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The Effect of Wind and Currents on Gas Exchange in an Estuarine System

Final Technical Report

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Final technical report for NASA grant NAGW-667 "The Effect of Wind and Currents on Gas Exchange in an Estuarine System

INTRODUCTION

The objectives of the proposal were to develop a non-volatile tracer to use in gas exchange experiments in laterally unconfined systems and to study new applications of deliberate tracers in limnology and oceanography. Progress has been made on both fronts but work on the development of the non-volatile tracer proved to be more difficult and labour intensive than anticipated so no field experiments using non-volatile tracers have been performed as yet. In our search for a suitable non-volatile tracer for an ocean scale gas exchange experiment we have discovered a tracer which does not have the required sensitivity for a large scale experiment but is very easy to analyze and will be well suited for smaller experiments such as gas exchange determinations on rivers and streams.

Sulfur hexafluoride, SF_6, was used successfully as a volatile tracer along with tritium as a non-volatile tracer to study gas exchange rates from a primary stream. To our knowledge this is the first gas exchange experiment in which gas exchange rates were determined on a head water stream where significant groundwater input occurs along the reach. In conjunction with SF_6, ^{222}Radon measurements were performed on the groundwater and in the stream. We are currently studying the feasibility of using a combination of SF_6 and radon to determine groundwater inputs and gas exchange rates in streams with significant groundwater input without using a non-volatile tracer.

DISCUSSION

Development of a non-volatile tracer

For gas exchange experiments in systems which are laterally unbounded, a non-volatile tracer is needed in addition to a volatile tracer in order to distinguish between concentration decrease due to lateral dispersion and concentration decrease due to gas exchange. Open systems which require further study are rivers and streams where biological oxygen demand can be increased drastically due to release of organic wastes and in which gas exchange of oxygen is the major mechanism of keeping the water "healthy". Short term gas exchange rates over the ocean are not well constrained and the parameters controlling the rates are poorly understood. Better knowledge of the gas exchange is essential to predict the impact of the ocean on the atmospheric level of "greenhouse gases" such as CO_2 and CH_4 . Our long term goal is to determine gas exchange rates in open ocean experiments and to relate the gas exchange to environmental forcing functions.

A non-volatile tracer has to be stable in the water column, non-toxic, and measurable down to concentration of 10^{-15} mol/L for ocean work. Although tritium would be ideal for such work it would be difficult to field this tracer since bomb produced tritium is still used extensively as an oceanic tracer, and unfavorable public opinion about using radio tracers in the environment.

Our approach is to use a halogenated acid, extract it from the water phase, alkylate it to make it volatile, and analyze it by electron capture detection gas chromatography. This method of analysis is orders of magnitude more sensitive for halogenated compounds than measuring the compounds in a liquid matrix. Moreover, using the appropriate reactants can increase the sensitivity of the derivitized compound for analyses.

The initial compound which was tried was pentafluorobenzoic acid, PFBA which has been used successfully as a groundwater tracer (Stetzenbach et al., 1982). Esters were formed with methanol, using a BF_3/methanol mixture (figure 1a); with Bromo-2,3,4,5,6-pentafluorotoluene, using an extractive alkylation technique with tetrabutylammonium hydrogen sulfate (figure 1b); and using trichloro ethanol. The last two methods will yield esters with additional halogen atoms thereby increasing the sensitivity of the derivative. Since alkylation with a halogenated reactants will make most organic acids present in natural waters sensitive to electron capture analyses, many more peaks appear on chromatograms with associated problems of peak interference. The yields of the alkylation reactions appeared to be very low for all the reactants which is attributed to the strong acidity of pentafluorobenzoic acid acid (pK=1.7).

One of the compounds which was tried as an alternative was decafluorobenzhydrol (DFBH). DFBH can be extracted quantitatively from water with hexane and it can be analyzed directly in the organic phase without prior synthesis. DFBH has a distribution coefficient between sediments and water of about 20, and thus particle reactive which would be a problem for long term experiments but for short term tracer releases the loss rate will be negligible. DFBH can be detected down to 10^{-14} moles. Due to the strong partitioning into the organic phase samples can be concentrated by extraction into a small volume of hexane and further concentration can be accomplished by partial evaporation of the hexane. Since decafluorobenzhydrol is not very soluble in water, the compound is dissolved in methanol prior to injecting a spike into water.

