

Draft Assessment Report (DAR)

- public version -

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

CALCIUM PHOSPHIDE

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

Volume 3, Annex B, part 4, B.8

October 2007

Annex B

Calcium phosphide

B-8: Environmental fate and behaviour

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.8 Environmental fate and behaviour

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

B.8.1.1 Route of degradation (Annex IIA 7.1.1.1)

B.8.1.1.1 Aerobic degradation

ACTIVE SUBSTANCE

Recent, “state-of-the-art” investigations according to current guidelines for the elucidation of the degradation pathway of calcium phosphide in soil do not exist. It is also expressly noted here that calcium phosphide is an inorganic molecule, and therefore “biological degradation” can intrinsically not be a relevant removal mechanism in the environment. Instead, hydrolysis leading to the evolution of phosphine and residual calcium cations will prevail. The former is expected to either partition to the atmosphere due to its volatility, or become re-adsorbed onto soil. In both cases, oxidative processes are effective in finally transforming phosphine to phosphate anions.

B.8.1.1.2 Anaerobic degradation

ACTIVE SUBSTANCE

Justification for non-submission

The submission of data or the performance of a test on anaerobic degradation of calcium phosphide is not considered to be required, since products containing calcium phosphide are applied for fumigation in underground tunnel systems and in this open field environment are not expected to be subject to anaerobic conditions. According to laboratory studies performed in 2 soils the maximum DT₅₀ of PH₃ in the gas phase was found to be 15 d. For further information please refer to B.8.1.1.1 and B.8.1.2.1.

RELEVANT METABOLITES

Justification for non-submission

The submission of data or the performance of a test on anaerobic degradation of relevant metabolites of calcium phosphide are not considered to be required, since products containing calcium phosphide are applied in open field environment or in storage and therefore are not expected to be subject to anaerobic conditions.

B.8.1.1.3 Soil photolysis

ACTIVE SUBSTANCE

Justification for non-submission

The submission of data or the performance of a test on soil photolysis of calcium phosphide is not considered to be required, since the calcium phosphide molecule is not expected to absorb

light at relevant wavelengths (for details, refer to EU-dossier chapter AII-2.5.1). In contrast, the active substance is degraded in contact with humid soil to phosphine gas.

B.8.1.2 Rate of degradation (Annex IIA 7.1.1.2; Annex IIIA 9.1.1)

B.8.1.2.1 Laboratory studies

RELEVANT METABOLITES

Calcium phosphide is degraded in soil to yield phosphine gas as an intermediate, and calcium cations. Theoretically, any phosphine generated during hydrolysis of will either be volatilised and subsequently subject to oxidative degradation by reaction with OH-radicals, or it will become re-adsorbed onto soil and subsequently be degraded.

Reference number: IIA 7.1.1.2.2
Author: Vahldiek, M., (1985);
Title: Untersuchung zur Beständigkeit von Phosphorwasserstoff (PH₃) im humusfreien Mineralboden, unpublished report. (BOD 97-00505)
Date: September 1985
Guideline: BBA method and method MB 36 (modified)
GLP: no (investigations were performed at a time when GLP was not mandatory)
Validity: Not applicable, supplemental information

Materials and Methods:

In this laboratory trial, three soils were used which were be characterised as follows:

Table B.8.1-1: Description of soils used in the study

Soil type	„Leichtweiß“	„Banteln“	„Gartenerde“
characterisation	sandy soil, low clay and silt	clay silt soil	loess soil, carbonate-rich
Org. carbon (%)	0.02 %	0.09 %	high *
max. water capacity	19.8 %	32.6 %	not stated
pH	not stated	not stated	not stated

*: not stated

Test item: POLYTANOL, batch no.: not stated, purity: 21.3 % calcium phosphide (Ca₃P₂) or 7.9 % phosphine. The product POLYTANOL was used as a source of phosphine in these experiments. The phosphine source was added to the soils, and the flasks were closed with a gas-proof silicone septum. Soils with different humus contents were tested with different levels of Ca₃P₂. The soils were reactivated by adjustment to 40 % of the maximum water capacity in the dark at a temperature of 20 ± 0.5 °C. 100 g soil were incubated in 300 mL Erlenmeyer flask with POLYTANOL up to the 2-fold application rate (3.4 - 10 mg/100 g soil), closed with a gas proved ground glass stopper. The decomposition of phosphine was determined by sampling the head-space with a gas-tight syringe in defined intervals from the flasks. Samples were analysed by gas chromatography.

