Donahaye, E.J., Navarro, S. and Varnava, A. [Eds.] (1997) Proc. Int. Conf. Controlled Atmosphere and Fumigation in Stored Products, 21–26 April 1996, Printco Ltd., Nicosia, Cyprus, pp. 59–71

EFFECTS OF CARBONYL SULPHIDE ON *SITOPHILUS GRANARIUS* (L.) (COLEOPTERA: CURCULIONIDAE), *FUSARIUM CULMORUM* AND *FUSARIUM AVENACEUM* (SACC.) (DEUTEROMYCOTINA: HYPHOMYCETES), AND CORROSION ON COPPER

R. PLARRE[1, 2] AND C. REICHMUTH[1]

[1]*Federal Biological Research Centre for Agriculture and Forestry, Institute for Stored-Product Protection, Königin-Luise-Straße 19, D-14195 Berlin, Germany*

[2]*Present address: Stored-Product Insects Research Unit, USDA ARS, Department of Entomology, 1630 Linden Drive, University of Wisconsin, Madison, Wisconsin, USA*

ABSTRACT

All life stages of *Sitophilus granarius* (L.) were tested for their susceptibility to different concentrations and exposure times of carbonyl sulphide (COS) at 20°C and 70% r.h. Complete kill of *S. granarius* occurred at concentrations of 18 g m^{-3} COS for 120 h or 32 g m^{-3} COS for 72 h. The eggs were most tolerant to the toxic gas, followed by pupae and adults. Larval stages were most susceptible to the fumigant. Sublethal dosages prolonged the developmental periods of the immature life stages. Lethal dosages on *S. granarius* also caused growth inhibition in *Fusarium culmorum* and *F. avenaceum*, though the fungi recovered fully after treatment. In the presence of high relative humidity, COS is degraded partly to H_2S, which causes corrosion on copper. Carbonyl sulphide is discussed as being a possible alternative to methyl bromide.

INTRODUCTION

The treatment of stored products or storage facilities with fumigants is a common and effective method to control stored-product pests. In comparison with contact insecticides applied either as dusts, wettable powders or emulsifiable concentrates, fumigants have the advantage of penetrating the treated commodities completely. This becomes extremely important when grain, legumes or nuts are infested internally (Reichmuth, 1990). In general, fumigations leave either very low residues or none at all in the treated products and are also very time-effective. Therefore, fumigants impact heavily on import and export quarantine procedures. Nevertheless, the hazardous properties of fumigants, their carcino-

genic potential and concerns about worker safety, as well as environmental threats, have led in recent years to the recession of licensed and registered formulations. Because methyl bromide (MB) potentially contributes to the depletion of the ozone layer, its use will be heavily regulated even though it is one of the most commonly applied fumigants worldwide. Although the actual impact of anthropogenic produced MB is still vigorously debated (Detmers, 1993), in the near future its use will be restricted, and eventually it will be banned (Anon., 1994a). Either existing fumigation techniques must be modified in order to reduce emission of fumigants into the environment after aerating a treated facility (Reichmuth, 1990; 1993; Schreiner, 1993), or new alternative active agents and techniques for their safe application must be developed.

Carbonyl sulphide (COS) is regarded as one future alternative to MB (Catley, 1993). The Commonwealth Scientific and Industrial Research Organization in Canberra, Australia, has already filed a worldwide patent covering the use of COS as a fumigant in pest control (CSIRO, 1993). Although COS is not a novel chemical, its additional uses as a fumigant to protect stored products such as grain, in treating empty storage facilities, for soil fumigation and as a quarantine fumigant must be regarded as new fields of application (Anon., 1994b). COS showed toxic effects on such pest insects as stored-product Coleoptera and Lepidoptera, as well as on aphids, fruitflies and termites. It has been shown to be lethal to mites, nematodes and fungi. No residues have been recorded on wheat, rice or barley after treatment with COS. Nor does COS negatively affect germination (Desmarchelier, 1994a). Possible control of such rodents as rats and mice with COS has also been mentioned (Falbe and Reglitz, 1989).

COS appears naturally in the atmosphere at a concentration of approximately 1.5 $\mu g\ m^{-3}$, and it is the most common form of sulphur in the stratosphere. It is emitted from soil, marshes, manures, compost and most combustible products (Catley, 1993; Desmarchelier, 1994a). Furthermore, COS is found in a variety of industrial and natural gases (Ferm, 1957). The physical and chemical properties of COS have been described in detail by Stock and Kuss (1917), as well as by Ferm (1957) and Hommel (1993). It boils at –50.2°C and melts at –138°C. The vapor pressure is 1.1 MPa (11 bar) at 20°C. The specific weight is 124 $kg\ m^{-3}$, and the molecular weight is 60.07. Purified COS is a colorless, odorless and tasteless gas. It is highly flammable, burning with a slightly luminous blue flame ($2COS + 3O_2 \rightarrow 2SO_2 + 2CO_2$). In the absence of humidity, COS is a very stable compound. Thermal decomposition occurs at either 600°C ($2COS \rightarrow CO_2 + CS_2$) or 900°C ($COS \rightarrow CO + S$). With water or in the presence of water vapor, COS slowly reacts to form carbon dioxide and hydrogen sulphide ($COS + H_2O \rightarrow CO_2 + H_2S$).

