## Conclusion

Our study in real situations showed that cross-contaminations of oilseeds by post-harvest insecticide residues exist, and can sometimes lead to residues above the regulatory limits.

The highest risk of contamination for rapeseed appears when cereals are systematically treated at receipt, at the same time than rapeseed receipt, using the same conveyer circuits. The other identified cases can also lead to slighter contamination. But, silo operators have to concentrate on accumulation of several risky cases, which can worsen the contamination.

Other sources of insecticide residues can occur in storage facilities, but we couldn't check them in this investigation. This include leak of insecticide by the application equipment.

We noticed differences in cross-contaminations between sunflower and rapeseed, especially because of the harvest period. But also this new investigation was carried out in the new regulatory context in which dichlorvos and malathion are forbidden for cereal treatment. Thus storage operators have new grain protection strategies, with more preventive strategies to protect cereals against pests.

So in order to reduce these cross-contaminations, we can advise to avoid sharing same receipt circuits when cereals are systematically treated, and to avoid accumulation of risky situations. It is also very important to verify the insecticide treatment equipment. This investigation allowed us to make the storage companies aware of this issue, and to help them to understand how cross-contaminations can occur in their silos and how to avoid them, knowing that each silo is different of the others.

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## 17 - Fumigants in Stored Product Protection

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## Abstract

Since man began to store huge amounts of harvested cereal grains and other products in large bulks the application of fumigants was the method of choice for thorough disinfestations. Only these molecules are suitable to meet all the stages of pests even hidden within the products and kill them without moving the stored produce. Some boundary conditions are linked to effective use of fumigants for pest control:

- The product of premise must be sealed to a high degree of gas tightness – for instance by use of tarpaulins, glue, sticky tapes, poly urethane foam, silica glue or other appropriate materials – to keep the concentration of the gas for some length of tome sufficiently high.
- The temperature must be sufficiently high to allow penetration of the poison into the insect body and reaction at the target site within the insect.
- The concentration must be sufficiently high for a considerable length of time to control all stages or the target stage of the pest at a mortality rate of at least 99.9% (to avoid selection for resistance).

Only a few fumigants remain as registered compounds for this purpose:

- metal phosphide products for the release of phosphine gas
- carbon dioxide as inert atmosphere for replacement of oxygen; also under high pessure
- nitrogen [as inert atmosphere without need for registration as plant protection product]
- [hydrogen cyanide as gas for use as biocide]

The specific features of the fumigants including the efficacy against pests and fields of applications will be discussed.


Today‘s Situation: The economical importance and the impact of stored product pests, especially insects, has been highlighted and described quite often (Reichmuth et al. 2007). The elements of Integrated Management of these organisms (Reichmuth 1994b) comprise besides biological, physical and technical approaches a variety of chemicals and especially fumigants. These are especially required to control insect pests in products that are stored in bulk like in silo bins, granaries or deep ship holds during transit (Leesch et al. 1994). Also container fumigation is nowadays an important issue of pest control. The following fumigants are regulated in Germany (Bundesamt für Verbraucherschutz und Lebensmittelsicherheit, 2009) according to the Plant Protection Law:

1 Phosphine
2 Sulfuryl Fluoride
3 Carbon dioxide [including registration for High Pressure + CO2] and as biocide
4 Hydrogen Cyanide.

According to new definitions, a registration for nitrogen as inert fumigant does not seem to be necessary any more. Fumigants registered in various other countries around the world for pest control in general:

5 Carbonyl Sulfide (Australia)
6 Ethyl Formate (+CO2) (Australia)
7 Ethane Dinitrile (Australia)
8 Propylene Oxide (United States of America, [USA])
9 Methyl Iodide (USA, Japan) Against microbes
10 M(ethyl)-I(so)-T(hio)-C(yanate) (France, USA) Against microbes
11 Chloropicrin (USA)

The following table gives a raw description of advantages and disadvantages of the different fumigants:

