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In Situ Sampling and Storage of Soil Gases

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Introduction

Gas concentration and composition profiles can be used to measure the flux of gases into or out of soil (de Jong and Schappert, 1972; Cook *et al.*, 1998; Topp *et al.*, 1997), plant and animal tissues. Numerous gas samplers have been developed for collection of environmental and biological gases. Magnusson *et al.* (1989) used a gas sampler with a gas permeable watertight membrane (Gor-tex) for sampling gases in saturated soils and showed they were effective in obtaining a representative gas profile from peat soils. However, the response time of this sampler and the sample volume, were too large for our purposes and we describe here a smaller sampler with a shorter response time suitable for the rapid collection of gases from saturated or unsaturated soils.

When transporting gas samples from the field to the laboratory there is a need to securely store the samples. Traditionally, gas tight syringes have been used, but these are expensive and not well suited to longer term storage. Blood collection vials have been used previously by Covert *et al.* (1995) for the storage of gas samples prior to analysis by gas chromatography. They are cheap and well suited for use in the field. We tested the efficacy of Vacutainer[®] Brand (Becton Dickenson) tubes for the collection and storage of gases from the gas samplers and measured the changes to gas composition over a two week period. We also tested the tubes for residual atmospheric gases and calculated the error this would have imparted to our analyses.

Method

Design of the gas samplers

The gas samplers were constructed from 150 mm long, 10 mm diameter PVC rod. A 4 mm diameter hole was drilled down through the centre of the rod to within 15 mm of the base. A 20 mm long slot was cut through the wall of the sampler near the base to connect with the internal cavity. A 3 μm PTFE mesh (Gor-Tex[®] - W.L. Gore & Associates) membrane was wrapped over the slot and sealed in place with an epoxy resin (Araldite[™]). A 5.5 mm diameter hole was drilled from the top down through the sampler to a depth of 9 mm and a 6 mm butyl rubber septum was used to seal the tube. Gas samples were extracted from the sampler through the septum (Fig. 1).

Response time of gas samplers

The response time of the gas samplers was measured in the laboratory using a 250 mL Erlenmeyer flask equipped with side inlet ports. The flask was flushed with gas from 1 of 2 cylinders at a flow rate of 250 mL min⁻¹. The first cylinder contained N₂ but had a residual O₂ concentration of 1.7 %. The second contained a mixture of 52 % O₂ in N₂ (V:V). The flask was vented to atmosphere through a flow meter via a second side port. With the septum removed, the sampler and flask were flushed with N₂ from the first cylinder for at least 10 min. The septum was then sealed into the top of the sampler and N₂ run through the flask for a further 10 min. Samples were then taken from both the N₂ supply, and from the sampler using septum sealed gas tight syringes and double ended needles. Gas from the second cylinder (O₂ = 52 %) was then supplied to the flask, and more samples taken from within the sampler at 0, 2, 5, 10, 15, 30, 60, 90, 120, 180, 240 and 300 min. Needles and syringes were flushed with either the N₂ supply or O₂ (52%) supply prior to extraction of a gas sample. At each extraction, a compensating volume of N₂ was injected into the sampler to maintain

constant pressure. The composition of gas from within the sampler was measured using a gas chromatograph and compared to the theoretical composition of the gas in the flask using two possible mixing models.

Storage of gas samples

A total of 10 spent 2 mL Vacutainer[®] tubes were used to test their gas storage ability over 14 days. The empty tubes with suba seals removed were filled underwater with water. Whilst keeping the tubes submersed and inverted, they were then filled by displacement with a standard reference gas mixture containing N₂ (66.43%), O₂ (7.03%), CH₄ (4.5%), CO (7.04%) and CO₂ (15%) by volume. New suba seals were inserted and the tubes stored in the laboratory for up to 14 days prior to analysis. Two tubes (replicates) were analysed immediately, and a further 2 tubes analysed at 1, 3, 8 and 14 days. Two pseudo-replicate analyses from each of the two replicate tubes were analysed at each sampling time.