The low solubility of the compound in water, the tendency to adsorb onto particles, and lack of extreme sensitivity limits the use of this tracer to short term lake or stream experiments. For ocean experiments we are currently investigating pentafluorophenylacetic acid as a possible choice. It is not as strong an acid as pentafluorobenzoic acid and the alkylation reaction appears to yield a higher and more reproducible yield. Although preliminary work has been very encouraging, more work remains to be performed before we can adequately assess the suitability of this tracer for oceanic purposes.

New applications of deliberate tracer work using SF_6

A collaborative effort between Dr. P. Mulholland and Dr. G. Elwood of the environmental science division of Oak Ridge National Laboratories and our group has shown the feasibility of using SF_6 for determining gas exchange rates in shallow head water streams. Prior stream work has concentrated on larger, slower moving streams with little groundwater inflow along the reach using ^{85}Krypton and tritium (Tsivoglou, 1967) or propane and dye (Rathbun, 1979) as volatile and non-volatile tracers, respectively. Although the first tracer pair works very well, current use is severely limited due to the radio activity of the compounds. Especially ^{85}Kr is considered an environmental hazard. Dye and isopropanol are not completely conservative and the compounds do not have a very low sensitivity for detection. In the experiment in the West Fork of the Walker Branch in Oak Ridge, Tn we used SF_6 and tritium as volatile and non-volatile tracer and used the ^{222}Rn concentration in the stream to locate groundwater inputs. Our ultimate goal is to use SF_6 and ^{222}Rn to determine gas exchange coefficients and groundwater inflow rate in streams without having to resort to a non-volatile tracer.

In the experiment 4 liter of water containing 10×10^{-9} Ci of tritium and 5×10^{-5} moles of SF_6 was injected into the stream over a period of four hours such that a dynamic equilibrium between inflow, dilution and escape of SF_6 was reached. Samples were taken at 10 m intervals along the 300 m reach. Figure 2 shows the increase in flow of the river deduced from the dilution of the tritium downstream of the injection point. The radon concentration profile in the stream which is influenced by high radon groundwater input and gas exchange shows increases at points of high inflow (figure 3). Groundwater samples taken at springs had an average concentration of 495 pCi/L with a standard deviation of 25 pCi/L which indicates that all the groundwater inputs had similar concentrations.

In this experiment the gas exchange coefficient, k was calculated from the change in ratio between the volatile and the non-volatile tracer according to:

$$k = \frac{h}{\Delta t} \ln \frac{R_i}{R_f}$$

where h is the depth of the stream; R_i and R_f are the initial and final ratios of volatile to non-volatile tracer in the stream (see figure 4); and Δt is the time interval. The gas exchange coefficient did not change significantly along the reach although the slope and the geometry differed for different parts of the stream. The average gas exchange coefficient was 27 cm/hr which is an order of magnitude greater than the average observed in lakes (Wanninkhof et al. 1987). Since the input concentration of Rn is constant and the ground water does not contain any SF_6, it should be possible to deduce the gas exchange rate and inflow of ground water if the inflow rate of water spiked with SF_6 and ^{222}Rn and SF_6 concentrations are measured at closely spaced intervals during the experiment. This can be illustrated with a simple box model (see figure 5). The inflow into the "box' can be determined from the SF_6 in the spike container, the inflow rate of the spike into the stream and the concentration in the stream. The concentrations, area, and stream velocity can be measured which leaves three independent equations and three unknowns: the ground water input, the outflow, and the gas exchange rate.

This method was not used for the experiment in the Walker Branch since not enough radon measurements were performed in the stream and the radon measurements were taken two days prior to the spike release to avoid excessive handling of the tritiated water. The night before the release a cloud burst caused the flow of the west Fork to double making comparison of gas exchange coefficients and concentrations before and during the spike experiment very ambiguous.