**Tab. 1** Survey on some advantages and disadvantages of fumigants for stored product protection

| | **Advantages** | **Disadvantages** |
|---|---|---|
| Phosphine,<br>PH3 | The alternative for commodity disinfestation<br>Fairly economic<br>With prospects even for perishables | Exposure time of several days<br>Corrosion of copper and electronics<br>Risk of resistant strains |
| Sulfuryl fluoride,<br>SO2F2 | Quick lethally acting<br>Very good penetration characteristic<br>Excellent for empty space treatment<br>No long lasting residues of sulfuryl fluoride | Less effective against eggs of insects than against other stages<br>F- residues in fumigated products conflict with existing MRLs.<br>Global Warming Potential (GWP) fairly high compared with the GWP of carbon dioxide |
| Carbon dioxide,<br>CO2 gas mixtures with low residual oxygen content, modified (MA) or controlled | No significant residues in treated products<br>Obtainable also from natural sources<br>Suitable for organic products<br>Fairly quickly acting at elevated temperatures | Fairly long exposure period of several weeks at 20°C<br>High degree of gas tightness of treated objects required |

| | Advantages | Disadvantages |
|---|---|---|
| atmosheres (CA) | above 30°C | |
| Carbon dioxide, $CO_2$, in combination with high pressure of about 20 bar | Very quick acting method in hours<br>Suitable for organic products<br>Suitable for bulk products | Expensive pressure tight metal chambers necessary<br>Good logistics necessary |
| Nitrogen, as inert gas with very little residual oxygen content, produced from cylinders, pressure swing absorption (PSA) machines or semi permeable membrane machines with pressurized air | Residue free disinfestations of all stages of arthropods<br>No registration required<br>Worker safety high<br>Easy production in the field | Long lethal exposure periods of several weeks required<br>High degree of gas tightness necessary to avoid gas losses and back diffusion of oxygen<br>Costly treatment |

In previous publications the fumigants phosphine (Bell and Watson 1999, Hasan et al. 2007, Reichmuth 1990, 1994a,c, 1998, 1999, 2007, Klementz and Reichmuth 2004, Reichmuth et al. 2006, 2008, Shazali and Reichmuth1999, WHO 1988), methyl bromide (Bell et al. 1996, Bond 1984, Monro 1969, MacDonald and Reichmuth 1996, Reichmuth 1998) hydrogen cyanide (Reichmuth 1990, 1998), nitrogen (Adler et al. 2000, Reichmuth 2000) and carbon dioxide (Adler et al. 2000, Corinth and Reichmuth 1991, Reichmuth 2000, Hashem and Reichmuth 1992/1993, Mitsura et al. 1973, Reichmuth 2000, 2002, 2007a, Reichmuth and Wohlgemuth 1994, Stahl et al. 1985) are discussed at length.

This paper therefore focuses on some theoretical considerations, concerning all fumigants and especially sulfuryl fluoride.

Figure 1 describes the dependency of the lethal ct product - required for effective fumigation of all stages of the red flour beetle Tribolium castaneum other than eggs with SF at 25°C. The purple line represents a parameter curve to obtain a ct product of 113 gh/m³ with various concentrations of sulfuryl fluoride and exposure times in the laboratory. The dotted line indicates the corresponding times and concentrations of sulfuryl fluoride for a ct product of 300 gh/m³, being necessary from experience to provide lethal control under practical conditions when uneven concentration, temperature and insects hidden in cracks and crevices limit the direct transfer of laboratory data into practice.

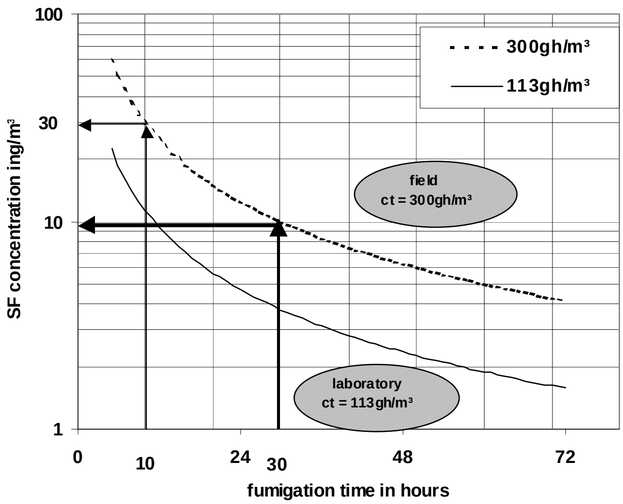


**Fig. 1** Model for the control of adults, larvae and pupae of the red flour beetle *Tribolium castaneum* at 25°C with sulfuryl fluoride; possible dosages (t and c) to obtain a lethal ct product of 113 gh/m³ (lower line) or a higher lethal ct product of 300gh/m³ (dotted upper line) to compensate for some leakage, limited gas distribution and temperature gradients; the arrows demonstrate two cases of dosage selection with either 10 g/m³ for 30 hours or 30 g/m³ for 10 hours, both resulting in the same lethal ct product of 300 gh/m³.

