

TITLE PAGE

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ABSTRACT

The program for International Collaboration on CO₂ Ocean Sequestration was initiated December 1997. Preliminary steps involved surveying a suite of biogeochemical parameters off the coast of Kona on the Big Island of Hawaii. The preliminary survey was conducted twice, in 1999 and 2000, to obtain a thorough data set including measurements of pH, current profiles, CO₂ concentrations, microbial activities, and water and sediment chemistries. These data were collected in order to interpret a planned CO₂ injection experiment. After these preliminary surveys were completed, local environment regulation forced moving the project to the coast north east of Bergen, Norway. The preliminary survey along the Norwegian Coast was conducted during 2002. However, Norwegian government revoked a permit, approved by the Norwegian State Pollution Control Authority, for policy reasons regarding the CO₂ injection experiment. As a result the research team decided to monitor the natural CO₂ flow off the southern coast of the Big Island. From December 3rd-13th 2002 scientists from four countries representing the Technical Committee of the International Carbon Dioxide Sequestration Experiment examined the hydrothermal venting at Loihi Seamount (Hawaiian Islands, USA). Work focused on tracing the venting gases, the impacts of the vent fluids on marine organisms, and CO₂ influence on biogeochemical cycles. The cruise on the *R/V Ka'imikai-O-Kanaloa* (KOK) included 8 dives by the *PISCES V* submarine, 6 at Loihi and 2 at a nearby site in the lee of the Big Island. Data for this final report is from the last 2 dives on Loihi.

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INTRODUCTION

World concern about the increase in atmospheric CO₂ has initiated investigation of a broad range of technologies for anthropogenic CO₂ sequestration. Currently, potential locations for CO₂ sequestration are in mines, forests and the ocean. The world's oceans are the largest potential sinks for deposition of anthropogenic CO₂. Work over the last few years has focused on laboratory and modeling efforts for CO₂ sequestration (Handa and Ohsumi 1995, Herzog, 1996; Omerod, 1997). Results from these efforts warrant field studies to validate and ground truth predictive data. The Project Agreement for International Collaboration on CO₂ Ocean Sequestration was initiated December 1997 to foster increased understanding of the ocean as a CO₂ sink. The initiation of the program was accomplished through a union of research efforts of laboratories from three countries; 1) Research Institute of Innovative Technology for the Earth (Japan), 2) the Norwegian Institute for Water Research (Norway); and 3) the Massachusetts Institute of Technology (USA). Recently, Canadian Institute of Ocean Science, the US Naval Research Laboratory and ABB Switzerland have joined this program. Permission to conduct this research off the coast of the Big Island and the western coast of Norway was requested denied. As a result of this regulation work on carbon sequestration was conducted at approximately 1300 m depth on Loihi, a new forming island off the coast of the Big Island. In the center of this region are active hot flows of dissolved CO₂ commonly referred to as dissolved inorganic carbon (DIC). The NRL Code 6114 contributions to this international project were; 1) measuring the impact of the DIC on the microbial production, and 2) coupling radiocarbon isotope measurements of the DIC with pH measurements to determine the region(s) most influenced by the venting activity.

EXPERIMENTAL

A. *PISCES V* and *RV KOK*

Ship board activity was on the *RV KOK*. This vessel was the support ship for the manned research submarine *PISCES V*. Eight dives were conducted during the research cruise. Loihi was visited 6 times and 2 control sites were sampled. The *PISCES V* was equipped with two mechanical arms for sampling. These were used to obtain sediment cores, manipulate Niskin bottles to collect water samples, and set and retrieve experimental cages. The submarine was equipped to navigate and measure salinity and temperature. The dive depths for this project on Loihi were characteristically 1360 m.

