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Contract Report 99/052/VK
DEMONSTRATION PROJECT MP/SYR/98/028: ALTERNATIVES TO METHYL BROMIDE FUMIGATION FOR THE DISINFESTATION OF BAGGED WHEAT IN SYRIA

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1. Summary

Techniques for using phosphine generated from 34 g sachets of aluminium phosphide, or supplied as a 2% mixture in bottled liquid carbon dioxide, together with techniques of using carbon dioxide as a treatment atmosphere by itself, were demonstrated at the Sarico Storage Site near Homs, Syria, in comparison to treatment with methyl bromide. The programme and key findings are presented in the following summary table.

Summary of treatments and results

Treatments applied to sets of three 25.7 tonne stacks of bagged wheat inside a shed or in the open	**Mean amount dosed (g per tonne)**	**Mean gas concentration or level achieved (mean of 3 stacks)**	**Days of exposure**	**Survival of test insects /number treated**	**Mean CTP* achieved (g h m^{-3})**
Methyl bromide indoors	30.7	16.8 g m^{-3}	<1	0 /2400	335
outdoors	30.3	15.2 g m^{-3}	<1	0 /2400	305
Carbon dioxide indoors	3002	53.4%	15	0 /3200	-
PH_3/CO_2 indoors	3.2	1.60 g m^{-3}	7	0 /3200	269
outdoors	5.7	1.46 g m^{-3}	6	0 /3200	210
PH_3 from sachets indoors	4.7	1.75 g m^{-3}	8	0 /3200	336
outdoors	6.5	1.51 g m^{-3}	8-9	0 /3200	311

* Concentration time product (for phosphine or methyl bromide)

2. Introduction

Methyl bromide is currently used in Syria to control infestations encountered in bagged wheat. Bag stacks of up to 250 tonnes may be fumigated with either methyl bromide or phosphine, but there is particular concern about the risk of fire when using phosphine to treat stacks built in the open. At the Homs Sarico Storage Site of the General Establishment for Cereal Processing and Trading, there are normally sufficient sheds to store the grain under cover but this is not true of some other sites, particularly those in the north of the country. However discussions with local officials revealed that because of low rainfall the 1999 harvest was much less than the 4 million tonnes sometimes achieved, and hence the need for outside storage was much reduced this year. Nevertheless the treatment of stacks both indoors and outdoors was conducted in the current programme.

The fumigation of bagged cereals and other commodities with phosphine releasing formulations has been carried out routinely in many parts of the world for many years (Cogburn and Tilton, 1963; Bond, 1984). The gas is released from commercial formulations of aluminium or magnesium phosphide containing various other ingredients to slow the rate of release of gas. Phosphine works at very low concentration levels but requires a long time in contact with some insect stages to achieve complete control. It is highly penetrative of commodities and airs off rapidly after treatment. There is normally little sorption of the gas during treatment.

Mixtures of phosphine in air exceeding 1.8% by volume are spontaneously combustible but this level should not be reached during normal fumigation practice. Vacuum should not be used with phosphine as this threshold for explosive combustion is reduced. Phosphine works best at high temperatures and should not be used below 10-15°C. There may be problems for the breakdown of formulations if the humidity is too low - for wheat, a crop moisture content of below 10% can cause this problem. There is, of course, no such humidity limit for the action of phosphine released from cylinders. The toxicity of phosphine is well known for common pest species and dosage schedules are available (EPPO, 1993), but resistance is becoming a problem in tropical countries, requiring the use of longer exposures under better conditions of gas containment for effective control.

Carbon dioxide (CO_2) is not currently used in Syria for the disinfestation of wheat. Its use in other parts of the world extends back two decades, much of the early development work being done by Australian and other extension agencies in S. E. Asia with particular reference to bagged rice (Annis and Greve, 1984; Nataredja and Hodges, 1990). Carbon dioxide offers a relatively safe, non-toxic treatment method for commodity disinfestation. The treatment method requires a complete seal of the enclosure because high levels of gas (over 40% in air) need to be held for at least two weeks, even at warm temperatures, to achieve complete control of all insect stages. Normally stacks are dosed to contain over 70% CO_2 at the outset of a treatment (Annis, 1990). Specially fashioned canopy sheets, tailored for a set stack size, are glued to a base sheet of a similar material. Polyethylene is not a suitable material for this purpose as it is quite permeable to CO_2, and best results are obtained using sheets containing PVC.

Gluing can be problematical as the impermeable nature of the sheets restricts the evaporation of solvent so that the glue takes a long time to dry. This makes stacks vulnerable to any disturbance in the period following construction. For a single dosing of CO_2 to be sufficient for the total duration of the treatment, the seal on the stack needs to be sufficient to pass a negative pressure half life test of 10 minutes (Annis, 1990). The alternative approach is to monitor the gas levels in the stack at regular intervals and to redose and reseal as necessary.

The aim of the current project was to demonstrate that use of cylinders of CO_2 from a local supply, or use of phosphine, supplied from a conventional solid formulation (aluminium phosphide sachets) or from the new cylinder-based source of 2% phosphine in CO_2, offered viable alternatives to the use of methyl bromide in terms of efficacy, safety and cost.

3. Materials and Methods

The CSL team arrived in Syria on 21st June to start the trials programme. There were delays in obtaining the release of the trials equipment from Customs and it was only possible to begin the programme at the Sarico grain store near Homs on 1st July with the setting up of the first stacks on ground and base sheets. Supplies of methyl bromide, CO_2 and aluminium phosphide sachets were obtained locally, but the cylinder-based formulation of 2% phosphine in CO_2 had to be imported from Cyprus via the UK. The phosphine sachet formulation available in Syria, trade name Gastoxin, was manufactured by Caso Barnardo, Brazil.

3.1. Experimental Stack Design and Construction

Twelve stacks of wheat, bagged in hessian sacks, were constructed at the Sarico site (Fig. 1). Six stacks were built in a large concrete store (stacks A to F) and six were built outside (stacks G, H and J to M). Prior to stack building the floor area was swept clean of loose grit or gravel to minimise damage to sheets. Each stack was built on a 6 m x 6 m base sheet beneath which was a 125 μm polythene sheet to protect the base sheet from damage.

Inside the store stacks A, B and C were built on 50 μm polythene base sheets and stacks D, E and F were built on Powerplas 528 fumigation sheets. Outside the store stacks G, H and J were built on 50 μm polythene base sheets and stacks K, L and M were built on Powerplas 528 fumigation sheets. Powerplas 528 fumigation sheets are UV proof and manufactured using double sided PVC membrane supported on a scrim mesh. They were chosen because of their high impermeability to CO_2.

Each stack contained 7 layers of 32 bags of wheat, 224 bags in all, and was about 4.5 m square by 2 metres high (Figs 2 and 3). The mean mass of eight bags weighed at random was 114.8 kg and so each stack contained approximately 25.7 tonnes of wheat. Stacks A, B, C, G, H and J were constructed with a layer of pallets between the bottom layer of bags and those above to provide a gap for later insertion of solid phosphine preparations. Gas sampling lines, K type thermocouples and insect cages were placed across a transept of each stack at positions 1, 2 and 3 (Figs 2 and 3) before sealing the stacks.

3.2. The insect bioassay

A laboratory strain of the rice weevil *Sitophilus oryzae* (L.) was selected for the bioassays. The older immature stages of this species are highly tolerant of control using either phosphine or CO_2. The bioassay samples were prepared specially for the project at the Central Science Laboratory at York, UK. The insect cultures were brought to Syria in secure containers and at the time of fumigation each comprised upwards of 300 individuals at all stages of development. In the case of the stacks dosed with phosphine or CO_2 extra insect cultures were inserted at the bottom corner position to be removed at an intermediary time during the exposure, before the day of unsheeting. For the tests with CO_2, these samples were removed on the 10th day of the 15-day exposure, for tests with the solid formulation of phosphine on the 5th day of the 8-day exposure, and for the 2% phosphine in CO_2 tests, on the 4th day of the 6- or 7-day exposure.

After treatment, fumigated and control samples were examined for survival and were returned to the laboratory for incubation at 25°C. In addition to the bioassay, the wheat used in the stack tests was sampled for the presence of any natural infestation. The examination of samples was initially carried out in Syria and thereafter at CSL.

3.3. Stack Sealing and Dosing with Methyl Bromide

The stacks were sheeted using 9 m x 9 m fumigation sheets fitted with two 1.5 inch ports sealed with caps (Figs 2 and 3). The ports were positioned so that one was within 20 cm of the ground on the mid point of one side of the stack and the other was on the top of the stack towards the opposite side. To fasten the canopy sheet to the fumigation base sheet, the two were rolled together at the joins and the seal was reinforced with sand bags.

Stacks D, E, F, K, L and M were dosed with methyl bromide at the summer rate used on site at Sarico, about 25 g m^{-3}, via the port at the top of the stack. The dosage rates applied are given in Table 1. The concentration of methyl bromide was monitored using a thermal conductivity meter and the temperature was monitored using the thermocouples. Stacks D, E and F were aired after 21 hours and stacks M, K and L were aired after 24 hours. After airing some bags were removed to gain access to the insect bioassay samples which were removed from positions 1, 2 and 3 for assessment of mortality, and replaced with new samples in preparation for subsequent tests.

3.4. Stack Sealing and Dosing for Tests with Carbon Dioxide

To provide an additional level of seal for tests on CO_2, the top sheets were sealed to the base sheets using PVC glue before the joined edges were rolled and weighed down with sand bags. In each stack a polythene sleeve was placed in the join between the top and base sheets near position 3 to provide access for removal of bioassay samples on the 10th day of the treatment without disturbing the seal. After sealing, stacks D, E and F were fitted with valves at the ports near the ground. The pressure in each stack was then reduced using an industrial vacuum cleaner. When the pressure had been reduced below 1000 Pa the valve was closed and the time taken for the pressure to change from 1000 Pa to 500 Pa and the time taken for the pressure to change from 500 Pa to 250 Pa were recorded. This was repeated three times for each stack. Pressure tests were also done on stacks K, L and M in the open. However, on the night after performing the tests wind damaged the seals, preventing the subsequent dosing with CO_2.

The indoor stacks D, E and F were dosed with CO_2 from a vaporiser via the valves fitted at the ports near the ground and with the ports at the top open. The concentration of CO_2 at the top of each stack was monitored using an Anagas CD95 infra-red CO_2 analyser. When the concentration was greater than 70 % at all points, dosing was stopped. The valve was then closed and the cap was screwed on to the port at the top of the stack. The concentration of CO_2 in the stacks was monitored daily using the Anagas CD95 and the temperature was monitored using the thermocouples. The stacks were re-dosed whenever necessary to maintain a concentration of more than 40 % CO_2 at all points. Insect samples were removed from position 3 in each stack after 10 days using the polythene sleeve. After 15 days the stacks were unsheeted and the remaining insect samples were removed.

3.5. Sealing and Dosing with Phosphine

Stacks for dosing with the solid formulation of aluminium phosphide sachets incorporated a pallets laid between the bottom two layers of bags (see 3.1. above). As for the stacks treated with CO_2, top sheets were sealed to the base sheets using PVC glue before the joined edges were rolled and weighed down with sand bags. Stacks A, B and C, were dosed at a rate of 4.7 g/tonne using 11 bags of aluminium phosphide preparation in each stack. The outdoor stacks G, H and J were dosed at a rate of 5.1 g/tonne using 12 bags of aluminium phosphide preparation in each stack. The bags were placed in the spaces created by the layer of pallets so that they were not in contact with the floor. The winds caused damage to the seal between top sheet and base sheet of stack G and the sealing had to be repaired daily. The loss of gas in stack G caused by the wind damage meant that it had to be re-dosed after 5 days with 10 bags of aluminium phosphide preparation making the total dose 9.4 g/tonne in stack G.

The concentration of phosphine was analysed using an Agridox phosphine monitor and the temperature was monitored using the thermocouples. Insect samples were removed from position 3 in each stack after 5 days using the polythene sleeve. Stacks A, B, C, H and J were aired after 8 days and stack G was aired after 9 days. The stacks were partly dismantled to retrieve insect samples from positions 1, 2 and 3. In stacks A, B and C fresh insect samples were put in place and the stacks were then rebuilt and re-sealed ready for the trials with phosphine from cylinders.

Stacks A, B, C, K, L and M were dosed with a mixture of 2 % phosphine in CO_2 from cylinders via a regulator through the valves fitted at the ports near the ground. The initial dosage rate chosen for the stacks was set as 3 g per tonne. The concentration of phosphine and the temperatures were monitored as before. Stack M at the windward end of the outdoor stacks encountered the strongest winds which caused damage to the glue seal between top sheet and base sheet and the sealing had to be repaired daily. The loss of gas in the stack caused by the wind damage meant that it had to be re-dosed after 2 days and again after 4 days. After 7 days (or 6 days outdoors) the stacks were aired and the insect samples were retrieved.

4. Results

4.1. Methyl Bromide

Sampling of the grain before the tests did not reveal the presence of a resident population of pest insects in the shed. Stacks D, E and F indoors, and stacks K, L and M outdoors were dosed with about 0.7 - 0.9 kg of methyl bromide (Table 1). The effectiveness of a fumigation is usually assessed as the concentration - time product (time in hours multiplied by concentration in mg/l or g per cubic metre, = g h m^{-3}) achieved by the end of the fumigation. The concentration time products (CTP's) of methyl bromide achieved were more than sufficient to achieve complete control of insects at the high temperatures prevailing throughout the treatments, all exceeding 150 g h m^{-3} (Tables 1 and 2). There was some variation of temperature at the different positions in the stacks and considerable variation in the methyl bromide levels during the first hours after dosing (Figs 4-9). During the 20-h exposures, concentration levels fell by up to two thirds for the indoor stacks (Figs 4-6), but in two of the outdoor stacks, by the 20th hour concentrations had fallen to about one fifth of the starting levels. The prevailing high winds at the site (Table 2) had undoubtedly caused increased leakage of gas from the enclosures and the mean CTP's for the outside stacks were 10% lower than those inside (Table 3). There was no survival in the insect bioassay.

4.2. Carbon dioxide

It proved impractical to dose the outdoor stacks with CO_2 but good results were obtained indoors. With some redosing CO_2 levels were kept above 40% throughout the 15-day exposures (Figs 10-12, Table 4). The CO_2 stack F nearest the front entrance caught the sun during the day and perhaps some wind, and required the addition of CO_2 every second day to keep levels above 40% (Fig. 12). As a result this stack required the addition of over twice as much CO_2 during the treatment as stacks D and E (Table 4). Temperatures remained high throughout the exposures, averaging over 30°C inside the stacks with day time maxima in the shed of 32 °C (Table 5).

