The impact of temperature, moisture content, grain quality and their interactions on changes in storage vessel atmospheres

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Abstract

Knowledge of grain respiration is of interest in several areas of stored-products technology. In this study, insect-free wheat (moisture contents ranging from 9–13.2%) was sealed in storage vessels kept at temperatures ranging from 15–35°C. Changes in storage atmosphere were measured and rates of carbon dioxide production and oxygen consumption calculated. Carbon monoxide production was also measured.

Carbon dioxide production rates ranged from 1×10^{-5} to 450×10^{-5} mol/t/day. Oxygen consumption varied from 1×10^{-3} to 72×10^{-3} mol/t/day. Carbon dioxide production and oxygen consumption increased with temperature and relative humidity. Most variation in storage atmosphere composition could be modelled by a polynomial regression of log transformed rates against absolute humidity. Carbon monoxide levels observed ranged from 0 to 550 ppm. Higher temperatures led to higher concentrations of carbon monoxide across the range of moisture contents. Carbon dioxide and monoxide levels were closely correlated.

In a second experiment, changes in storage atmospheres of 8-year-old ASW grade wheat (moisture content 10.8%) were followed for 300 days. Carbon monoxide concentration reached 2363 ppm. Carbon dioxide and monoxide production rates were 3.3×10^{-4} and 1.35×10^{-4} mol/t/day. The oxygen consumption rate was 3.60×10^{-3} mol/t/day.

Introduction

In order to improve the efficacy of gaseous treatments, grain storage in sealed structures is becoming more common. This may lead to changes in storage atmospheres, which in turn may have important occupational health and safety implications. There is some possibility that these changes may also be helpful in maintaining the grain in an insect-free condition (Banks 1981; Navarro and Calderon 1980). In hermetic storage, atmosphere changes are due to metabolic activity of the grain, insects and fungi contained within a sealed storage environment. Oxygen (O_2) is lowered as it is used up by oxidative processes and carbon dioxide (CO_2), the end product of these processes, is elevated (Annis 1990; Banks 1981).

Bailey (1918) showed that carbon dioxide production of wheat increased with increasing moisture content. His measurements varied from 0.12 to 2.66 mol/t/day at 12.5–17.1% moisture content (m.c.) incubated at 37.8°C. He also found that some varieties of wheat had higher respiration rates than others. He concluded that a temperature of 55°C was optimal for carbon dioxide production of wheat (7.21 mol/t/day at 17% m.c.).

Robertson et al. (1939) found that the respiration rate of wheat, oats and barley increased with increasing relative humidity (r.h.). For wheat they reported carbon dioxide production rates as low as 0.002 mol/t/day at a relative humidity of 57.6% (approximately 13% m.c.) and as high as 7.85 mol/t/day at 98% r.h. (>22% m.c.). Bailey (1940) reported that, when the logarithm of respiration rate of wheat was plotted against moisture content it approached a linear form, and proposed a simple model that predicted the amount of carbon dioxide produced by grain with moisture contents between 11 and 17%. He also derived formulae for the respiration of rice, barley and oats.

Ragai and Loomis (1954) studied the respiration of maize with moisture content of 14–24% and above at temperatures ranging from 8–30°C (carbon dioxide production at 30°C: 0.22 mol/t/day at 15% m.c. to 29.02 mol/t/day at 23% m.c.) They found that respiration depended partly on the storage atmosphere. They also treated grain with fungicides in an attempt to prevent carbon dioxide production by fungal respiration but observed little difference in the respiration of treated and untreated grain. Hummel et al. (1954) reported that mould-free grain showed low respiration rates, even at high moisture contents (15–31%), and at 30°C.