In a separate trial, we analysed the headspace gas of 20 brand new Vacutainers[®]. The tubes had a total volume of 5.5 mL composed of a nominal 2 mL sample volume (present as a vacuum), and 3.5 mL of headspace gas. We brought the internal pressure up to atmospheric pressure by either injecting ‘make-up gas’ consisting of high purity dry, O₂ scrubbed He gas from the GC carrier gas line, or atmospheric air. The concentration of gases in the Vacutainers[®] was then measured by gas chromatography.

Gas Chromatography

Gas chromatography was carried out on a Packard 427 GC equipped with a thermal conductivity detector (TCD). The GC was fitted with a CTR-1 column packed by Alltech and the oven temperature maintained at 25 °C. The carrier gas was dry high purity O₂ scrubbed He at a flow rate of 50 mL min⁻¹. The TCD filament temperature was 290 °C. Analogue output from the GC was captured and integrated using a Shimadzu CBM-10A and Class LC-10 chromatogram analysis software. The analysis time for CH₄, N₂, O₂/Ar, CO₂ and CO was less than 5 min per sample.

Results

We were unable to detect O₂ in excess of that present in the N₂ gas (1.7%) in samples taken from the gas samplers prior to introduction of O₂ into the flask from the second cylinder, irrespective of the syringe/needle flushing protocol. The potential O₂ concentration within the sampler from residual O₂ in the needle when flushed with 52 % O₂, is only 0.2 %. This is below the limit of detection by our GC using TCD, and below the residual O₂ in the N₂ cylinder. Therefore, preflushing the syringe and needle with N₂ was unnecessary.

The volume of the samplers is 1.8 mL. Due to the large volume difference between the samplers and the flask, the concentration of O₂ in the flask was unaffected by the removal of sample from the samplers, but the O₂ within the sampler was diluted by the introduction of N₂ to compensate for sample removal. When calculating the response time of the samplers following introduction of 52 % O₂ in N₂ into the flask, we compensated for the change in O₂ concentration within the samplers by using a constant mass loss algorithm thus:-

$$C_g = (C_i \times (V_s - 1) + C_o)/(V_s) \quad (1)$$

Where C_g is the O₂ concentration in the sampler after dilution, V_s is the volume of the sampler in mL, and C_o is the residual O₂ in the N₂ supply (ie 1.7%). Within the sampler, we calculated the O₂ concentration at the theoretical elapsed time t^* - the time at which the calculated O₂ concentration after dilution was equal to the measured O₂ concentration (see Appendix I for calculation of t^*). Because dilution reduces the O₂ concentration within the sampler, t^* will always be less than the actual elapsed time t .

We then calculated the theoretical O₂ partial pressure difference between the atmospheres within the flask at time t and the sampler at time t^* . Two different mixing models were used to estimate the O₂ concentration within the flask at time t . The first, a displacement model comprising piston flow assumes the original N₂ atmosphere within the flask was completely exchanged after one volume change. The second, a perfect mixing model assumes instantaneous turbulent mixing and continuous dilution of the gas within the flask by inflowing gas from the supply cylinder. The mixing models are representative of the best and worst case scenarios unless there are preferential flow paths. The diffusion rate across the membrane was calculated based on the theoretical partial pressure difference between the flask at time t and the sampler at t^* for each gas.

For the piston flow model with the sampler located midway between the inlet and outlet ports, the time for the N₂ atmosphere at the sampler to be completely replaced by 52 % O₂ from the incoming gas (t_o) is given by:

$$t_o = \frac{V_f}{2f} \quad (2)$$

where V_f is the volume of the flask (mL) and f is the flow rate of the gas through the flask (mL min⁻¹). In our experiments $V_f = 250$ mL and $f = 250$ mL min⁻¹, so $t_o = 0.5$ min.