The level of seal obtained on the stacks varied from 14 to 25 seconds (Table 6), well below the level required for a one-shot CO_2 treatment. Difficulties were encountered with the glue seal of the canopy to the base sheet because of the dusty conditions and the long time required for the glue to set. Also, because the sheets were intended for general use after the demonstration trial they were not fashioned into canopies for the current experimental 25 tonne stacks, and as a result sheets had to undergo gluing and rolling at the corners to improve the level of seal. With the monitoring and redosing strategy applied to all stacks, mean concentrations of CO_2 were held above 50% at all positions. The best results were obtained with stack E which, in spite of having the shortest pressure test half life, required only a single redosing during the 15-day treatment (Fig. 11). All test insects inserted in the stacks, whether removed after 10 or 15 days, were killed.

4.3. Phosphine: 2% in CO_2 from cylinders

Dosing of stacks A, B and C with phosphine from cylinders to a level of about 3 g per tonne of wheat gave consistently good results. After the first day the concentration profiles were similar throughout the stacks at 2.1 to 2.6 g m^{-3} and at least 0.7 g m^{-3} phosphine remained at the end of the 7-day exposure (Table 7, Figs 13-15). There was no need to top up the dose of phosphine. Outdoors the daily strong winds (Table 8) adversely affected gas retention in all stacks (Figs. 16-18). Stack M at the leeward end of the three stacks faired best with concentration levels holding up to 0.6 g m^{-3} by the sixth day (Fig. 15). Stack K in the direct path of the wind had to be resealed and redosed on two occasions, the combined dose for this stack rising to over 10 g of phosphine per tonne of wheat. Stack L in the central position escaped redosing but only a trace of gas remained at the time of unsheeting (Fig. 17).

Temperatures in the outdoor stacks appeared higher than those under cover but it was suspected that some readings were increased by the effect of solar heating of the jackpoint used for plugging in the digital thermometer. Average ambient temperatures were about 5 degrees higher outdoors because of the sun (Table 8). No test insects survived the 4 or 6/7 day exposures in any stack, probably as a result of the prevailing high temperatures.

4.4. Phosphine: Aluminium Phosphide Sachets

Once again consistently good results were obtained from the stacks in the shed. Concentrations built up to a maximum during the second and third days of the treatment as gas evolved from the solid formulation (Figs 19-21). Concentrations of phosphine at the end of the 8-day exposures ranged from 0.6 to 1.4 g m^{-3}, and CTP's ranged from 250 to 405 g h m^{-3} (Table 9). There was more variation between sampling positions within stacks, and between stacks, than for the indoor treatments with phosphine from cylinders. Temperatures were slightly higher than in other trials, reaching a maximum of 34°C indoors (Table 10).

Outdoors the same windy conditions encountered in other trials broke the seal of stack G at the front of the row (Fig. 1), necessitating resealing and redosing at day 5 (Fig. 22). Progressively higher concentrations were achieved in stacks H and J, concentrations in the latter exceeding the upper limit of quantification (about 3 g m^{-3}) between days 2 and 5 (Figs 23 and 24). All CTP's exceeded 150 g h m^{-3} and all test insects were killed.

Mean CTP's for indoor treatments for the two formulations revealed that in spite of a 30% lower dose applied for the stacks treated with the phosphine/ CO_2 formulation, the mean CTP achieved was only 20% lower (Table 11). Outdoors the frequent breaking of seals affected the stacks facing the wind for both formulations and prevented meaningful comparisons other than seeing lower CTP's being achieved than indoors.

5. Discussion

5.1. Efficacy

The aim of this project was to demonstrate that viable alternatives exist to treatment with methyl bromide for bagged wheat, a crop with a long residence time available in store. Hence two longer acting alternatives were demonstrated, phosphine and carbon dioxide. Treatments have to be designed to control the full range of pests likely to be present and in warm climates this includes the khapra beetle *Trogoderma granarium* Everts, a notoriously destructive cereal pest of international quarantine status. The larvae of *T. granarium* are highly tolerant of carbon dioxide when in diapause (Spratt et al., 1985) but can be controlled easily by the high dosages of phosphine set for the tolerant older immature stages of weevils of the genus *Sitophilus* (Hole et al., 1976; Bell et al., 1984, 1985). At high temperatures in the presence of food the high tolerance of *T. granarium* can be avoided as under these conditions larvae do not enter or remain in diapause (Bell et al., 1984). The current programme was conducted under warm summer conditions, an ideal time following the harvest for action against pests.

With the need to control *T. granarium* in mind options were considered for the choice of test insect for the field bioassays. The rice weevil *Sitophilus oryzae* has a high tolerance of CO_2 levels (Annis, 1987) which rivals that of *T. granarium* larvae in diapause, especially at higher temperatures. As mentioned above it is a member of a genus with very high tolerance of phosphine, and also is a species that occurs widely on grain stored throughout the world, including Syria. *Tribolium castaneum* (Herbst) and *Oryzaephilus surinamensis*

(L.) which also commonly occur on wheat in Syria are by comparison quite susceptible to both gases, though *T. castaneum* is more tolerant to methyl bromide. Choosing the rice weevil as the bioassay species for these tests thus presented a strong challenge for both alternative treatment methods. The fact that after prolonged incubation no survival was obtained of any fumigated samples of this species indicates that all would have been effective in combatting any insect pest outbreak. An estimated minimum total of 3,200 insects (about 2,400 for methyl bromide because of the lack of a second, shorter exposure time withdrawn from stack position 3), as judged from subsequent emergence in the controls, were exposed in each indoor and outdoor treatment with each of the control measures tested.

The rigorous attention to sealing, monitoring and redosing to maintain lethal atmospheres in the stacks dosed with phosphine or CO_2 resulted in success for these demonstration tests, but the question has to be asked how such measures will be practical for routine treatments. The problems encountered in the gluing of canopies to base sheets showed that the technology developed in S. E. Asia was not so easily transferred to a hot dry situation with dust and wind to contend with. It is true that had canopies been fashioned beforehand to the fit the stacks more exactly to the base sheets better results may have been obtained, at least indoors, but there was still the need for lengthy undisturbed periods for the PVC glue seals to set. In practice the use of a glue seal to assist the process of securing the top sheet to the base, together with rolling joins and weighing down with dunnage, as performed in the trials reported here, may be implemented rather than the extremely time consuming and rigorous application of gluing a specially fashioned canopy sheet to a base sheet to achieve a pressure test standard for a one shot application. If this is indeed the case then the use of CO_2 as an alternative treatment method will be limited to situations where there is the continual presence of experienced personnel, because monitoring of stack gas retention and redosing of stacks will be needed throughout the long treatment exposures.

The principal factor of high potential threat to efficacy is the effect of wind speed on outdoor treatments. In some stacks the winds actually broke the seal, necessitating resealing and redosing. This occurred in spite of the use of many sand bags to reinforce the seal. There are clearly some prospects for success with phosphine in sheltered situations with perhaps 5 to 7 days for exposure, but the much longer exposures required for CO_2 effectively rule out this alternative as a viable option outdoors in Syria.

5.2. Safety

The use of any measure providing an atmosphere toxic to insects requires stringent attention to safety. Respiratory equipment with appropriate canisters for use with phosphine (type A2B2E2K2P3) and methyl bromide (also AX) should be available for personnel involved with gas application and warning notices should be placed near stacks to warn all personnel to keep away from the treatment area. During fumigation and airing, appropriate detector tubes should be available to measure atmospheric levels, especially when fumigating inside a building. Carbon dioxide applications present less risk but it is necessary to have detector tubes available to monitor gas levels adjacent to stacks in case of a large undetected leak source.

The use of phosphine also requires some further consideration when dosing because of the risk of spontaneous combustion if gas is released rapidly into a confined space. This can occur when a large amount of formulation is exposed at one position in an enclosure under warm, moist conditions. Care needs to be taken to ensure that the formulation is spread out as much as possible at dosing and that on release from solid formulation gas is free to permeate throughout the whole enclosure and not be confined to a particular area. The problem is not normally serious for bagged grain, particularly under dry conditions with a low moisture content commodity, such as Syrian wheat.

However, discussions with local staff responsible for fumigation in Damascus and on site at Sarico revealed that there had been instances of stacks catching fire when using phosphine releasing formulations to treat stacks in the open. The current practice for dosing phosphine in Syria is to string sachets across the sides of stacks before sheeting. This method has been used without incident for indoor stacks but problems had occurred outdoors. The CSL team had encountered this problem before and were able to diagnose the cause. Placing the sachets on strings at the side of stacks left many of them in contact with the sheet. Extreme temperature variations between day and night encountered outdoors could give rise to condensation on the sheets and sachets in this position were at risk of direct contact with water. In designing the demonstration treatments with phosphine this was taken into account and steps were taken to avoid sachets from coming into contact with water.

The secret was to provide a layer of pallets near the base of the stack to create spaces for later insertion of the sachets. To avoid damage to the ground sheet these were placed on top of the first layer of bags and the stack was then built on top. After sheeting and sealing, sachets were spread out on trays and, using the sleeve ports provided across the canopy base sheet seal, were pushed well under the commodity away from any likely moisture arising from condensation or another source. The spaces provided by the pallets also assisted the distribution of gas in all treatments. This technique should remove the possibility of any problems in this area and alleviate concerns over there being a fire risk associated with the use of solid phosphine formulations.

5.3. Costs

A detailed cost analysis of the different pest control methods is difficult to prepare. The issue is complicated by the use of the regular on site work force to conduct fumigation operations and the lack of a ready reckoner to estimate the true cost of this input, resulting in a potentially greatly exaggerated contribution to the costings by the fumigant formulations themselves. In comparison with methyl bromide, the aluminium phosphide formulation offers a slightly cheaper option whereas the phosphine in carbon dioxide formulation at approximately £250 (GB pounds) is about twice as expensive if applied at the same dosage rate. Cylinders of CO_2 are locally available at about £12 per cylinder, plus rental and transport charges. From the trial results at least two carbon dioxide cylinders are required per stack, increasing the cost to, say, £25. However one phosphine/ CO_2 cylinder will be sufficient to dose at least seven 25 tonne stacks at the rate of 3 g per tonne (about 4 kg of the CO_2 mixture), and in addition for successful application of CO_2 a vaporiser is needed and the cost of this item is £1,934, a high capital investment. Furthermore the reduced dose of 3g per tonne of phosphine/ CO_2 as compared with 5 g per tonne for the solid formulation of phosphine erodes the cost differential between the two formulations, although with better sealing it may be possible to reduce the dose of solid formulation also, at least indoors (Table 11).

The solution to the cost equation also depends on local availability. At present the nearest source for the cylinder-based formulation of phosphine is Cyprus and a trading link and local approval would need to be obtained for importation. In principle all the options could be made economically competitive in favourable circumstances.

6. Recommendations

6.1. Phosphine can be used as a safe cost effective alternative to methyl bromide, both indoors and outdoors in sheltered situations, but some changes to existing fumigation practice are recommended.

6.2. The alternative fumigants to methyl bromide that can be recommended require much longer times of exposure to be effective. As a result it is essential to make improvements to the method of sealing enclosures. Firstly the use of ground sheets is recommended. Before stack building the surface should be swept and fumigation base sheets should be protected by a polythene ground sheet if on an uneven surface. PVC-based sheeting is suitable for use with both phosphine and CO_2. It is recommended that canopy and base sheets be sealed together with PVC glue, with subsequent rolling of the joins to further improve the seal. Heavy reinforcement with sand bags is necessary, especially for outdoor treatments.

6.3. For stack fumigations using the readily available aluminium phosphide formulations releasing phosphine gas, the use of pallets is recommended to create spaces below or near the bottom of the stacks for insertion of the formulation at various points spread out on trays. In this way any possible contact of the formulation with ground water or condensation can be avoided. If wooden pallets are available these can be used to bear 1 tonne loads of bags that can be built into stacks using fork lift trucks. If only metal pallets are available, then because these will damage the sheets if applied directly, it is recommended that they be laid on an initial layer of bags during stack building.

6.4. The possibility of making available a supply of a cylinder-based supply of phosphine in Syria, either phosphine in CO_2 or phosphine in nitrogen, should be explored. The nearest supply of phosphine in CO_2 is in Cyprus (Ecofume or Phosfume), and of phosphine in nitrogen, Germany (Frisin). Cylinder-based formulations lack the problem of having to dispose of spent residues after treatment, gain at least a day on the exposure time required because of the comparatively rapid dosing and mixing of gas, and remove the risk of combustion arising from contact with water.

6.5. Carbon dioxide could offer a cost effective alternative to methyl bromide if available locally to the store and if used for stacks inside buildings protected from the weather. The level of seal required is stringent and exposures of 10 to 15 days are required at temperatures around 30°C. For effective use of CO_2, a vaporiser needs to be available during dosing to prevent stoppage of flow because of freezing the line, and concentrations in the stack will need to be monitored to judge whether redosing is needed.

6.6. For both phosphine and CO_2 the exposure time and not the dose level is greatly influenced by temperature. For effective treatments at 30°C, phosphine requires a minimum exposure of 4 days (EPPO, 1993), this being achievable by use of the phosphine/ CO_2 but not by solid formulations which require an additional day to release the gas, increasing to a 7-day exposure at 25°C and 14 days at 20°C. For CO_2 exposure times increase from 10-15 days to 20 days as temperatures fall towards 20°C. Around 20°C and below this exposure time will need to be substantially increased if there are prospects of *T. granarium* or *Sitophilus spp* being present.

6.7. The methods demonstrated were largely new to Syria and there is a need for further extension work to enable the successful widespread implementation of the technology.