After termination of the tests, 10 mL of sulphuric acid (10 %) were injected into each flask to determine the residual, unreleased PH_3 . After 2 h, the PH_3 content of the head space was analysed again. Since the degradation of phosphine is supposed to be very rapid, the determination had to be carried out in shorter intervals than scheduled by the guideline MB 36.

Findings:

In all trials, the maximum level of PH_3 release was reached after 2 h. The next 2-4 days the PH_3 release was constant or degradation was very slow. This interval was longer if more substance was added. After 4 days a precise degradation was observed. In one soil the half-life was dependent on the initial concentration, increasing with higher concentrations upon initiation. In all trials with low-humus soils (0.02 % and 0.09 % organic carbon), the DT_{50} was between 2 and 13 days. In the soil ("Gartenerde") with high humus content (not stated), the half-life was only 8 h. This result conforms to other tests conducted by the same testing facility with humus soils, where DT_{50} -values of 3-11 h were determined. Since the addition of sulphuric acid after termination of the test did not result in an increase of PH_3 -concentration, it was established that this substance had been totally decomposed during the test.

Conclusion:

The rate of degradation of phosphine in soil may be expected to proceed with DT_{50} values in the range 2-13 days in soils with low organic matter content, but more rapidly in soils with high organic matter ($\text{DT}_{50} = 3-11$ hours). The results of the study are plausible. However, this study can only be classified as supplemental information.

B.8.1.2.2 Field studies

Reference: IIA 7.1.1.1.1
Author: Koch, E.;
Report: Messungen des Diffusionsstromes von PH_3 im Boden, report no.: P/W/K 82. (BOD 2005-67)
Date: April 26, 1982
Guidelines: BBA- Leaflet No. 36
GLP: no
Validity: Not applicable, supplemental information

Material and methods:

In the study the diffusion stream of phosphine in soil was analysed.

Calcium phosphide (POLYTANOL), active substance: 26 %.

Choice of soil: Soil with relative high amounts of sand.

The mean humidity of soil was 13.5 %.

Dosage of POLYTANOL = 5 g, in underground 5, and 10 cm, respectively.

Atmospheric pressure = 1012 mbar

Performance of the field trials:

A tin case was placed on one part of the surface of the soil. After defined time the air contained in the tin case was analysed for its phosphine content. For the analysis of the gas area a Dräger gas detector pump with Dräger tube for phosphine, was used.

Findings:

The results are summarised in the following table.

Table B.8.1-2: Chart of results

Layer thickness of soil (cm)	Maximum phosphine concentration (ppm)	Time for maximum phosphine concentration (min)	Time of the half-life period of phosphine (min)	Maximum diffusion stream of phosphine (mg PH ₃ /m ² •h)	Time for the maximum diffusion stream (min)
10	1060	~ 150	~ 375	66	120
20	75	~ 420	~ 575	1.9	240
25	18	~ 420	~ 575	0.2	360
30	0.2	~ 420	~ 575	0.004	420

Conclusion:

In the field trials the extension of phosphine in soil in the horizontal line was estimated to about 30 cm, in vertical line to about 25 cm. The half-life period of phosphine was estimated to 6 – 10 hours. After two days the degradation of phosphine was complete. The degradation products were non-hazardous phosphates, e.g. hydroxyl apatite. The study results are plausible and can be used as additional information.

B.8.1.2.3 Soil residue study**Justification for non-submission**

The submission of data or the performance of a test on field studies on the residues of the product in soil is not considered to be required since there are no restrictions in extrapolating from the data provided for the active substance and relevant metabolites, degradation and reaction products.

B.8.1.2.4 Soil accumulation study**Justification for non-submission**

The submission of data or the performance of a test on field studies on the accumulation of the product in soil is not considered to be required since there are no restrictions in extrapolating from the data provided for the active substance and relevant metabolites, degradation and reaction products.

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

B.8.2.1 Adsorption and desorption (Annex IIA 7.1.2)

ACTIVE SUBSTANCE and RELEVANT METABOLITES

Justification for non-submission

The performance of “state-of-the-art” adsorption/desorption experiments with calcium phosphide is not considered to be required for the following reasons:

- All high-resolution analytical methods for calcium phosphide are based on the principle of liberating phosphine gas, with subsequent head space gas chromatography. Thus, a discrimination between the parent compound calcium phosphide and any phosphine already present would not be possible in experimental settings.
- The preparation of a solution in water for the subsequent adsorption/desorption experiments is not possible. As a result, this renders the performance of such studies as technically and scientifically unfeasible.