For a perfect mixing model, the gas in the flask is constantly diluted by inflowing gas at the dilution rate. The instantaneous O₂ concentration within the flask at any time (t) is given by (Appendix I):-

$$C_f = C_s - (C_s - C_o)\exp(-Vt/f) \quad (3)$$

where C_f is the O₂ concentration in the flask, C_s the O₂ concentration in the supply from the cylinder (52%), and C_o is the O₂ concentration in the flask at $t = 0$ from residual O₂ in the N₂ supply (1.7%).

The temporal change of C_f for the two models is shown in Fig 4. We obtained the transfer coefficient for each sampler by fitting each of the mixing models to the time-corrected measured data (Fig 3a and Fig 3b) using SigmaPlot (SPSS, 2001). The transfer coefficients were the same ($p > 0.05$) for each of the samplers ($1.7 \pm 0.4 \times 10^{-3}$ s⁻¹) (Table 1) and for both mixing models although the piston flow model fitted the measured data more closely. Using these estimates of the transfer coefficients, Fig. 3 shows the samplers will reach 99 % equilibrium with the surrounding atmosphere in about 4×10^3 s or 1.1 hours.

Storage of gas samples

Analysis of the test gas mixture stored in the Vacutainer[®] tubes indicated no statistically significant change in the relative gas composition during the 14 day test period (Table 2).

The tubes had a nominal 2 mL sample volume and 3.5 mL of headspace gas for a total volume of 5.5 mL. The mass of O₂+Ar¹, N₂ and CO₂ measured in the sample when both He and atmospheric air were used as the make-up gas are given in Table 3. The volumes of each of the component gases in the 0.5 mL of injected sample were then calculated from the measured injected mass of each component gas by using the universal gas law. The mass of a particular component gas comes from both the headspace gas and the ‘make-up’ (sample) gas and is calculated by:

$$m_x^s = M_x^n - M_x^o \quad (4)$$

where m_x^s is the mass of gas x in the make-up (sample) gas, M_x^n is the mass of gas x measured by the chromatograph, M_x^o is the mass of gas x in the headspace.

The total volume occupied by measurable gases in the injected gas is calculated by summing the individual volumes of the component gases using:

$$V_s = \sum [M_x^n / \rho_x^o] \quad (5)$$

where ρ_x^o is the density of gas x in mg mL⁻¹ at 25 °C. When He was used as the make-up gas, V_s was 0.35 mL. The volume shortfall between the calculated total gas volume and the injection volume of 0.5 mL represents the volume of He which is not detected by the GC. When air was used as the make-up gas, V_s was 0.52 mL (Table 3). The difference in volume between these two samples (0.17 mL) is the calculated volume of air as the make-up gas. Extrapolating from the sample volume to the tube volume of 5.5 mL indicates a measured sample volume in the tubes of 1.87 mL compared to the nominal sample volume of 2.0 mL. The actual sample volume measured by adding water to an empty tube to bring the internal pressure up to atmospheric pressure and then weighing was 2.09 ± 0.01 mL ($n = 5$). This suggests that the total error in the mass measurement with the GC is 6.5%.

The molar (and volume) ratio of O₂+Ar to N₂ in the make-up gas where air was used are shown in Table 3. O₂+Ar constitutes 18 % by volume and N₂ is 82 %. We also detected CO₂ but the amount was not quantifiable based on the limit of quantitation of the detection system, whilst other atmospheric gases were below the limit of detection or not measurable on our system.

Discussion

The initial flushing of the gas sampler and flask replaced residual atmospheric gases with 1.7 % O₂ in N₂ from the first supply cylinder. When switched to the second supply cylinder containing 52 % O₂ in N₂, the O₂ concentration in the flask does not reach 52 % instantaneously, but will increase as mixing and dilution of the existing gas with the incoming gas occurs. With perfect turbulent mixing, the composition of

¹ Ar and O₂ are not separated by our GC using a CTR-1 column. Ar makes up 1 % of atmospheric gases and its atomic mass (39) is sufficiently similar to molecular oxygen (32) to enable the O₂/Ar molar concentration to be combined for volume determination.

the gases in the flask changes asymptotically over time towards the composition of the inflowing gas. After 10 min, the O₂ concentration in the flask is predicted using Equation 2 to be 51.701 %. So a 10 min flushing - equivalent to 10 flask volumes – replaces 99.4% of the original volume, which, based on the limit of quantitation of our GC, is effectively a complete change of atmosphere within the flask.