In its pure form, COS does not corrode polished copper. However, contamination by as little as 1 ppm of elemental sulphur or hydrogen sulphide causes it to discolor copper. Information about its action on other metals is not available, but it is said to be corrosive toward concrete. The molecular structure of COS has been a matter of controversy. Nonlinear and linear configurations have been proposed, with the latter being favored. Intramolecular bonds vary between three possible structures: O=C=S; $^{+}O{\equiv}CS^{-}$; and $^{-}O{\equiv}CS^{+}$. The third structure, containing the triple carbon–sulphur bond, is the least impor-

tant; the first two structures predominate. The best method for making COS in the laboratory is the hydrolysis of metallic thiocyanates with mineral acids ($KCNS + 2H_2SO_4 + H_2O \rightarrow COS + KHSO_4 + NH_4HSO_4$).

Lethal effects of COS on insects and mites, including stored-product pests, have been reported by Desmarchelier (1994b). The most important results are those on *Rhyzopertha dominica* (the lesser grain borer) and *Sitophilus oryzae* (the rice weevil) because the immature life stages of these insects develop inside grain kernels. At 25°C, COS concentrations of 20 mg L^{-1} for an exposure time of 168 h, a concentration of 30 mg L^{-1} for 72 h and a concentration of 40 mg L^{-1} for 48 h all resulted in a complete kill of all the rice weevil's life stages. Damage caused by *R. dominica* can be ignored in temperate climatic conditions where it is negligeable (Chittenden, 1911; Weidner, 1983); although the occurrence of *S. oryzae* is increasing (Reuter and Bahr, 1988; Hallas, 1992; Stengård Hansen, 1994), economically the most important pest of stored grain in Central Europe is still the granary weevil *S. granarius*. The effect of COS on this weevil has not been investigated.

In a stationary fumigation chamber located at the Institute for Stored-Product Protection of the Federal Biological Research Centre for Agriculture and Forestry in Berlin, seven developmental stages including eggs, larvae, pupae and adult weevils of *S. granarius* were tested for their susceptibility to different concentrations and exposure times of COS at 20°C. Also of interest were the potential fungicidal and growth inhibition fungistatic effects of COS on mycotoxin-producing storage fungi. Short exposure times with high gas concentrations and long exposure times with low gas concentrations, both at dosages lethal to the granary weevil, were tested for their effects on two *Fusarium* species, *F. culmorum* and *F. avenaceum*. The possible corrosion effects of COS on copper, under European climatic conditions with high relative humidities, were also investigated.

MATERIALS AND METHODS

To obtain the necessary developmental stages of *S. granarius*, a quantity of 2.0 cm^3 of adult weevils were transferred weekly on to 600 cm^3 wheat substrate at 25°C and 70% relative humidity (r.h.). Adult weevils were sifted out of the culture after 3–4 d. Cultures 1–3 d old contained eggs; cultures aged 1 week, 2 weeks, 3 weeks and 4 weeks contained first, second, third and fourth instar larvae, respectively. Pupae (just prior to adult emergence) were expected after 5 weeks. Mesh-wire 8.8-cm^3 tubes were filled with approximately 3 g wheat kernels infested with the designated life stages. Fifty adult weevils, together with approximately 3 g uninfested wheat kernels, were caged in the same way. Seven tubes, one for each developmental stage, were stacked in perforated metal probes which could be inserted into a stationary airtight fumigation chamber of approximately 0.5 m^3 (Reichmuth, 1981).

The fumigant COS with a quality of N17 (97%) was procured from Air-Liquide, Branch Alphagaz.

The COS from a filled gas sampling tube was released into the fumigation chamber by a pump-driven circulation system. To obtain effective gas concentrations, the evacuated

gas-sampling tube was filled with a precalculated weight of COS using a pressure system of approximately 200 kPa (2 bar). The actual effective gas concentration inside the fumigation system was measured by a Miniature Infra Red Analyzer (MIRAN) [1A General Purpose Gas Analyzer, Foxboro Analytical (WILKS)] through absorption of COS at 4850 nm. For this purpose three 5.0-ml samples were taken with a gas syringe from the fumigation volume and then injected into the MIRAN analyzer (see Table 1). After the designated exposure times (see Table 1), two metal probes, each containing all seven life stages of *S. granarius*, were taken out of the system without opening the chamber and/or disturbing the effective gas concentration.