CONCLUSION

Steady advances have been made in development of the non-volatile tracer. The synthesis and chromatography of the fluorinated compounds have been worked out. Although our initial choice of tracer, pentafluorobenzoic acid did not fulfill our objective, the work has proved worthwhile in chosing other compounds. One of the compounds, decafluorobenzhydrol will be fielded shortly in a stream release to test the stability of the compound in nature. Work has started on another halogenated acid, pentafluorophenyl acetic acid with encouraging results. Suitable extraction methods and chromatographic peak interference for natural water samples has not been fully resolved.

Our volatile tracer, SF_6, has been used successfully in conjunction with tritium to determine gas exchange coefficients in a primary stream with large ground water inputs. It appears to be feasible that by using radon and SF_6 simultaneously the groundwater inputs and gas exchange coefficients in such streams can be determined without elaborate measurements of stream flow or use a non-volatile tracer. Since non-volatile tracers do not degrade while volatile tracers escape to the atmosphere it is probable that opposition to injecting volatile tracers will be less than using non-volatile tracers. Furthermore this method gives a direct measure of the radon burden to the local atmosphere from streams.

Continuation of the development of tracer methods for an open ocean experiment will be sponsored by the NSF chemical oceanography division and NASA oceanographic processes division with emphasis on establishing a relationship between gas exchange coefficients and radar back scatter form satellite scatterometers.

PUBLICATIONS ACKNOWLEDGING GRANT: NASA-NAGW-667:

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Tsivoglou, E.C. Tracer measurements of stream reaeration. USDI, Federal water pollution control administration. Washington D.C., 1967.