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Tables 1-3. Methyl Bromide Treatments

Table 1. Dosage Rates and Concentration-Time Products For The Methyl Bromide Treatments

Location	Stack	Dose (Kg)	Dosage Rate (g/tonne)	CTP (ghm^{-3})		
				Position 1	Position 2	Position 3
Inside	D	0.90	35	366.3	472.8	346.0
	E	0.70	27	234.4	192.7	336.3
	F	0.78	30	286.9	358.1	422.3
Outside	K	0.76	30	359.5	237.5	276.8
	L	0.80	31	374.4	338.5	370.4
	M	0.76	30	305.0	172.1	308.2

Table 2. Wind and Temperature Data For The Methyl Bromide Treatments

Location	Stack	Mean Temperature (°C)			Wind Speed (m/s)		Ambient Temperature (°C)	Maximum - Minimum Temperature (°C)
		Position 1	Position 2	Position 3	Average	Maximum Gust		
Inside	D	29.4	34.8	31.1	-	-	26	31-24
"	E	30.2	35.2	31.9				
"	F	31.2	33.6	30.4				
Outside	K	37.9	30.5	37.5	4.5	9.6	-	-
"	L	35.2	29.8	36.9				
"	M	35.0	34.1	38.9				

Table 3. Average Concentration-Time Products For The Methyl Bromide Treatments

Location	Mean Dosage Rates (g/tonne)	Mean CTP ($g\ h\ m^{-3}$)
Inside	30.7	335.1
Outside	30.3	304.7

Tables 4-6. Carbon dioxide treatments

Table 4. Dosage Rates and Concentration Data For Trials Using Carbon Dioxide

Stack	Initial Dose(Kg)	No. of Times Redosed	Total Dose (Kg)	Mean Concentration (%)		
				Position 1	Position 2	Position 3
D	46.32	4	61.68	50.5	50.9	52.1
E	42.70	1	46.70	54.8	55.4	57.3
F	61.94	7	123.10	51.9	52.3	55.8
Mean	-	4	77.16	53.4		

Table 5. Temperature Data For Trials Using Carbon Dioxide

Stack	Mean Temperature (°C)			Average Ambient Temperature (°C)	Maximum - Minimum Temperature (°C)
	Position 1	Position 2	Position 3		
D	30.2	31.0	31.0	27	32-22
E	29.9	32.6	30.4		
F	30.6	32.7	32.2		

Table 6. Pressure Test Data For Stacks D, E & F

Pressure Decay (Pascals)	Stack D Average half life (seconds)	Stack E Average half life (seconds)	Stack F Average half life (seconds)
1000-500	22.73	14.87	18.94
500-250	24.70	16.76	21.40

Tables 7-11. Phosphine treatments

Table 7. Dosage Rates and Concentration-Time Products For Trials Using 2% Phosphine in Carbon Dioxide

Location	Stack	Initial Dose (Kg of mixture)	No. of Times Dosed	Total Dose (Kg of mixture)	Dosage Rate (g/tonne of phosphine)	CTP (ghm^{-3})		
						Position 1	Position 2	Position 3
Inside	A	4.18	1	4.18	3.25	291.0	285.2	327.3
	B	4.02	1	4.02	3.12	261.8	263.0	301.9
	C	4.14	1	4.14	3.22	215.7	214.2	261.3
Outside	K	4.46	3	13.22	10.29	190.5	187.0	189.2
	L	4.66	1	4.66	3.63	206.8	200.5	206.4
	M	4.05	1	4.05	3.15	237.8	233.2	236.9

Table 8. Wind and Temperature Data For Trials Using 2% Phosphine in Carbon Dioxide

Location	Stack	Mean Temperature (°C)			Wind Speed (m/s)		Average Ambient Temperature (°C)	Maximum - Minimum Temperature (°C)
		Position 1	Position 2	Position 3	Average	Maximum Gust		
Inside	A	27.9	27.7	30.4	-	-	27	32-22
	B	28.4	28.4	29.6				
	C	28.2	28.4	30.2				
Outside	K	33.5	29.6	29.3	4.0	9.3	31.8	-
	L	32.1	33.5	35.1				
	M	-	32.3	37.1				

Table 9. Dosage Rates and Concentration-Time Products For Phosphine Trials Using Solid Formulation

Location	Stack	Initial dosage rate (g/tonne of phosphine)	Top-up dosage rate (g/tonne of phosphine)	CTP (ghm^{-3})		
				Position 1	Position 2	Position 3
Inside	A	4.7	0	267.8	249.6	320.2
	B	4.7	0	351.3	329.2	405.2
	C	4.7	0	375.5	329.9	397.0
Outside	G	5.1	4.3	171.6	166.7	174.5
	H	5.1	0	306.3	314.8	308.6
	J	5.1	0	450.2	441.4	461.7

Table 10. Wind and Temperature Data For Phosphine Trials Using Solid Formulation

Location	Stack	Mean Temperature (°C)			Wind Speed (m/s)		Average Ambient Temperature (°C)	Maximum - Minimum Temperature (°C)
		Position 1	Position 2	Position 3	Average	Maximum Gust		
Inside	A	28.2	32.8	30.1	-	-	28	23-34
	B	28.3	33.3	30.5				
	C	28.4	33.3	30.4				
Outside	G	33.5	36	32.1	2.5	8	32.5	-
	H	32.3	34.3	33.3				
	J	32.9	37.0	33.3				

Table 11. Average Concentration-Time Products For The Phosphine Treatments

Location	Formulation	Mean Dosage Rates (g/tonne)	Mean CTP ($g\ h\ m^{-3}$)
Inside	Aluminium phosphide	4.7	336.2
Inside	Phosphine in carbon dioxide	3.21	269.0
Outside	Aluminium phosphide	6.5	310.6
Outside	Phosphine in carbon dioxide	5.69	209.8

