



Physical Sciences & Mathematics

Measuring Air-Sea Gas Exchange of Nitrogen, Oxygen, Argon and Carbon Dioxide by Micrometeorology and Mass Spectrometry

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Abstract

Advancement in the mass spectrometric analysis of air permits measurement of small gradients in N_2 , O_2 , Ar, and CO_2 . This work shows the potential of the gradient method for detecting air-sea fluxes of N_2 , O_2 , Ar, and CO_2 , though only on a qualitative basis. Difficulties were encountered due to meteorological conditions, though possible effects due to thermal diffusion were shown to be insignificant. Refinement of the technique may eventually lead to qualitative assessment of air-sea fluxes.

Introduction

Understanding the interaction of the atmosphere and the ocean has become increasingly important for global change studies. As anthropogenic activities produce and consume a variety of gases, the chemistry of the atmosphere has been significantly altered. Coupled with chemical changes in the atmosphere are changes in the dissolved constituents of the ocean, as the two reservoirs try to equilibrate. Fluxes of trace atmospheric constituents (e.g. CO_2) across the air-water interface have been well-studied, however little attention has been paid to the major constituents of the atmosphere, N_2 , O_2 , and Ar. This is due to the difficulties encountered in measuring small changes in concentration of such prevalent species. Recent technologic advances have allowed measurement of small changes in atmospheric oxygen with important applications to understanding the global carbon cycle (Keeling and Shertz 1992). Moreover, improvements in the precision of mass spectrometry make it possible to apply this tool to the study of major atmospheric constituents (Bender *et al.* 1994). Here we present results of a study measuring gradients in N_2 , O_2 , Ar, and CO_2 above the sea surface at the end of the Scripps Institution of Oceanography's 320 meter pier.

Background

Studying air-sea exchange of N_2 , O_2 , Ar, and CO_2 has the potential to tell us a great deal about global change. Previous measurement of atmospheric O_2 concentrations has shed light on the 'missing sink' for carbon (Keeling *et al.* 1996) including an oceanic component-the so-called 'biological pump' of planktonic organisms that takes up CO_2 and releases O_2 . Studying N_2 , O_2 , Ar, and CO_2 air-sea fluxes can also enhance our understanding of the influence of changing ocean temperature on gas exchange (Keeling *et al.* 1993). Warming of the oceans by the greenhouse

effect would lead to exsolution of dissolved gases, including greenhouse gases. This would be a positive feedback and lead to enhanced warming. Warming may also lead to enhanced biological activity, and the biological pump would draw down CO_2 while releasing O_2 . The thermal O_2 flux is difficult to separate from the biological O_2 flux, but it is possible by measuring fluxes of N_2 , O_2 , and Ar (Keeling *et al.* 1993). For atmospheric oxygen measurements O_2 is ratioed to N_2 , however they dissolve in the ocean in a different ratio than they are found in the air. In air, $\text{N}_2:\text{O}_2:\text{Ar}$ is 78:21:1, in sea water, it is 36:20:1 (Keeling *et al.* 1993). Since the sea-to-air flux of a species is primarily dependent on its concentration in the ocean, the solubility change due to temperature change would lead to increased fluxes of O_2 relative to N_2 while the O_2/Ar ratio would remain almost unchanged. An increase in O_2 flux due to biological activity would change both ratios - thus measuring N_2 , O_2 , and Ar is quite useful.

A variety of micro-meteorological techniques are available for the study of gas exchange, with the most widely-used being eddy correlation. Another promising technique is the gradient method, the technique employed in our study. The gradient method measures differences in concentrations between levels to yield a concentration gradient. The theory behind the method is that a sink or source for a gas will produce a slightly higher or lower concentration of the gas in the atmosphere around the source or sink. Thus above a forest that is producing O_2 , higher concentrations will exist nearer the forest than in the atmosphere above. The gradient method benefits from the fact that most instruments have better precision than accuracy (Baldocchi *et al.* 1988) and thus it is possible to more easily measure relative differences than absolute values. It has been successfully applied to terrestrial studies of trace gas species (Simpson *et al.* 1997), though gradients in CO_2 over the ocean have been measured with only limited success (Fairhall *et al.* 1999). This study is the first attempt to measure gradients in N_2 , O_2 , and Ar over the ocean, and the feasibility of making such measurements is unknown.

Methods

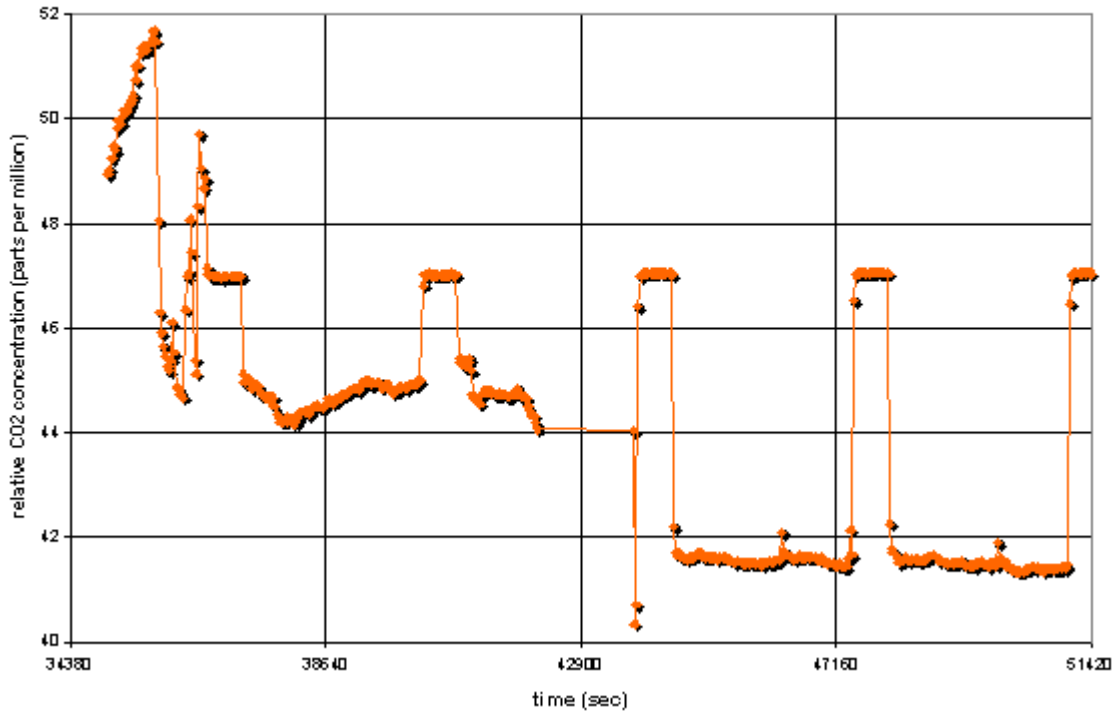
We found measurement of gradients in N_2 , O_2 , Ar, and CO_2 to be quite difficult. The gradient of a given gas above the sea surface goes with $1/z$, where z is the height above the sea surface (Fairhall *et al.* 1999). Detection of a gradient is then aided by measuring as close to the sea surface as possible, a measurement of obvious difficulty given the presence of surface waves. Wave height on sampling days was on the order of 1 m, thus 1 m was chosen as the closest possible measurement. These measurements were alternated with measurement at 2 m, as initial work showed that any measurement further above 2 m yielded no significant increase in the gradient. A tubing system was lowered off the end of the pier by rope and pulley and stabilized by diving weights lowered into the water. Sampling was conducted for 10 minutes at each height to maximize the number of measurements taken while minimizing possible effects on gas exchange from changes in wave height, tide, wind speed and solar radiation (due to clouds). 15 liters of air per minute is continuously pulled from the end of the pier through the tubing system and into the laboratory.