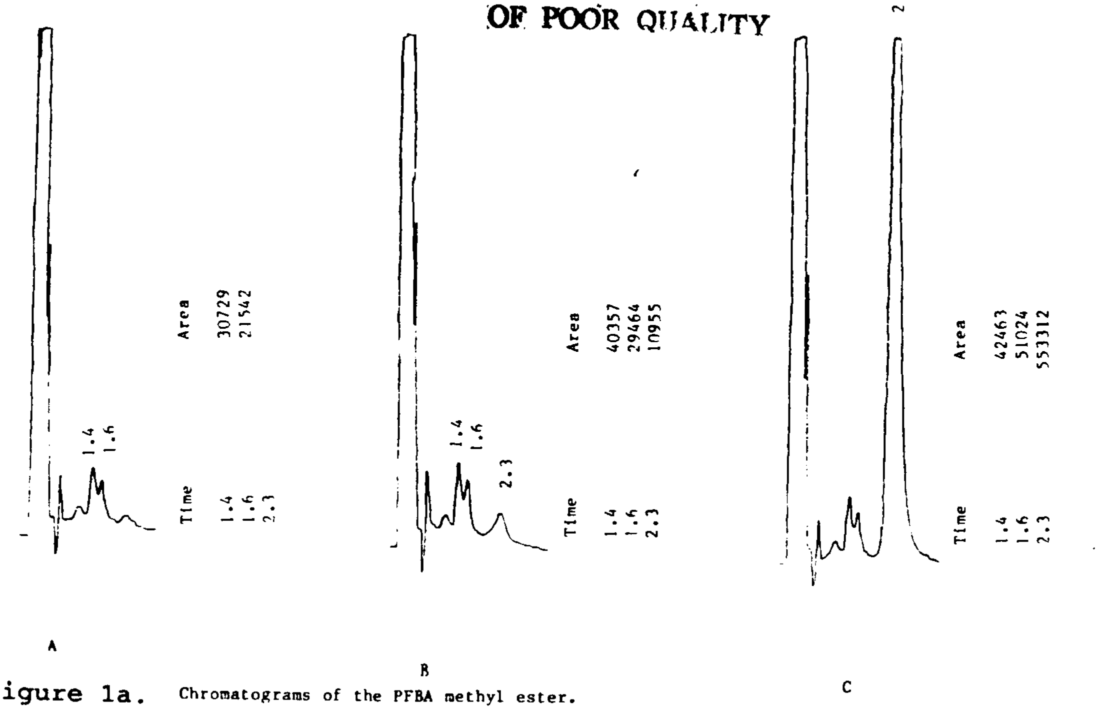


Figure 1a. Chromatograms of the PFBA methyl ester.
A. Blank, extraction of organic molecules from 1.66 ml tap water and subsequent esterfication.
B. Extraction of 1.7 ml of 10^{-7} mol/l PFBA in Hexane
C. Extraction of 25 μl of 10^{-4} mol/l PFBA in Hexane
2 μl injections. Column 4 % SE-30, 6 % OV-210 on 80/100 Chromosorb WHR. Column temperature 100 °C, flow rate 40 ml/min. The ester elutes at 2.3 minutes. Assuming 100 % yields and linear response the peak area on Chromatogram C should be 10 times that of Chromatogram B. The lower observed response in B is attributed to incomplete reaction of PFBA in presence of excess hexane.

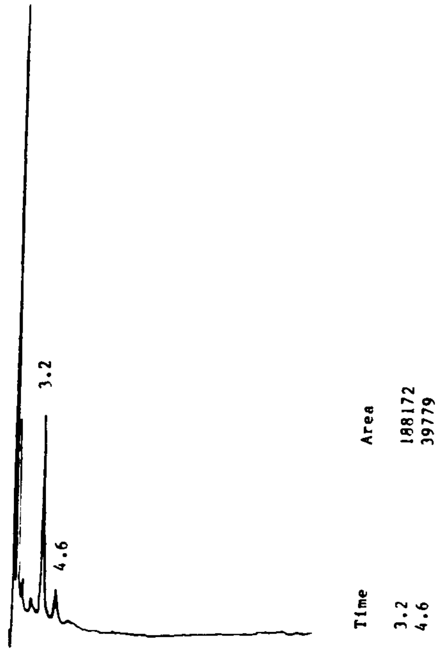


Figure 1b. Chromatogram of the PFBA pentafluorobenzyl ester. The ester elutes at 4.6 minutes. This sample does not show the interference described in the text since the solution is diluted down a factor of 10^3 after the reaction. The peak at 3.2 minutes is excess α-bromo pentafluorotoluene.
2 μl injection. Column 4 % SE-30, 6 % OV-210 on 80/100 Chromosorb WHR. Column temperature 160 °C, flow rate 40 ml/min.