Bartholomew and Loomis (1967) examined carbon dioxide production of maize at 30°C. The grain used was viable or had been rendered non-viable by chemical treatments. The oxygen levels of the storage environments were controlled at 0, 21 and 100%. They found that carbon dioxide production rates of viable maize ranged from 0.001 mol/t/day at 2.4% m.c. and 0% oxygen to 0.008 mol/t/day at 12.6% m.c. after 10 days of storage. Non-viable maize produced 0.004 mol/t/day at 1.6% m.c. and 0% oxygen and a maximum of 0.006 mol/t/day at 13% m.c. and 21% oxygen. They reported that carbon dioxide production decreased with increasing storage time.

Carbon monoxide (CO) production of quiescent grain has only recently been recognised (Whittle et al. 1994). Even low concentrations of this gas may form a safety hazard. The threshold limit value (TLV) is set at 25 ppm (Anon 1992) and the short term exposure limit is 125 ppm. Many of the measurements reported by Whittle et al. (1994) exceeded these recommendations substantially.

The aims of the work described here are:

- to assist in modelling of head space concentrations of carbon dioxide, oxygen, and carbon monoxide.
- to develop a model that expresses the relationship between storage conditions, grain quality, and the composition of storage vessel atmospheres.

Results are expected to be useful in studies concerned with hermetic storage, aeration, and drying of wheat.

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Materials and Methods

The main observations were carried out on wheat from a single source (variety, Corella; grade, ASW; harvest, 1988). Moisture contents were determined according to ISO recommendation R 712-1968(E). Relative and absolute humidity were calculated on the basis of dewpoints measured with a condensation dewpoint hygrometer. Viability was measured according to methods suggested by the International Seed Testing Association (Anon. 1976). Fungal contamination was determined by direct plating wheat grains onto a suitable medium — dichloran 18% glycerol agar (Hocking 1991; Hocking and Pitt 1980).

Analysis of gas samples was carried out using a Fisher model 1200 Gas Partitioner with 80–100 mesh Columpak™ PQ (6.5 feet × 1/8 inch) and 60–80 mesh Molecular Sieve 13X (11 feet × 3/16 inch) columns in series. The conditions used were: carrier gas, helium at a flow rate of 30 mL/minute; oven temperature, 50°C. Concentrations were calculated on the basis of peak areas. Peak areas were calibrated periodically using a standard gas mixture with known carbon dioxide, oxygen, carbon monoxide and nitrogen composition.

The grain used had been stored in sealed screw-top jars each containing approximately 500 g of wheat. Moisture contents of these samples had been adjusted to four different levels before sealing. Storage temperatures were 15, 25 and 35°C. Accounting for all possible combinations of moisture content and temperatures, 12 jars were set up. From these jars, 200 g subsamples were obtained and placed in hermetically sealed flasks.

Before use, the grain samples were passed through a Börner divider to remove residual CO_2 and to ensure that subsamples were representative. The storage containers used were round-bottomed, 250 mL flasks sealed with a stopper containing a stopcock and a septum. These were designed to allow gas sampling through a septum without breaking the hermetic seal. The flasks were kept under the same conditions as the original samples. With replicates, 24 flasks were available for sampling. One of the flasks leaked during the experiment and a total of 23 yielded useable data.

Moisture content, humidity, viability and fungal contamination were measured at the beginning of the experiment. The atmospheres in the flask were sampled weekly, and in triplicate, over a period of 18 weeks. The volume of the sample taken was 1.2 mL which was replaced with dry air. Actual CO_2 and O_2 volumes in the flasks were computed from the free gas volume of the flasks and the measurements obtained from the gas partitioner. Carbon dioxide and O_2 volumes were calculated for all weekly measurements over the duration of the experiment.

Rates of gas production were calculated based on the averages of the replicate measurements. Regression analysis was carried out using *SAS* (Statistical Applications System, SAS Institute, 1987) and were based on the rates of CO_2 production and O_2 consumption.

An additional experiment was carried out using 8-year-old, ASW grade wheat. This had previously been stored in a 3 L sealed flask for 7 years. The moisture content and viability of this grain were measured as above. The wheat was split into 2 subsamples of approximately 1 kg each and resealed in 1 L flasks. The atmospheres in the flasks were sampled and analysed at approximately 4-week intervals over one year with each flask being sampled in triplicate. The volume of the samples taken was 1.2 mL which was replaced as detailed above.

