

The environmental profile of metaldehyde

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ABSTRACT

Since 1937 the dry alcohol metaldehyde has been known to act as a molluscicide. Detailed studies have shown that the main effect on slugs is that the mucus cells are irreversibly damaged. Mucus cells are part of important physiological structures typical of molluscs. Metaldehyde is not phytotoxic and in no cases have negative effects been recorded on the carabid beetles *Poecilus cupreus*, *Carabus granulatus*, *Pterostichus melanarius*, *Harpalus rufipes*, the staphylinid beetle *Aleochara bilineata*, the honey bee (*Apis mellifica*), the aphid parasitoid *Aphidius rhopalosiphi* and the predatory mite *Typhlodromus pyri*. No adverse effects were found on three earthworm species (*Lumbricus terrestris*, *Allolobophora chloroti* and *Eisenia fetida*). Studies with wild living mammals, hedgehogs (*Erinaceus europaeus*) fed with metaldehyde-contaminated slugs and wood mice (*Apodemus sylvaticus*) exposed to metaldehyde slug pellets did not show any signs of disturbance. No adverse effects on tilapia (*Tilapia mossambicus*), carp, milkfish (*Chanos chanos*) and on Crustacea were found in aquatic systems. Metaldehyde does not show any tendency to accumulate in soils, water bodies, plants and mammals. Under natural conditions it completely degrades to CO₂ and H₂O.

THE ACTIVE INGREDIENT METALDEHYDE

The first systematic reporting of Metaldehyde as a slug control agent goes back to Gimingham & Newton in 1937. From this year on it attracted the attention of agricultural research as a molluscicide and the first commercial formulations appeared on the market, offered to farmers, vegetable and ornamental growers. Metaldehyde was first discovered by von Liebig in 1835. It is the cyclic tetramer of acetaldehyde (Fig. 1), forming tetragonal prisms.

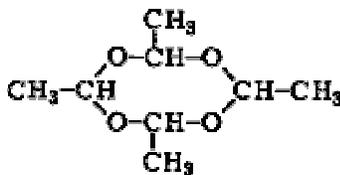


Figure 1. Chemical structure of Metaldehyde.

It can be considered as a solid alcohol, a pure hydrocarbon that degrades to acetaldehyde, then to acetic acid and thereafter into water and carbon dioxide (CO₂). Acetaldehyde is a naturally occurring substance and an intermediate in the degradation chain of ethanol in mammals.

The mode of action of metaldehyde on slugs was investigated in detail in several studies by Triebkorn *et al.* (Triebkorn, 1989; Triebkorn & Ebert, 1989; Triebkorn & Schweizer;

1990; Tribskorn *et al.* 1998). The main findings of these studies were that the mucus cells of slugs, typical for land molluscs, essential for land-life, are irreversibly destroyed. Metaldehyde acts very fast in slugs or snails inducing severe alterations and ultrastructural destructions in mucocytes independent of the exterior conditions, independently also at low temperatures and high precipitation rates. These findings also enlighten the fact that Metaldehyde is a highly specific molluscicide active ingredient, as will be shown in this paper.

DEGRADATION AND FATE OF METALDEHYDE IN THE ENVIRONMENT

In top soils under aerobic conditions Metaldehyde completely get degraded within a few days. In average German agricultural soils a DT_{50} of 5.3 to 9.9 days are observed (Lonza proprietary data).

Similar observations can be made in water sediments under moderate temperature conditions (Fig. 2). Metaldehyde is completely degraded with a DT_{50} of about 12 days. It's only metabolite acetaldehyde is formed transiently and finally mineralised to CO_2 . The original carbon from metaldehyde is recovered as carbon dioxide.

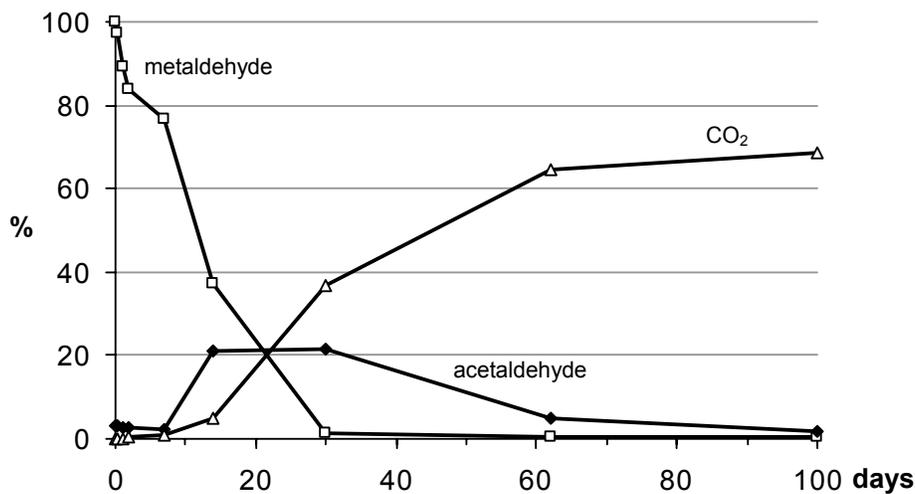


Figure 2: Degradation of Metaldehyde in water sediment over a 100 day period at moderate temperatures (Lonza proprietary data).