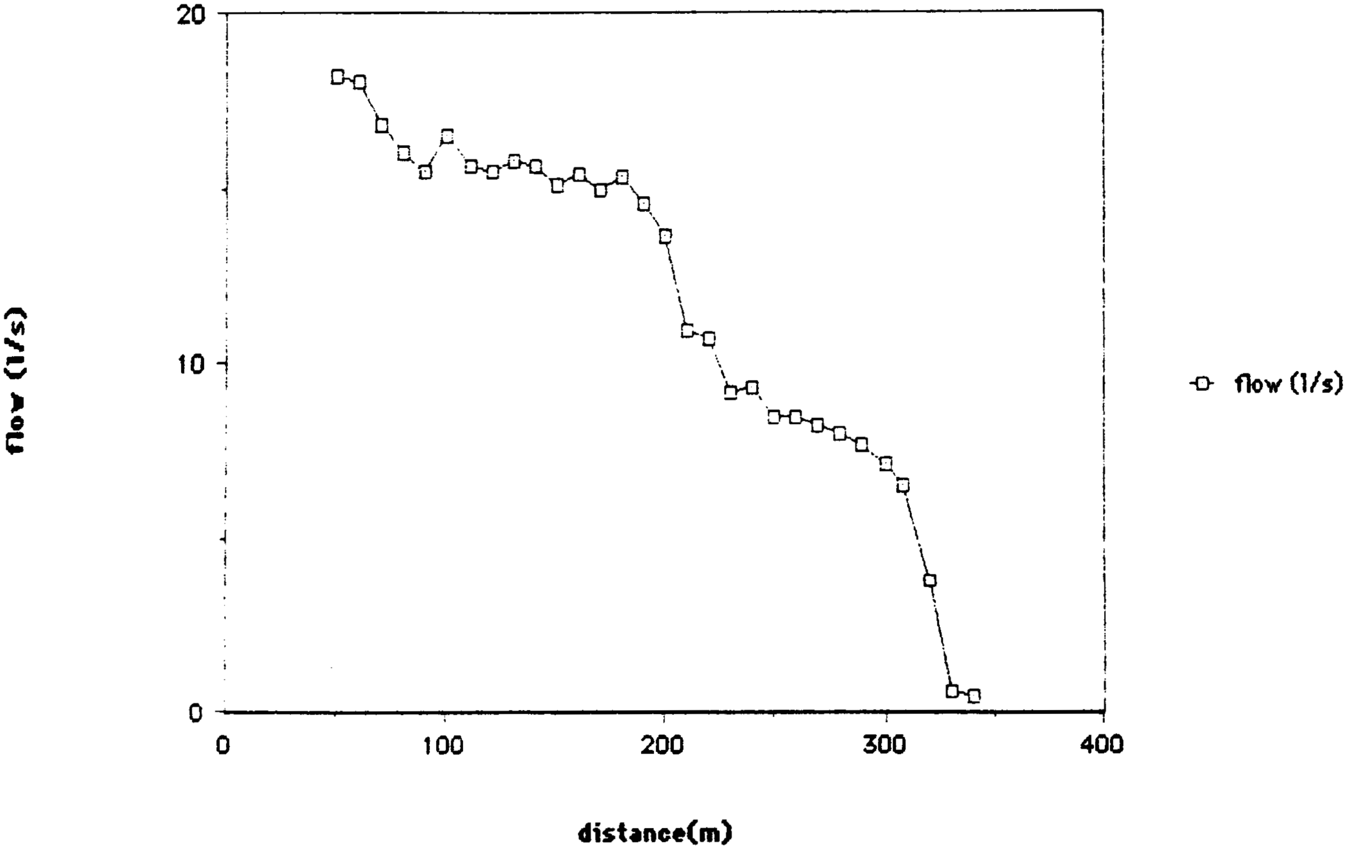


Figure 2. Flow of West Fork of Walker Branch, Oak Ridge Tn. during the tracer experiment. The flow is determined from the dilution of the tritium spike. The distance is measured upstream from a weir. The tracers were injected at 342 m.