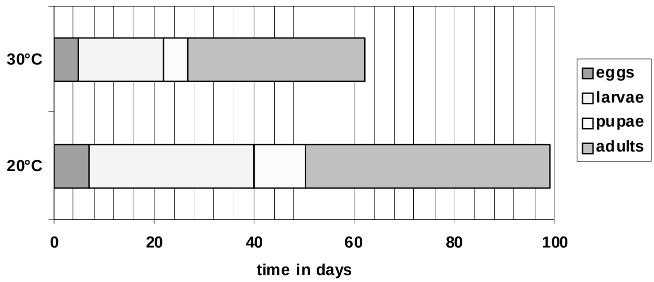


**Fig. 2** Model for the control of the red flour beetle *Tribolium castaneum* at 25°C with sulfuryl fluoride; different developmental times of the three pre immature developmental stages of the beetle and different life times of adult beetles at 20°C and 30°C, respectively

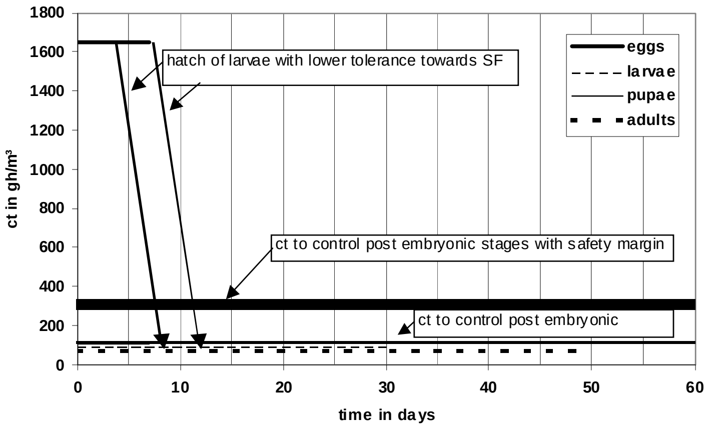


**Fig. 3** Model for the control of the red flour beetle *Tribolium castaneum* at 25°C with sulfuryl fluoride; egg hatch starts after about four days to continue for further four days to result in larvae with low tolerance towards SF; the ct product of about 300 gh/m³ during the first fumigation controls all post embryonic stages (larvae, pupae, adults); a second fumigation about two weeks after the first with about the same ct product of 300 gh/m³ would wipe out all those larvae that had hatched from eggs surviving the first fumigation.

As shown in figure 3, pronouncedly different ct products are required to control either the egg stage or all the other stages including the adults. Following fumigation with about 300 gh/m³, only the more tolerant eggs would remain as survivors. After a waiting period of about 12 days, a second consecutive fumigation again with 300 gh/m³ should be sufficient to kill all the larvae. Since the adult beetles had already been controlled by the first fumigation, no more eggs could have been laid between the two treatments. These twin fumigations should achieve full control with altogether 600gh/m³. The obviously necessary length of time (pulse) between two consecutive fumigations with 300 gh/m³ to achieve full control of all present stages including eggs, seems to be in the range of at least 14 days.

## Discussion – efficacy of SF

Baltaci et al. (2006) have presented laboratory data for the temperature dependency of the ct products of SF to obtain 50%, 95% and 99% mortality (LD50, LD95 and LD99), respectively, for control of *Oryzaephilus mercator*.

From the presented data it is obvious that there is a pronounced temperature effect on the lethal dose. Increase of temperature by 5°C leads to reduction of the LD99 of about 10%. For demonstration purpose, the difference of the ct product between control mortality of 95% and 99% is given. The necessary ct product for control of 99% of the merchant grain beetle even at 15°C is still far lower than the registered 1500 gh/m³ (Bundesamt für Verbraucherschutz und Lebensmittelsicherheit 2009). Again, there is clear indication that significant increase of the dosage is required to control only 4% more and ensure a higher rate of control of all the present stages.

These facts have to be taken in consideration when discussing the selection of the appropriate dosage for application of SF as fumigant for insect pest control.

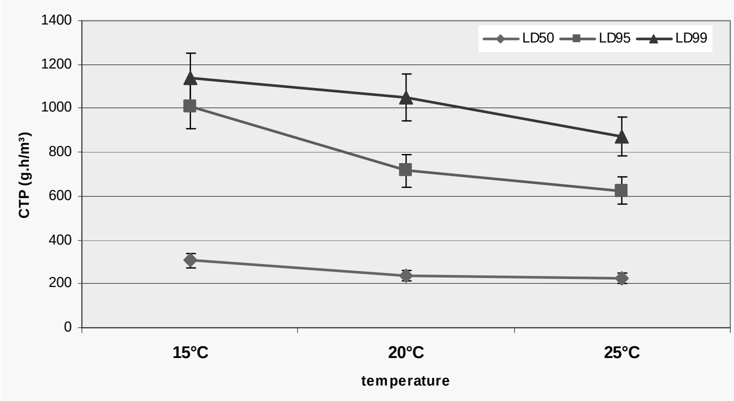


**Fig. 4** Dependency of the ct product for control of the merchant grain beetle Oryzaephilus mercator of the temperature between 15°C and 25°C; the indicated standard deviation covers a range of 5%.