Fig. 1. Plan Showing Layout Of Stacks Inside and Outside Store

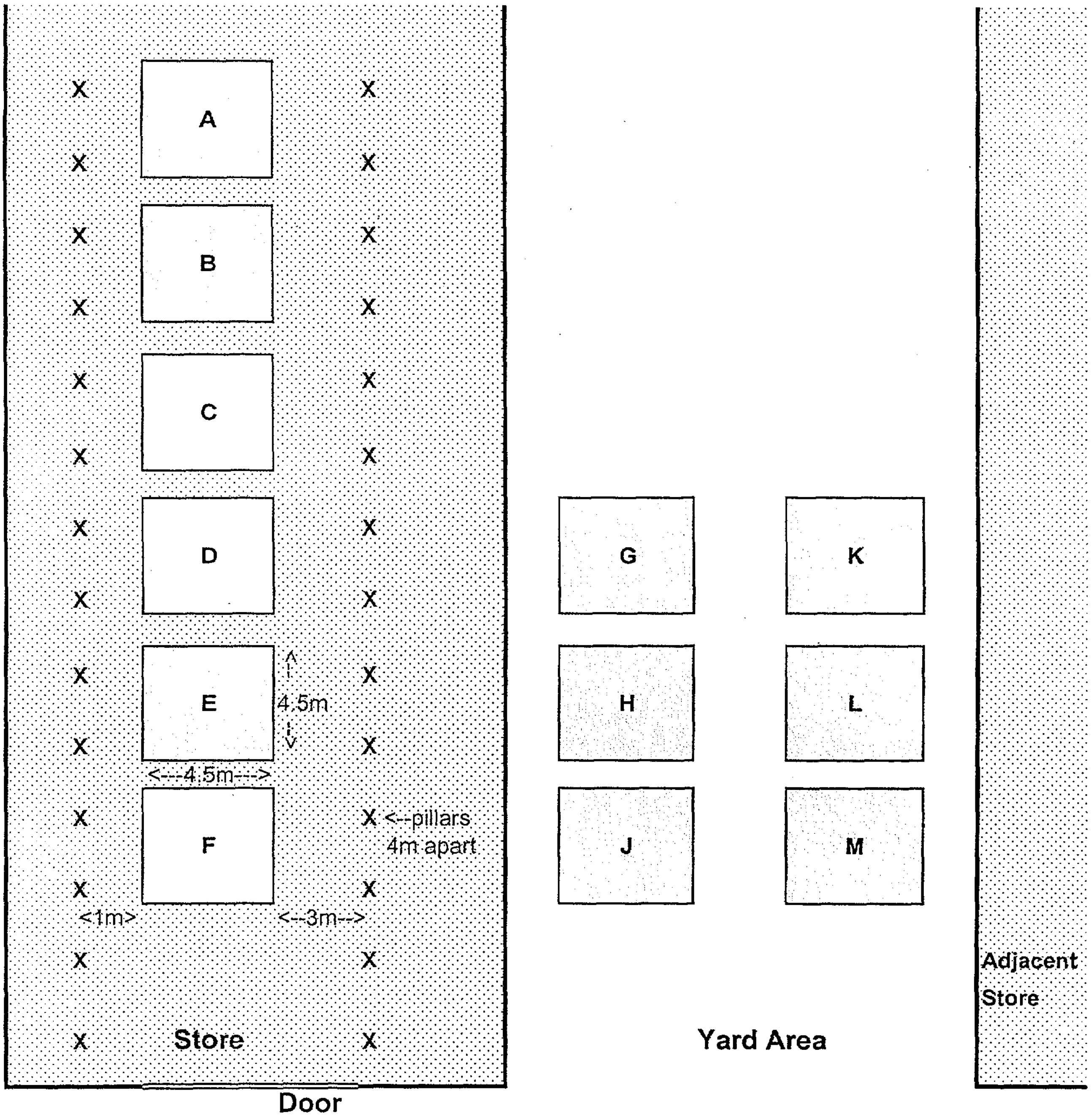

Fig. 2. Plan of a Stack Showing Sampling Positions

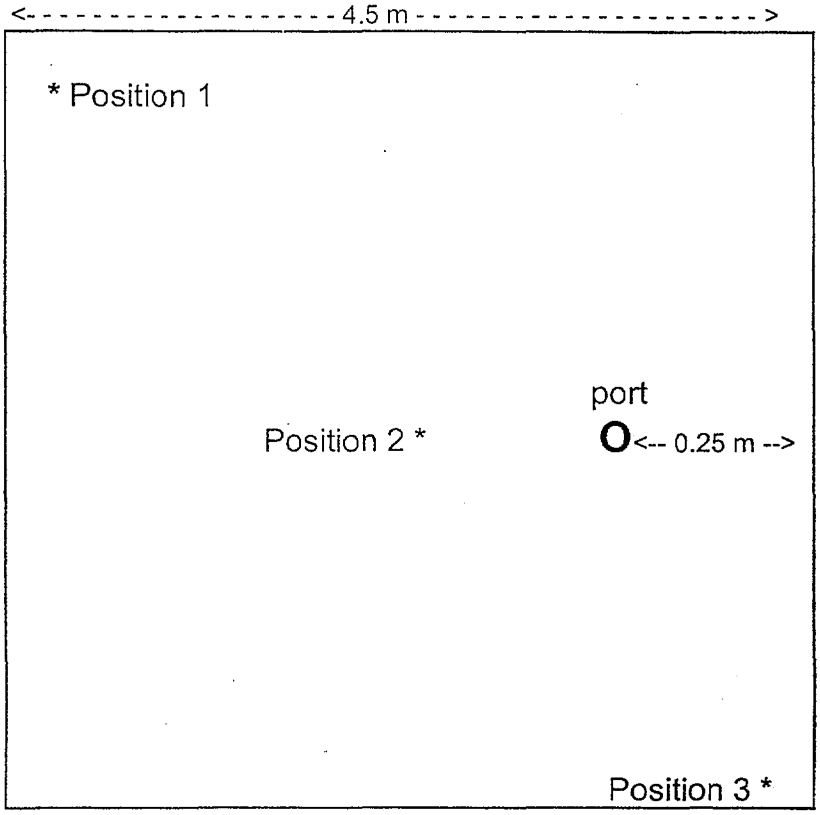

Fig. 3. Side View of a Stack Showing Sampling Positions

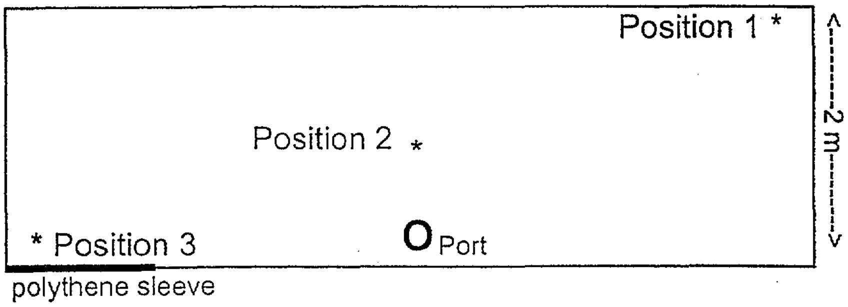

Fig. 4. Concentration of methyl bromide in stack D

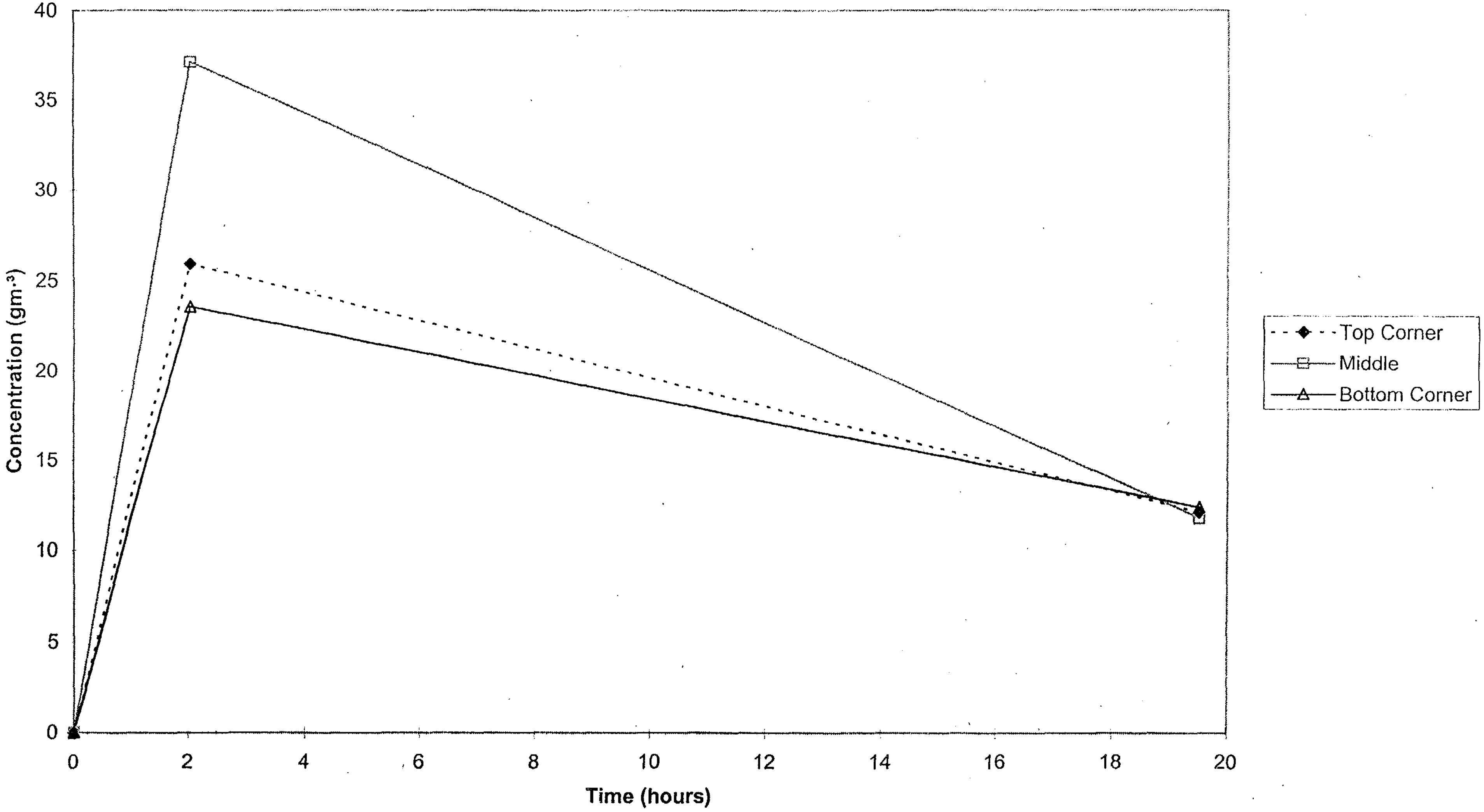

Fig 5. Concentration of methyl bromide in stack E

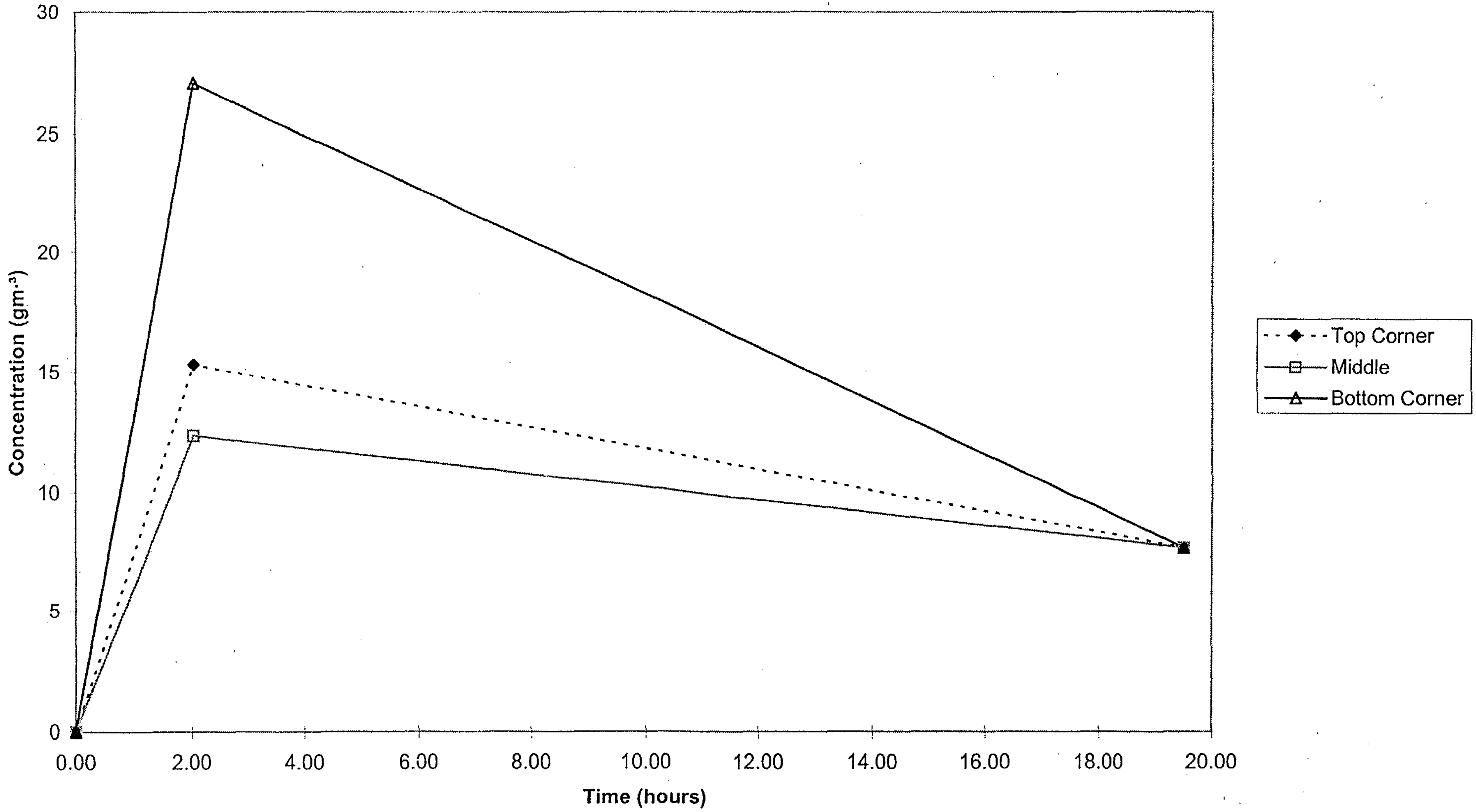

Fig 6. Concentration of methyl bromide in Stack F

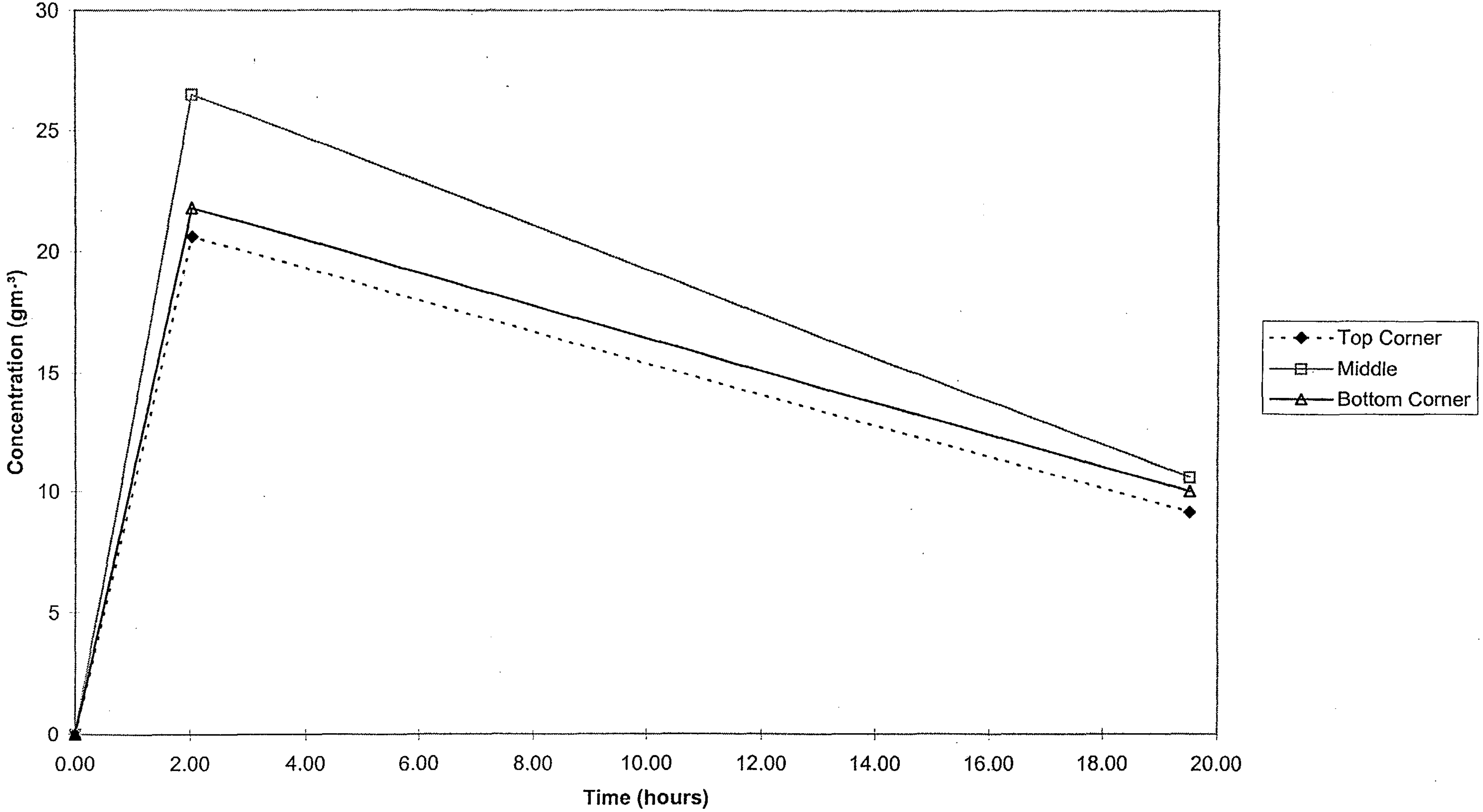

Fig. 7. Concentration of methyl bromide in stack K