TABLE 1
Effective COS-concentrations and exposure times for treatment of *Sitophilus granarius*

COS concentration (g m^{-3})	Exposure times (h)
15.12 ± 0.47	12/24/48/72
18.11 ± 0.41	120
18.27 ± 0.59	18/24/48/72
18.93 ± 0.64	96
28.39 ± 0.34	15/24/48/72
32.31 ± 1.08	19/24/48/72

All treatments were carried out at a temperature of 20 ± 1°C and a r.h. of 70 ± 10%. After the probes were taken from the fumigation chamber and the mesh-wire tubes emptied, the infested wheat samples were kept in an incubator for another 8 weeks at 25°C and 70% r.h. An equal number of infested samples was prepared in the same manner and held for the same times at 20°C and 70% r.h., but not exposed to COS. These untreated control samples were also transferred to the incubator as described. The number of emerging adult weevils was recorded weekly.

Mortality resulting from COS was calculated by correcting the observed mortality in the treated samples by the naturally occurring mortality in the untreated control samples (Abbott, 1925). Mortality of treated adult weevils was recorded immediately after exposure and again 48 h later. Uninfested wheat kernels were exposed together with adult weevils during fumigation, and they were incubated as described in order to check both for possible egg deposition during treatment and for the possible hatch of an F_1-generation.

The possible corrosion effect on copper caused by COS degradation under high relative humidities was tested on polished copper pennies which were exposed to the gas during fumigation. Changes in weight before and after exposure, together with discolorations, were compared to those in untreated pennies.

The *Fusarium* species *F. culmorum* and *F. avenaceum* were exposed to COS in 6300-ml desiccators. Strains No. 65219 and 64218 of *F. culmorum* and No. 64211 and

64854 of *F. avenaceum* were obtained from the Institute for Microbiology of the Federal Biological Research Centre for Agriculture and Forestry in Berlin. Each strain was cultured on a Bacto Potato Dextrose Agar (PDA from DIFCO) and on a Synthetic low Nutrition Agar (SNA) (Table 2).

TABLE 2
Nutritional compositions of PDA and SNA

PDA	Potato extract from 200 g; 20 g Bacto Dextrose; 15 g Bacto Agar in 1000 ml H_2O
SNA*	1 g KH_2PO_4; 1 g KNO_3; 0.5 g $MgSO_4 \times 7H_2O$; 0.6 ml NaOH; 0.2 g glucose; 0.2 g saccharose; 22 g agar-agar in 1000 ml H_2O

*Developed in the Institute for Microbiology of the Federal Biological Research Centre for Agriculture and Forestry.

The fungal cultures were transferred into the desiccators 2 d after an initial growth period and exposed at 20°C and 70% r.h. to COS concentrations of either 30 g m^{-3} for 72 h or 20 g m^{-3} for 120 h. These COS concentrations and exposure times were those necessary for complete kill of *S. granarius* as ascertained earlier. The actual effective gas concentrations in the desiccators were again measured in the MIRAN, as described above (Table 3).

TABLE 3
Effective COS-concentrations and exposure times for treatment of *Fusarium* strains

Species	Strain	Medium	COS (g m^{-3})	Exposure time (h)
F. avenaceum	64211; 64854	PDA; SNA	20.64 ± 1.78	120
F. culmorum	65219; 64218	PDA; SNA	23.28 ± 0.17	120
F. avenaceum	64211; 64854	PDA; SNA	30.06 ± 1.77	72
F. culmorum	65219; 64218	PDA; SNA	26.97 ± 3.73	72

The areas covered by fungal mycelia on the respective media were recorded prior to the fumigation (0 h), directly after the fumigation (72 or 120 h) and again after an additional incubation period (240 h) at 20°C and 70% r.h. Possible fungicidal or growth inhibition effects of COS could be determined by comparison to *Fusarium* cultures identically cultivated without any gas exposure.

RESULTS

The mean number (with standard deviation) of emerging weevils and the survival of adults in the untreated control samples are shown in Table 4. Because 3 g of wheat infested with the designated developmental stages were used for experiments, the increasing number of emerging weevils from egg to pupal stage was easy to follow. The older the immature

TABLE 4
Mean emergence and survival with standard deviation of granary weevils in untreated control samples

Developmental stage	Number of weevils (mean ± SD)
Eggs	43.0 ± 10.6
Larvae 1	46.5 ± 6.3
Larvae 2	47.5 ± 7.3
Larvae 3	54.1 ± 7.8
Larvae 4	63.1 ± 8.5
Pupae	74.9 ± 5.3
Adults	49.8 ± 0.3
Eggs*	53.7 ± 7.5

*Deposited during fumigation.

instar, the more kernel substance material metabolized by the insect and the greater resulting weight loss of the grain. Therefore, the larger number of infested kernels compensated for the weight loss per kernel with increasing larval age.

The effects of the four different COS concentrations for different exposure times are plotted in Fig. 1, in which given mortality is corrected with the natural mortality of the untreated control samples. The first to third instar larvae were most susceptible to COS. A mortality of 90% occurred at a concentration of ca. 15 g m^{-3} for an exposure time of 72 h. COS-concentrations of ca. 18 and 28 g m^{-3} for 48 h caused mortality of over 95 and 100%, respectively. At ca. 32 g m^{-3} COS, a 95% kill occurred after 19 h of exposure.