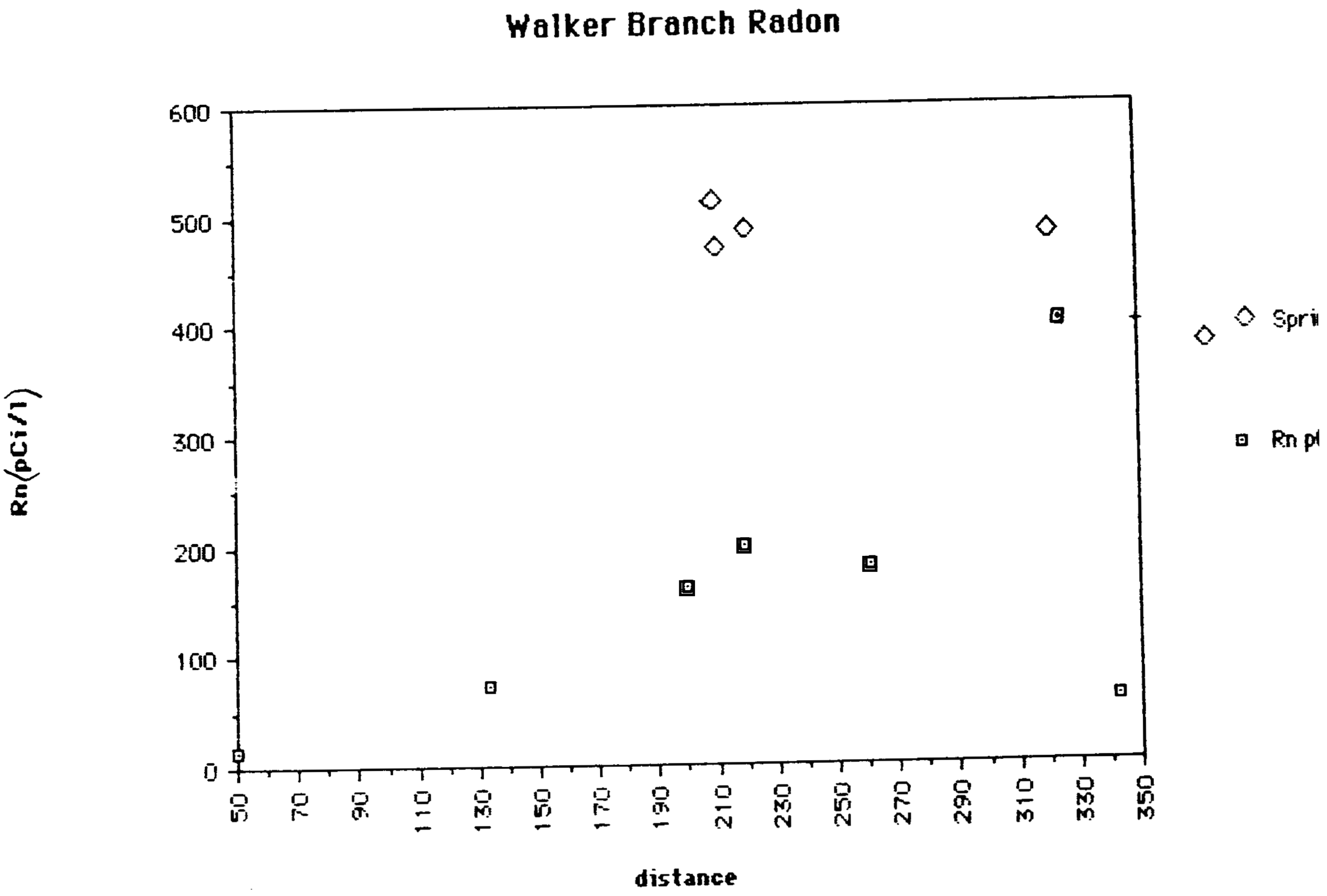


Figure 3. Radon concentrations in the stream. The concentrations increase at locations with high groundwater input.