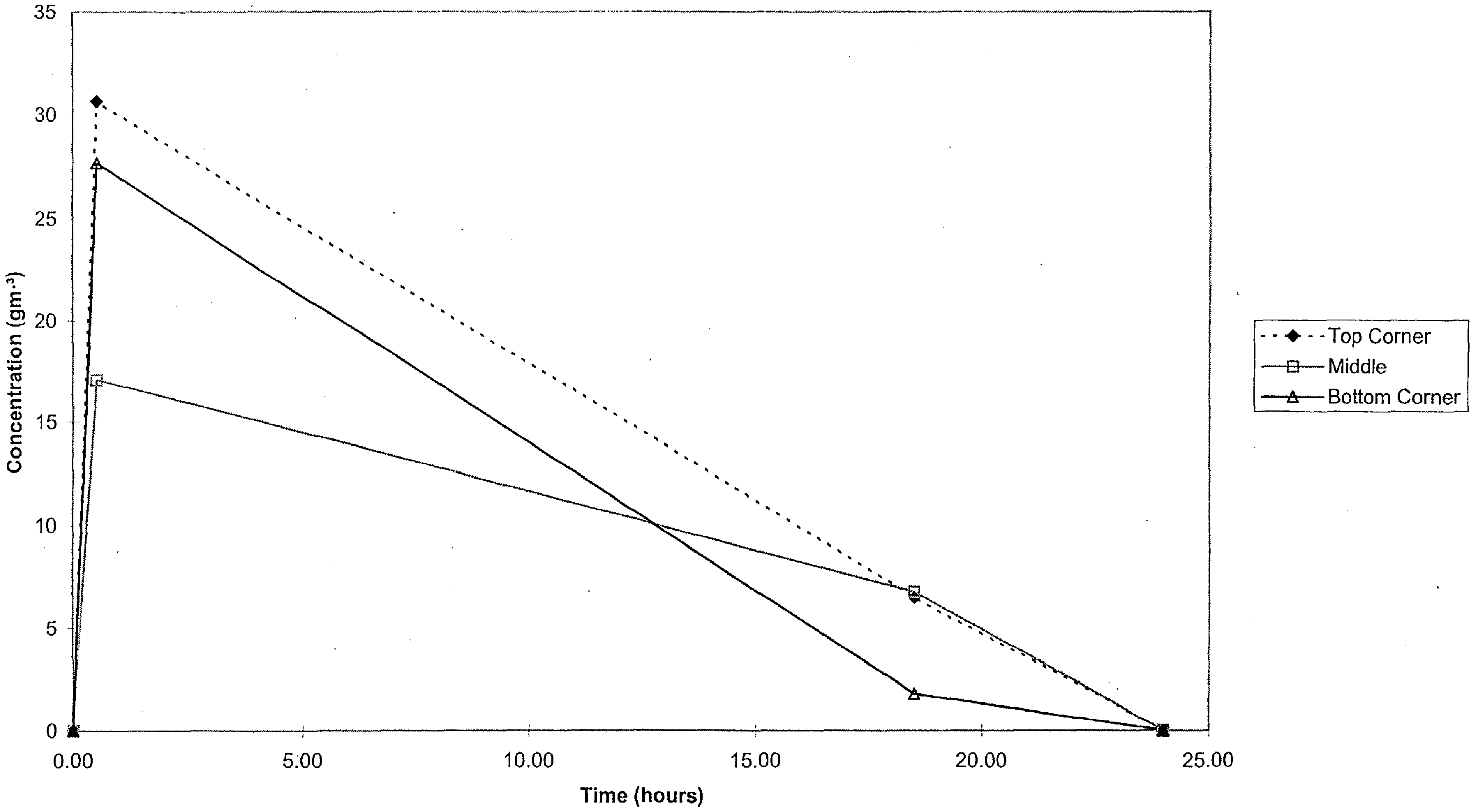

Fig. 8. Concentration of methyl bromide in stack L

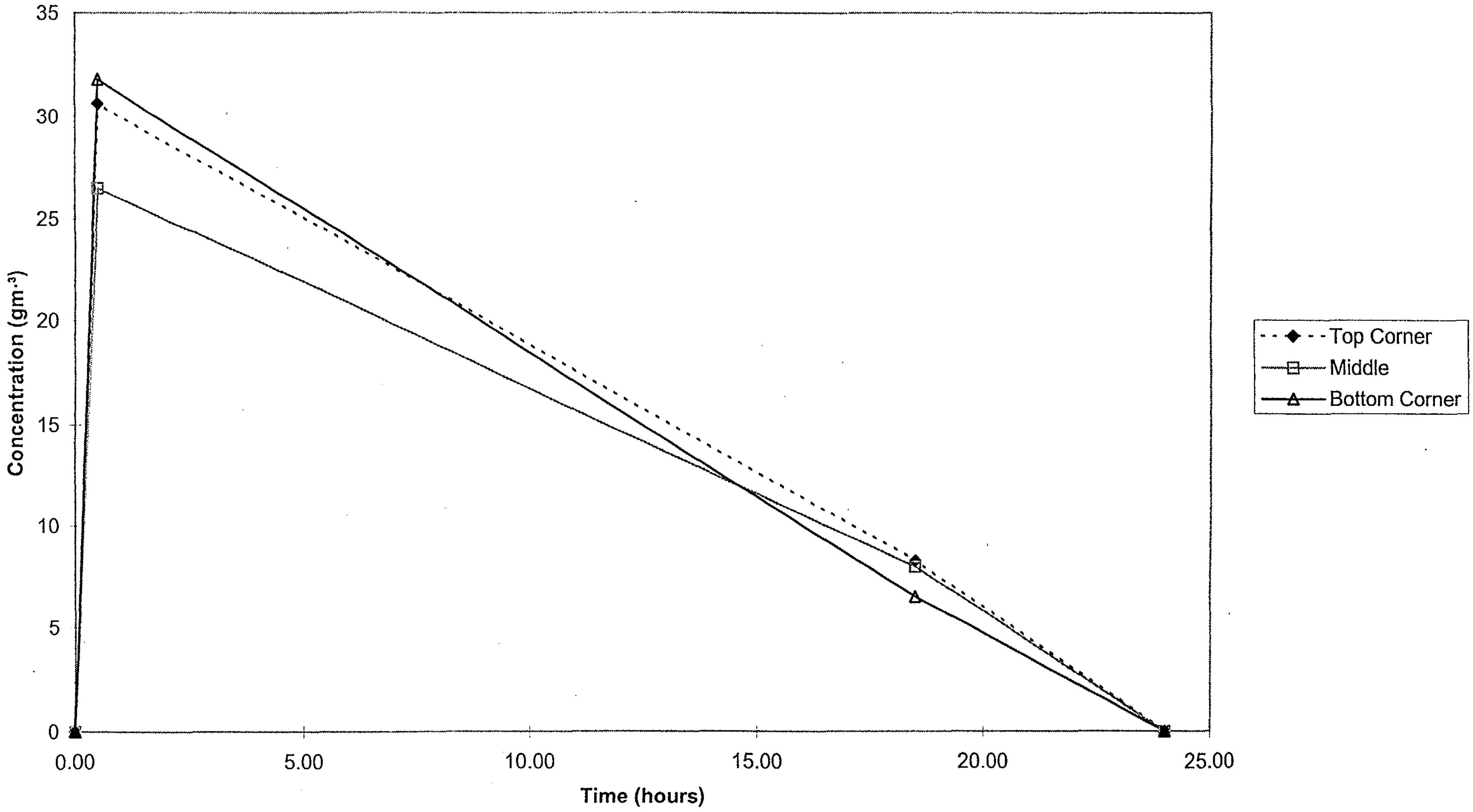

Fig. 9. Concentration of methyl bromide in Stack M

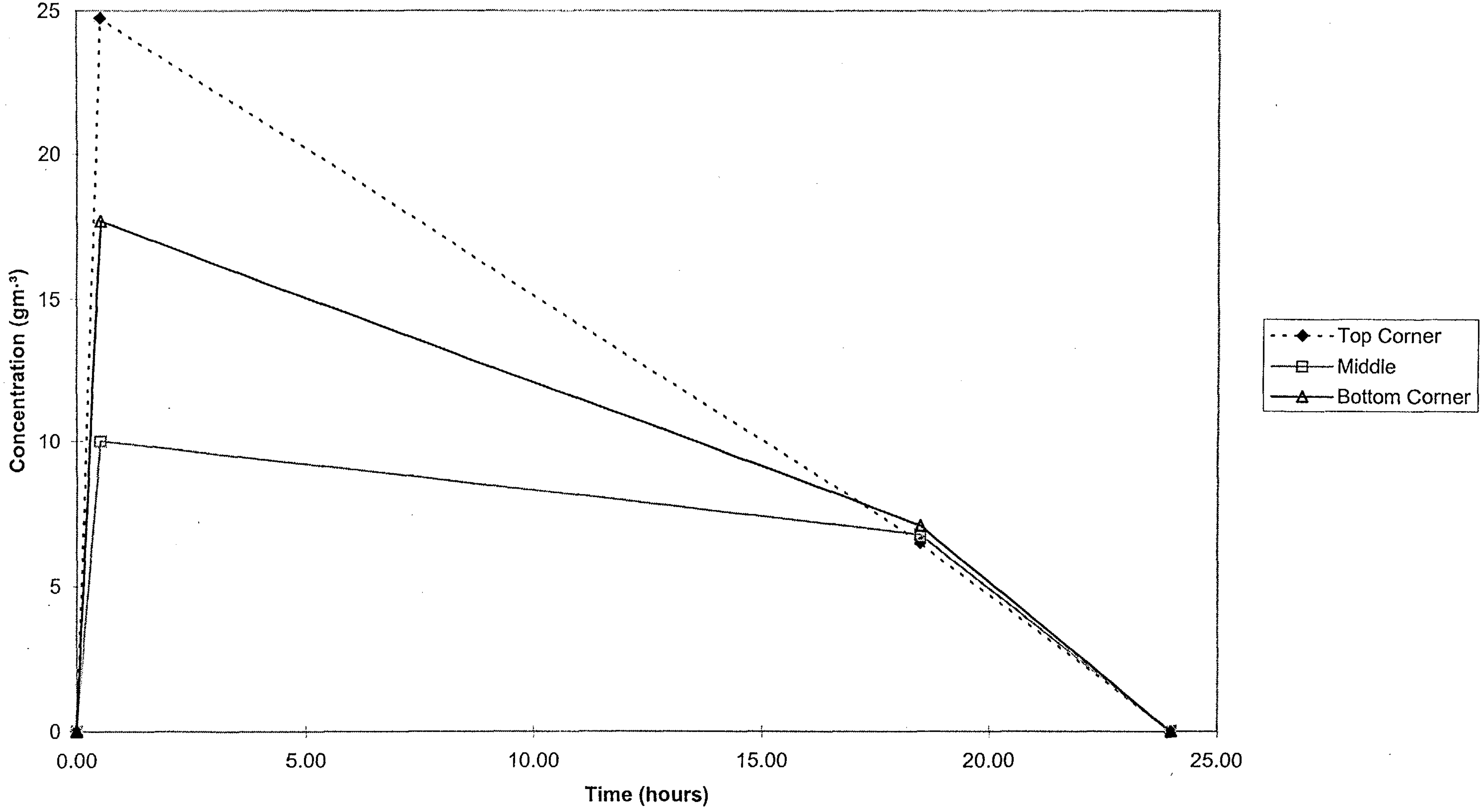

Fig 10. Concentration of carbon dioxide in stack D

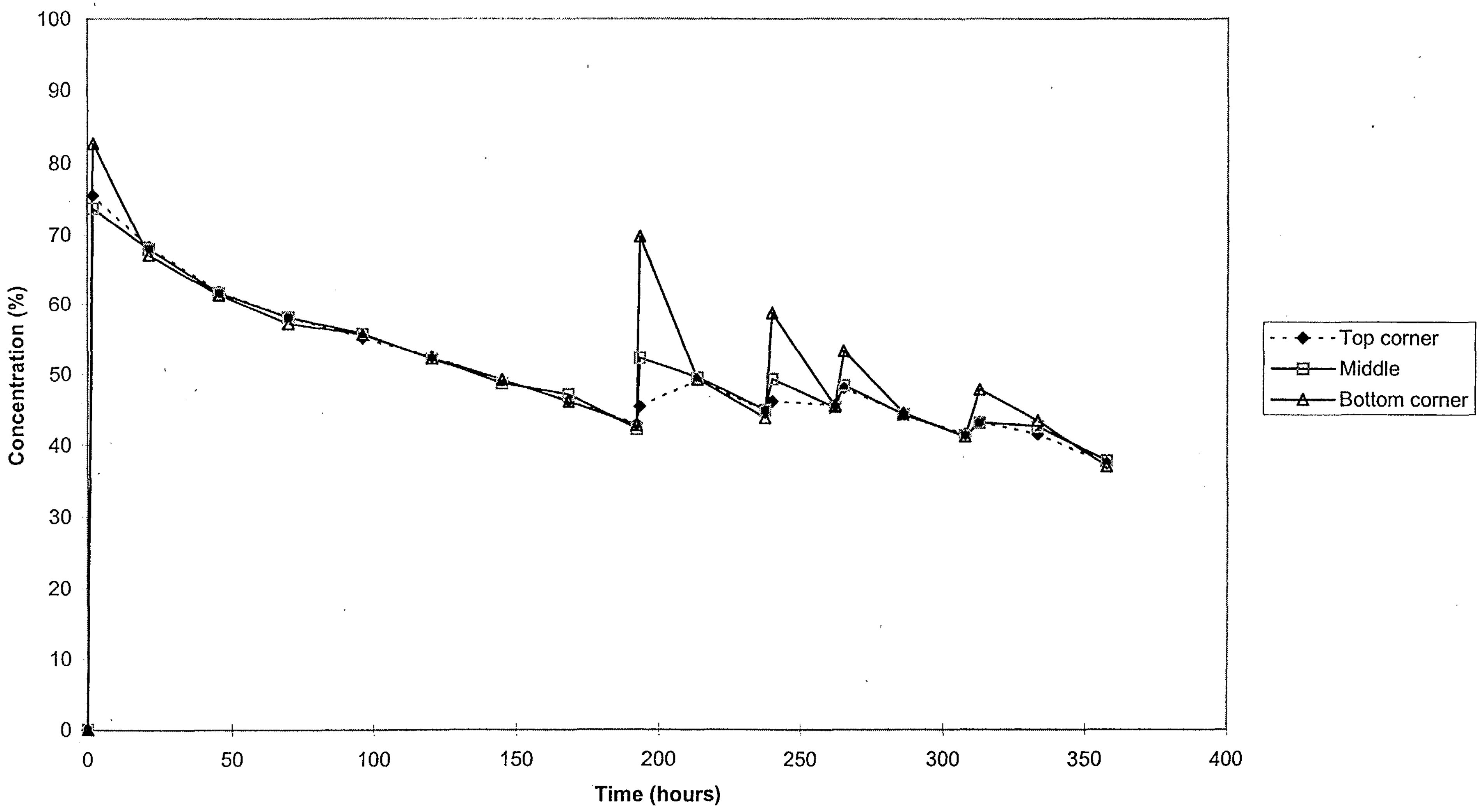

Fig 11. Concentration of carbon dioxide in stack E

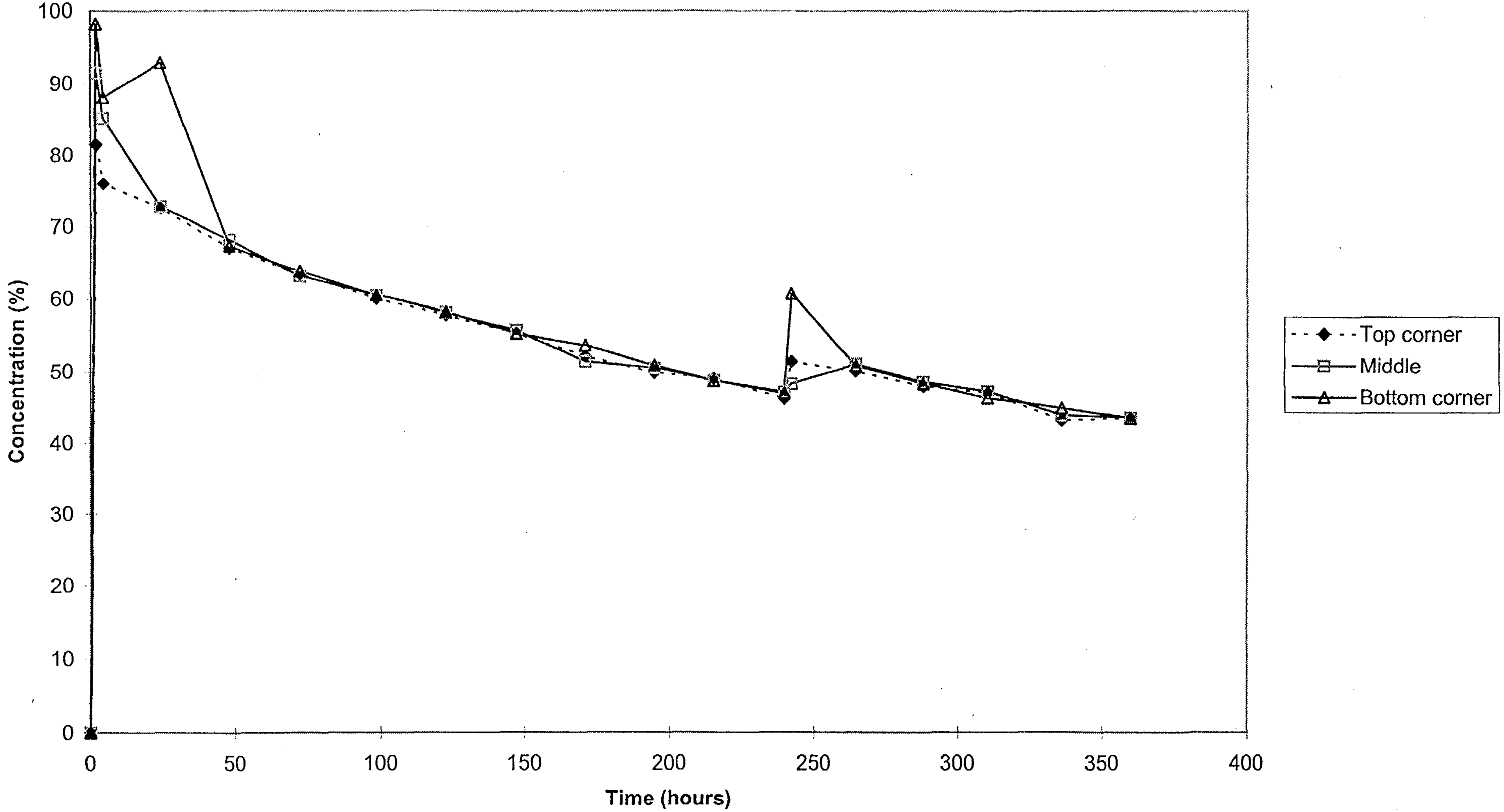

Fig 12. Concentration of carbon dioxide in stack F

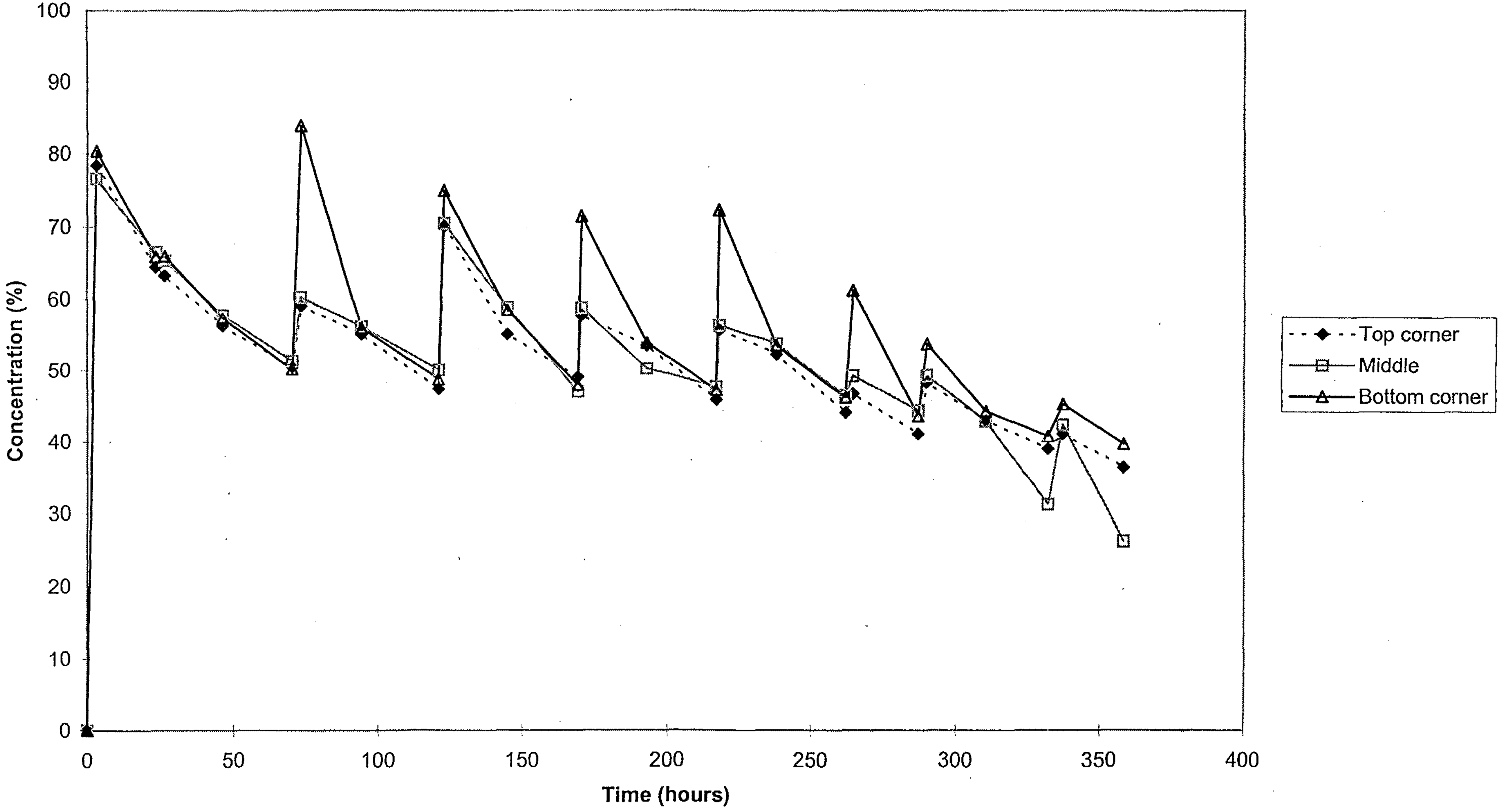

Fig 13. Concentration of phosphine in stack A in the 2% phosphine in carbon dioxide treatment

