possible to estimate a daily dose for an insectivorous

B.9.4.7 Tunnel testing to investigate effects of feeding on contaminated honey

No study available.

B.9.4.8 Summary of Effects on Bees

No data available.

B.9.4.9 Exposure and risk assessment for bees

Taking into consideration the intended use of the product the risk to bees can be considered negligible.

B.9.5 Effects on other arthropod species

No study available.

B.9.5.1 Effects of the active substance and formulations on non-target terrestrial arthropods

No study available.

B.9.5.2 Summary of exposure and risk assessment of the active substance and formulations on non-target terrestrial arthropods

Regarding that calcium carbide is intended to use underground, terrestrial arthropods may be exposed to calcium carbide degradation product phosphine. Phosphine is used not only as a

rodenticide but also as insecticide. Phosphine acts on two main enzymes, oxidase cytochrome and catalase. These two enzymes regulate the conditioning of oxygen to enter the mitochondrion. Blocking their action makes it impossible for oxygen to penetrate into the cells leading to the formation of super oxides, which are the true biocidal agents. Since phosphine acts in the respiratory chain, insects with a low respiratory rhythm, such as in the case of low temperatures or for stages with low respiratory rates like eggs or pupae, need much longer exposure to gas than those with high respiratory rhythm such as larvae or adults. Presently adult insects can withstand concentrations of 1000-2000 ppm, whereas a susceptible insect dies in a few hours at 30 ppm (Ducom, nd¹).

Regarding the low content of calcium phosphide in the technical product (0.025-0.05 w/w), at the maximum application rate of 10 Kg product/ha, the maximum concentration of calcium phosphide in soil is 0.0066mg/kg. Regarding that the substance that might cause adverse effects to soil organisms is phosphine gas, and that the release of phosphine from calcium phosphide is gradual, and that underground this substance is adsorbed and degraded to phosphates, the concentration that soil insects can be exposed should be much lower than the estimated, so the risk to non-target soil arthropods can be considered very low.

B.9.6 Effects on earthworms

B.9.6.1 Acute toxicity to earthworms

B.9.6.2 Sublethal effects on earthworms

No study available.

B.9.6.3 Acute toxicity of the formulations to earthworms

Toxicity to Earthworms (preliminary test)

Grunert, B.

Guidelines and GLP: Not mentioned.

Material and methods:

Ten adult earthworms were exposed to POLYTANOL, a product containing 28% calcium phosphide (Ca_2P_2), which represents 10% of phosphine (PH_3), for 14 days. Two vessels with substrate were tested for each tested concentration, containing 5 earthworms each. The test substrate contains the substrate medium (500g synthetic soil dw), the test substance and deionised water. The water content comprises about 28% of the dry weight of the substrate medium. Only a preliminary test was conducted in which two concentrations were tested, 100 mg/kg test substrate dw and 400 mg/kg test substrate dw of POLYTANOL.

Findings:

No mortality was observed at test concentrations of 100 mg/kg dw and at 400 mg/kg dw of POLYTANOL, during the period of 14 days.

¹ Ducom, Patrick. The issue of Phosphine insecticide efficacy. Laboratoire National Denrées Stockées. Bordeaux.

Table 9-8 - Number of dead earthworms when exposed to POLYTANOL

Concentration mg/kg test substrate dw	Observation day 1	Observation day 2	Observation day 3
100 (vessel 1)	0	0	0
100 (vessel 2)	0	0	0
400 (vessel 1)	0	0	0
400 (vessel 2)	0	0	0

Comments: The study was considered not reliable. First, there is no information about the guideline followed, and about GPL. In absence of detailed information on study procedures is not possible to accept the study conclusions. In addition, in the study report only the results for the first 3 days were presented, but the conclusion of the number of mortalities presented in the preliminary test is for the period of 14 days. Moreover, the study was conducted with a different technical product.

Although is not possible to accept this study, for the previous reasons, this study can contribute with useful information about phosphine. As mentioned before the phosphine is a very toxic substance, that acts on respiratory chain. Earthworms can be affected by this substance too, so the release of phosphine in soil should be considered. Regarding phosphine action, acute effects will be expected on earthworms when exposed to this gas. In this study, only the first three days results were presented, no lethal effects were observed when earthworms were exposed to 400 mg POLYTANOL/kg, i.e. 40mg phosphine/kg soil. Regarding that the technical calcium carbide contains only 0.05% of calcium phosphide and this study was developed with a product with 28% of calcium phosphide, it is possible to conclude that the expected content of phosphine released in soil after the application of PRONTOX Wuhlmausgas would be significantly lower.

B.9.6.4 Sublethal effects of the formulation on earthworms

No study available.

B.9.6.5 Field tests - residue content of earthworms

No study available.

B.9.6.6 Summary of effects on earthworms

No data is available.

B.9.6.7 Exposure and Risk assessment for earthworms

Calcium carbide technical is a repellent containing 80% w/w calcium carbide and minor quantities (0.025-0.05% w/w) of calcium phosphide, is intended to be applied directly underground, in voles tunnels and mole burrows, at application rate of 2.5-10 kg/ha of technical calcium carbide. After application tunnels and burrows should be covered.

Calcium carbide placed in tunnels and burrows in contact with soil moisture breaks down rapidly to produce the gas acetylene, solid calcium hydroxide and minor quantities of gas phosphine, very toxic substance. Phosphine is produced by calcium phosphide, one impurity of technical calcium carbide.