B.8.2.2 Mobility in soil (Annex IIA 7.1.3; Annex IIIA 9.1.2)

Reference: IIA 7.1.1.1.1
Author: Koch, E.;
Report: Messungen des Diffusionsstromes von PH_3 im Boden, report no.: P/W/K 82. (BOD 2005-67)
Date: April 26, 1982
Guidelines: BBA- Leaflet No. 36
GLP: no
Validity: Not applicable, supplemental information

Material and methods:

In the study the diffusion stream of phosphine in soil was analysed.

Calcium phosphide (POLYTANOL), active substance: 26 %.

Choice of soil: Soil with relative high amounts of sand.

The mean humidity of soil was 13.5 %.

Dosage of POLYTANOL = 5 g, in underground 5, and 10 cm, respectively.

Atmospheric pressure = 1012 mbar

Performance of the field trials:

A tin case was placed on one part of the surface of the soil. After defined time the air contained in the tin case was analysed for its phosphine content. For the analysis of the gas area a Dräger gas detector pump with Dräger tube for phosphine was used.

Findings:

The results are summarised in the following table.

Table B.8.2-1: Chart of results

Layer thickness of soil (cm)	Maximum phosphine concentration (ppm)	Time for maximum phosphine concentration (min)	Time of the half-life period of phosphine (min)	Maximum diffusion stream of phosphine (mg PH ₃ /m ² •h)	Time for the maximum diffusion stream (min)
10	1060	~ 150	~375	66	120
20	75	~420	~575	1.9	240
25	18	~ 420	~575	0.2	360
30	0.2	~ 420	~575	0.004	420

Conclusion:

In the field trials the extension of phosphine in soil in the horizontal line was estimated to about 30 cm, in vertical line to about 25 cm. The half-life period of phosphine was estimated to 6 – 10 hours. After two days the degradation of phosphine was complete. The degradation products were non-hazardous phosphates, e.g. hydroxyl apatite. The study results are plausible and can be used as supplemental information.

B.8.2.2.1 Aged residue column leaching studies**Justification for non-submission**

The submission of data or the performance of a test on laboratory studies on mobility of the product in soil is not considered to be required, since there are no restrictions in extrapolating from the data provided for the active substance and relevant metabolites, degradation and reaction products.

B.8.2.2.2 Lysimeter studies or field leaching studies**Justification for non-submission**

The submission of data or the performance of a test on lysimeter studies or field leaching studies of the product is not considered to be required, since there are no restrictions in extrapolating from the data provided for the active substance and relevant metabolites, degradation and reaction products.

B.8.3 Predicted environmental concentrations in soil (PEC_{soil}) (Annex IIIA 9.1.3)

Reference:	IIIA 9.1.3
Author:	Köhler, U.;
Report:	Estimation of predicted environmental concentration in soil (PEC _{soil}); unpublished, (BOD 2005-79)
Date:	1990
Guidelines:	not GLP
Validity:	Approach comprehensible, but not applicable for the proposed use pattern (no application on hectare basis)

Estimations by the Notifier

The conventional calculation of predicted environmental concentrations, i.e. (i) predicted initial environmental concentration ($PEC_{initial}$), (ii) predicted time-dependent actual concentrations (PEC_{act}), and (iii) the time-weighted average concentrations (PEC_{twa}) to which an organism may be exposed at certain time points or, respectively, during a certain period after the last application, was not considered appropriate, since a direct application of the plant protection product to soil is not a GAP use. POLYTANOL is placed underground at a recommended rate of 8–10 g / run or tunnel with 18 % active ingredient. Based on the resulting maximum expected rate of application of 10 kg /ha the application rate of the active ingredient calcium phosphide is 1.8 kg as /ha. However, the following worst case estimation was performed in order to derive a range for the maximum achievable PEC_{soil} .

On a hypothetical basis, assuming a total and immediate transfer of the entire calcium phosphide content of POLYTANOL to the soil surface layer, a homogeneous distribution of compound in the upper 15- 25 cm of soil, and a soil bulk density of 1.5 g/cm³, a hypothetical, maximum predicted initial environmental soil concentration of 0.90 mg/kg ($PEC_{theor-max}$) soil can be calculated.

However, under practical conditions of use it must be assumed that

- complete and immediate transfer is an unrealistic assumption because of the GAP use (i.e. application of POLYTANOL underground)
- approx. 90 % of the POLYTANOL degrades within 4 - 5 days after contact with soil to calcium compounds and phosphine. Phosphine is oxidised to inorganic phosphites, phosphates and phosphoric acid. These are natural soil components and plant nutrients.
- Thus, under practical conditions of use, it appears a reasonable assumption that a maximum of 10 % of the calcium phosphide would not be degraded within 4 – 5 days, so that as a consequence it would appear a sufficiently conservative approach to assume that only 1 % of the total active ingredient would at any time penetrate to the soil surface layer, leading to the following assumptions:

$$PEC_{initial} = 0.01 \times PEC_{theor-max} = 0.01 \times 0.90 \text{ mg/kg soil} = 9.0 \text{ } \mu\text{g/kg soil}$$

Further time-dependent PEC_{soil} were not calculated in view of these minimal initial soil concentrations, and since, based on the data presented in B.8.1.1, any calcium phosphide transferred to soil may be expected to be converted quantitatively to phosphate anions within a period of max. 14 days.