More rapid degradation of Metaldehyde is reported by Calumpang *et al.* (1995) in rice paddies in Philippines. The maximum concentration measured in the water body reaches 1.58 mg/l, whereas the Metaldehyde content fell below the detection limit within 9 days after treatment. The calculated half-life time is 0.27 day. A complete degradation of Metaldehyde in the soil was observed. The Metaldehyde content with a peak of 0.127 mg per kg soil fell in the soil below the analytical detection level within 22 days after treatment. The authors concluded that the use of Metaldehyde as a molluscicide in rice production does not lead to persistent residues in the various components of a rice paddy ecosystem. Similar results were found by Coloso *et al.* (1998), where the Metaldehyde content constantly fell to 1 % of its original concentration in the sediment of fish ponds within 15 day. In the water body the Metaldehyde content decreased to 16 % of the maximum concentration in the same time range.

For higher vertebrates there is no risk for accumulation in the organism, if it would be ingested at low doses. Metaldehyde gets metabolised in the same way as ethanol, a substance that naturally occurs in small but clearly measurable amounts in almost any ripe fruit.

EFFECT OF METALDEHDE ON NON TARGET ORGANISMS

In the last decades the knowledge of the sometimes highly sensitive interactions within our agroecosystems increased and with the growing awareness about the agronomic value of the beneficial organisms, high attention was given to know the effects of the used agrochemicals on those organisms.

Earthworms

Obviously earthworms are the most exposed beneficial organism during slug control measures. Slugs and earthworms are soil organisms and share the same habitats. It is assumed that for small slugs earthworm burrows serve as important refuges to survive cold or dry periods in deeper soil layers.

Molluscicides are applied in form of pellets. For food collection, earthworms examine the soil surface around their burrows for algae or litter peaces to bring into their burrows. Earthworms of treated fields therefore also get in direct contact with slug pellets. Because of the important functions of these animals for our soils slug treatments should not endanger or deactivate the earthworms.

In several studies by Bieri et al. (1989), Fayolle and Stawietcky (1990), Högger et al. (1992) did not found any behavioural change on *Lumbricus terrestris* L. and *Allolobophora chlorotica* exposed to Metaldehyde slug pellets in the laboratory. Even at doses far beyond the field application rate the animals did not show any reverse effects. Bieri et al. (1989) found that the exposed animals must have ingested considerable doses of Metaldehyde.

The NOEL of *Eisenia fetida* is more than 1000 mg Metaldehyde per kg soil, measured according to OECD procedure Nr. 207.

Beneficial Arthropods

The other important group of soil dwelling animals are the predatory arthropods. In semi-field trials Büchs *et al.* (1989, 1990) investigated the effects of slug pellets on *Poecilus cupreus*, *Carabus granulatus*, *Pterostichus melanarius* and *Harpalus rufipes* of the Carabid family in the laboratory in semi-field tests as well as in the field. In the laboratory *Carabus granulatus* showed sensitivity against Metaldehyde pellets, whereas in an extended laboratory test and in the semi field test the natural mortality clearly exceeds that found in the laboratory plots with Metaldehyde pellets at application rates of 4.5 to 5.3 times of the recommended rate by the pellet producers.

The effect of Metaldehyde slug pellets on the predatory roof beetle *Aleochara bilineata* was investigated by Samsøe-Petersen *et al.* (1992) in the laboratory. *Aleochara bilineata* females were brought in jars of a diameter of 3.5 cm with at least one slug pellet. This gives an over dosage of 30 to 33 times of that of the field rate. No mortality could be observed due to Metaldehyde slug pellets and the number of eggs laid per female did not differ compared to the control.

In a field test where each plot was fenced by iron sheet stripes, the effect on soil dwelling arthropods of scattered slug pellets were recorded by Bieri et al. (1989). Some plots were treated with about 4 times the field rate of Metaldehyde slug pellets. The numbers of arthropods was measured with pit fall traps placed in the centre of each plot. In no case an effect on spiders, ants, millipedes, staphylinid and carabid beetles could be observed in the areas where Metaldehyde slug pellets were applied.

In different laboratory tests no effects on beneficial arthropods were observed. Honey bees after exposed to direct contact or oral exposure to Metaldehyde and did not show any adverse reactions (Lonza proprietary data). The predatory mite *Typhlodromus pyri* and the aphid parasitoid *Aphidius rhopalosiphii* did not show any signs of irritation when exposed on a Metaldehyde containing surface (Lonza proprietary data).