The real mixing scenario will be somewhere between the mixing and piston models, if preferential flow paths are ignored. With mass flow occurring and the likelihood of a preferential flow path causing the inflowing gas to be directed towards the membrane, the atmosphere adjacent to the sampler would more closely resemble that of the inflowing gas more quickly, than if the gases were perfectly mixed.

Magnusson *et al.* (1985) suggested that their samplers would contain a representative gas sample after 8 hours. We have shown here that our samplers will reach 99 % of equilibrium in 1.1 hours due to the smaller sampler volume used. Additionally, the smaller internal volume of the sampler we describe here, will reduce the extent of contamination from gaseous diffusion out of samplers following deployment into the surrounding soil, than would otherwise occur with samplers of larger internal volume.

In practice, a 5.5 mL Vacutainer[®] tubes with a 2 mL collection volume contains 3.5 mL of headspace gas. If the tubes are to be used without opening and re-evacuating, the composition of residual headspace gas must be accounted for when calculating the concentration of the gases in samples. Previous studies indicate that the composition of residual headspace gas in Vacutainer[®] tubes is variable, especially for minor gases, particularly CO₂ and CH₄ (Roberts and Smith, 1988; Covert *et al.*, 1995). Covert *et al.* (1995) suggested that the composition was inconsistent, requiring that they be opened and evacuated prior to use as gas sampling and storage vessels. Results from this study show there is residual N₂ and O₂/Ar in quantifiable concentrations, but that CO₂ although present was only just detectable, and not quantifiable. This study also shows the variability between tubes was within the limits of experimental sampling error. The presence of near-atmospheric concentrations of N₂ and O₂/Ar in the headspace gas precludes the use of brand new Vacutainer[®] tubes for gas storage when differences between samples is likely to be smaller than the sampling variability between duplicate samples. In this case, replacement of the headspace gas with He and re-evacuation prior to use would be required.

The results also showed gas exchange by diffusion through the Suba-seal was not significant and that gas sample integrity was maintained for at least 14 days for all the gases tested.

Conclusion

Samplers that use a Gor-tex membrane to collect soil gases have a small equilibrium time making them suitable as sampling devices. The samplers we have described here can be deployed and a gas sample retrieved in less than 2 hours. When deployed in the field, gas samples from the samplers can be stored in Vacutainers[®] tubes for transport back to the laboratory for analysis subject to the caveats mentioned above, and the pre-treatment of the tubes will depend on which gases are being analysed, the expected concentrations range, and the magnitude of the differences expected between treatments.

For this reason Vacutainers[®] tubes are suitable for the collection and storage of gases for later analysis. Additionally, they are widely available and are inexpensive because of their widespread use in the veterinary and medical industry for blood collection.

Acknowledgements

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Appendix I

Diffusion into gas sampler

For diffusion across a thin membrane the rate of transfer across the membrane can be written as;

$$\left. \frac{dC}{dt} \right|_t = -k[C_o(t) - C(t)] \quad (\text{A1})$$

where $C(t)$ and C_o are respectively the concentration in the sampler and the concentration in the flask at time, t , and k is the transfer coefficient. For the piston flow model the flow within the flask is considered to occur by piston flow and hence the initial conditions are;

$$\begin{aligned} t = t_o, & \quad C(t) = C_n \\ t > t_o, & \quad C_o(t) = C_o \end{aligned}$$

where C_o is the concentration of the invading gas, t_o is given in eqn (2) in the text and C_n is the initial concentration in the of the flask. The solution of eqn (A1) for these initial conditions results in:

$$t = \frac{1}{k} \ln \left[\frac{C_n - C_o}{C - C_o} \right] + t_o \quad (\text{A2})$$

During the first period of accumulation it is easily deduced that the corrected time, $t^* = t - t_o$. The value of k for this first time period is calculated with eqn (A2). The value of t_o for the next accumulation period is calculated with eqn (A2) with $C = C_g$ (calculated using eqn (1) in the text). The procedure is repeated until the last accumulation period. A mean value of k can then be calculated from each of the k 's calculated during each accumulation period.