The stage most tolerant to COS was the egg of *S. granarius*, oviposited into the kernel prior to fumigation. Low COS concentrations of approximately 18 g m^{-3} required exposure of at least 120 h for a complete kill. For lower exposure times, the COS-concentration required to achieve 100% mortality after 72 h had to be over 32 g m^{-3}. Eggs were more susceptible when they were laid during the exposure to the fumigant. This was determined by incubating the originally uninfested wheat kernels placed together with adult weevils during the exposure to COS. In these cases ca. 18 g m^{-3} for 72 h, and over 32 g m^{-3} for 19 h, were sufficient to achieve 95% mortality.

Adult weevils were completely controlled at concentrations of ca. 18 g m^{-3} for 72 h or 28 g m^{-3} for 48 h. Over 95% mortality was achieved at a concentration of ca. 15 g m^{-3} for 72 h.

Fourth instar larvae and pupae of the granary weevil were more tolerant to the tested COS concentrations and exposure times than were the adults. The fourth instar larvae seemed to be slightly more susceptible to lower COS concentrations than were the pupae. A 95% kill of fourth instar larvae occurred at ca. 18 g m^{-3} COS for 72 h, and an exposure time of 96 h resulted in 100% mortality. A complete kill of pupae required at least 120 h of exposure at this COS concentration. Above a concentration of ca. 28 g m^{-3}, differences in mortality between fourth instar larvae and pupae disappeared.

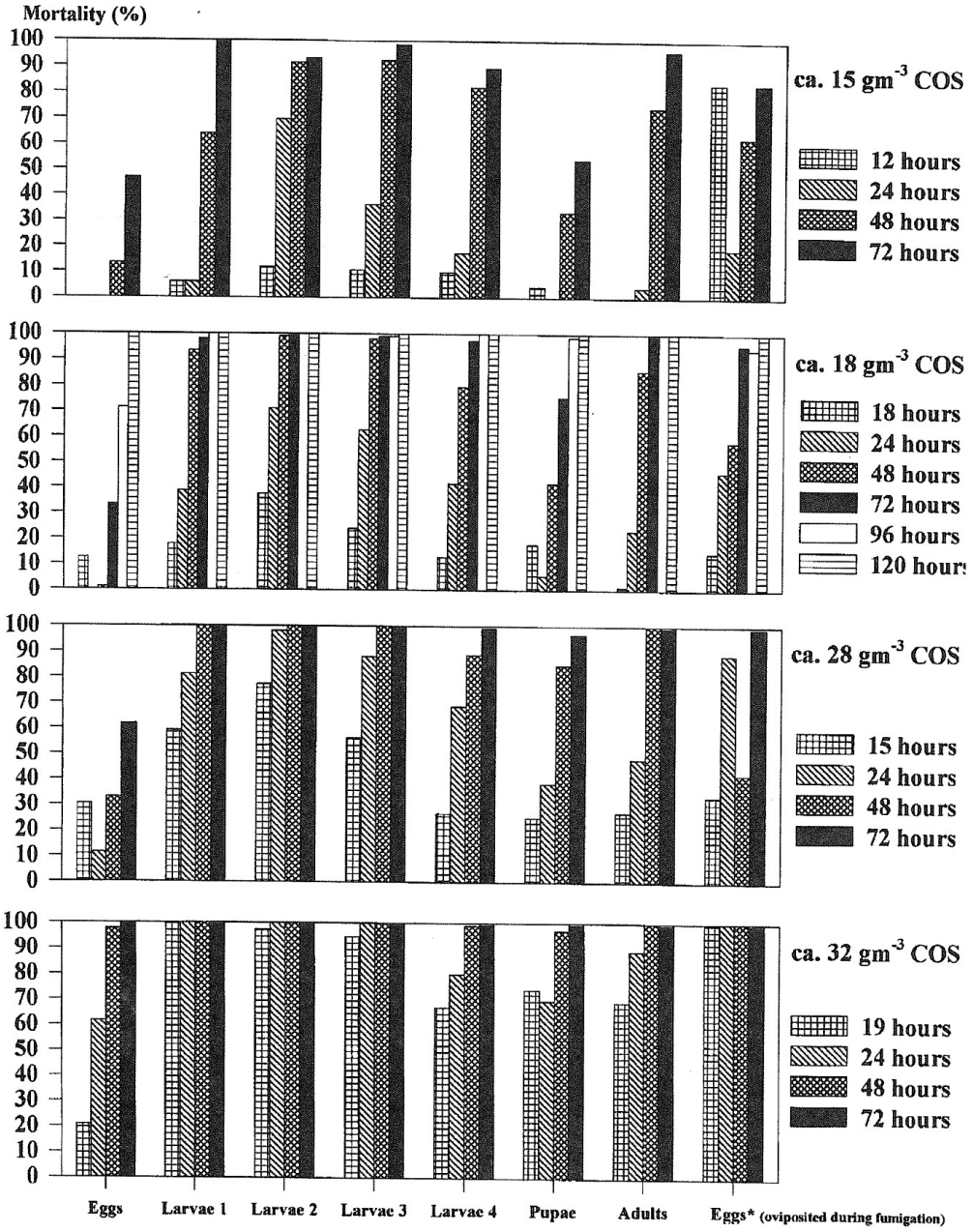

Fig. 1. Effects of four concentrations of carbonyl sulphide on life stages of the granary weevil *Sitophilus granarius* at different exposure times at 20°C and 70% r.h.