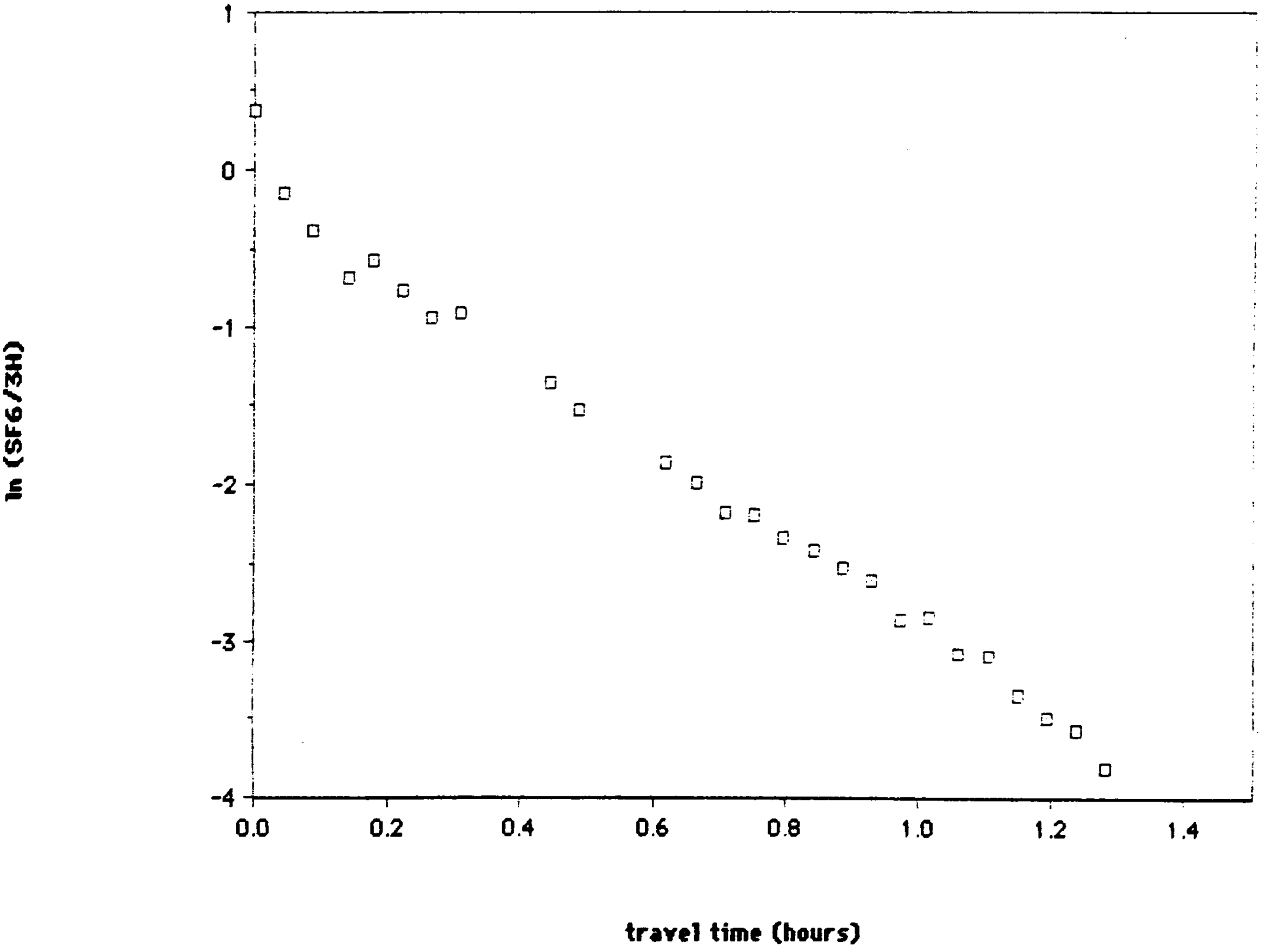
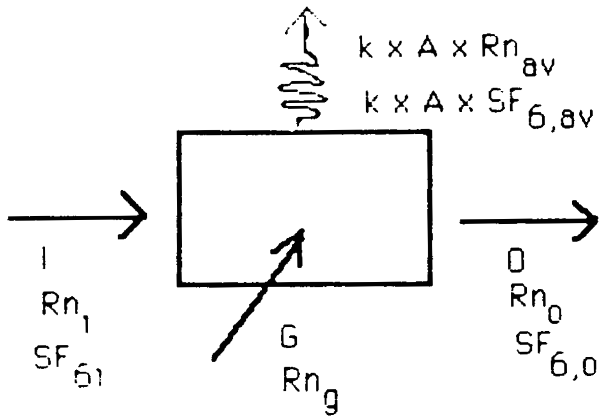


Figure 4. Change in ratio of SF_6 to tritium in the stream. From the slope of the line and the average depth, the gas exchange coefficient can be determined (see text). To obtain the travel time of a water parcel an average stream flow of 225 m/hr was used determined from the rate at which the front of the tracer patch moved downstream.



Flow balance $I + G = O$

Radon balance $I \times Rn_1 + G \times Rn_n = O \times Rn_n + k \times A \times Rn_{av} \times dt$

SF_6 balance $i \times SF_{6,1} = O \times SF_{6,0} + k \times A \times SF_{6,av} \times dt$

Figure 5. Diagram of how gas exchange coefficients can be determined using a gaseous deliberate tracer, such as SF_6 and radon.