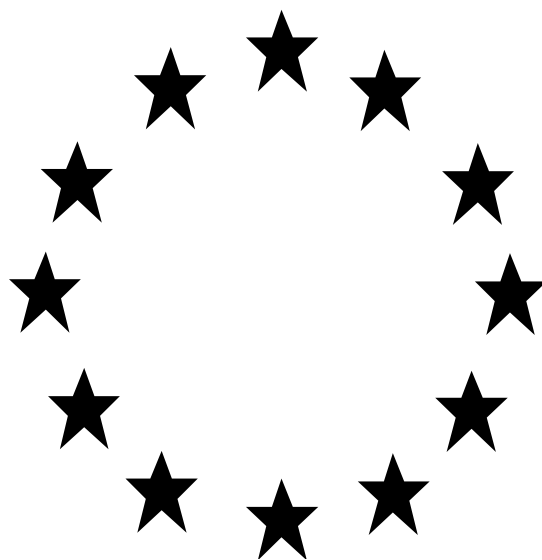




Draft Assessment Report (DAR)

- 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 4, B.8

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B.8 Environmental Fate and Behaviour

A dossier was submitted for the evaluation of the active substance calcium carbide.

For the proposed use (repellent), technical calcium carbide needs to contain calcium phosphide (0.02%w/w) for the production of phosphine in the presence of moisture. Phosphine has a garlic odour and in fact it is the repellent active substance.

Experts present in the PRAPeR 06 Meeting, organised by EFSA, agreed that the RMS should evaluate and report the active substance calcium phosphide. Due to the fact that phosphine is a very toxic gas, it was also agreed by those experts that the RMS would set a range in the specification (minimum and maximum purity) of calcium phosphide, to prevent having a different function for this active substance, e.g. rodenticide, if the content of calcium phosphide present in calcium carbide would be much higher.

Thereafter calcium carbide has been assessed as a technical product with a very low content of calcium phosphide.

The technical calcium carbide is sold unformulated, i.e., the PRONTOX Wuhlmausgas is the technical. There is no difference between the technical active substance (Annex II) and the plant protection product (Annex III) assessment.

No information was submitted by the applicant on chapter 5 of environmental fate and behaviour and chapter 6 of ecotoxicology. Only five studies with low reliability were submitted. The RMS tried, as far as possible, to construct a comprehensive document on calcium carbide fate and behaviour in environment with assessment of possible risks to non-target organisms. The following report was based on the RMS assessment of the applicant dossier, from Doc. A to J and Tier III, chapter 1 to 4 and 7 and RMS research.

B.8.1 Route and rate of degradation in soil

B.8.1.1 Aerobic degradation in soil

Chemical Properties and Ecological Effects of POLYTANOL

Koch, E (1981).

Guidelines and GLP:

No guideline and no GLP. Unpublished.

Findings:

The substance POLYTANOL is a technical calcium phosphide and consists of 28% calcium phosphide and approximately 72% hydroxyl apatite. Water or diluted acids break down POLYTANOL while creating hydrogen phosphide PH_3 .

POLYTANOL breaks down relatively quickly when exposed to air. It produces primarily hydroxyl Apatite and Calcium oxide (CaO) as decomposition products. Calcium phosphide (CaP and Ca_3P_2) could no longer be verified in any instance. Hydrogen phosphide is highly volatile. Moreover, hydrogen phosphide is a rather inert compound that does not react on a larger scale. This has been confirmed by various research results, e.g. H. Rauscher, Frankfurt/main (1973). The results of these tests, which were performed using the Reclaiming methods test, on about 80 different types of products, determined that hydrogen phosphide is apparently the safest gas medium to use in terms of residue metabolites. Phosphine is a very strong poison, the awareness threshold (olfactory) from phosphine is approx. 0.02 mg/kg.

The decomposition products of POLYTANOL are substances that occur as natural mineral phosphates and lime catenations and are essential substances of human body as well as animal and plant organisms.

Comments:

This report can not be considered relied on, because it is not a study neither a document supported by technical and scientific information, moreover it describes a different technical product, with a significant higher content of calcium phosphide. However information about the behaviour of calcium phosphide in environment can be considered useful. This information was included in the Annex IIA 7.1 by the applicant, however the RMS considered that this is not appropriate, not only because of the previous reasons but also because it did not include available information of calcium carbide behaviour in soil.

B.8.1.2 Supplementary studies

B.8.1.2.1 Anaerobic degradation in Soil

No study available.

B.8.1.2.2 Soil photolysis

No study available.

B.8.1.3 Field studies

No study available.

B.8.1.4 Summary and assessment of the route and rate of degradation in soil

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 as a repellent for voles (*Arvicola terrestris*) and moles (*Talpa europaea*). The useful recommended mode of application is at rate of 10g per tunnel for voles and at rate of 20g per burrow for moles of technical calcium carbide. Depending on the infestation level, the application rate should range between 2.5-10kg/ha of technical calcium carbide. The product is intended to be applied once only.