The following series shows the increasing susceptibility to COS: egg → pupae → 4th instar larvae → adult → 2nd, 1st and 3rd instar larvae.

Table 5 shows the necessary exposure times required to achieve LT_{50}, LT_{95}, LT_{99} and $LT_{99.9}$ for the corresponding COS concentrations, as calculated using the computer software "Table Curve".

Sublethal concentrations and exposure times of the fumigant prolonged the developmental periods in the juvenile stages of *S. granarius*. Onset and duration of weevil hatch from kernels infested with the designated stage and exposed to the fumigant were compared to those of untreated control samples. In all cases, especially after long exposure times but also at the higher concentrations, the onset of adult emergence was delayed. The prehatching duration of eggs increased with increasing sublethal dosages. The pupal stage was least affected; prolongation of development was most marked in the larval stages.

No fungicidal effect of COS was observed at concentrations and exposure times which were lethal to all stages of the granary weevil. Growth of both *Fusarium* species on both media was inhibited during exposure to COS. The higher concentrations of approximately 27 g m^{-3} or 30 g m^{-3} for a shorter exposure time of 72 h suppressed mycelial growth more than did the lower concentrations of ca. 23 g m^{-3} or 21 g m^{-3} for a longer exposure time of 120 h (Fig. 2). Additionally, a discoloration of the mycelia (to a whitish yellow) was

TABLE 5

Calculated exposure times in hours to obtain LT_{50}, LT_{95}, LT_{99}, and $LT_{99.9}$ at COS-concentrations of ca. 15, 18, 28 and 32 g m^{-3} for different developmental stages of the granary weevil

COS ($g\ m^{-3}$)	LT	Eggs	L1	L2	L3	L4	Pupae	Adults	Eggs*
15	LT_{50}		44.14	20.19	28.02	34.86	54.91	53.44	40.94
15	LT_{95}		62.42		51.49			63.38	
15	LT_{99}		68.80						
15	$LT_{99.9}$		71.56						
18	LT_{50}	79.84	27.44	20.07	22.03	30.99	51.76	34.02	32.81
18	LT_{95}	116.55	48.84	35.65	40.85	65.08	95.93	55.63	89.69
18	LT_{99}	119.11	73.25	48.00	50.44	86.63	105.19	68.44	107.52
18	$LT_{99.9}$	119.68		64.88			108.01	84.92	114.57
28	LT_{50}	62.45	12.44	10.03	14.21	17.26	28.14	23.90	17.22
28	LT_{95}		36.24	21.27	30.65	59.87	64.36	44.90	27.24
28	LT_{99}		47.43	26.07	40.36	76.08		50.70	39.29
28	$LT_{99.9}$		53.88	31.48	46.06			52.94	
32	LT_{50}	21.65		02.84	03.59	09.87	19.42	13.32	
32	LT_{95}	43.45		12.19	15.29	39.86	40.27	32.78	
32	LT_{99}	48.38		18.49	22.67	54.92	56.05	48.75	
32	$LT_{99.9}$	50.04		25.75	29.11	62.96	69.25	56.64	

*Deposited during fumigation. L1, L2, L3 and L4 = first, second, third and fourth instar larvae.