<u>Why using Fumigants for Pest Control</u>?

In the light of reduced acceptability of toxic pesticides for use in pest control, the point has to be stressed, that these fumigants are a very important and nearly the only final tool in Integrated Pest Management to be able to control pests in certain situations of storage. Despite increased efforts to avoid pest infestation in the first place by various mechanical and other methods, insect infestation of large bulks of stored harvested products have to be thoroughly disinfested. Otherwise, large amounts of stored food or feed stuff will be lost. The question is allowed to be asked: What if we would not have access to these chemicals? What did man do before he used them? Long term storage without this tool seems to be very difficult. To some extent, construction of gas tight storages (Newman 1989) combined with right concepts of aeration (Reed and Arthur 2000, Navarro and Noyes 2002), and cooling (Armitage and Burrell 1978, Meier 1994) might be a promising approach. The knowledge of this complicated strategy is around but difficult to apply. A high degree of expert knowledge and understanding of the physics limits access to this technique. Costs may be another constraint. There are some examples in history (Cyprus bins), that show the possibilities and limits of this approach. Hermetic storage with aspects of reducing oxygen in the storage environment goes along with this concept (Adler et al 2000). Scientific data in abundance on the effects and use of inert atmospheres with low residual oxygen content (Bailey 1955, 1956,1957, Bailey and Banks 1975, Banks 1981, Banks et al 1990, Oxley and Wickenden 1963, Stahl et al. 1985, Adler et al. 2000, Corinth et Reichmuth 1991, Reichmuth and Wohlgemuth 1994, Reichmuth 2000, 2002, 2007a, Calderon and Barkai-Golan 1990, Navarro et al. 1994, Navarro et al. 1993, Bell) is inviting the application of this alternative. Constraints are the long lethal exposure times, the necessities concerning the structure and linked to gas tightness the costs. Toxic fumigants of these days bring along the high degree of efficacy in a fairly short time without leaving toxic residues in the treated commodities. Therefore, these few chemicals are especially suitable, useful and indispensable for effective and thorough pest control

- in large infested structures and space and
- in bulky infested commodities including large stacks of bags and boxes.

View from the roof of the main building of the Research Centre towards the Fumigation station of the department for Stored Product Protection (green churchlike-shaped building) and Skyline of Berlin

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## 18 - Ozonation – What is the potential? Application of ozone as an alternative to traditional fumigants

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### Abstract

Ozonation, the process in which stored products are exposed to a mixture of ozone gas and air in order to terminate unwanted biologic activity is presented as potential method to control pest infestation.

Following a historical resumée of the scientific research on ozonation, the s shown that in at least some cases Ozonation seems to be very effective against infestation. A brief summary on some of the studies relating to the effects on the crops treated with Ozone is given. It is shown that the reported effects in most cases are not causing any harm to the crops.

How are laboratory test results transferred to full scale storage facilities? A number of considerations are discussed; and results from field trials are discussed. It is shown that the amount of Ozone generated is critical, and that the distribution in larger facilities is also critical.

What are the advantages of Ozonation? The potential advantages of the use of Ozone are discussed in relation to the following: effectiveness as a 100% killer, immunity, environment, safety and economical issues.

A brief look to the future of Ozonation is attempted.

### Introduction

<u>Research on ozone as a fumigant</u>

- More than 100 scientific articles have been published on the subject.
- Several scientific studies have demonstrated that low ozone contents in air - like 50 ppm - are sufficient to kill insects, mites, molds, bacteria and other organisms.

Ozone as a strong oxidizer is traditionally used for sterilization of water. It eliminates flavour and color and can also purify air.

Results of initial tests on effects of ozone mixtures (50 ppm ozone in air) on *Aspergillus flavus* and maize germination showed:

- 66 % reduction in survival of surface conidia
- Complete inhibition of Hyphal growth and sporulation
- 97% reduction of aflatoxin production
- No reduction of maize germination
  (Ref.: Linda Mason et al, Perdue University)