Calcium carbide technical reacts in contact with soil moisture to gas acetylene, small quantities of gas phosphine and solid calcium oxide (calcium hydroxide). Calcium hydroxide reacts with carbon dioxide to calcium bicarbonate and calcium carbonate, other calcium carbide impurities as carbon, aluminium oxide, iron oxide and silicon dioxide are ubiquitous and stable in the soil

At soil surface acetylene gas is subject to rapid atmospheric degradation upon volatilisation. Several articles mention the importance of acetylene in soil to inhibit nitrification in soil. Since it is very volatile at soil surface, sources of acetylene such as calcium carbide that allow slow releases into soil should be used. Acetylene inhibits the activity of nitrifying bacteria involved in transformation of ammonium (NH_4^+) in nitrates (NO_2^-) involved in the nitrogen cycle (Freney *et al*, 2000¹; Maeyer *et al*, 2002²). The inhibition of nitrification in soil has been pursued as a strategy to improve

¹Freney, J.R.; Randall, P.J., Smith, J.W.B, Hodgkin, J.; Harrington, K. J. & Morton T.C. (2000). Slow release sources of acetylene to inhibit nitrification in soil. Nutrient Cycling and Agroecosystem journal. Springer Netherlands. Volume 56, Number 3/March, 241-251 pp.

²Maeyer, R.L.; Kjaer, T. & Revsbech N.P. (2002). Nitrification and Denitrification near a Soil-Manure Interface Studied with a Nitrate-Nitrite Biosensor. Soil Science Society of America Journal. Volume 66:498-506

recovery of fertilizer nitrogen (N) by crops through lowering losses by leaching of nitrate or denitrification in order to benefit yields and the environment (Randall *et al*, 2002¹), this may assume particular importance in agricultural soils exposed to successive fertilizations.

Phosphine is the substance responsible for the repellent action by its characteristic garlic-like smell. Because of its high vapour pressure (40 mm Hg at 129.4°C) and Henry's Law Constant (0.1 atm m³/mol), phosphine at the soil surface is expected to rapidly dissipate into the atmosphere (World Health Organization, 1988, cit in EPA, 1999²). Several published laboratory studies suggest that phosphine below soil surface is quickly adsorbed and degraded (Hilton and Robinson, 1972; Eiseman *et.al.*, 1997; Berck and Gunther, 1970, *cit. in*. EPA, 1999). Gaseous phosphine added to soil headspace at 1000mg/kg dry soil in closed containers degrades 50% after approximately five days in air dried soil and 11 days in water saturated soil (Hilton and Robinson, 1972 *cit. in*. EPA, 1999). Smaller quantities of phosphine may be removed by soil by faster mechanisms because phosphine added at lower concentrations (0.35 µg/kg) was undetectable in 50 minutes (Eiseman, Glindemann, Bergman and Kuschik, 1997). Diffusion through the soil environment is expected to be slow because phosphine is sorbed in seconds when pushed through several types of soil in a nitrogen carrier (Berck and Gunther, 1970 *cit. in*. EPA, 1999). Phosphine gas trapped below the surface soil will degrade to phosphates in a matter of days. Phosphine has a low potential for contaminating ground and surface water (EPA, 1999).

Regarding the intended uses, the calcium carbide properties and the expected degradation process the accumulation in soil of calcium carbide or its degradation products is not expected.

B.8.2 Adsorption, desorption and mobility in soil

B.8.2.1 Adsorption and desorption of the active substance and relevant metabolites

No study available.

B.8.2.3 Aged residue column leaching

No study available.

B.8.2.4 Lysimeter and field leaching studies

No study available.

B.8.2.5 Summary and assessment of adsorption/desorption and mobility in soil

No data available.

B.8.3 Predicted environmental concentration in soil (PECs)

The PEC in soil was not submitted. However, regarding fate and behaviour of calcium carbide and its degradation products in soil, as well as the intended use of the product, the predicted concentration of the active substance and degradation products in soil should be negligible.

¹ Randall, P.J.; Freney, J.R.; Hodgkin, J. & Morton, T.C. (2002). Effect of acetylene generated from carbide on nitrification soil, yield of irrigated maize and growth of maize seedlings. *Developments in Plants and Soil Sciences*. Volume 92. Plant nutrition. Volume 92: 774-775.

² EPA – United States Environmental Protection Agency, Office of prevention, Pesticides and toxic substances (7505C). Pesticide Fact Sheet, Conditional Registration, Dec. 1999.

B.8.4 Fate and behaviour in water

B.8.4.1 Hydrolysis rate of relevant metabolites, degradation and reaction products

B.8.4.2 Direct phototransformation of relevant metabolites, degradation and reactions products in water

No study available.

B.8.4.3 Ready biodegradability of the active substance

No study available.

B.8.4.4 Water/sediment study

No study available.

B.8.4.5 Degradation in the saturated zone of active substance, metabolites, degradation and reaction products

No study available.

B.8.4.6 Summary and assessment of the fate and behaviour in water

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 rates of 2.5-10 kg/ha of technical calcium carbide. After application tunnels and burrows should be covered.