In the lab, air is passed through a Siemens ULTRAMAT 3 CO_2 Analyzer, and then through a Micromass IsoPrime mass spectrometer system to measure N_2 , O_2 , and Ar. All gases are measured relative to a working tank of known concentration. However, absolute concentrations of the species were not determined, as this experiment was chiefly concerned with relative changes and not absolute measurements. Consequently, O_2 and Ar values are ratioed to N_2 and reported in per Meq units, as described by (Keeling and Shertz 1992). Time values are presented as seconds since the beginning (12 am) of the day.

Results & Discussion

The most apparent aspect of our data is the noise of the signal. The CO₂ values, in particular, are quite noisy (Figure 1).

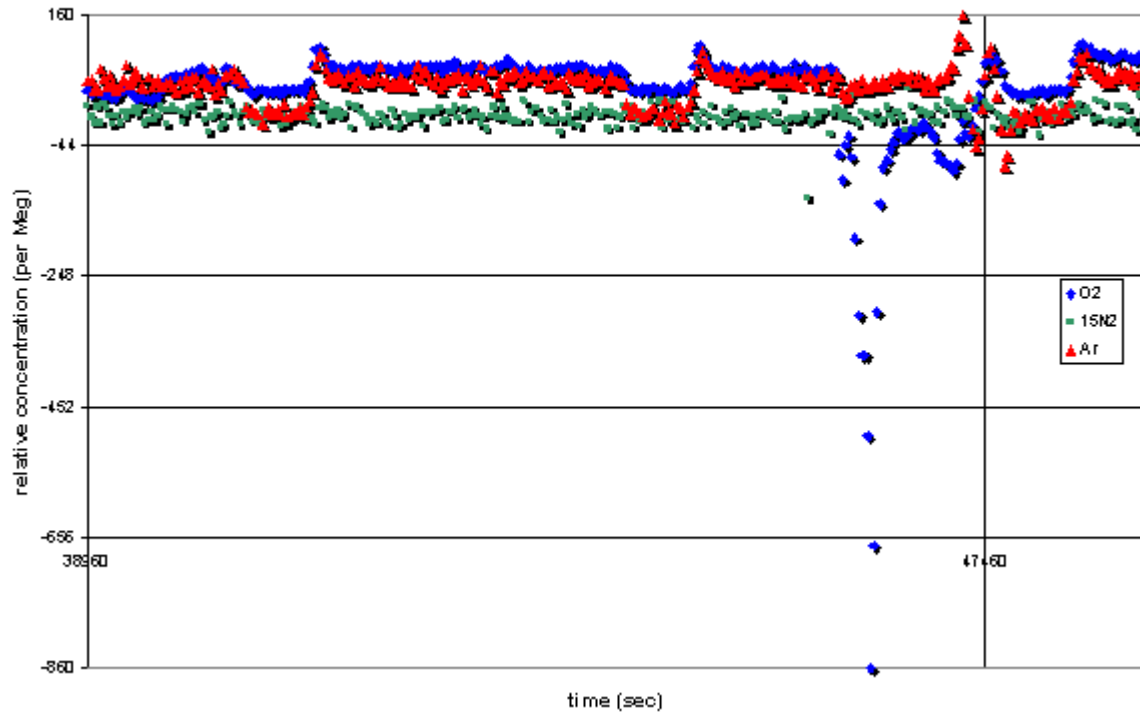
Figure 1: 7-21 CO₂ Time Series



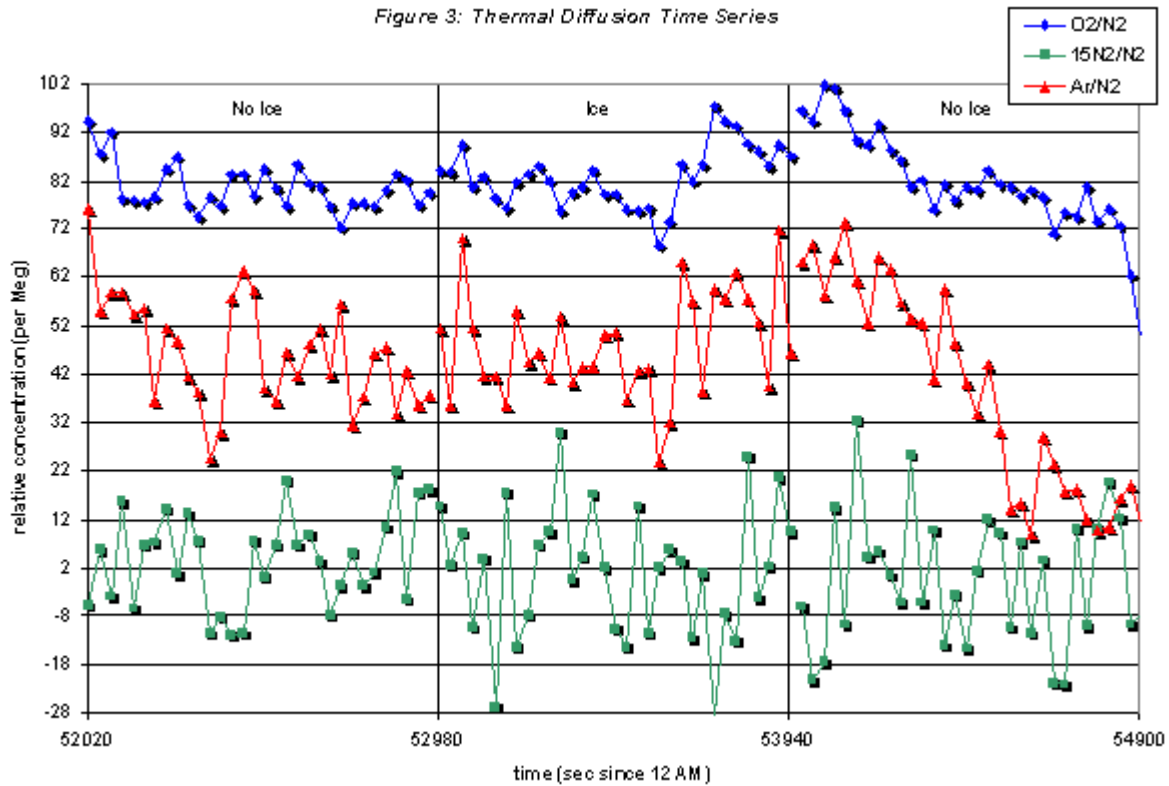
This is due to air pollution, as clear plumes of exhaust are evident on 7-21 in the beginning of the measurement period. These higher CO₂ values are corroborated with low values in oxygen on 7-21 as well. The pollution effect is on the order of 10's to 100's of ppm, and masks any 0.5-1 ppm gradient. It is then necessary to have a good southwest wind to accurately measure CO₂: any easterly or northerly component brings air is coming from inland areas to the east or from Los Angeles to the north. Unfortunately, there was no full measurement period during which CO₂ was unaffected by pollution.