Conclusion

The RMS considers the approach presented by Köhler (1990) as not acceptable and therefore not valid. The approach is not applicable for the proposed use pattern of calcium phosphide. Instead the RMS considers that the emission scenario document for biocides used as rodenticides should be used for PEC_{soil} estimations.

Estimations by the RMS

Based on estimations using an emission scenario document for biocides used as rodenticides the following PH_3 -concentrations were estimated by the RMS:

PT14 Emission Scenarion Document for Biocides used as Rodenticides

Exposure of Rodenticides in open Areas (Chapter 2.5.3.2 Emission to Soil Gassing)

Purpose

Gassing against water voles and moles is performed to protect dikes and embankments.

The burrow of moles are slightly oval, approx. 5 cm wide and 4 cm high, located in a depth of 5 to 100 cm of which the main parts are located in a depth of 10 to 20 cm. The area covered by the galleries is depending on the amount of food available.

The home range for water voles were observed to vary from 6 to 4000 square meters per individual water vole. As voles prefer to stay in family groups the total area may be large. A realistic gassing area is estimated to be 2 ha (=20 000 m²)

The water voles entrance holes are 6-8 cm in diameter.

In case of metal phosphide the phosphine gas is transformed into phosphorous compounds with a half-life of a few to 20 days [WHO1988]. In this case it may be sufficient to estimate the local emission of active substance to soil after each application (0.2 kg product to 2 ha) instead of the emission to soil per campaign.

The number of emission days per application is one day, but the exposure period is longer.

Chemical: Ca₃P₂

Definitions

d := 86400s g := 10⁻³ kg µg := 10⁻⁹ ng := 10⁻¹² kg

S = set value provided by applicant

D = default value

O = result output

Input

Amount of product used in control campaign per treated area	Q _{prod} := 16000 g
Fraction of active substance in product e.g. Ca ₃ P ₂	F _{as} := 0.18
Number of application	N _{app} := 1
Fraction of product released to soil	F _{release_soil} := 0.99
Fraction of phosphine formed out of rodenticide	F _{formed} := 0.3.7.3

Output

Local emission of as to soil after campaign (fumigation scenario)

$$E_{\text{local soil campaign}} := Q_{\text{prod}} \cdot F_{\text{as}} \cdot N_{\text{app}} \cdot F_{\text{release soil}} \cdot F_{\text{formed}}$$

$$E_{\text{local soil campaign}} := 1.063 \times 10^3 \text{ g}$$

The exposed soil area is assumed to be the burrow wall surrounding an 8-cm diameter tunnel, with the mixing soil depth of 10 cm and up to 30 cm around the tunnel with a length of 2000 m.

Volume of exposed soil around burrow

$$\text{Radius of exposed soil around the hole} \quad \text{Radius}_{\text{soil}} := 0.14 \text{ m} \quad \text{D}$$

$$\text{Radius of hole} \quad \text{Radius}_{\text{hole}} := 0.04 \text{ m} \quad \text{D}$$

$$\text{Length of exposed hole} \quad \text{Length} := 2000 \text{ m} \quad \text{D}$$

$$\text{Soil volume exposed to rodenticide} \quad \text{O}$$

$$V_{\text{soil exposed}} := (\text{Radius}_{\text{soil}}^2 - \text{Radius}_{\text{hole}}^2) \cdot \pi \cdot \text{Length}$$

$$V_{\text{soil exposed}} := 113.097 \text{ m}^3$$

Local concentration in exposed soil at area per campaign

$$\text{Density of wet exposed soil TGD} \quad \text{RHO}_{\text{soil}} := 1700 \text{ kg} \cdot \text{m}^{-3} \quad \text{D}$$

$$\text{Local concentration in soil after campaign} \quad \text{O}$$

$$C_{\text{local soil}} := \frac{E_{\text{local soil campaign}}}{V_{\text{soil exposed}} \cdot \text{RHO}_{\text{soil}}}$$

$$C_{\text{local soil}} = 5.531 \text{ mg} \cdot \text{kg}^{-1}$$

Table B. 8.3-1: Estimation of PH₃-concentrations in soil

Amount of product per treated area (= 1000 m = 1 ha) length of exposed hole)	PH ₃ PEC _{soil} (mg/kg)
5 kg	3.457
8 kg	5.531
10 kg	6.914

Predicted environmental concentrations in soil (PEC_{soil}) for relevant metabolites

Not relevant, since the ultimate degradation products are calcium and phosphate ions, via phosphine gas as an intermediate, the latter being either subject to volatilisation or re-absorption and degradation to the aforementioned reaction products.