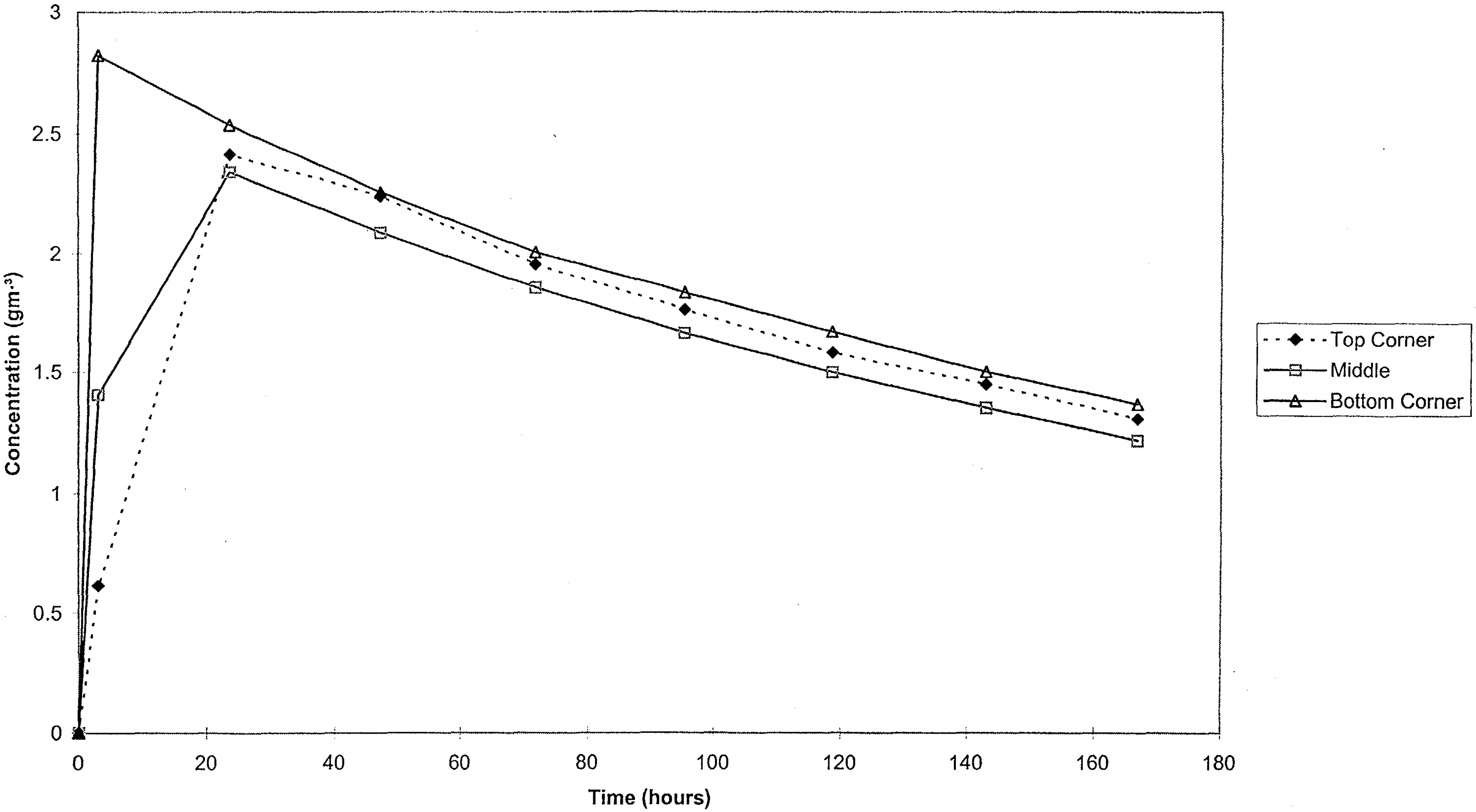

Fig 14. Concentration of phosphine in stack B in the 2% phosphine in carbon dioxide treatment

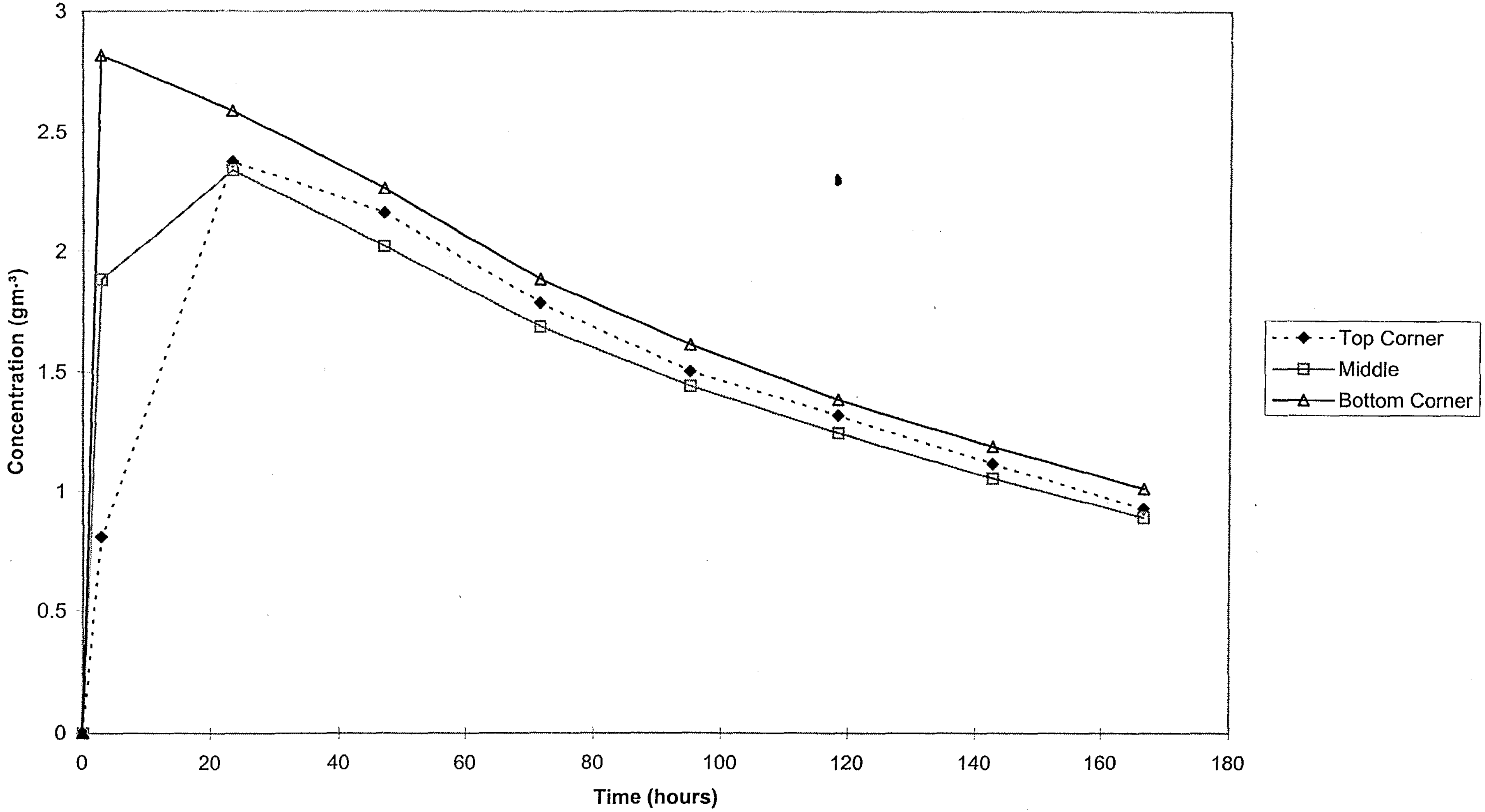

Fig 15. Concentration of phosphine in stack C in the 2% phosphine in carbon dioxide treatment

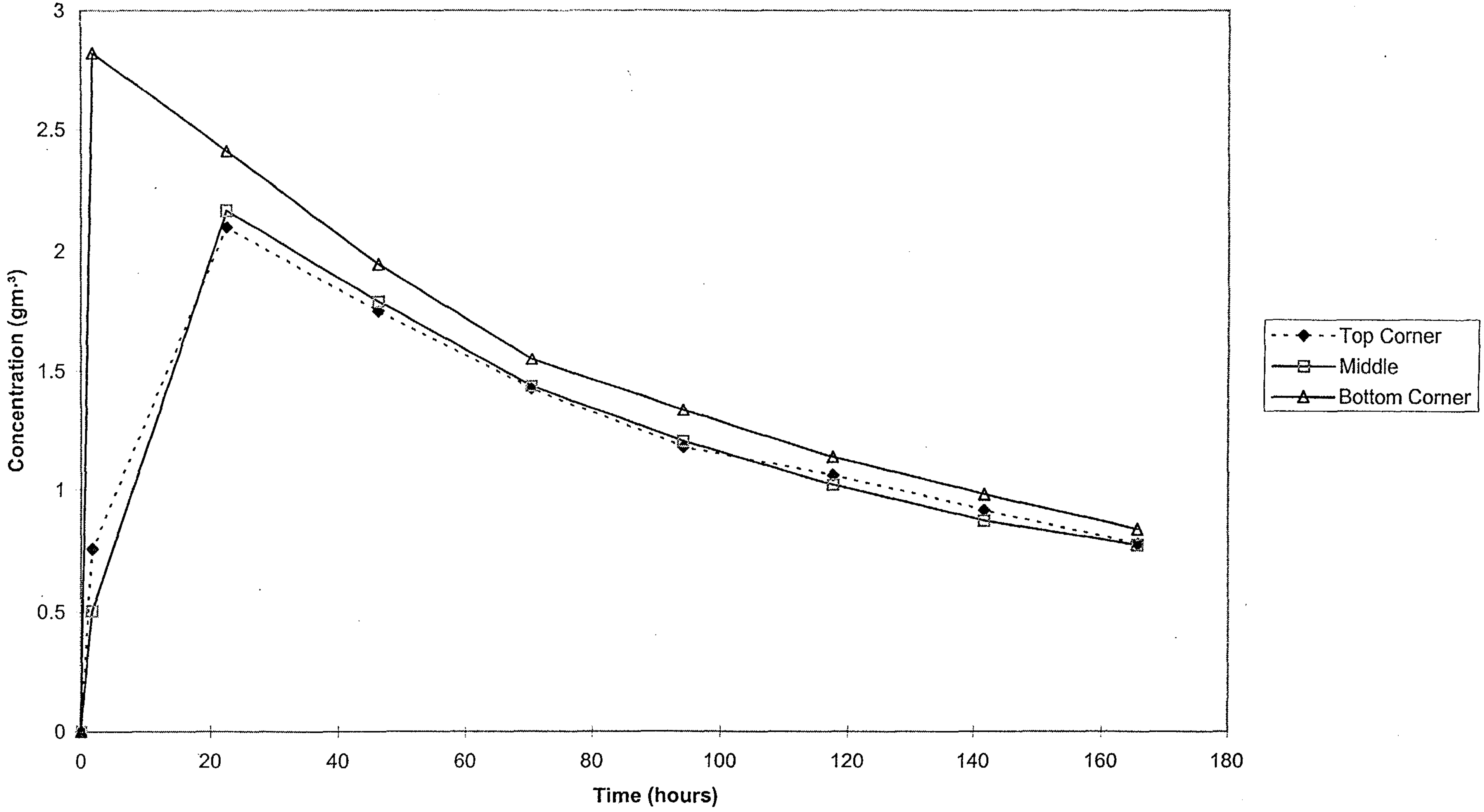

Fig 16. Concentration of phosphine in stack K in the 2% phosphine in carbon dioxide treatment