Other noise in the data are the very large peaks visible in Figure 2.

Figure 2: 7-21 Time Series

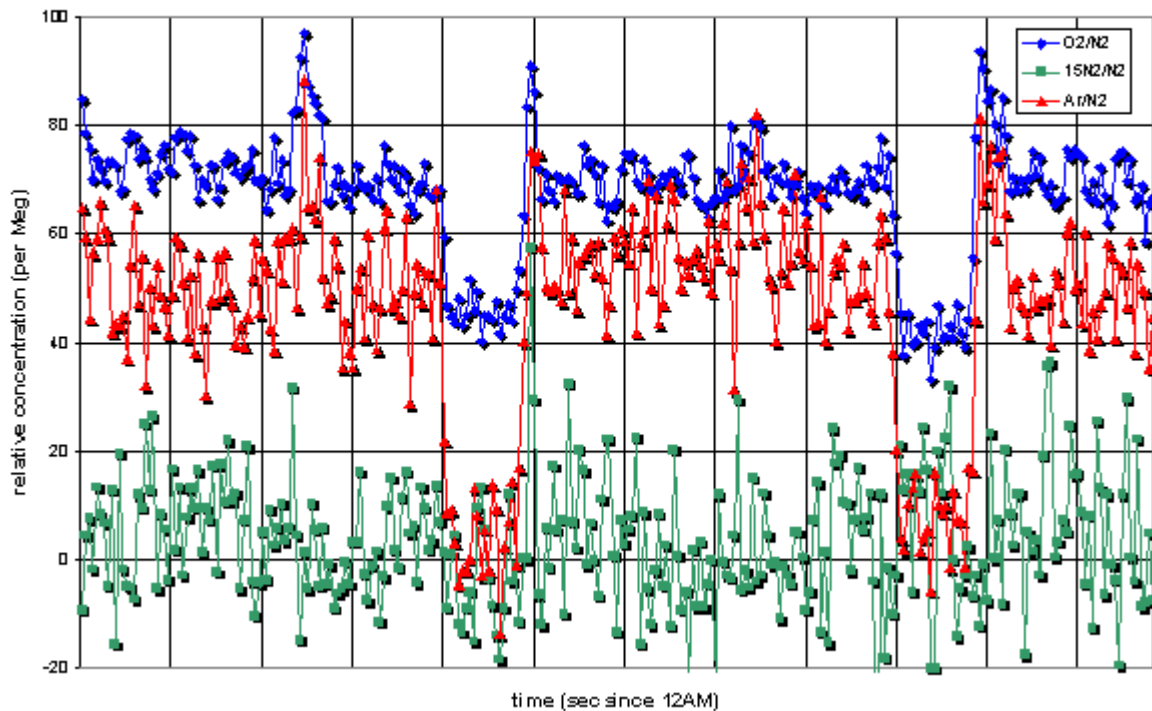


These are real features measured by the mass spectrometer, not single erroneous points. We are uncertain of their cause. One possible effect we considered is that of thermal diffusion, whereby a given gas will become enriched in heavier isotopes in colder areas (Grew and Ibbs 1952). This effect has been identified in sand dune gases by Severinghaus *et al.* 1996. Their work indicated that gases containing heavier isotopes indeed congregate in areas of lower temperature, and that air itself should show this fractionation. The idea is that air itself should fractionate, with gases of higher molecular weights tending to concentrate in slightly colder areas. Heating or cooling of the air lines that run along the pier could theoretically fractionate the air in the tube, leading to the observed peaks. To this end, we conducted an experiment where ice was placed on approximately 1 m of air line to observe possible fractionation due to thermal diffusion. CO₂, N₂, O₂, and Ar were measured for 16 minutes, and then ice was placed on the tubing for 16 minutes, then removed again for 16 minutes (these times were chosen to get as long of a continuous record as possible while avoiding the hourly working tank calibration). No observable fractionation can be gleaned from the data, certainly not of the magnitude of the peaks observed during some of the sampling (Figure 3).



Moreover, Severinghaus *et al.* (1996) observed fractionation of ^{15}N -N relative to N_2 of ~ 0.2 per mil, which would be almost 200 per Meg and is clearly not present in our data. The only other possible effect is that of pressure changes, which would lead to fractionation of air as it is pulled into the mass spectrometer. This possibility warrants further work, as peaks are also evident after switchover from the working tank (Figure 4).

Figure 4: 7-27 Time Series



The fact that thermal diffusion does not have a dramatic signal is a benefit to future use of the gradient method for measuring fluxes. It is plausible that thermal diffusion could cause a gradient of its own, as heavier gases would congregate closer to the sea surface where the air is colder than above, but if a temperature change of 10's of degrees due to ice had no effect, a change of .1's of a degree is obviously of no significance.

The finer features of our data are difficult to resolve visually within the large scatter of the data. The $^{15}\text{N-N}$ signal shows no trends and is of no value, however trends in O_2 and Ar are statistically resolvable. Figures 5 through 9 show the raw data with trendlines (least squares fit). This analysis was chosen over a more quantitative assessment because averaging values masks the noise of the data.