B.8.4 Fate and behaviour in water (Annex IIA 7.2.1; Annex IIIA 9.2.1; 9.2.3)**B.8.4.1 Hydrolytic degradation (Annex IIA 7.2.1.1)****ACTIVE SUBSTANCE**

Reference: IIA 7.2.1.1
Author: Martens-Menzel, R.
Report: Report about the Gas Development from Soil Fumigants Containing Phosphides. (WAS 2005-48)
Date: June 26, 1998
Guidelines: not applicable
GLP: on principles of GLP in accordance with PSD
Validity: Not applicable, supplemental information

Material and methods:

The gas development behaviour of POLYTANOL pellets is examined continuously by means of an IR spectrometer and compared with the gas development behaviour of two preparations containing magnesium phosphide and calcium phosphide, respectively, under the influence of atmospheric humidity.

IR Absorption Spectroscopy (MIRAN), GC-MS Spectrometry, (Chromatography: Shimadzu GC-17A, Detector: Shimadzu GCMS – QP5000)

The gas development experiments were performed in a thermostat fumigation chamber. The chamber volume was 2.5 m³. With every gas development experiment the dosage was 1g PH₃/m³, so 2.5 g PH₃ for the fumigation chamber with 2.5 m³ volume. Every gas development experiment was performed at least three times.

Table B.8.4-1: Chart of materials

Properties	Magtoxim	Phosfinon-P	POLYTANOL-Pellets
Producer/dealer	Degesch, Frankfurt/Main	Casa Bernado, Brazil	Chemische Fabrik Wülfel, Hannover
Active substance	magnesium phosphide	aluminium phosphide	calcium phosphide
Content of the active substance in %	66	57	18
Content of the active phosphorus in %	30	30	6
Weight of the preparation for 1g PH ₃ in g	3.0	3.0	16.0

Findings:

The results are summarised in the following tables.

Table B.8.4-2: Comparison of the Gas Development Data, 55 % Atmospheric Humidity

Parameters	Magtoxin	Phosfinon-P	POLYTANOL pellets
Maximum rate of gas development in $\mu\text{L/L}\cdot\text{h}$	78	34	38
Time of maximum rate of gas development in h	4.0	9.1	4.8
Time with 60 $\mu\text{L/L}$ (LC_{50} of the rat) in h	1.2	2.4	2.1

Table B.8.4-3: Comparison of the Gas Development Data, 75 % Atmospheric Humidity

Parameters	Magtoxin	Phosfinon-P	POLYTANOL pellets
Maximum rate of gas development in $\mu\text{L/L}$	136	45	80
Time of maximum rate of gas development in h	1.9	9.1	2.3
Time with 60 $\mu\text{L/L}$ (LC_{50} of the rat) in h	0.8	2.0	0.9

Conclusion:

It is not possible to perform a standard hydrolysis study (instant decomposition of the active compound), this study can be classified as supplemental information. The most important period of every gas development is a 24 hours range from the beginning. The gas development characteristics of Magtoxin and Phosfinon-P showed much higher concentrations than those, calculated from the content of active substance, announced by the producer. To make it possible to compare with POLYTANOL pellets, all results were transformed on the assumption that at most the whole content phosphine (1g/m^3) can be developed, e.g. under 75 % atmospheric humidity. Thus, a volume ratio of 710 $\mu\text{L/L}$ will be reached. Under 55 % atmospheric humidity the experiments concerning Magtoxin and POLYTANOL pellets showed a weaker total phosphine development fewer than 75 %. The proportion is 96 % by Magtoxin and 75 % by POLYTANOL pellets. Phosfinon-P develops the same total phosphine portion, under both humidity values. Under 55 % atmospheric humidity the maximum volume ratios are as shown beneath: 680 $\mu\text{L/L}$ Magtoxin, 710 $\mu\text{L/L}$ Phosfinon-P and 530 $\mu\text{L/L}$ POLYTANOL pellets. The results of the study are plausible.

B.8.4.2 Photochemical degradation (Annex IIA 7.2.1.2)**Justification for non-submission**

The submission of data or the performance of a test on the direct photo-transformation for calcium phosphide is not considered to be required, since the substance does not absorb light at relevant wavelengths to any significant degree.