Results

Moisture content, humidity, viability and fungal contamination

The moisture contents of samples at the beginning of the experiment are shown in Table 1. The maximum relative humidity measured was 60%. Absolute humidity (moisture content of the storage atmosphere) was in the range 3.6–23.4 g/m^3. Viability of wheat samples varied from 0 to 93.2%. Temperature and moisture content both had an impact on the viability of the samples. Viability decreased with rising temperature, reaching zero in samples of high moisture contents at 25°C. At 35°C most samples were no longer viable with the exception of the low moisture content samples (Table 1).

The percentage of grains contaminated by fungi ranged from 0 to 98%. Fungal contamination appeared to be dependent on moisture content and temperature. Contamination was high in samples whose moisture content ranged from 9–12% and that were kept at 15 and 25°C. Samples that were kept at 35°C showed low contamination except in the low moisture content range.

Table 1. Viability, fungal contamination, carbon dioxide production rate and oxygen consumption rate for wheat held in sealed vessels under a range of condition.

Temperature (°C)	Moisture content (%)	Relative humidity (%)	Absolute humidity (g/m^3)	Viability (%)	Fungal contamination	$CO_2 \times 10^{-5}$ (mol/t/d)	$O_2 \times 10^{-3}$ (mol/t/d)
15	9.0	27	3.6	90.8	98	1.0	7.500
	11.3	41	5.3	93.2	96	1.0	8.550
	11.6	48	6.1	78.4	92	1.0	7.250
	13.3	60	7.7	89.2	22	1.5	8.400
25	9.0	28	6.5	90.4	92	2.0	6.325
	10.9	44	10.0	83.6	44	3.5	6.075
	11.6	47	10.8	91.6	6	5.0	7.400
	13.1	58	13.4	2.8	0	9.5	1.008
35	8.9	27	10.7	80.4	12	5.5	7.850
	10.6	43	16.6	0	0	10.5	9.250
	11.3	44	17.6	0	0	140.0	12.450
	12.9	59	23.4	0	0	450.0	72.000

Carbon dioxide production and oxygen consumption

Carbon dioxide production rates ranged from 1×10^{-5} to 450×10^{-5} mol/t/day. As storage temperature increased, more CO_2 was produced. Similarly, increases in relative humidity appeared to lead to higher CO_2 production rates. Low viability occurred in samples with high CO_2 production rates. Samples with high fungal contamination had lower CO_2 production rates than those with low or no contamination (Table 1). Oxygen consumption rates varied from 1×10^{-3} to 72×10^{-3} mol/t/day. In general, oxygen consumption followed the trends of carbon dioxide production described above (Table 1).

Statistical analyses were performed using stepwise regression procedures. The most important predictors of log transformed carbon dioxide production and oxygen consumption were temperature, relative and absolute humidity and, to some extent, viability. A substantial amount of carbon dioxide production (adjusted $r^2 = 0.98$) could be described by a polynomial regression model ($F = 276.16$, df = 4,18, $p < 0.0001$) describing a curvilinear regression of log transformed carbon dioxide production rate against absolute humidity (Fig. 1):

$$\log(CO_2) = -3.79 - 0.6671AH + 0.1160AH^2 - 0.0070AH^3 + 0.0001AH^4 \quad \ldots (1)$$

where AH is the absolute humidity in g/m^3 and carbon dioxide production rate is in mol/t/day.

Similarly, oxygen consumption was successfully modelled (adjusted $r^2 = 0.91$, $F = 74.81$, df = 3,19, $p < 0.0001$) using a cubic term and could be described as follows (Fig. 1):

$$\log(O_2) = -2.22 + 0.0433AH - 0.0061AH^2 - 0.0003AH^3 \quad \ldots (2)$$

with the same units as in the carbon dioxide equation.