For the mixing model $C_o(t)$ from eqn (2) is substituted into eqn (A1) and the initial value problem with the initial values of

$$t = 0, \quad C_o(t) = C_n$$

solved to give:

$$\begin{aligned} C(t) &= C_x - \frac{C_x - C_n}{k - V/f} \left[k \exp(-Vt/f) - \frac{V}{f} \exp(-kt) \right], \quad k \neq V/f \\ C(t) &= C_x - \frac{C_x - C_n}{k - V/f} (1 + Vt/f) \exp(-Vt/f), \quad k = V/f \end{aligned} \quad (\text{A3})$$

Eqn (A3) was used to correct the time in the first two accumulation periods (up to 300 s). There is little error introduced by using the procedure described above for the piston model after 300 s (see figure A1), so that procedure was used when $t > 300$ s.

Table 1. Transfer coefficient calculated for the 3 samplers

Sampler No.	Transfer coefficient, k (s^{-1})	
	Piston flow model	Perfect Mixing model
1	$2.4 (\pm 0.5) \times 10^{-3}$	$2.2 (\pm 0.4) \times 10^{-3}$
2	$1.9 (\pm 0.4) \times 10^{-3}$	$1.8 (\pm 0.2) \times 10^{-3}$
3	$1.2 (\pm 0.5) \times 10^{-3}$	$1.1 (\pm 0.2) \times 10^{-3}$
All samplers	$1.7 (\pm 0.4) \times 10^{-3}$	$1.6 (\pm 0.1) \times 10^{-3}$

Table 2. Relative gas concentrations normalised to initial concentration at $t=0$ for each gas in the test gas mixture. Each data value represents the mean of two pseudo replicates of two true replicates. The standard deviation for all samples is < 0.1 .

Elapsed Time (d)	Relative gas concentration (%)						
	Air/CO	[†] CH ₄	CO ₂	O ₂	N ₂	*CH ₄	CO
0	100	100	100	100	100	100	100
1	91	97	96	97	106	113	114
3	89	95	91	95	105	114	114
8	102	107	102	93	101	108	108
14	101	105	106	95	101	106	108

[†] from outer column

* from inner column

Table 3. Measured injected mass and calculated volume (at 25 ° C) for N₂ and O₂ in the injected samples (0.5 mL injection volume) when He and air were used as make-up gas, and the calculated mass and volume of air used as make-up gas.

Sample	Replicates	Mass ¹ (μg)		Volume (μL)		Calculated Volume (mL)
		O ₂	N ₂	O ₂	N ₂	
He as make-up gas	10	90 ± 3	320 ± 10	69 ± 2	279 ± 9	0.35 ± 0.01
Air as make-up gas	27	129 ± 5	480 ± 10	98 ± 4	418 ± 9	0.52 ± 0.01
Air		40 ± 8	160 ± 20	30 ± 6	139 ± 17	0.17 ± 0.02

¹ Values are mean ± std dev

Figure Captions

Figure 1. Schematic diagram of a gas sampler, showing a cross-sectional view and a top view of the end of the sampler with the membrane removed to show the slot.

Figure 2. Schematic diagram of the experimental apparatus used for testing the gas samplers.

Figure 3. Equilibration of O₂ within the samplers based on calculated O₂ concentration in the flask and corrected for the mass loss during sampling by; a) piston model and b) mixing model. The fitted equations are of the form $C(t) = a \ln t^* - b$, where C is the O₂ concentration (%m³ m⁻³) with a regression coefficient, $r^2 = 0.87$ and 0.72 for the piston and mixing models respectively .