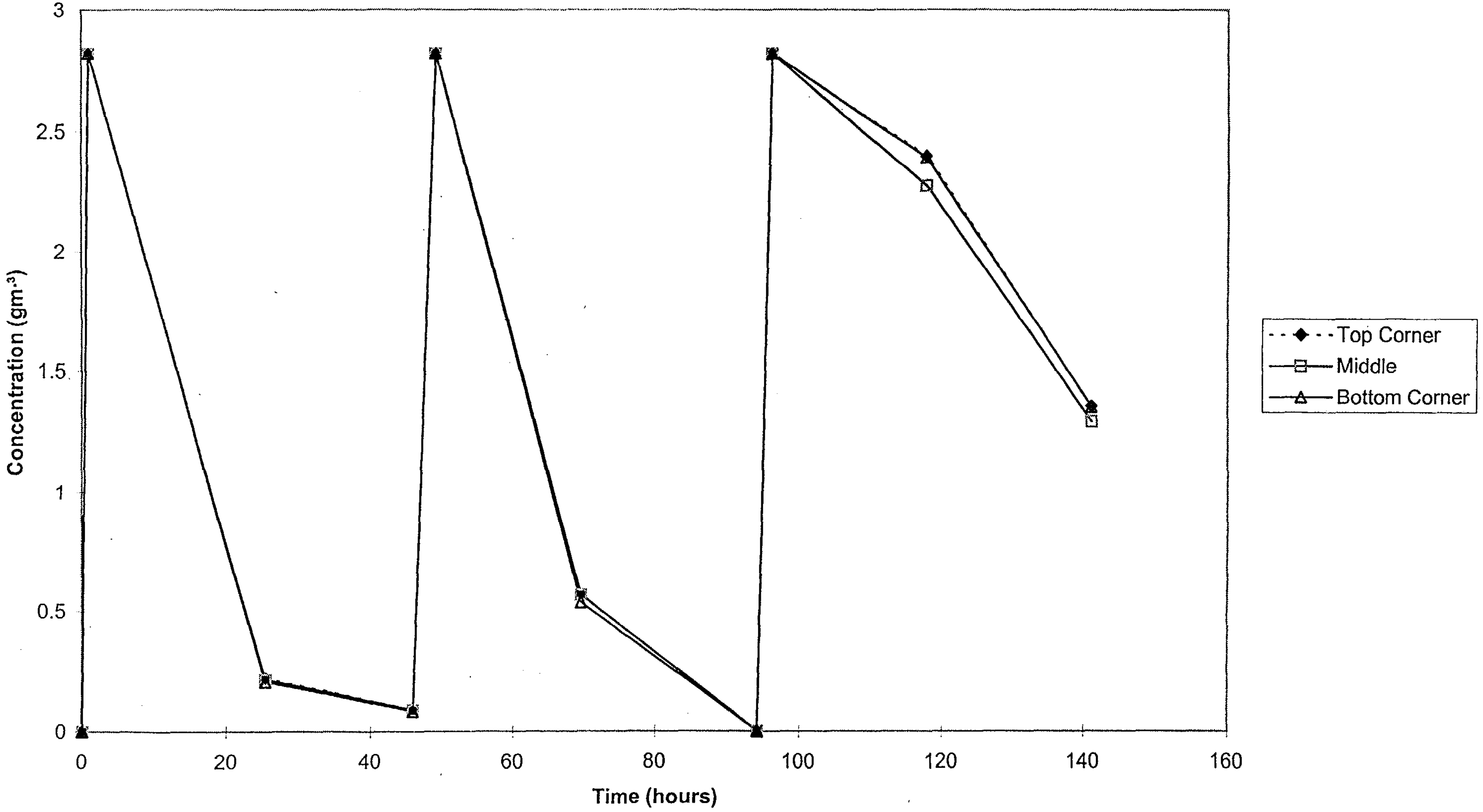

Fig 17. Concentration of phosphine in stack L in the phosphine in carbon dioxide treatment

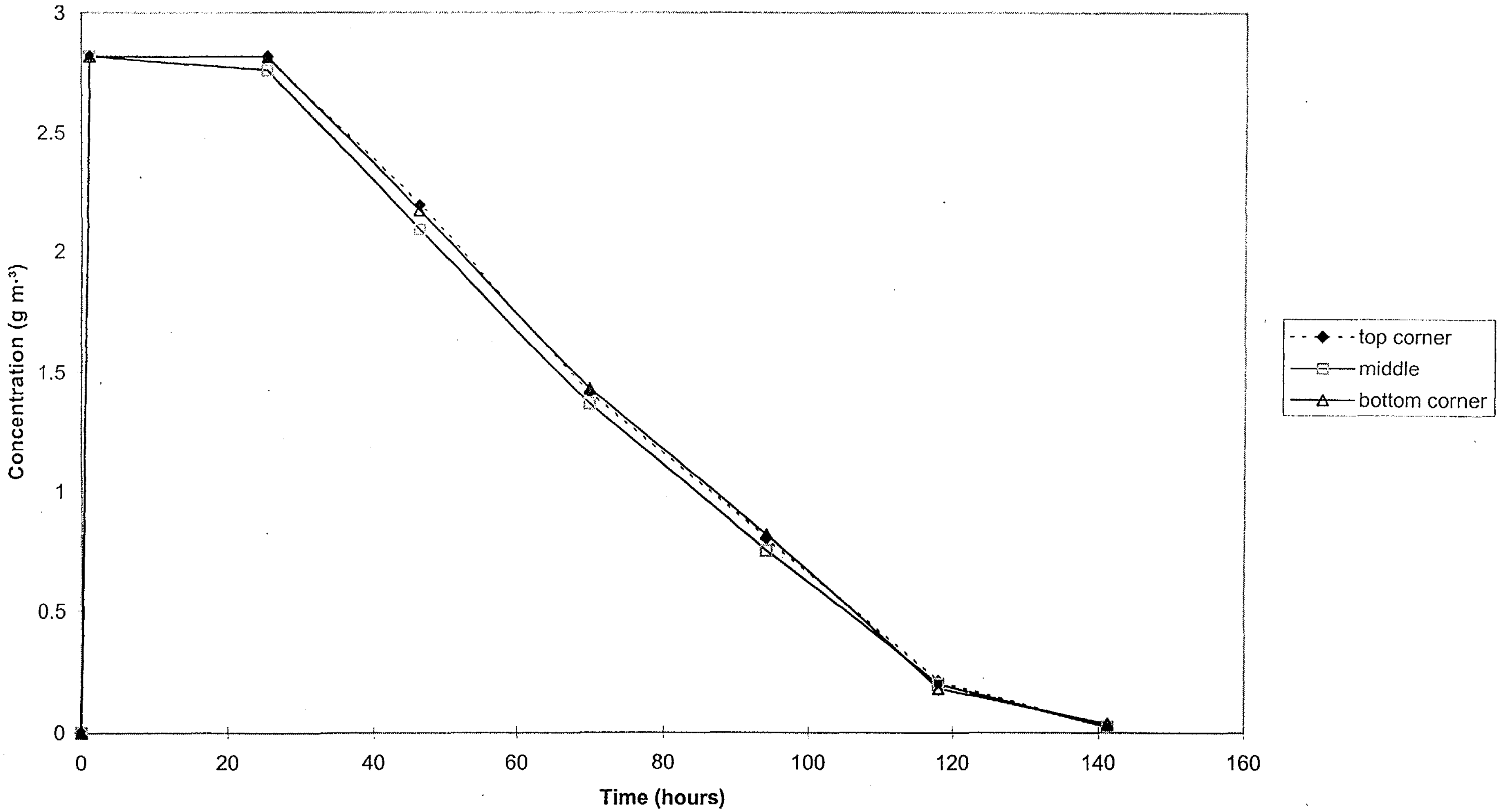

Fig 18. Concentration of phosphine in stack M in the 2% phosphine in carbon dioxide treatment