Carbon monoxide production

Carbon monoxide levels observed ranged from 0 to 550 ppm (mean = –1104, n = 1185), 64% of observations had no measurable amounts of carbon monoxide (< 250 ppm). The data were considered insufficient to calculate production rates or carry out detailed statistical analysis, but yielded some interesting trends. Concentrations between 250 and 300 ppm were found in 14% of all samples. Higher concentrations of carbon monoxide were not as commonly found and samples with carbon monoxide levels above 450 ppm comprised less than 4% of measurements taken.

The amount of carbon monoxide produced varied with temperature and moisture content. It appeared that higher temperatures led to higher concentrations of carbon monoxide across the range of moisture contents. Moisture content seemed to have less impact on carbon monoxide production than temperature (Fig. 2).

There was a strong correlation between the averaged CO_2 measurements and levels of carbon monoxide produced in the storage vessels ($r = -0.72$). When measurements of CO less than the limit of detection were dropped from the analysis, carbon dioxide became an excellent predictor of CO levels ($r = 0.93$). Oxygen consumption rate and CO concentration were negatively correlated, but the relationship was not very strong ($r = -0.24$ for all averaged measurements and $r = -0.39$ if zero measurements were disregarded).

Head space composition of 8-year-old wheat

The moisture content and viability of the wheat were 10.8 and 57.0%, respectively. After 21 days there was an almost linear rise in carbon dioxide and carbon monoxide concentrations with time. Oxygen concentration decreased almost linearly over the same period. The carbon monoxide concentration reached 2363 ppm in 299 days (Fig. 3).

The average CO_2 and CO production rates based on changes in gaseous composition after 21 days were 3.3×10^{-4} and 1.35×10^{-4} mol/t/day. The average O_2 consumption rate was 3.60×10^{-3} mol/t/day.

Discussion

Carbon dioxide production rates were quite low in all treatments with a maximum of 450×10^{-5} mol/t/day from samples stored at a relative humidity of 59% and 35°C. Oxygen consumption increased with temperature and humidity up to 72×10^{-3} mol/t/day at the maximum temperature and relative humidity used (35°C and 60% r.h.). Differences between oxygen consumption rates at low humidity were, however, minimal. Most of the variation in the composition of storage atmospheres could be described by a curvilinear regression using absolute humidity as a single factor (equations (1) and (2), Fig. 1). It appears that levels of carbon dioxide production and oxygen consumption depend mainly on the amount of moisture present in the storage atmosphere.

Samples stored at low humidity and temperatures had higher levels of fungal contamination then those kept at higher humidity and temperatures. None of the samples examined provided moisture levels (> 70% r.h.) suitable for significant fungal growth (Pitt and Hocking 1991). The contamination is therefore likely to be fungi producing viable spores and resting hyphae rather than actively growing. Fungal spores may be rendered sterile if exposed to 35°C over extended periods of time (Parrey and Pawsey 1984; Deacon 1984). Low moisture content may help preserve fungal spores under these conditions. In this respect, fungal spores may behave like seeds and lose viability, if they do not germinate, under conditions of high temperature and moisture content.

Viability of wheat was found to be dependent on temperature, moisture content and storage time as was expected from the literature (e.g. Villiers 1980). At 35°C most samples became non-viable during the 18 weeks of the experiment. The exception was samples kept at 9% m.c. which tolerated the temperature well. Samples which showed low viability had high carbon dioxide production and oxygen consumption rates. This may be due to the fact that low viability occurred with high humidity and storage temperatures. Viability is a factor which greatly depends on the amount of moisture present in the storage environment. The relationship between carbon dioxide production and viability may therefore be explained in the context of a regression of changes in storage atmospheres against absolute humidity.

Fungal contamination, which like viability was highest at low moisture contents and temperatures, was also negatively related to carbon dioxide production, possibly for similar reasons. In all cases fungal respiration could be discounted as a contributing factor to carbon dioxide production, as the most highly contaminated samples showed the lowest carbon dioxide production rates.