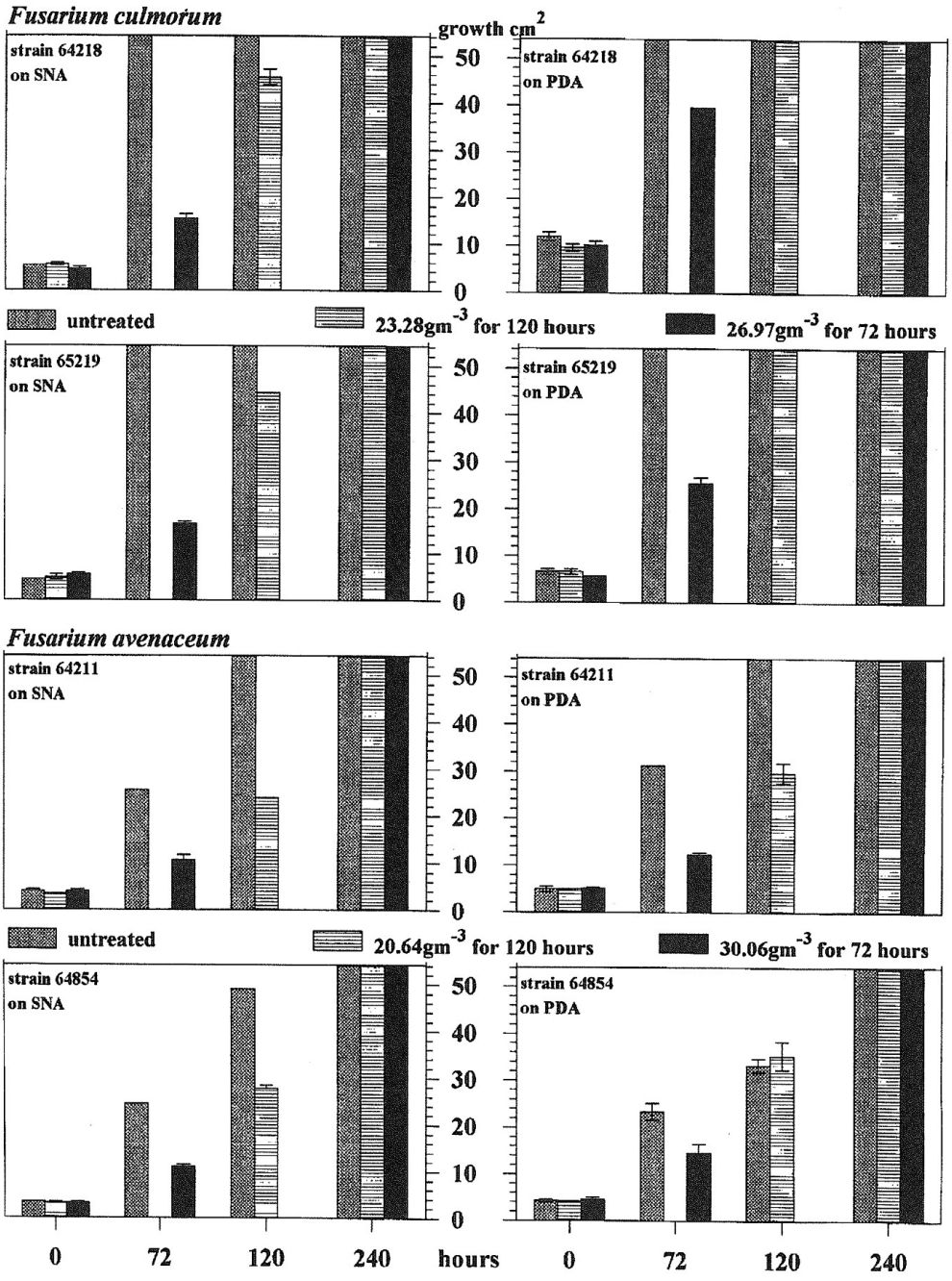

Fig. 2. Growth inhibition by carbonyl sulphide on *Fusarium culmorum* and *F. avenaceum.*

observed. The untreated control cultures did not show a change in color. An analysis of the treated and untreated culture media for changes in the pH-value and sulphide concentration showed no changes. After COS treatment the fungi recovered fully and, as with the untreated control samples, the growth pattern reached the boundaries of the petri dishes within a few days. The discoloration was retained.

At high r.h., COS is partly degraded to hydrogen sulphide, which causes corrosion on copper. This was indicated by the discoloration of copper pennies (which altered to a bluish color) and by a gain in weight of the magnitude of 10^{-4} g.

DISCUSSION

The possibility of controlling the granary weevil, including all of its immature stages, with atmospheres enriched with COS was demonstrated. Depending on the COS concentration, at 20°C exposure times of 120 h at ca. 18 g m^{-3} or 72 h at over 32 g m^{-3} were necessary to achieve complete kill of *S. granarius*. Comparable COS concentrations of 30 g m^{-3} or 20 g m^{-3}, for similar exposure times of 72 or 168 h, respectively, were needed to control the rice weevil *S. oryzae*, including all its immature stages (Desmarchelier, 1994b). Because these findings were recorded at 25°C, the granary weevil might be regarded as more susceptible to COS than the rice weevil. This remains to be verified. It can be assumed, though, that insect metabolism increases with a rise in temperature which results in a higher respiratory activity and a faster intake of the toxic gas.

The egg stage of *S. granarius* was most tolerant to COS when eggs were oviposited prior to treatment. Eggs deposited into grain kernels while females were exposed to the fumigant were far more susceptible. Several explanations are possible. During oviposition, or while still in the female's body, the egg could be more exposed to the toxic fumigant than when already inside the grain kernel. The sealed kernel might provide excellent protection for the immobile egg of relatively low metabolic activity. As long as the egg-laying channel has not been sealed by the female, direct contact between COS and the egg is a possibility, and this could also result in a higher mortality.