Wild Vertebrates

In European countries hedgehogs (*Erinaceus europaeus* L.) are protected animals. They are beneficials and are known to be slug eaters. Many people take the presence of hedgehogs as an indication of a sound biotop. So it is a logic reaction that there is concern that hedgehogs, as slug predators, could be affected by slug pellets. At the German Research Station of Agriculture and Forestry in Münster Gemmeke (1995) exposed in specially equipped cages dead slugs after having ingested Metaldehyde slug pellets to six hedgehogs (Another six animals were used as control animals). From all of the six hungry hedgehogs offered dead slugs no adverse symptoms could be observed even on those animals having eaten almost all or all 200 slugs offered per cage. Gemmeke (1995) could not observe any effects or behavioural changes at the hedgehogs having consumed Metaldehyde containing slugs. Schlatter cited in Esser (1984) found in his investigations a dose of 500 mg / kg body weight as unproblematic for hedgehogs.

Tarrant et al. (1990) studied the effect of Metaldehyde slug pellets on the wood mice (*Apodemus sylvaticus* L.) population in a newly-sown field of winter cereals. They got no indication of exposure (none of the wood mice analysed contained detectable residues of Metaldehyde) nor of adverse effects on individual wood mice or on the population.

Several tests for studying the effect on bird species indicated that Metaldehyde pellets are not attractive to birds at recommended application rates.

Aquatic animals

For more than a decade Metaldehyde formulations are in use against aquatic snail pests mainly in South East Asia. Cheng (1989) reported on the control of the introduced snail *Pomacea lineata* invading rice paddies in Taiwan. According to his studies Metaldehyde is quite selective for *P. lineata* having no effect on fresh water shrimps and fishes. It is the only molluscicide allowed to be used in Taiwan in ponds, irrigation ditches and other water systems whenever fish toxicity is a concern.

Tilapia and Carps exposed to paddy rice treatments with Metaldehyde formulations did not show any mortality in the directly exposed cages positioned in the treated area (Calumpang et al. 1995).

Borlogan *et al.* (1996) exposed in a study juvenile Milkfishes (*Chanos chanos*) in test basins to Metaldehyde formulations (10 % a.i.) with application rates of 0, 25, 50, 75, 100, 125, 150 and 175 kg/ha. No mortality could be observed within 7 days at the exposed animals of 1 to 2 g life weight.

Investigations on Metaldehyde exposure of the fish species *Tilapia mossambicus*, the shrimp species *Penaues monodon* and *Metapenaues ensis*, the crap *Scylla serrata* and the small crustacean *Artemia salina* by Coloso & Borlogan (unpublished data) showed, that Metaldehyde applications present no risk to these animals.

PHYTOTOXICITY

Metaldehyde is used for many years in all kind of crops and all over the world. For all these years no records on observations on phytotoxicity were reported. Ester A. & H.J. Nijënstein (1995) investigated

the effect of Metaldehyde on the growth of the perennial ryegrass (*Lolium perenne*) after seed treatment. Even at rates of 320 g a.i. per kg seed no phytotoxicity could be observed on the seedlings and at plant growth.

CONCLUSIONS

An ideal pest control agent acts highly specific and efficient against the target organism at all weather conditions. But it should have no effects on the crops to be protected and does not deter the ecosystems. Especially the full complex of beneficials supporting the farmer in keeping down pest populations or maintaining an active soil should not be disturbed by the control measure. Finally the applied ingredient has to break down completely into simple, harmless and naturally occurring molecules within few days and no accumulation of the active ingredient occurs.

In reviewing the environmental profile of Metaldehyde it can be concluded that it is a slug control agent that fulfils the prerequisites of an ideal pest control agent. Because of its mode of action on the typical mucus cells of molluscs it acts highly specific and efficient against slugs and snails in aquatic and terrestrial systems. None of the beneficial organisms investigated showed adverse effects caused by Metaldehyde. But also no phytotoxic effects ever were observed. Metaldehyde basically is an alcohol that first it breaks down into acetaldehyde. Acetaldehyde is a widespread naturally occurring molecule that subsequently easily gets degraded by micro organisms into CO₂ and H₂O.

LITERATURE

Anonym (1984) *OECD procedure* Nr. 207.

Bieri M; Schweizer H; Christensen K; Daniel O (1989). The effect of Metaldehyde and Methiocarb slug pellets on *Lumbricus terrestris* Linne. In: *Slugs and Snails in World Agriculture*, ed. I F Henderson, pp. 237 – 244. BCPC Monograph No. 41.