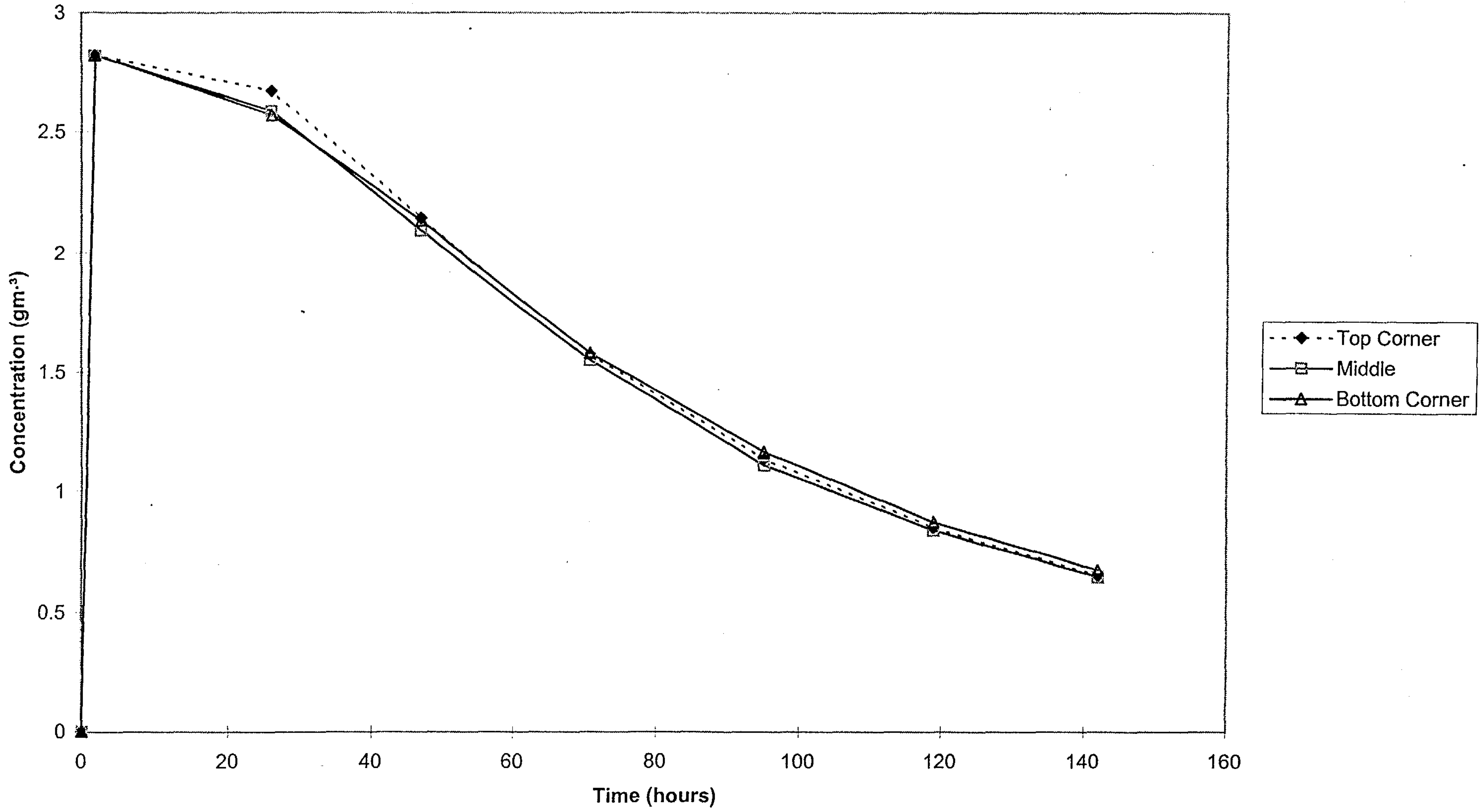

Fig 19. Concentration of phosphine in stack A in the solid formulation treatment

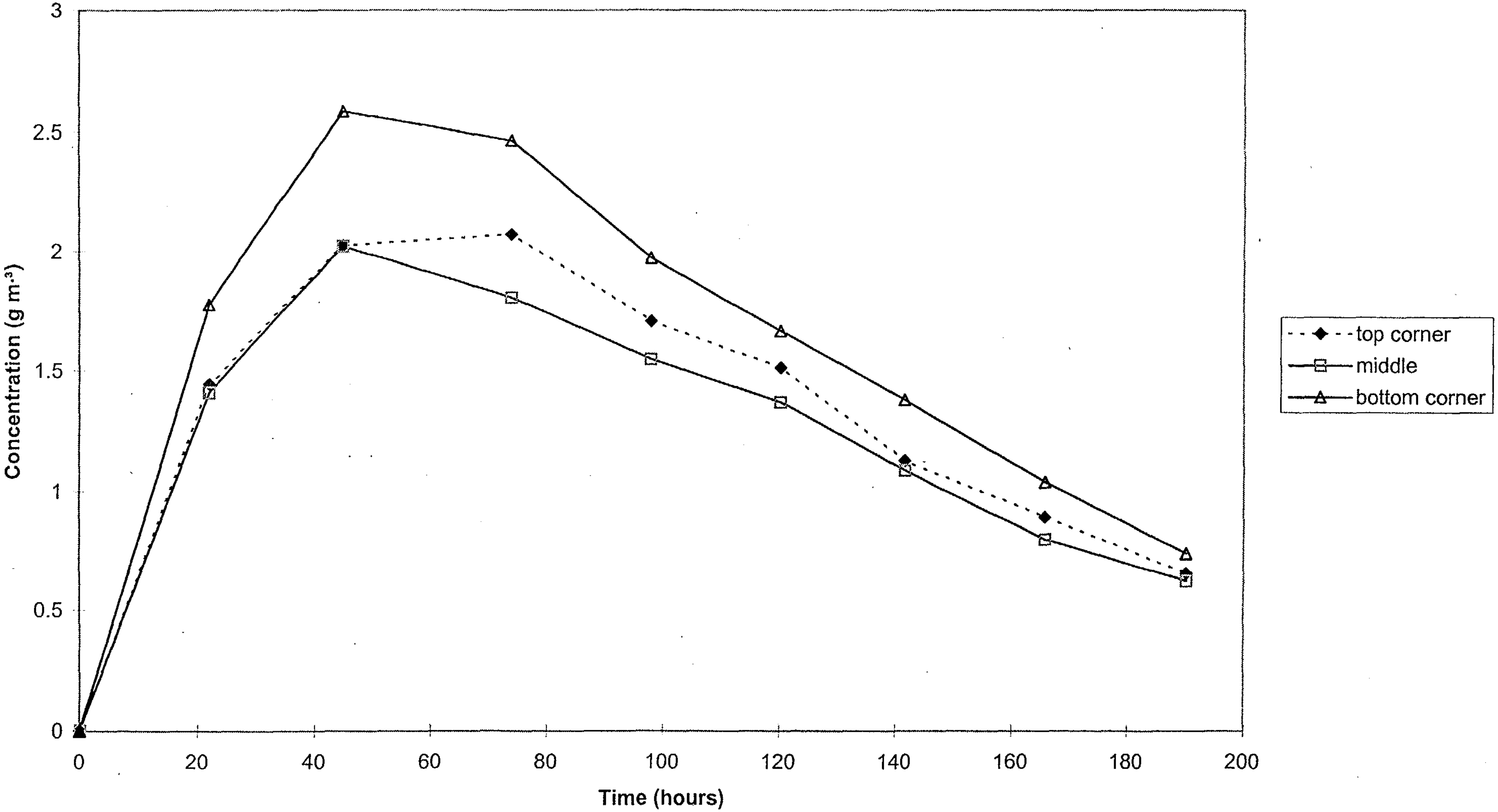

Fig 20. Concentration of phosphine in stack B in the solid formulation treatment

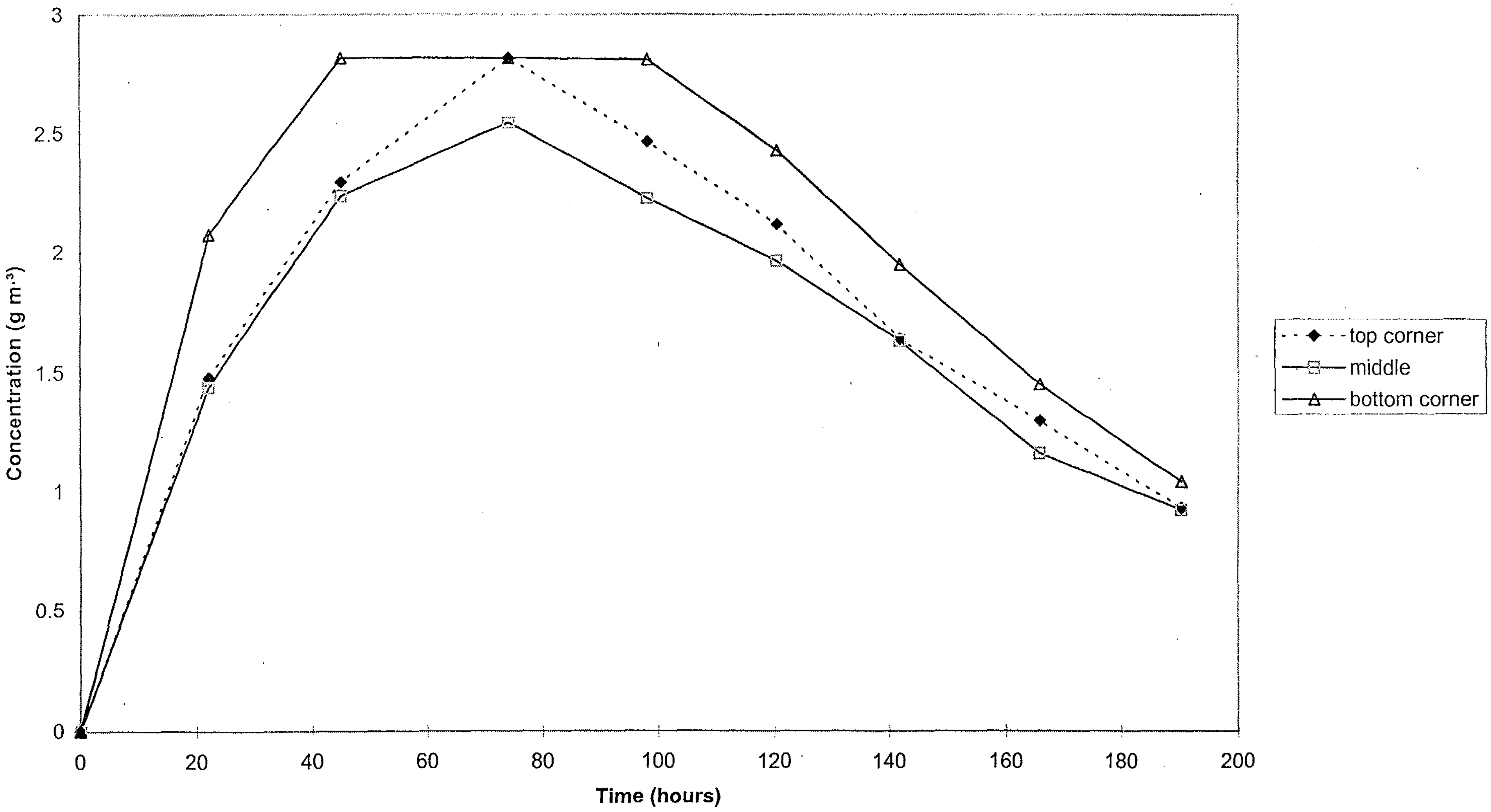

Fig 21. Concentration of phosphine in stack C in the solid formulation treatment

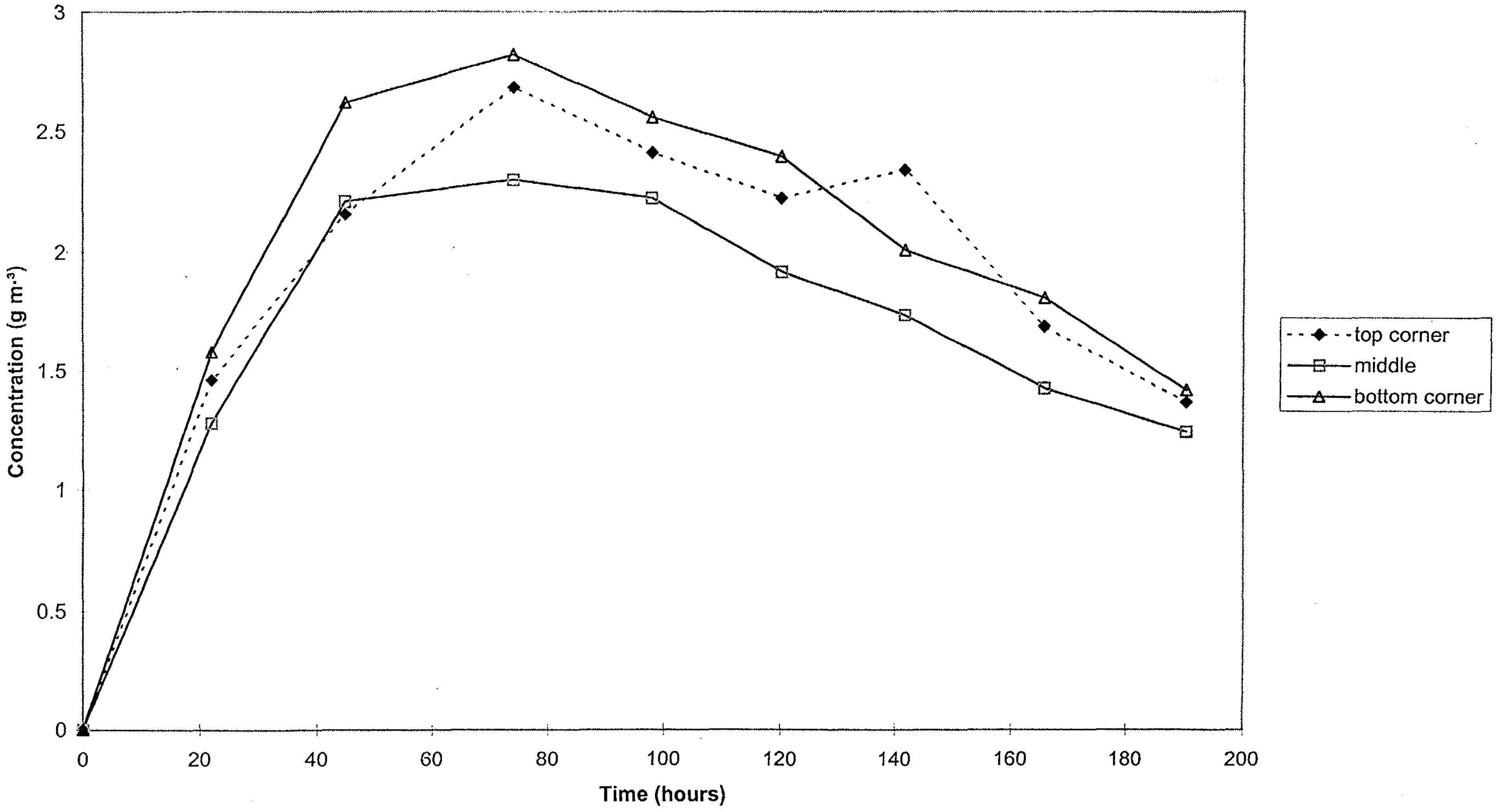

Fig 22. Concentration of phosphine in stack G in the solid formulation treatment

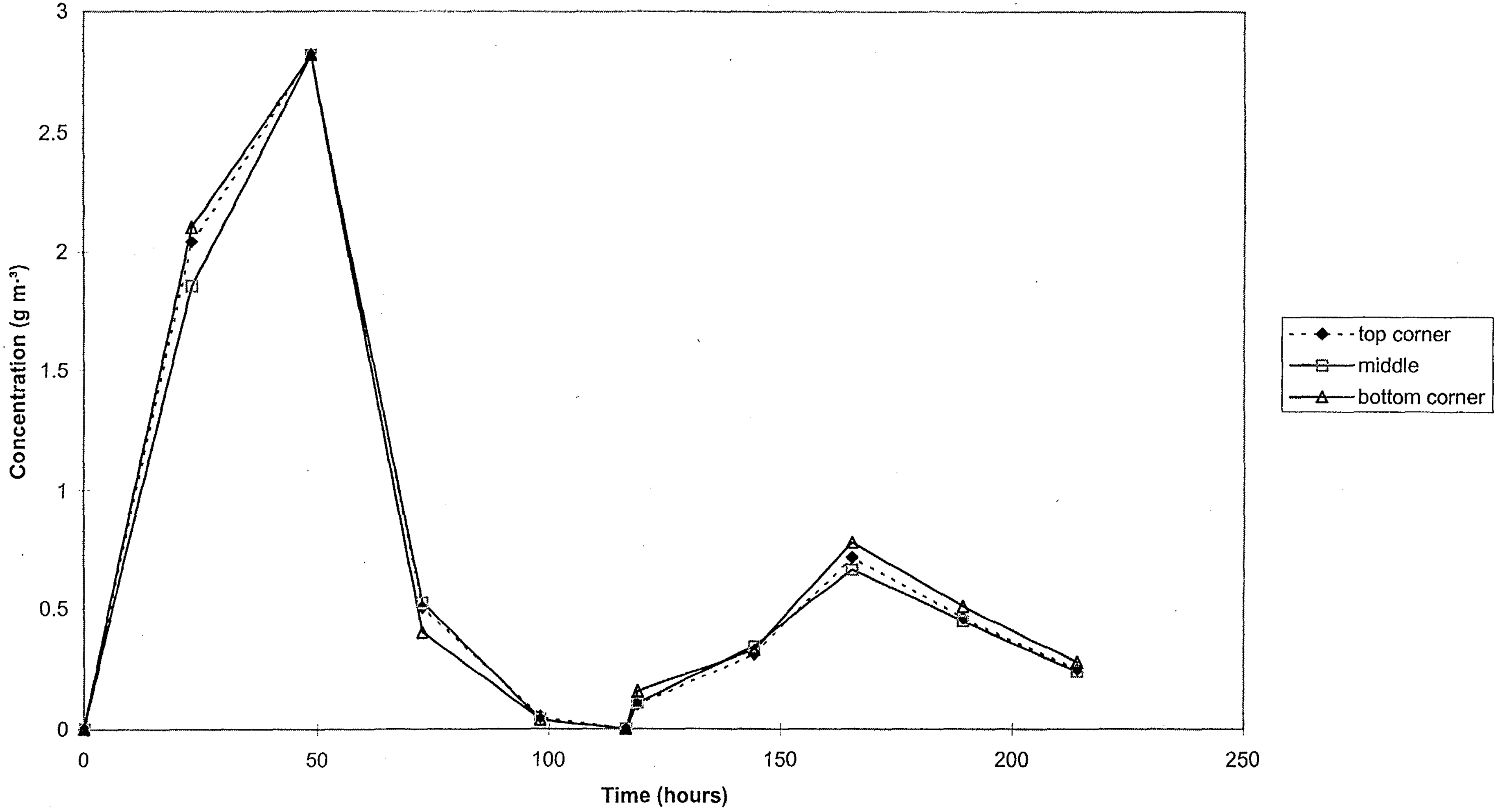

Fig 23. Phosphine concentration in stack H in the solid formulation treatment

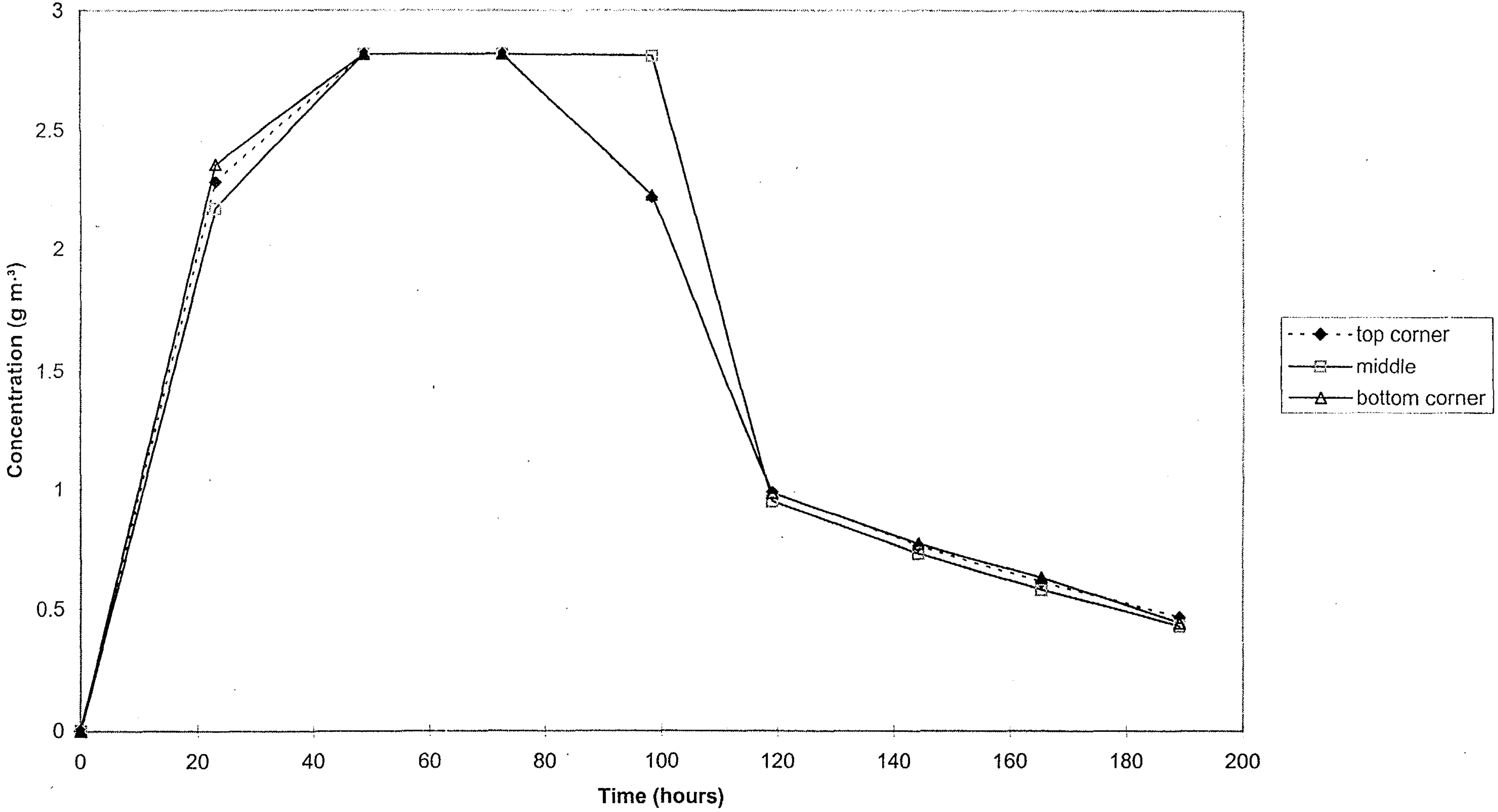

Fig 24. Phosphine concentration in stack J in the solid formulation treatment