Carbon monoxide production appeared to be temperature dependent (Fig. 2). Carbon dioxide levels were a good indicator of carbon monoxide concentrations above the limit of detection ($r = 0.92$). Some 36% of measurements taken showed carbon monoxide levels higher than the short-term exposure limit, that is above 125 ppm.

A combination of the equations given earlier should make it possible to model the gaseous composition for atmospheres in fully sealed enclosures. Estimates can be made of the changes in the enclosed atmosphere of real storage structures by including terms that describe the degree of sealing of the enclosure.

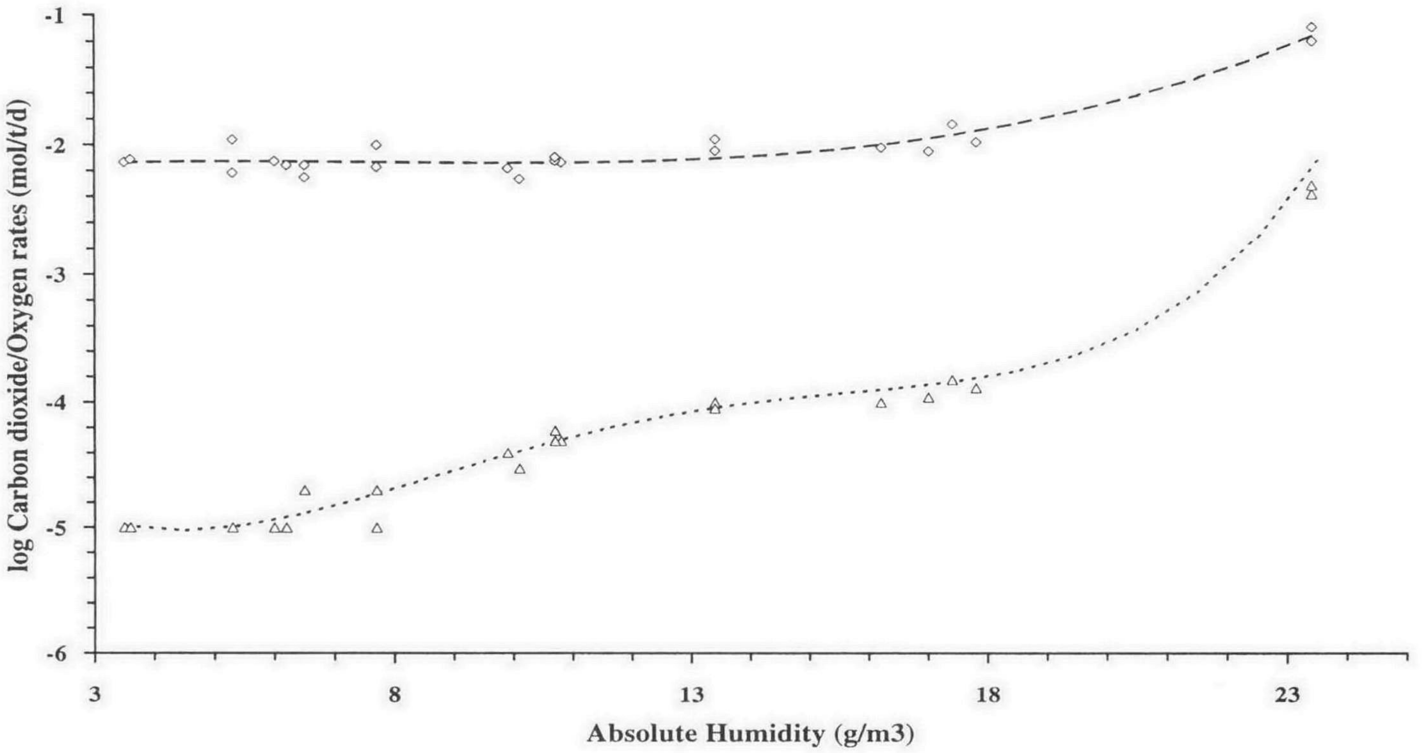

Fig. 1. Carbon dioxide production rate (Δ observed; modelled - - - -) and oxygen consumption rate (◇ observed; modelled – – – –) of wheat stored in sealed flasks. Data modelled using the polynomials of absolute humidity contained in equations (1) and (2).