Mass balance (accounting for 90 % of the applied radioactivity), identity of breakdown products, quantum yield, calculated theoretical life time in aqueous systems and photochemical half-life: Not required for reasons given above.

B.8.4.3 Biological degradation (Annex IIA 7.2.1.3)

B.8.4.3.1 Ready biodegradability

Justification for non-submission

The submission of data, or the performance of a test on biological degradation of calcium phosphide is not considered to be required, since calcium phosphide is an inorganic molecule, so that biological degradation can not be expected to contribute to any extent to the environmental fate of calcium phosphide. In contrast, abiotic hydrolysis in aquatic media will prevail, with subsequent release of phosphine gas.

B.8.4.3.2 Water/sediment study

Justification for non-submission

The submission of data or the performance of a test on water/sediment study of calcium phosphide is not considered to be required, since the active substance is not expected to access surface waters for the reasons given in B.8.4.3.1, and due to its GAP pattern of use.

B.8.4.3.3 Degradation in the saturated zone

Justification for non-submission

The submission of data or the performance of a test on degradation in the saturated zone of calcium phosphide is not considered to be required, for the following reasons: The use of plant protection products containing calcium phosphide as the active substance involves laying out of such products in underground tunnel systems and not area-wide. Due to its rapid degradation in the soil environment to normal soil constituents, no washing out into other soil layers or the ground water is to be expected.

B.8.5 Impact on water treatment procedures (Annex IIIA 9.2.2)

Justification for non-submission

The submission of data or the performance of a test for the impact on water treatment procedures of the product POLYTANOL is not considered to be required, since

- the degradation of calcium phosphide leads to either gaseous phosphine or by further degradation to phosphate and calcium ions, and
- these ubiquitous soil constituents are not expected to contaminate the ground water.

B.8.6 Predicted environmental concentrations in surface water and in ground water (PEC_{sw}, PEC_{gw}) (Annex IIIA 9.2.1, 9.2.3)

B.8.6.1 Predicted environmental concentrations in surface water (PEC_{sw})

The calculation of predicted environmental concentrations in surface waters (PEC_{sw}) for calcium phosphide following the GAP use of POLYTANOL is not considered to be required, since the use of the plant protection product merely involves laying out of ready-to-use calcium phosphide-containing granule on soil surfaces. Thus, any contamination of surface waters by events related in general to pesticides, such as over-spray, drift, run-off, atmospheric deposition etc. is not to be expected. In contrast, a contamination of surface waters is excluded by the specific conditions of use (please see above). Therefore, an estimation of predicted environmental concentrations in surface waters and consequently in sediments is not considered to be required.

B.8.6.2 PEC in ground water

Justification for non-submission:

The calculation of predicted environmental concentrations for calcium phosphide in ground water following the GAP use of the product POLYTANOL is not considered to be required, for the following reasons:

- PEC calculations for calcium phosphide in soil (subchapter B.8.3 above) following the GAP use of POLYTANOL have shown that only quantitatively insignificant amounts of active substance will reach the soil surface layer, even on a hypothetical worst-case basis.
- Calcium phosphide is degraded spontaneously in contact with water, hydrolysis of calcium phosphide leads to the formation of phosphine and calcium hydroxide.
- According GAP of calcium phosphide it is not allowed to use POLYTANOL in surface waters or ditches.

It is therefore concluded that there is no risk of contamination of ground water to any relevant degree.

Predicted environmental concentrations of relevant metabolites in ground water:

Justification for non-submission:

Not required for reasons set forth above.

Additional field testing:

Not required for reasons set forth above.

B.8.6.3 Monitoring data (Annex IIA 7.4)

To date, the applicant is not aware of any monitoring data that may be available for calcium phosphide. However, the existence of such data is also not likely in view of the environmental fate characteristics of the substance.

B.8.7 Fate and behaviour in air (Annex IIA 7.2.2; Annex IIIA 9.3)

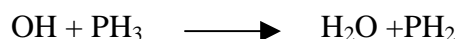
ACTIVE SUBSTANCE

Reference:	IIA 7.2.2
Author:	Fritz; B., et al.
Report:	Laboratory kinetic investigations of the tropospheric oxidation of selected industrial emissions, published in: Versino, B.; Ott, H. (Eds.): Physico - Chemical Behaviour of Atmospheric Pollutants, pp. 192-202, 1982 (LUF 2002-39)
Date:	1982
Guidelines:	not applicable
GLP:	no
Validity:	Acceptable

Material and methods:

Investigated substances are ethene oxide, phosphine, and hydrogen cyanide. In this study are report direct rate measurements for the reaction of OH radicals with ethene oxide, phosphine, and hydrogen cyanide, respectively, using an excimer laser photolysis/resonance fluorescence (LPRF) system are reported.