Figure 5a: 7-21 O₂ Data

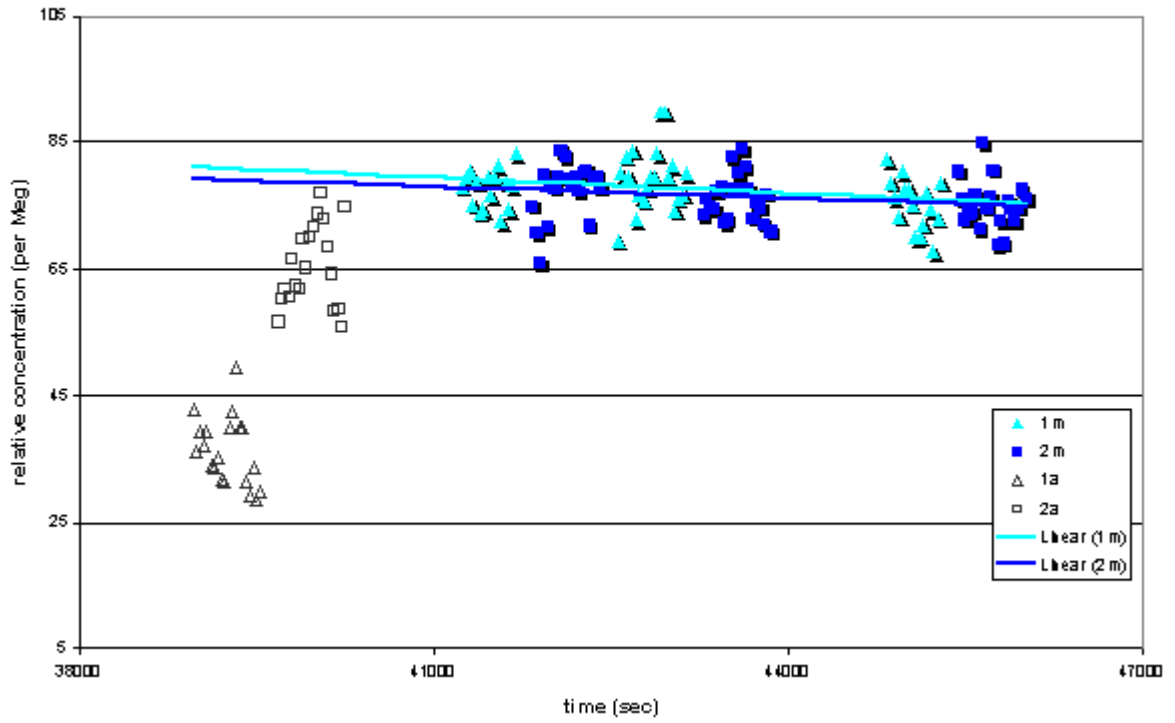


Figure 5b: 7-21 Ar Data

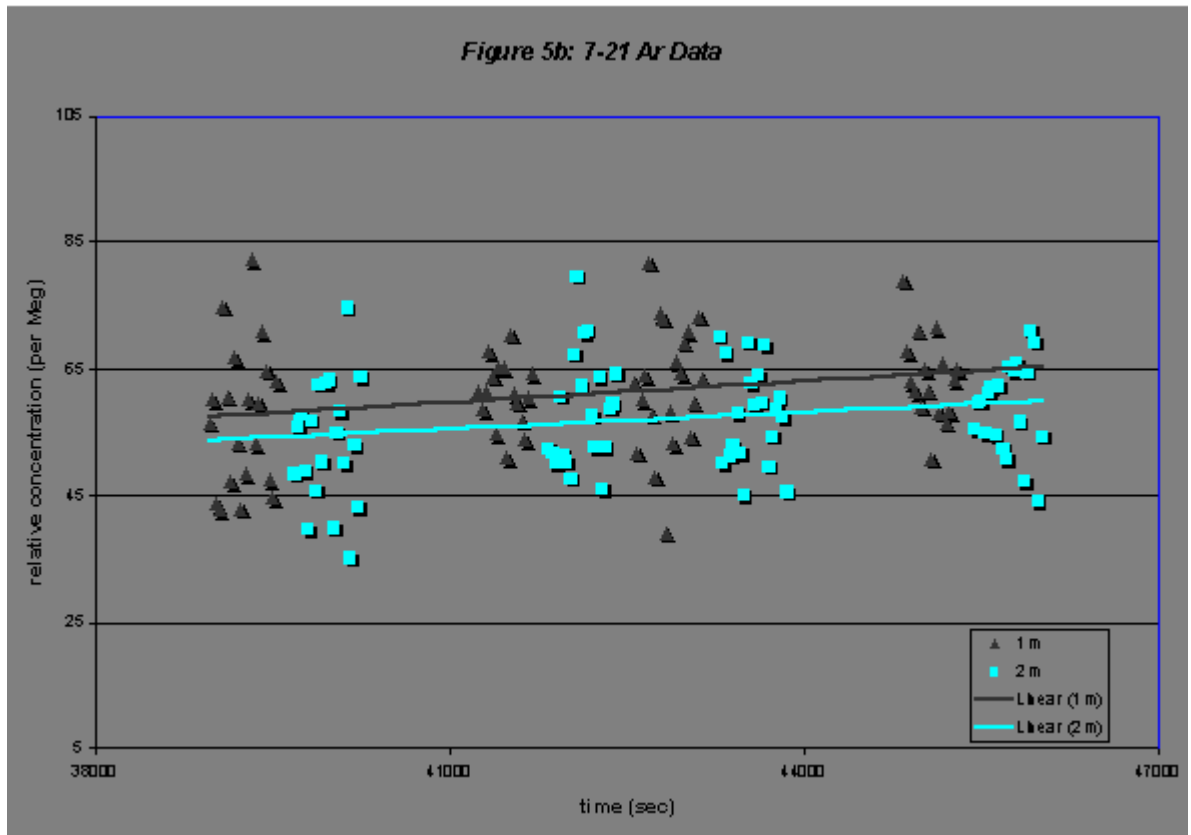


Figure 6a: 7-27 O2 Data

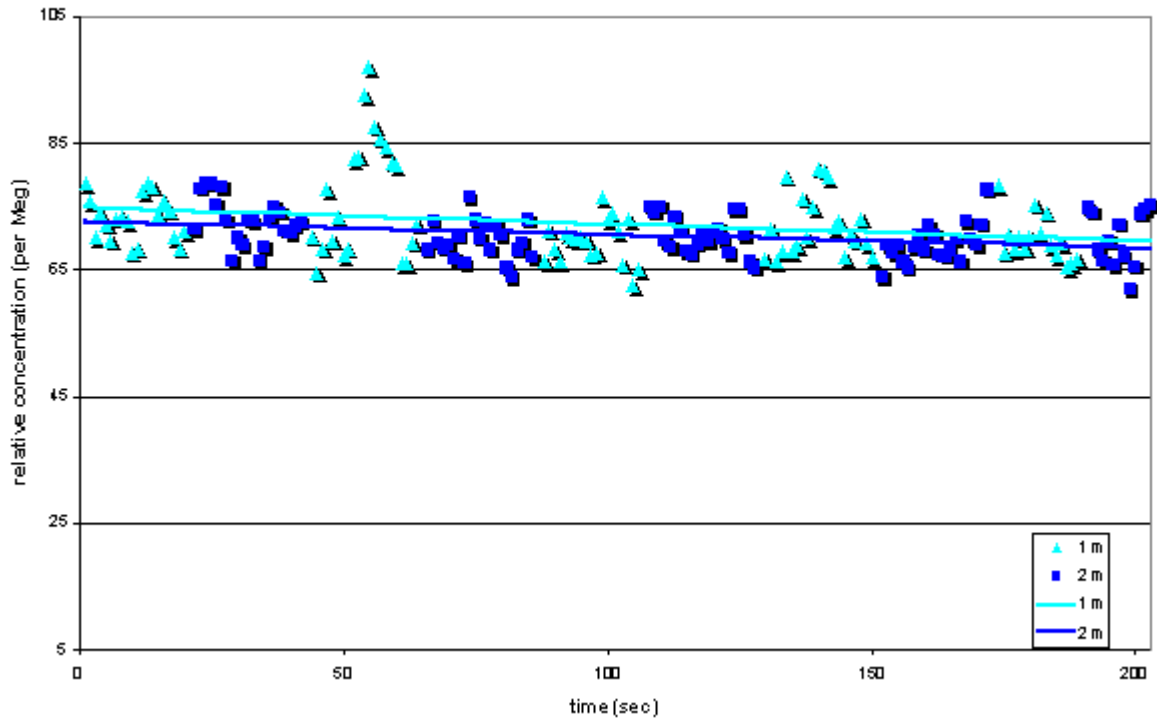


Figure 6b: 7-27 Ar Data

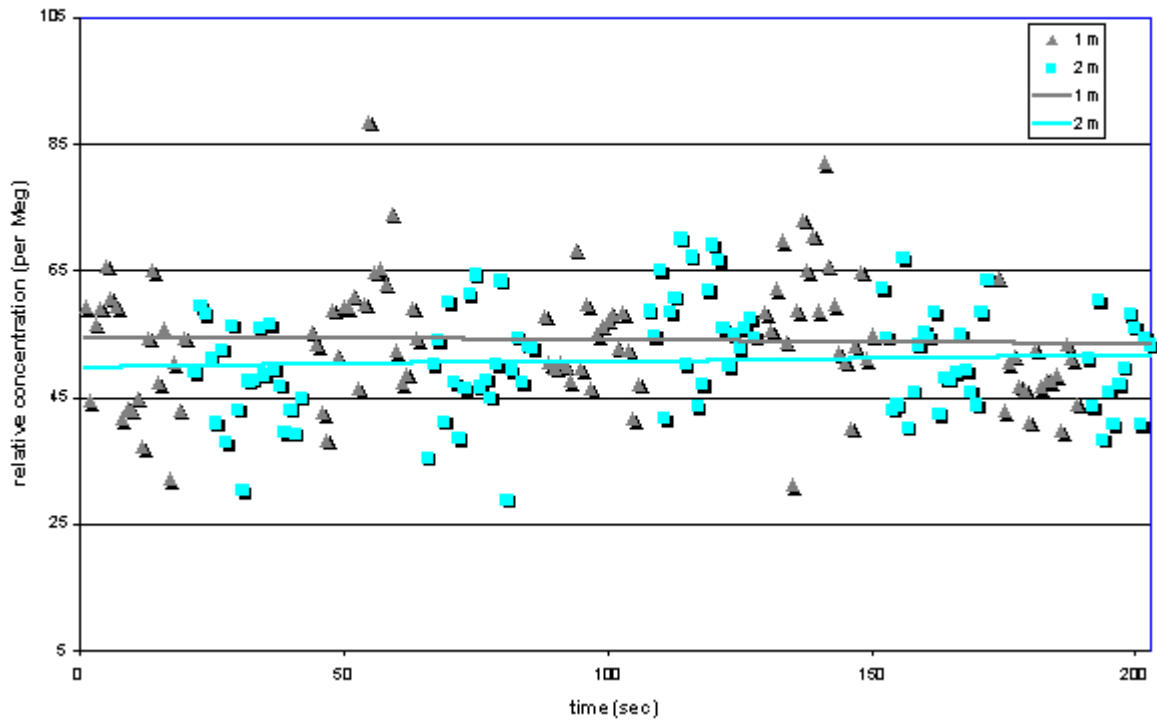


Figure 7a: 8-4 O2 Data

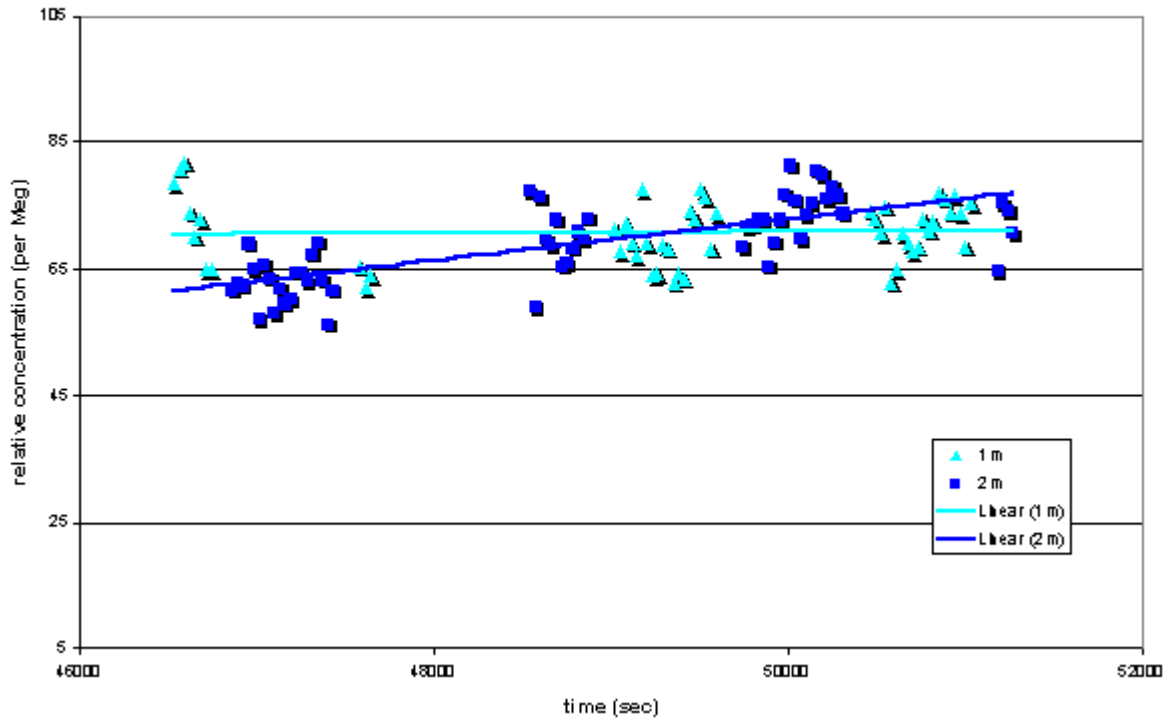