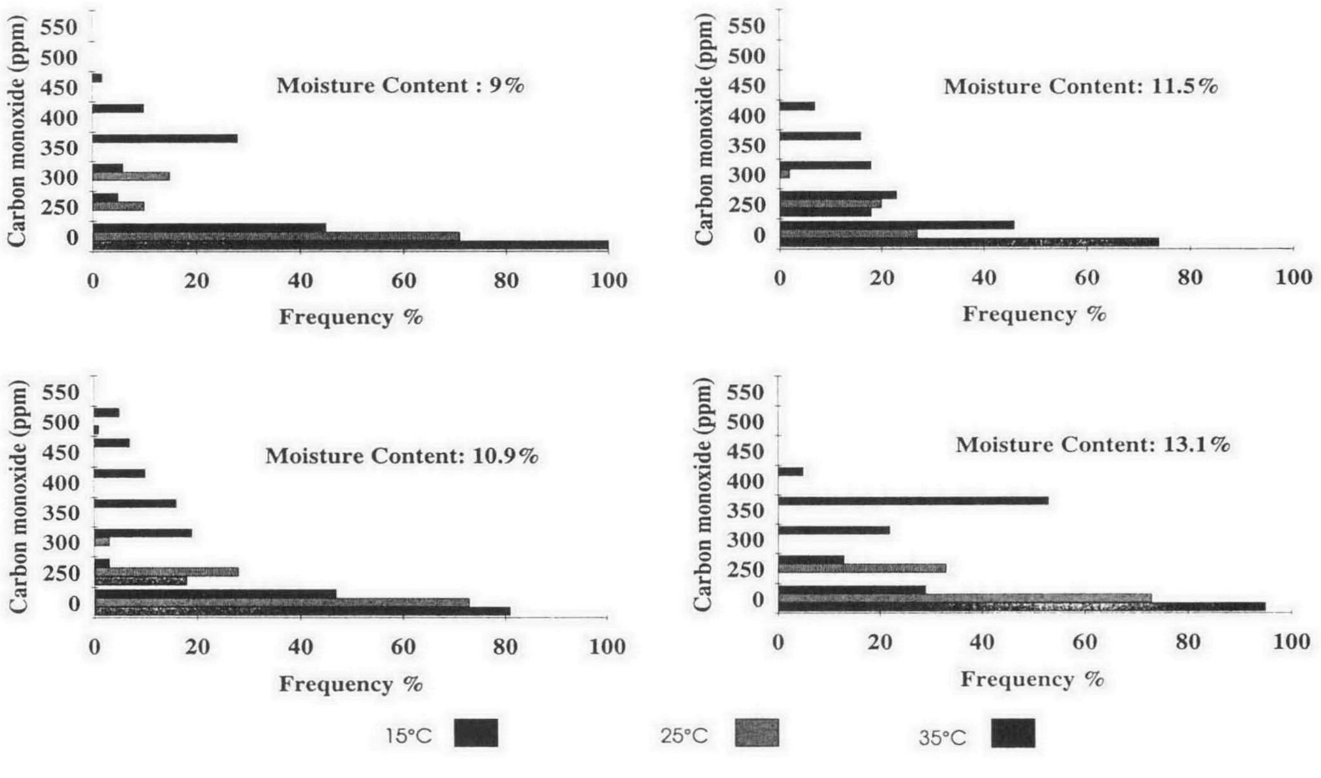

Fig. 2. Carbon monoxide content of storage atmospheres in wheat stored at various moisture contents and temperatures.