The other relatively immobile stage of the granary weevil, the pupa, not only showed a high level of tolerance to COS but its development time was also least affected by sublethal dosages. The tolerance of the pupal stage of *S. granarius* for other toxic fumigants, such as MB, phosphine (PH_3) and nitrogen-enriched atmospheres, has also been reported (Howe and Hole, 1966; Howe, 1973; Adler, 1992, respectively). The other immature stages of the granary weevil were more or less affected by sublethal dosages of COS, and their developmental times were prolonged. This might be a direct effect of the fumigant, but it is also possible that the larval stages actively reduced respiration to minimize exposure to the toxic gas. This is likely to be correlated with less metabolic activity and longer growth periods.

When fumigating with MB, where acting concentrations of the fumigant and exposure times are equally important to determine a certain lethal dosage, the product of concentration and exposure time (Ct-product) is constant. Applying the formula $c^n \times t = k$ (Zettler,

1993, according to Haber, 1924, and Winks, 1984) with c = concentration, t = exposure time, k = constant and $n < 1$, and using the calculated LT-values from Table 5, it can be shown that for COS the Ct-product is not constant. When varying the exposure time, the concentration necessary to achieve a certain lethal dosage needs to increase or decrease in proportion. Extending the exposure time results in a reduction of the necessary concentration, in multiples of the time, for a certain lethal dosage. In this regard COS acts very similarly to PH_3. This may have economic implications, such as in flour mill fumigation where the application of higher gas concentrations and shorter exposure times is desirable since a shut-down of the facility would result in greater financial losses than would the additional expense for the fumigant. Increasing gas concentration also carries the risk of higher gas losses when the treated commodities are improperly sealed. Applying sublethal dosages causes a delay in development, but it does not sufficiently control the very tolerant egg stage, and it also has potential risks. In order to avoid the propagation of tolerant strains, a complete control of the pest must be obtained.

F. culmorum and *F. avenaceum* are known as potential producers of mycotoxins on wheat in moderate climate zones (Miller, 1995). The application of COS concentrations and exposure times lethal to the granary weevil resulted in only temporary growth inhibition of the fungi. Similar findings have been reported for *Aspergillus flavus*, *A. parasiticum* and *Eurotium chevalieri* when treated with insecticidal dosages of PH_3 (Hocking and Banks, 1991). The discoloration of the mycelia can be regarded as a direct reaction of the fungi to the presence of the fumigant. An increase in sulphurous compounds or a change in pH-values of the treated culture media, which could also have been responsible for discoloration, were not detected. Exposure of fungi to such stress factors as fumigation can result in an increase of toxin formation. Unfortunately, analyses of toxin compounds and amounts were not possible. Nevertheless, fungal growth can be prevented by controlling insect pests which tend to form hotspots where higher temperatures and relative humidities favor fungi; dryer and colder grain storage also helps to prevent fungal growth.

Degradation of COS, already under high relative humidity, to hydrogen sulphide might cause severe problems of corrosion. This is of major concern. Because of it, COS does not appear to be a practical substitute for MB in moderate or temperate climatic regions such as Central Europe. In Australia, where the general climate is less humid and this new fumigant is highly regarded, COS might have a potential in pest control.

ACKNOWLEDGEMENTS

This research was supported through a research grant from the Federal Biological Research Centre for Agriculture and Forestry. The authors would like to thank Mrs Karacoglu and Mr Schmidt of the Institute for Stored-Product Protection for providing test insects and for excellent chemical analyses. We would also like to thank Dr Nirenberg of the Institute for Microbiology for providing *Fusarium* cultures and for very helpful suggestions and discussions. Carbonyl sulphide was obtained with the kind financial support of Binker

Company. We also thank W.E. Burkholder, J.K. Phillips and J.L. Zettler for carefully reviewing the manuscript.

REFERENCES

Abbott, W.S. (1925) A method of computing the effectiveness of an insecticide. *J. Econ. Entomol.* **18,** 265–267.

Adler, C. (1992) Zur Wirkung modifizierter Atmosphären auf Vorratsschädlinge im Getreide am Beispiel des Kornkäfers *Sitophilus granarius* (L.) (Col., Curculionidae). D 188 (Diss. Freie Univ. Berlin). Verlag Shaker, Aachen, Germany.

Anon. (1994a) *Report of the Methyl Bromide Technical Committee: Montreal Protocol on Substances that Deplete the Ozone Layer.* UNEP, Nairobi, Kenya.

Anon. (1994b) carbonyl sulphide being hailed as wonder new fumigant gas. *Int. Pest Control* **36,** 64.

Catley, A.C. (1993) Carbonyl sulphide, a potential methyl bromide substitute. *NAPPO Newsletter* **13,** 4, 2.

Chittenden, F.H. (1911) *The Lesser Grain Borer: Papers on Insects Affecting Stored Products.* USDA, Bureau of Entomology Bulletin No. 96, Part III, 29–47.

CSIRO (1993) Carbonyl Sulphide fumigant and method of fumigation. Intern. Appl. Publ. Patent Coop. Treaty (PCT), WO93/13659.