Figure 7b: 8-4 Ar Data

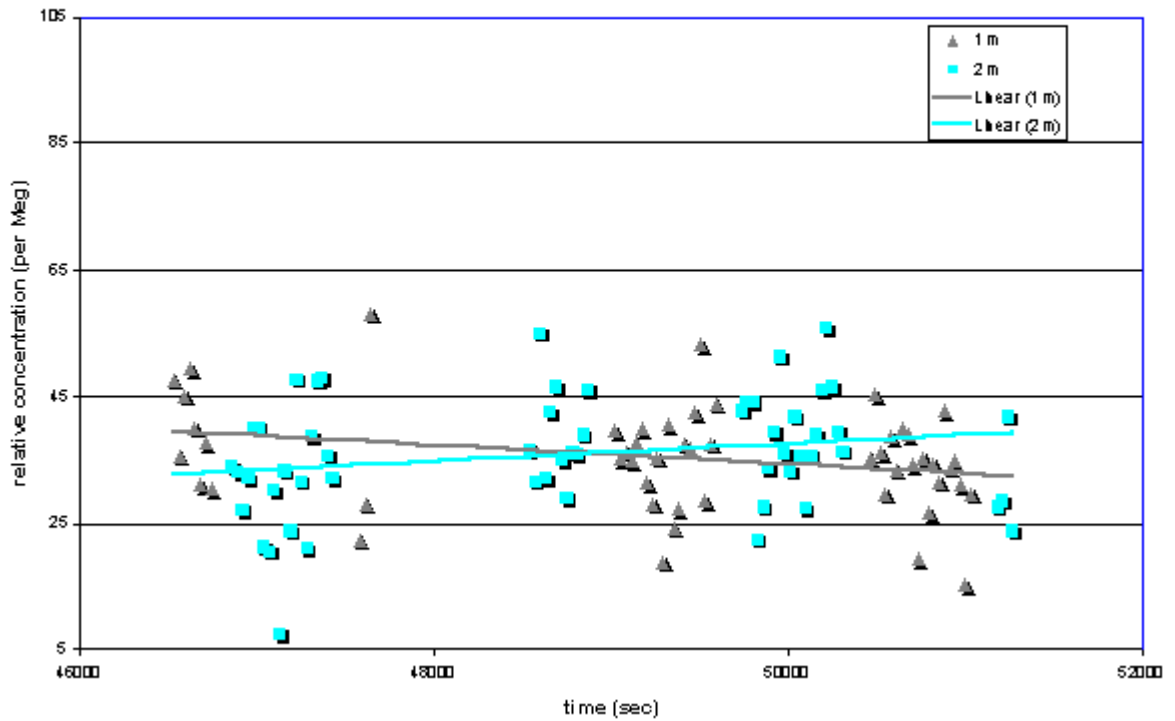


Figure 8: 8-12 O2 Data

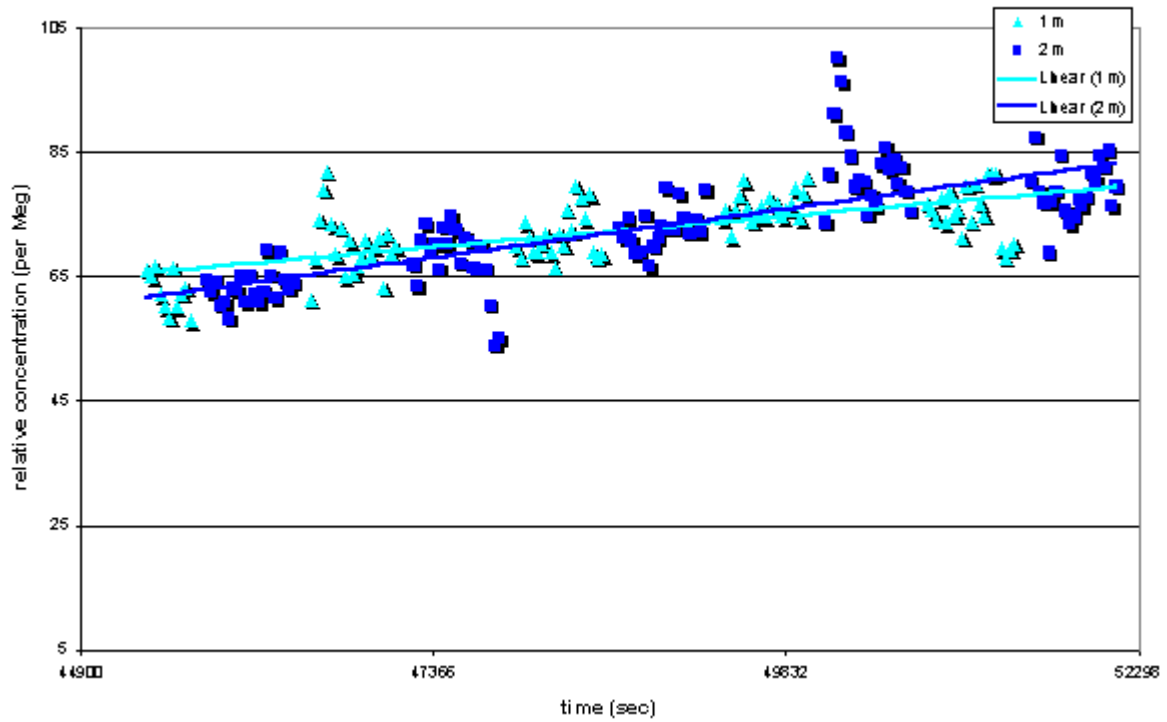
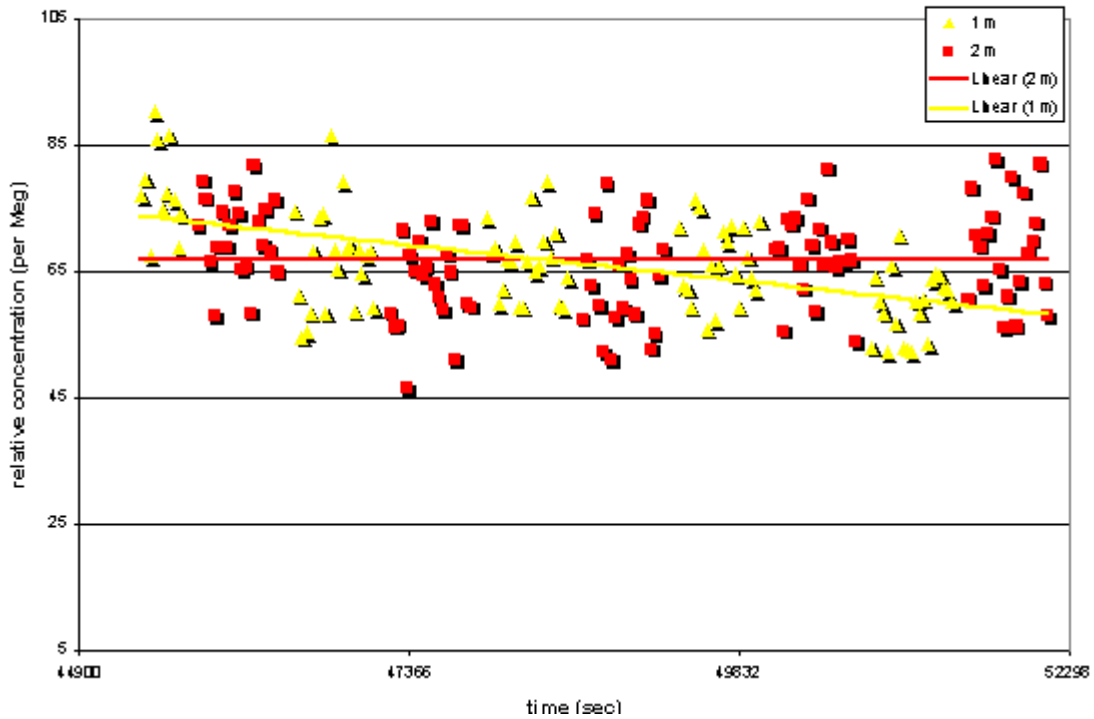


Figure 9: 8-12 Ar Data



Most of the noise seems to come in the form of peaks, clearly evident on 7-27 in Figures 6a and 6b. We envision these peaks as 'burps' from the sea surface, likely associated with gas flux from breaking waves. Any peaks with values 15 per Meg greater than the trendline have been identified

in the figures. Burps are more likely to be found at 1 m than 2 m, leading to increased concentrations closer to the sea surface, and qualitatively supporting our hypothesis.