Figure 4. Response of gas sampler to step change in gas concentration in surrounding air. The values of k used are the extremes of the measured range.

Figure A1. Oxygen concentration in flask as a function of time for the piston and mixing models.

Fig. 1

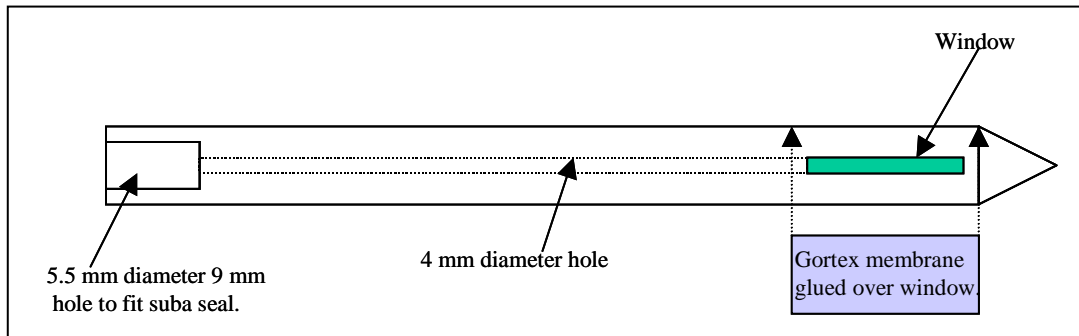


Fig.2