The reaction



is studied at 10 Torr total pressure of air in the temperature range $T = 249 - 438 \text{ K}$.

Findings

First order rate constants are strictly proportional to $[\text{PH}_3]$. The temperature dependence, however, is extremely weak. From the Arrhenius representation followed

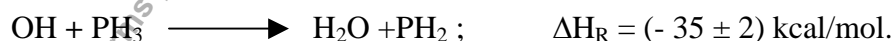
$$k(T) = (2.7 \pm 0.6) 10^{-11} \exp(-155/T) \text{ cm}^3/\text{molecule}\cdot\text{s}$$

which corresponds to a room temperature rate constant of

$$k(297 \text{ K}) = (1.6 \pm 0.3) 10^{-11} \text{ cm}^3/\text{molecule}\cdot\text{s}$$

Hence, PH_3 will be degraded very quickly in the atmosphere, having a lifetime of less than 1 day comparable to the most reactive organic compounds (e.g. C_3H_6 , CH_3CHO , Xylene).

Both, the magnitude of the rate constant and the thermochemistry suggest that the primary reaction proceeds by H atom abstraction:



Concerning the fate of PH_2 in the troposphere, one may only speculate by making recourse to a chemically similar species, NH_2 . Its dominant oxidation reaction is with O_3 . Hence, intuitively one may expect the following reaction for PH_2 :



Addition of NO_2 and subsequent hydrolysis could then yield hypophosphorous acid, H_3PO_2 .

Conclusion:

Phosphine is degrading very quickly in the atmosphere, having a lifetime of less than 1 day. In the troposphere the oxidation with ozone is dominant delivering phosphorous acids. A calculation performed by the RMS resulted in a reaction rate of $1.6 \times 10^{-11} \text{ cm}^3/\text{molecule}\cdot\text{s}$. This is in line with the study performed by the applicant. Therefore the study is acceptable and the results of the study are plausible.

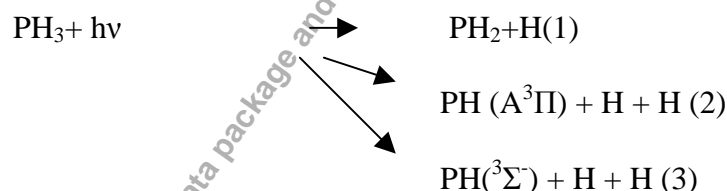
Reference:	IIA 7.2.2
Author:	Calvert, J.G. and Pitts, Jr., J.N.
Report:	Photochemistry – The Interaction of Light with Simple Molecules John Wiley & Sons, Inc., New York, page 204, 1966 (LUF 2002-158)
Date:	1966
Guidelines:	not applicable
GLP:	no
Validity:	not relevant

Material and methods:

Phosphine, flash photolysis under ultraviolet light

Findings

The absorption of UV light shows some banded structure at the long wavelengths (236, 232, 229.5, and 228 nm, respectively) and is continuous from the region 225 – 185 nm. The quantum yield of hydrogen formation in the long-wavelength absorption region is equal to about 0.56 independent of the pressure and the temperature. The flash photolysis studies show evidence of PH_2 formation in accordance with equation (1)



Below 200 nm, spectroscopic evidence is found for PH in both the $^3\Pi$ and $^3\Sigma^-$ states. If these species arise from a singlet excited state of PH_3 , then following spin conservation, molecular hydrogen cannot be formed (equations (2) and (3)).

Conclusion:

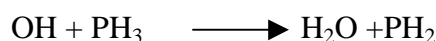
Phosphine absorbs UV light in the region 236 – 185 nm and decomposes in PH_2 , PH radicals, and hydrogen, respectively. This study is not relevant as there is no light absorption in the relevant wave length interval between 295 and 800 nm.

Reference: IIA 7.2.2
Author: Becker, K.H., et al. (Eds.)
Report: Phosphine, published in: Methods of the Ecotoxicological Evaluation of Chemicals. Photochemical Degradation in the Gas Phase, Vol. 6, p. 109, 1984 (LUF 2002-157)
Date: 1984
Guidelines: not applicable
GLP: no
Validity: acceptable

Material and methods:

Phosphine: An excimer laser is used as a short pulse monochromatic light source for the photolytic generation of OH radicals. The time dependence of OH is followed using conventional A-X resonance fluorescence excited by a microwave discharge of H₂O in Air. Resonantly scattered photons are collected by quartz optics via a 306 nm interference filter, focused on a photomultiplier and fed into a signal averager. The reaction was analysed in a range of temperature between 250 and 650 K.