These features vary between sampling days, possibly due to different meteorological conditions. The gradient method benefits from small waves, as mentioned before, and a SW wind is also ideal. Additionally, air-sea flux is dependent on wind speed. Increased fluxes are associated with higher winds, though the quantitative relationship is still unresolved in the literature (Liss and Merlivat 1986; Wanninkhof 1992; Wanninkhof and McGillis 1999). However, measurement of a gradient is only possible under less turbulent conditions. The presence of a gradient depends on the inability of the atmosphere to mix at the rate at which gas is added to or removed from the atmosphere, creating a measurable disequilibrium. 7-27 was extremely foggy and there was very low wind. This may have led to decreased fluxes in general, and the large peaks that are visible in Figures 6a & b may be the result of burps that stick out from the baseline data. 8-4 (Figures 7a & b) was extremely windy (>8 mps), resulting in the increased noise in the data and lack of a gradient observable in the trendlines. The conditions on 7-21 (Figure 4) were nearly ideal, but for the exhaust plume in the first set of sample points. O₂ shows little signal, but Ar has a clear and consistent gradient. Sampling was done on 8-11, when conditions were ideal, but laboratory difficulties prevented recovery of results. Wind speed and wave conditions on 8-12 were ideal, however the wind had a slight northerly direction. The gradient is clearly visible on 8-12 (Figures 8 and 9), with 1 m data being distinctly offset from the 2 m data, but the gradient changes signs. In Figures 10a & b and 11a & b, the first five sampling periods for both O₂ and Ar show a gradient with higher values closer to the sea surface and increasing with time.