Regarding the intended use of this product, phosphine will volatilise into the soil holes and burrows, i.e., phosphine could be retained in soil since the holes should be covered after application of the product. Earthworms can be exposed to calcium carbide degradation product, phosphine a very toxic substance. Regarding that phosphine released underground at low level can be quickly

adsorbed and degraded to phosphates the exposure of earthworms to this substance should be very low. No risks to earthworms are expected by the use of PRONTOX Wuhlmausgas.

B.9.7 Effects on other soil non-target macro-organisms

No study available.

B.9.8 Effects on soil non-target micro-organisms

No study available.

B.9.8.4 Summary of effects on non-target micro-organisms and exposure and risk assessment for non-target micro-organisms

Regarding the intended use of this product, phosphine will volatilise into the soil holes and canals, i.e., phosphine will be retained in soil since the opening holes should be covered after application of the product. Soil micro-organisms can be exposed to calcium carbide degradation products, including phosphine, a very toxic substance. Regarding the specific mode of action in the respiratory chain, it is possible to predict that all organisms with respiratory mechanisms can be affected by this substance. However, as mentioned before the level of phosphine released underground can be considered residual and at low concentrations soil can be quickly adsorbed and degraded. Acetylene underground can inhibit the activity of nitrifying bacteria. No other effects to microorganisms were registered for the technical product.

B.9.9 Effects on other non-target organisms (flora and fauna) believed to be at risk

No study available.

B.9.9.1 Summary of effects on other non-target organisms (flora and fauna) believed to be at risk

The product is intended to be used in agriculture soils, so plants (crops/ornamental) can be exposed to the product or degradation products, by roots. It is not foreseeable that calcium carbide affects plants. Moreover, the calcium carbide degradation products in soil, as calcium ions, bicarbonate and phosphates, are taken up and metabolised by plants as trace nutrients, so plants can benefit indirectly with the application of calcium carbide in soil.

B.9.10 Effects on biological methods of sewage treatment

No study available.

WARNING: This document forms part of an EC evaluation data package and should not be read in isolation. Registration must not be granted on the basis of this document.

B.9.11 References relied on

OECD data 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
--------------------------------------	-----------	------	---	--------------------------------	-------

Annex IIA

IIA 8.2 (cross ref. IIIA 10.2)	European Commission.	1995	Summary Record Commission Working Group on the Classification and Labelling of dangerous substances: Environmental Effects. 27-29 September 1995. ECBI/81/95 – Rev.2	N	
IIA 8.2 (cross ref. IIIA 10.2)	European Commission.	2000	Summary Record Meeting of the Commission Working Group on the Classification and Labelling of dangerous substances. Pesticides. ECB Ispra, 17-19 November 1999. ECBI/07/00 Rev.3 29 August 2000.	N	
IIA 8.2 (cross ref. IIIA 10.2)	EPA – United States Environmental Protection Agency	1999	Office of prevention, Pesticides and toxic substances (7505C). Pesticide Fact Sheet, Conditional Registration, Dec. 1999	N	
IIA 8.2.1; (cross ref. III 10.2.1.1)	Kleiner, R	1999	Acute fish toxicity test rainbow trout – Oncorhynchus mykiss according to OECD 203 calcium carbide Report no: 991048006 GLP. Unpublished	Y	Wülfel
IIA 8.3.1; (cross ref. IIIA 10.2.1.3)	Kleiner, R.	1999	Acute Immobilisation Test Daphnia-Daphnia magna according to OECD 202-I Calcium carbide, Report-no.: 991048007 GLP. Unpublished	Y	Wülfel
IIA 8.4, (cross ref. IIIA 10.2.1.11)	Kleiner, R.	1999	Algae Growth Inhibition Test Scenedesmus subspicatus according to OECD 201 Calcium carbide, Report-no.: 991048008 GLP. Unpublished	Y	Wülfel

Annex IIIA

IIIA 10.2 (cross ref. IIA 8.2)	European Commission.	1995	Summary Record Commission Working Group on the Classification and Labelling of dangerous substances: Environmental Effects. 27-29 September 1995. ECBI/81/95 – Rev.2	N	
IIIA 10.2 (cross ref. IIA 8.2)	European Commission.	2000	Summary Record Meeting of the Commission Working Group on the Classification and Labelling of dangerous substances. Pesticides. ECB Ispra, 17-19 November 1999. ECBI/07/00 Rev.3 29 August 2000.	N	

OECD data 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
IIIA 10.2 (cross ref. IIA 8.2)	EPA – United States Environmental Protection Agency	1999	Office of prevention, Pesticides and toxic substances (7505C). Pesticide Fact Sheet, Conditional Registration, Dec. 1999	N	
IIIA 10.2.1.1 (cross ref. IIA 8.2.1)	Kleiner, R	1999	Acute fish toxicity test rainbow trout – Oncorhynchus mykiss according to OECD 203 calcium carbide Report no: 991048006 GPL. Unpublished	Y	Wülfel
IIIA 10.2.1.3 (cross ref. IIA 8.3.1)	Kleiner, R.	1999	Acute Immobilisation Test Daphnia-Daphnia magna according to OECD 202-I Calcium carbide, Report-no.: 991048007 GLP. Unpublished	Y	Wülfel
IIIA 10.2.1.11 (cross ref. IIA 8.4)	Kleiner, R.	1999	Algae Growth Inhibition Test Scenedesmus subspicatus according to OECD 201 Calcium carbide, Report-no.: 991048008 GLP. Unpublished	Y	Wülfel
IIIA 10.6.2	Ducom, Patrick	nd	The issue of Phosphine insecticide efficacy. Laboratoire National Denrées Stockées. Bordeaux	N	

WARNING: This document forms part of an EC evaluation data package and should not be used for registration. Registration must not be granted on the basis of this document.