Desmarchelier, J.M. (1994a) Fumigant News: Carbonyl Sulphide. *Newsletter of Stored Grain Res. Lab. CSIRO*, 3.

Desmarchelier, J.M. (1994b) Carbonyl sulphide as a fumigant for control of insects and mites. In: *Proc. 6th Int. Working Conf. on Stored-Product Protection* (Edited by Highley, E., Wright, E.J., Banks, H.J. and Champ, B.R.), Canberra, Australia, 17–23 April 1994, CAB International, Wallingford, Oxon, UK, 78–82.

Detmers, H.-B. (1993) Empfindlichkeit der Entwicklungsstadien von *Prostephanus truncatus* (Horn) (Coleoptera: Bostrichidae) und *Teretriosoma nigrescens* (Lewis) (Coleoptera: Histeridae) gegenüber Methylbromid. Diss. Tech. Univ., Berlin, Germany.

Falbe, J. and Reglitz, M. (1989) *Römpp Chemie Lexikon.* Georg Thieme Verlag, Stuttgart and NY.

Ferm, R.J. (1957) The chemistry of carbonyl sulphide. *Chem. Rev.* **57,** 621–640.

Haber, F. (1924) *Fünf Vorträge aus den Jahren 1920–1923.* Verlag von Julius Springer, Berlin, Germany, 98 S.

Hallas, T. (1992) *Grain Pests: Official Examination of Consignments 1992.* Danish Pest Infestation Lab. Ann. Rep. 1992, 54–55.

Hocking, A.D. and Banks, H.J. (1991) Effects of phosphine fumigation on survival and growth of storage fungi in wheat. *J. Stored Prod. Res.* **27,** 115–120.

Hommel, G. (1993) *Handbuch der gefährlichen Güter.* Springer Verlag, Berlin, Heidelberg, NY, London, Paris, Tokyo, HK, Barcelona and Budapest.

Howe, R.W. (1973) The susceptibility of the immature and adult stages of *Sitophilus granarius* to phosphine. *J. Stored Prod. Res.* **8,** 241–262.

Howe, R.W. and Hole, B.D. (1966) The susceptibility of the developmental stages of *Sitophilus granarius* (L.) (Coleoptera: Curculionidae) to methyl bromide. *J. Stored Prod. Res.* **2,** 13–26.

Miller, J.D. (1995) Fungi and mycotoxins in grain: Implications for stored product research. *J. Stored Prod. Res.* **31,** 1–16.

Reichmuth, Ch. (1981) Inbetriebnahme der Begasungsstation des Instituts für Vorratsschutz der Biologischen Bundesanstalt für Land- und Forstwirtschaft in Berlin-Dahlem. *Nachrichtbl. Deut. Pflanzenschd.* **33,** 161–165.

Reichmuth, Ch. (1990) Toxic gas treatment responses of insect pests of stored products and impact on the environment. In: *Fumigation and Controlled Atmosphere Storage of Grain. Proc. of the Int. Conf.,* Singapore, 1989 (Edited by Champ, B.R., Highley, E. and Banks, H.J.), ACIAR Proc. No. 25. Brown Prior Anderson Pty Ltd, Canberra, 56–69.

Reichmuth, Ch. (1993) *Drucktest zur Bestimmung der Begasungsfähigkeit von Gebäuden, Kammern oder abgeplanten Gütern bei der Schädlingsbekämpfung mit Bemerkungen zur Begasungstechnik. Merkblatt 71 der Biologischen Bundesanstalt für Land- u. Forstwirtschaft.* Saphir Verlag, Ribbesbüttel.

Reuter, E. and Bahr, I. (1988) Zum Auftreten von Schadinsekten in Getreidevorräten. *Nachrichtenbl. Pflanzenschutz DDR* **42,** 225–229.

Schreiner, H. (1993) Recycling von Methylbromid nach Begasung im Mühlenbetrieb. *Getreide, Mehl und Brot* **48,** 10–12.

Stengård-Hansen, L. (1994) *Stored Product Pests: Official Examination of Consignments 1994.* Danish Pest Infestation Lab. Ann. Rep. 1994, p. 50.

Stock, A. and Kuss, E. (1917) Zur Kenntnis des Kohlenoxisulfides COS. *Berichte Deutsch. Chem. Ges.* **50, 159–164.**

Weidner, H. (1983) Vorratsschädlinge. In: *Leidfaden der Schädlingsbekämpfung. Band IV* (Edited by Heinze, K.). Wiss. Verlagsges, Stuttgart, 9–226.

Winks, R.G. (1984) The toxicity of phosphine to adults of *Tribolium castaneum* (Herbst): Time as a dosage factor. *J. Stored Prod. Res.* **20,** 45–56.

Zettler, J.L. (1993) Fumigant resistance. Practical Use of Fumigants and Pheromones. In: *Proc. of an Int. Technical Conf. and Workshop*, Lübeck, 117–122.