Figure 10a: 8-12 O₂ 1b-1d

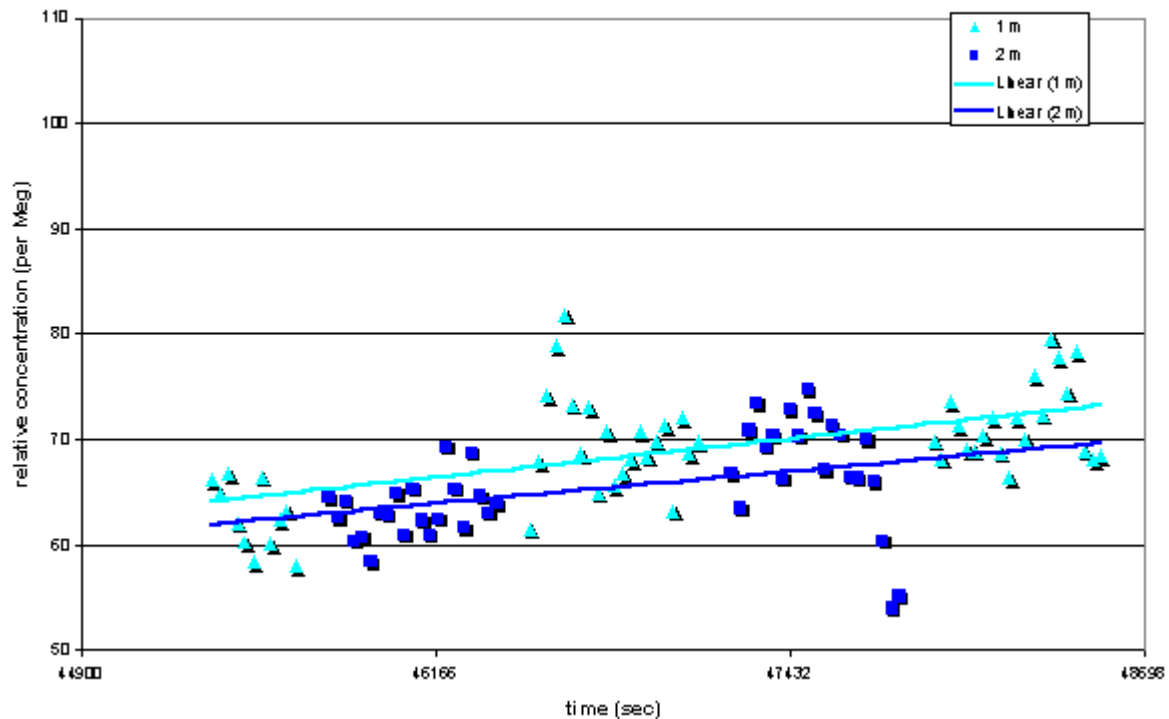


Figure 10b: 8-12 O2 2d-2f

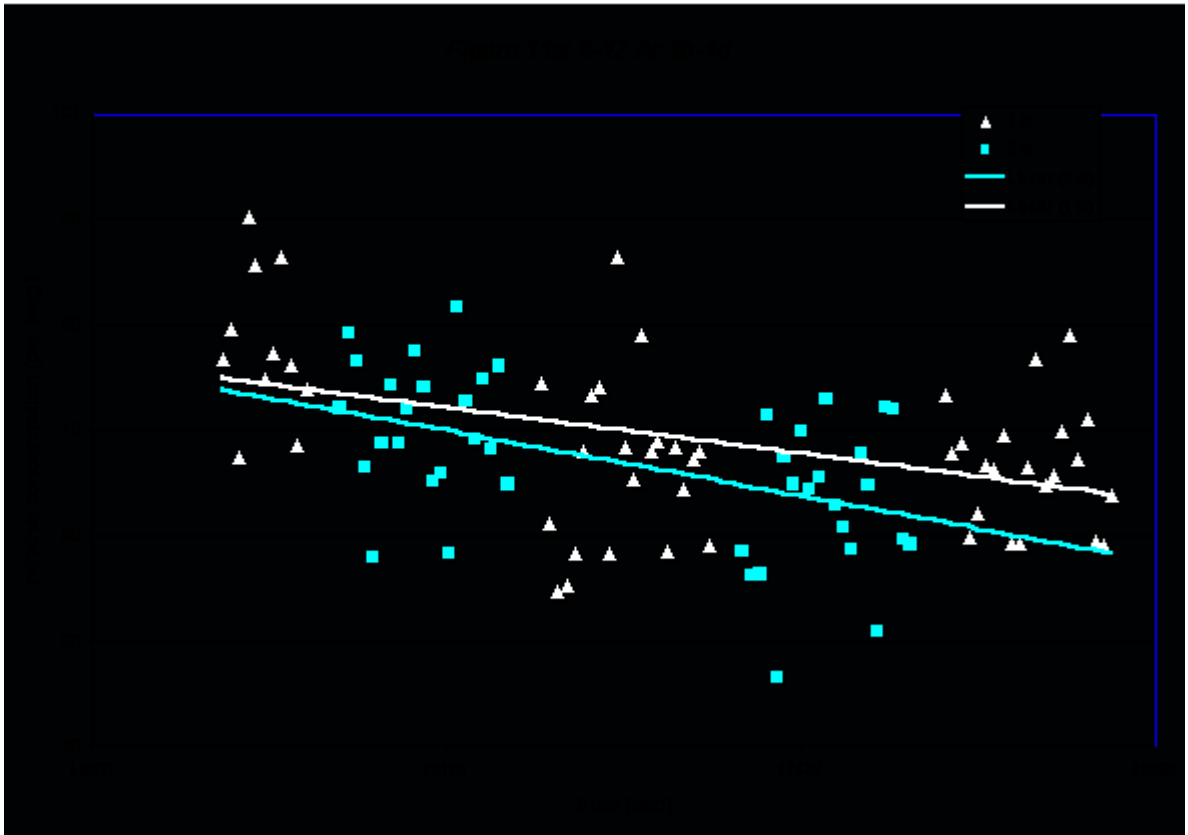
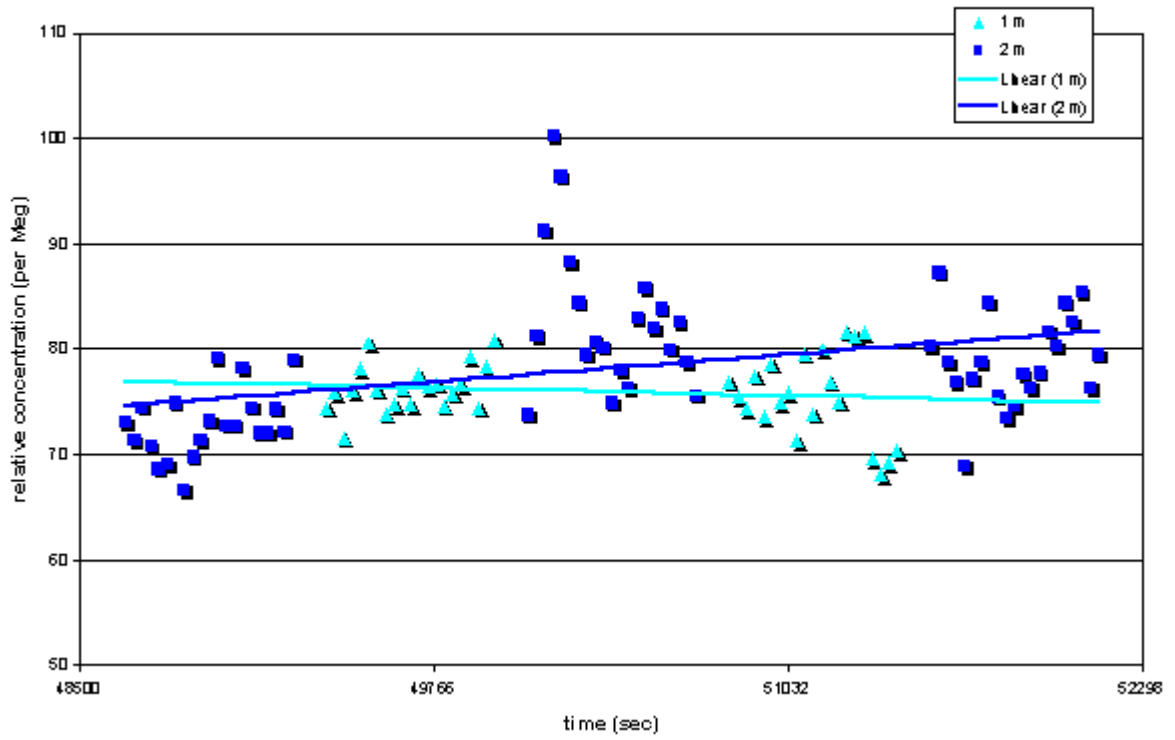
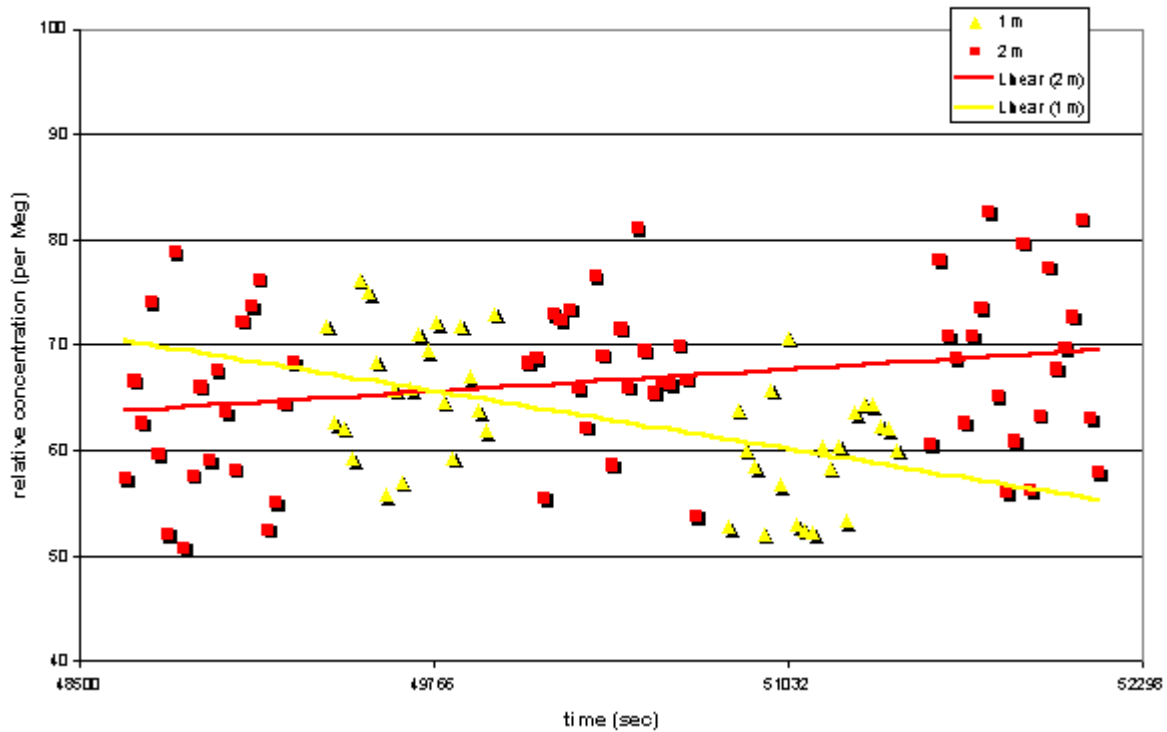


Figure 11b: 8-12 Ar 2d-2f



The second set of sample periods show a reverse in both gradients (Figures 10 and 11). An explanation for this eludes us.

The data are averaged and summarized in Table 1:

		O2 1 m	O2 2 m	O2 Gradient	Ar 1 m	Ar 2 m	Ar Gradient
21-Jul	average	77.649	76.261	1.389	60.846	57.114	3.732
	precision	1.022	0.914		2.089	1.980	
27-Jul	average	72.303	70.126	2.177	53.965	50.743	3.222
	precision	1.402	0.845		2.241	1.933	
4-Aug	average	70.731	68.946	1.785	35.262	35.830	-0.568
	precision	1.150	1.456		1.893	2.131	
12-Aug	average	72.112	63.512	8.600	66.255	58.877	7.378
	precision	1.293	1.953		1.864	1.784	

Increased concentrations are found nearer the sea surface in every case but Ar on 8-4. Yet in this case the gradient is insignificant compared to the standard deviation of the values. This is true for both gases on all days but 8-12. Ideal conditions on 8-12, despite the change in gradient sign, yielded the largest per Meg gradient. Nevertheless, the gradient is still quantitatively indistinguishable from the standard deviation, and we present our results merely as a qualitative observation.

Conclusion

The possibility of measuring air-sea gas fluxes of CO₂, N₂, O₂, and Ar by the gradient method and mass spectrometry is certainly real. Difficulties lie in resolving the noise associated with experimental set-up, but could be corrected with a more stable system-one floating on the sea surface would remove the difficulties associated with waves. Automation of the system would also allow collection of much more data. Furthermore, the data collected in this study represent only a snapshot of time and space. Collecting for years at a time and over different areas of the ocean could lead to a much-improved understanding of air-sea gas exchange. As it stands, the method seems qualitatively useful, with detectable gradients in O₂ and Ar most likely associated with summer warming of the waters off La Jolla. Further work could lead to quantification of air-sea gas fluxes-a large unknown in the global change equation.

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