The reaction



is studied at 13.3 hPa total pressure of air in the temperature range $T = 249 - 438$ K.

Findings:

The absolute rate constants measured are summarised in the following table

Table B.8.7-1: Absolute rate constants for the degradation of PH₃

T (K)	k (cm ³ /molecule•s)
249	$(1.4 \pm 0.3) \cdot 10^{-11}$
249	$(1.7 \pm 0.3) \cdot 10^{-11}$
256	$(1.3 \pm 0.3) \cdot 10^{-11}$
296	$(1.8 \pm 0.3) \cdot 10^{-11}$
296	$(1.2 \pm 0.3) \cdot 10^{-11}$
296	$(1.3 \pm 0.3) \cdot 10^{-11}$
370	$(1.8 \pm 0.3) \cdot 10^{-11}$
438	$(1.8 \pm 0.3) \cdot 10^{-11}$

Conclusion:

First order rate constants are strictly proportional to [PH₃]. The temperature dependence, however, is extremely weak. The study is acceptable. The results of the study are plausible and are supported by supplemental calculations of the RMS.

B.8.8 Predicted environmental concentrations in air (PEC_A) (Annex IIIA 9.3)

Justification for non-submission:

The submission of data or the performance of a test on fate and behaviour of the product POLYTANOL (calcium phosphide) in air is not considered to be required, since POLYTANOL as a solid substance minimises any dissipation to the air, and the vapour pressure of the active ingredient is very low. In contact with moist soil, calcium phosphide decomposes to phosphine which is subject to volatilisation and subsequent rapid atmospheric degradation.

B.8.9 Definition of the residue (Annex IIA 7.3)

Reference:	IIA 7.3
Author	Köhler, U. (2004)
Report:	Definition of residue (Chemische Fabrik Wülfel, Hannover, Germany) (BOD2005-71)
Date:	March 15, 2004
Guidelines:	not applicable
GLP:	no
Validity:	acceptable

Subject

Statement of the definition of residue by Köhler (2004).

The definition of a residue in plants is not considered to be required, since no residues of calcium phosphide in plants are to be expected due to the rapid hydrolysis of the compound. However, for formal reasons, concerning the definition of residues in the environment, the following is proposed: Residue analytical methods for calcium phosphide are principally identical to those for phosphine. Any calcium phosphide released to the soil or water environment may be expected to be associated with phosphine formation due to its inherent susceptibility to hydrolysis in aquatic media or in contact with soil moisture. Consequently, it is only logical to propose to define the relevant environmental residue of calcium phosphide as the sum of the released phosphine and calcium hydroxide.

Conclusion

The RMS considers the information as plausible and the conclusion as acceptable.

B.8.10 References relied on

Annex point/ reference number	Author(s)	Year	Title source (where different from company) report no. GLP or GEP status (where relevant), published or not BVL registration number	Data protection claimed Y/N	Owner
AIIA-7.1.1.1.1; AIIA-7.1.1.2.1; AIIA-7.1.3.3; AIIIA-9.1.1.1	Koch, E.	1982	Messungen des Diffusionsstromes von PH ₃ im Boden. not GLP, published BOD2005-67	N	-
AIIA-7.1.1.2.2; AIIIA-9.1.1.2	Vahldiek, M.	1985	Untersuchung zur Beständigkeit von Phosphorwasserstoff (PH ₃) im humusfreien Mineralboden. not GLP, unpublished BOD97-00505	Y	CFW
AIIA-7.2.1.1	Martens-Menzel, R.	2000	Report about the gas development from soil fumigants containing phosphides. GLP, unpublished WAS2005-48	Y	CFW
AIIA-7.2.2	Becker, K.H. et al.	1984	Photochemical degradation in the gas phase. Methods of the ecotoxicological of chemicals, vol 6, 109, 1984, 180-183 #161 not GLP, published LUF2002-157	N	-
AIIA-2.10; AIIA-7.2.2	Fritz, B. et al	1982	Laboratory kinetic investigations of the tropospheric oxidation of selected industrial emissions. Physico-Chemical Behaviour of Atmospheric Pollutants, 1982, 192-202 not GLP, published LUF2002-39	N	-
AIIA-7.3	Köhler, U.	2004	Definition of the residue. not GLP, unpublished BOD2005-71	N	CFW

Codes of owner

CFW: Chemische Fabrik Wülfel

¹ Only notifier listed