Borlogan I G; Coloso R M; Blum R A (1996). Use of Metaldehyde as molluscicide in Milkfish ponds. In: *Slug & Snail Pests in Agriculture*, ed. I F Henderson, pp. 205 – 212. BCPC Monograph No. 66.

Büchs W; Heimbach U; Czarnecki E (1989). Effects of snail baits on non target Carabid beetles. In: *Slugs and Snails in World Agriculture*, ed. I F Henderson, pp. 245 – 252. BCPC Monograph No. 41.

Büchs W; Heimbach U; Czarnecki E (1990). Untersuchungen zu Auswirkungen von Schneckenbekämpfungsmitteln auf einige Laufkäferarten (Coleoptera: Carabidae) bei Anwendung verschiedener Testverfahren im Labor und Halbfreiland. *Zeitschrift für Angewandte Zoologie* **77**, 479 – 500.

Calumpang S M F; Median M J B; Tejada A W; Medina J R (1995). Environmental impact of two molluscicides: Niclosamide and Metaldehyde in a rice paddy ecosystem. *Bull. Environ. Contam. Toxicol.* **55**, 494 – 501.

Cheng E Y (1989). Control strategy for the introduced snail, *Pomacea lineate*, in rice paddy. In: *Slugs and Snails in World Agriculture*, ed. I F Henderson, pp. 69 – 75. BCPC Monograph No. 41.

Coloso R M; Borlongan I G; Blum R A (1998) Use of metaldehyde as a molluscicide in semi commercial and commercial milkfish ponds. *Crop Protection* **17**, 669 – 674.

Esser J (1984) Untersuchungen zur Frage der Bestandesgefährdung des Igels (*Erinaceus europaeus*) in Bayern. *Bericht ANL* **8**, 22 – 62.

- Ester A; Nijenstein H J (1996). Control of field slug (*Deroceras reticulatum* (Müller)) by seed applied pesticides in perennial ryegrass assessed by laboratory tests. *Zeitschrift für Pflanzenkrankheiten und Pflanzenschutz* **103**, 42 – 49.
- Fayolle L; Stawiecki J (1990). Effet de deux molluscicides sur les vers de terre. *Phytoma* **416**, 28 - 33.
- Gemmeke H (1995). Untersuchungen über die Gefahr der Sekundärvergiftungen bei Igel (*Erinaceus europaeus* L.) durch metaldehydvergiftete Ackerschnecken. / Investigations on the hazard of secondary poisoning in hedgehogs (*Erinaceus europaeus* L.) from metaldehyde in slugs on arable land. *Nachrichten des Deutschen Pflanzenschutzdienst* **47**, 237 – 240.
- Gimingham C T; Newton H C F (1937). A Poison Bait for Slugs, *The Journal of the Ministry of Agriculture*, Vol. XLIV, 3: 242 – 246.
- Högger C H; Ammon H-U; Bieri M (1992). The Daniel Funnel Test in a Sequence of earthworm Tests of Agricultural Pesticides. In: *Ecotoxicology of Earthworms*. Eds. Greig-Smith P W; Becker H; Edwards P J; Heimbach F. pp. 220 – 224 Intercept Ltd. Andover, Hampshire UK
- Samsøe-Petersen L, Bieri M, Büchs W (1992) Interpretation of laboratory measured effects of slug pellets on soil dwelling invertebrates. *Aspects of Applied Biology* **31**, 87 – 96.
- Tarrant K A; Johnson I P; Flowerdew J R; Greig-Smith P W (1990). Effects of pesticide applications on small mammals in arable fields, and the recovery of their populations. *Brighton Crop Protection Conference – Pest and Diseases* pp. 173 – 181.
- Triebskorn R (1989). Ultrastructural changes in the digestive tract of *Deroceras reticulatum* (Müller) induced by a carbamate molluscicide and metaldehyde. *Malacologia* **31**, 141 -156.
- Triebskorn R; Ebert D (1989). The importance of mucus production in slugs' reaction to molluscicides and the impact of molluscicides on the mucus producing system. In: *Slugs and Snails in World Agriculture*, ed. I F Henderson, pp. 373 - 378. BCPC Monograph No. 41.
- Triebskorn R; Schweizer H (1990). Influence du molluscicide métaldéhyde sur les mucocytes du tractus digestif de la petite Limace grise (*Deroceras reticulatum* Müller). *ANPP Annales 1990. Conférence internationale sur les ravageurs en agriculture*, Versailles. Tome I, 183 – 190.
- Triebskorn R; Christensen K; Heim I (1998). Effects of orally and dermally applied metaldehyde on mucus cells of slugs (*Deroceras reticulatum*) depending on temperature and duration of exposure. *Journal of Molluscan Studies* **64**, 467 – 487.
- Von Liebig J (1844) *Chemische Briefe, 1. Auflage*, Brief 14, Justus Liebig Museum, Giessen.