Calcium carbide reacts very vigorously in water with spontaneous decomposition into calcium hydroxide, acetylene and small quantities of phosphine. Acetylene gas dissipates to the atmosphere and phosphine evolved in minor quantities is oxidized to phosphoric acids and phosphates. Calcium carbide reaction with water shows an alkaline reaction.

Regarding the physical and chemical properties of calcium carbide it is not expected that the active substance or any of the decomposition products persist in water. Moreover, regarding the intended use, application underground in tunnels or burrows, it is not expected that the product will reach surface waters.

B.8.5 Impact on water treatment procedures

No study available.

B.8.6 Predicted environmental concentrations in surface water and in ground water (PEC_{sw}, PEC_{gw})

B.8.6.1 Predicted Concentrations in Surface waters – PEC_{sw}

The PEC in surface water was not submitted. However, regarding the fate and behaviour of calcium carbide in water, as well as, the underground intended use, it is not expected that surface water will be exposed to this substance. PEC_{sw} should be negligible.

B.8.6.2 Predicted Concentration in Ground waters – PEC_{gw}

The PEC in ground water was not submitted. Regarding the fate and behaviour of calcium carbide and its degradation products in soil groundwater contamination is not expected with these substances. PEC_{gw} should be negligible.

B.8.6.3 monitoring data

No study available.

B.8.7 Fate and behaviour in air

B.8.7.1 Summary and Assessment of the fate and behaviour in air

The technical calcium carbide is intended to be applied directly below soil surface, at a rate of 2.5-10 kg/ha, in tunnels and burrows of agricultural soil, that should be covered after the application.

Calcium carbide technical is not volatile, but in contact with humid air reacts with spontaneous decomposition into calcium hydroxide, to acetylene gas and phosphine gas. Acetylene is a highly flammable gas and can form explosive mixtures with air. Phosphine in the atmosphere is rapidly degraded (WHO, 1988 *cit in* EPA 1999¹). The half-life in air is approximately five hours with the mechanisms of degradation being photoreaction with hydroxyl radicals. The dark half-life is approximately 28 hours. The expected reaction products of phosphine in air are oxyacids of phosphorous and inorganic phosphate which are non-volatile (EPA, 1999¹).

Regarding the intended uses of product, granules applied directly under soil surface, no releases of the product to air can occur. Considering that the volatile degradation products, acetylene and phosphine, will be trapped in soil, releases of those substances to air should be considered negligible. So, air will not be exposed to calcium carbide or to the degradation products.

B.8.8 Predicted environmental concentrations in air (PEC_{air})

The PEC in air was not submitted. Regarding the intended uses emissions to air are not expected also. PEC_{air} should be negligible.

B.8.9 Definition of the residue

Calcium carbide was shown to be very reactive in presence of water, soil moisture or air humidity, with degradation into calcium hydroxide, acetylene and small quantities of phosphine. Calcium hydroxide reacts into ubiquitous bicarbonate and carbonate calcium. Phosphine trapped below surface is quickly adsorbed and degraded in phosphates and acetylene may be used by soil microorganisms affecting indirectly the nitrogen cycle. In water calcium carbide reacts very vigorously into calcium hydroxide, acetylene gas, that dissipates to atmosphere, and minor quantities of phosphine that oxidized to phosphoric acids and phosphates. Since substances released in the environment from reaction of calcium carbide with soil moisture or water are ubiquitous no soil or water residue definition will be proposed.

Calcium carbide will be directly applied, in granules, in tunnels and burrows that should be covered, avoiding releases to air. Two of the degradation products acetylene and phosphine, had volatile properties but both will be trapped underground, his potential to reach surface will be very limited, so no residues in air will be considered.

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

B.8.10 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
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Annex IIA

IIA 7.3.	Frenay, J.R.; Randall, P.J., Smith, J.W.B., Hodgkin, J.; Harrington, K. J. & Morton T.C.	2000	Slow release sources of acetylene to inhibit nitrification in soil. Nutrient Cycling and Agroecosystem journal. Springer Netherlands. Volume 56, Number 3/March, 241-251 pp	N	
IIA 7.3.	Maeyer, R.L.; KJaer, T. & Revsbech N.P.	2002	Nitrification and Denitrification near a Soil-Manure Interface Studied with a Nitrate-Nitrite Biosensor. Soil Science Society of America Journal. Volume 66:498-506	N	
IIA 7.3.	Randall, P.J.; Frenay, J.R.; Hodgkin, J. & Morton, T.C	2002	Effect of acetylene generated from carbide on nitrification soil, yield of irrigated maize and growth of maize seedlings. Developments in Plants and soil Sciences. Plant nutrition. Volume 92: 774-775	N	
IIA 7.3; IIA 7.10.	EPA – United States Environmental Protection Agency	1999	Office of prevention, Pesticides and toxic substances (7505C). Pesticide Fact Sheet, Conditional Registration, Dec. 1999	N	

Annex IIIA

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