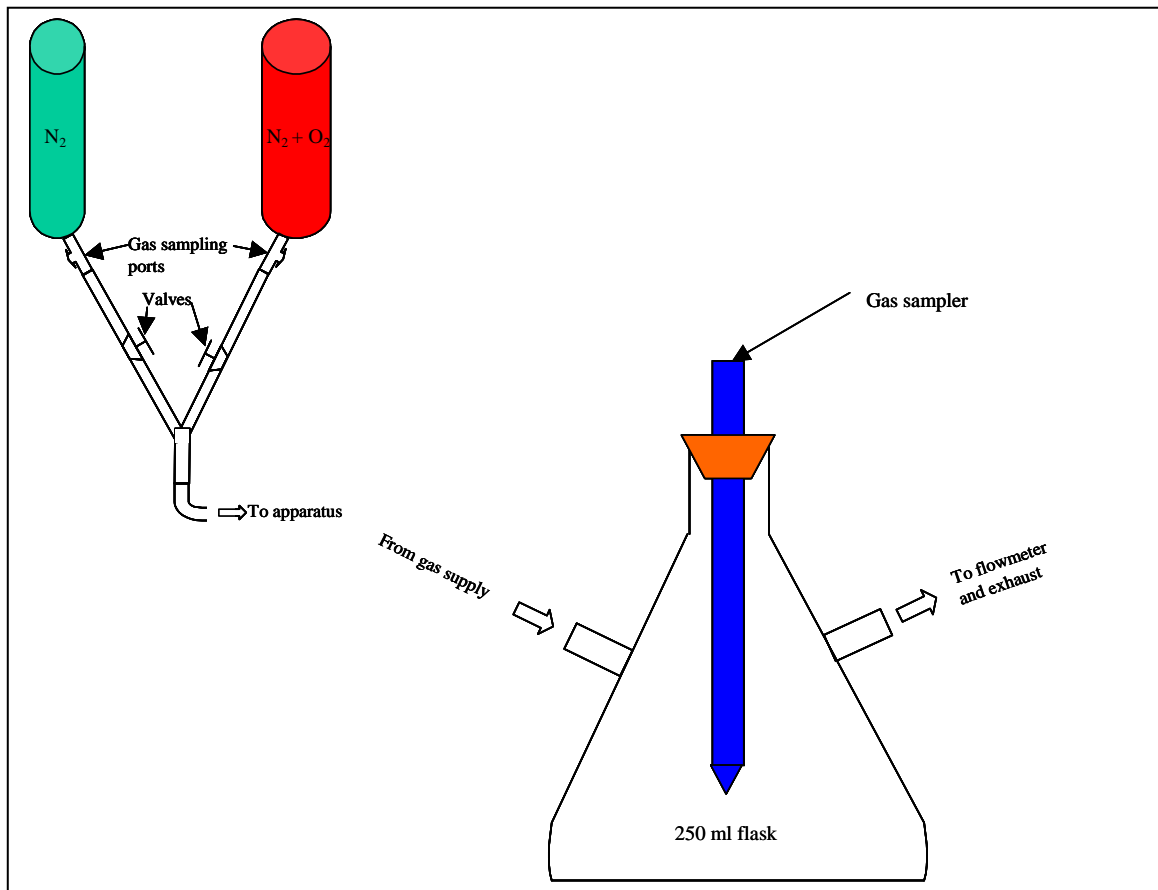


Fig. 3

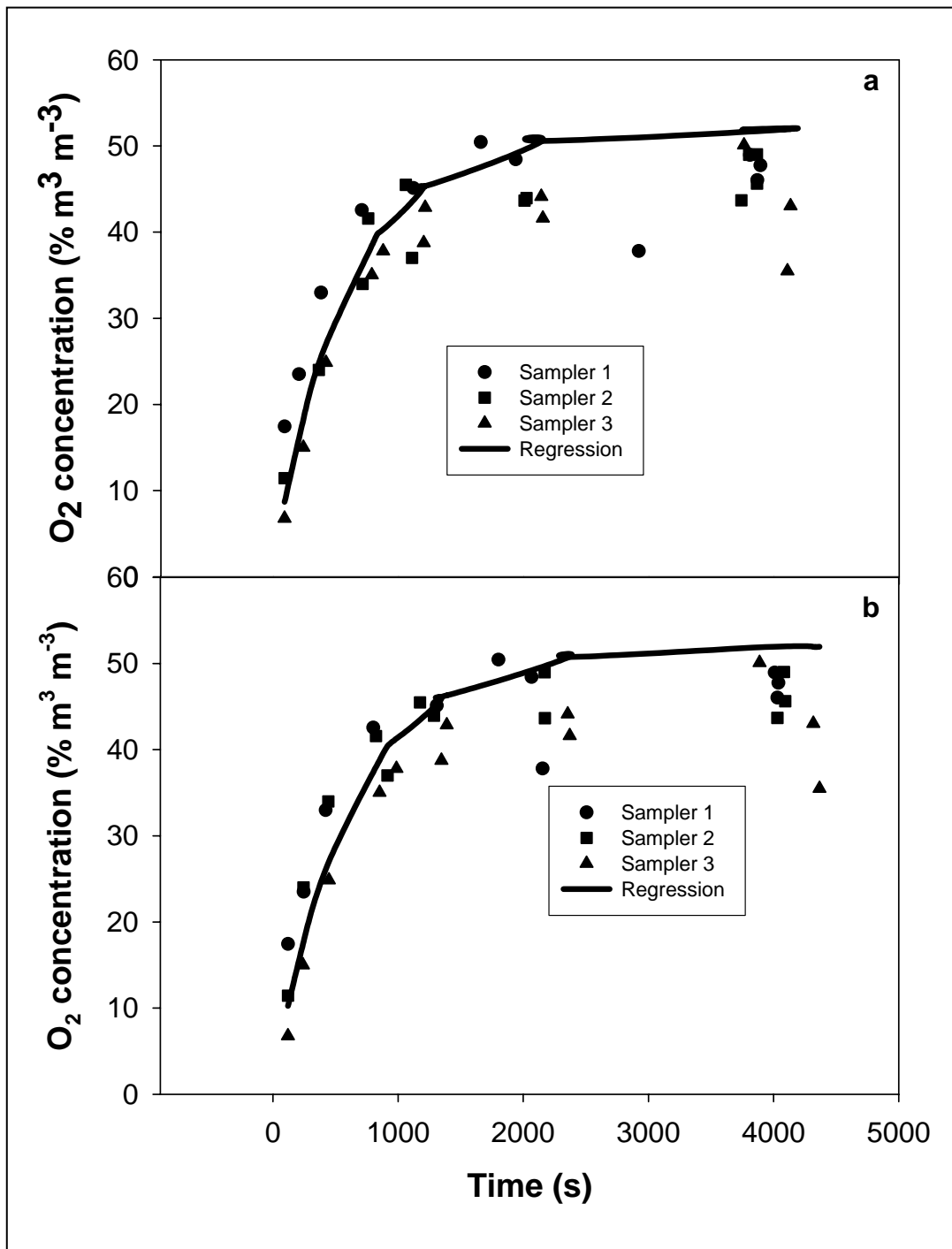


Fig. 4

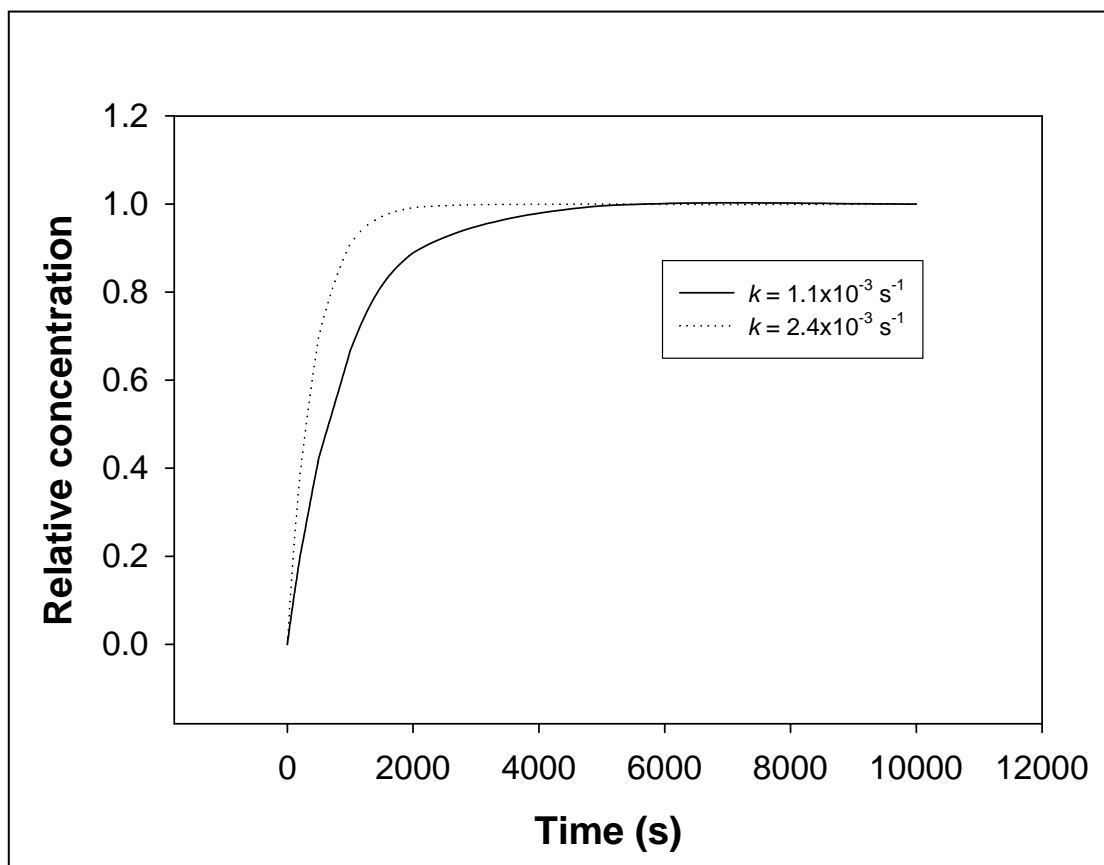


Fig. A1