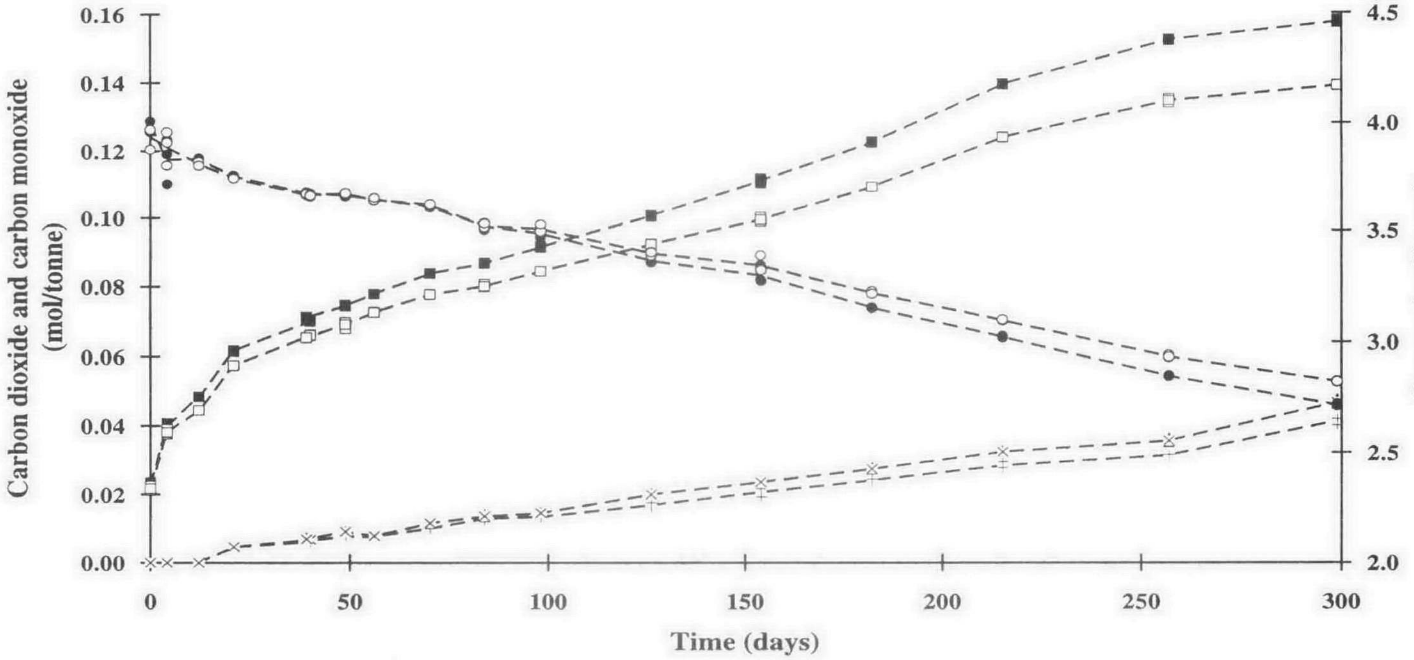

Fig. 3. Carbon dioxide (■ flask 1; ❑ flask 2), carbon monoxide (+ ×) and oxygen (● ○) concentrations in 8-year-old wheat stored in sealed flasks over a 300-day period. Symbols show individual observations for each of two flasks. The dashed lines connect the average values.

Conclusion

Carbon dioxide production and oxygen consumption rates of pest-free wheat stored at moisture contents of 9–13% at temperatures of 15–35°C were very low. Most variation in storage atmosphere composition could be explained by a curvilinear regression of log transformed rates against absolute humidity.

Long-term exposure of wheat to temperatures of 35°C appears to have fungicidal effects. At moisture contents likely to occur in wheat storage in Australia, fungal respiration is unlikely to contribute to modification of storage atmospheres.

Carbon monoxide levels occurring in the head space of wheat kept in sealed storage could present a hazard to workers that are required to enter storage facilities.

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