B. Radiocarbon Isotope Analysis

Radiocarbon isotope analysis ($\Delta^{14}\text{C}$) is calculated as:

$$d^n C = \left[\frac{R_s}{R_{std}} - 1 \right] \times 1000 \text{ (‰)}$$

where d^n is the radio carbon isotope ratio, R is the $^{14}\text{C}/^{12}\text{C}$ for radiocarbon, R_s is the sample ratio for the sample and R_{std} is the ratio for the standard, which is oxalic acid. Radiocarbon isotope analysis is used to determine a carbon source age and the relative input of thermogenic and new carbon sources to a variety of pools. Carbon derived from contemporary processes such as photosynthesis will have an abundant ^{14}C signature that is termed modern. At the sediment-water interface, mineralization of detrital organic material will introduce contemporary CO_2 into the water column. The $\Delta^{14}\text{C}$ signature of this CO_2 will be vastly different from thermogenic CO_2 which has no ^{14}C . This difference allows one to calculate the influence of vent gas to the total DIC sampled at the source and through the plume.

Radiocarbon is formed in the atmosphere when ^{14}N is altered by cosmic rays. Carbon that is isolated from contemporary biogeochemical cycling (i.e. in long-term sediment burial), will eventually become devoid of ^{14}C (which has a half life of 5370 years). As a result, $\Delta^{14}\text{C}$ of new organic matter recently produced in the ocean is greatly elevated relative to thermogenic carbon sources. In the ocean, $\Delta^{14}\text{C}$ ranges between approximately 100‰ and an undetectable value, near -1000‰. The wide range of dissolved organic carbon $\Delta^{14}\text{C}$ in the ocean is related not only to ocean-atmosphere coupling, but also to ocean circulation. Open ocean surface water $\Delta^{14}\text{C}$ range between -150‰ to -258‰. Deeper ocean water, below 1000 m, characteristically have $\Delta^{14}\text{C}$ that ranges between -393‰ to -525‰. A somewhat different range occurs for dissolved CO_2 , as reported in results of the World Ocean Circulation Experiment (WOCE) for the Pacific Ocean. In that work, the surface ocean waters have a $\Delta^{14}\text{C}$ range from about -50 to +150‰, while deeper waters below 1000 m have a range from about -160 to -220‰. These ranges still allow considerable resolution between the -1000‰ end member (geothermal CO_2) and typical deep ocean waters (-220‰ -525‰).

C. Bacterial Production

Bacterial productivity in seawater was determined by the leucine incorporation method (Kirchman et al., 1985) as adapted by Smith and Azam (1992). To convert the amount of ^3H -Leu incorporated into protein to bacterial organic carbon demand of the assemblage ($\text{g C mL}^{-1} \text{ h}^{-1}$), the formula of Simon and Azam (1989) was used:

$$\text{g C mL}^{-1} \text{ h}^{-1} = \left(\frac{\text{DPM}_{\text{sample}}}{\text{hr mL}} \right) \left(\frac{\text{mol leucine}}{\text{Y DPM}} \right) \left(\frac{2 \times 10^{17} \text{ Cells produced}}{\text{mol leucine}} \right);$$

$$\text{where Y} = \left(\text{specific activity} \right) \left(\frac{2.22 \times 10^6 \text{ DPM}}{\text{Ci}} \right)$$

We assumed a 20% metabolic efficiency, which is similar to that measured for low molecular weight organics in other aquatic systems (Bjornsen, 1986).

RESULTS AND DISCUSSION

A. Vent Plume Analysis

During the Loihi dives 7 and 8 water samples were taken with Niskin bottles for measurement of the pH and $\Delta^{14}\text{C}$ of DIC (Figure 1). Results through this sampling show a strong correlation between the pH and age of the carbon in the DIC pool. The oldest $\Delta^{14}\text{C}$ values were measured in the samples with lowered pH, taken at the mouth of the vent. The combination of data from the pH and $\Delta^{14}\text{C}$ in the DIC pool provides a good method to trace the region that is influenced by the thermogenic sources. Future work on this data set will provide a 3-D assessment to determine the volume of water that is impacted by this point source.

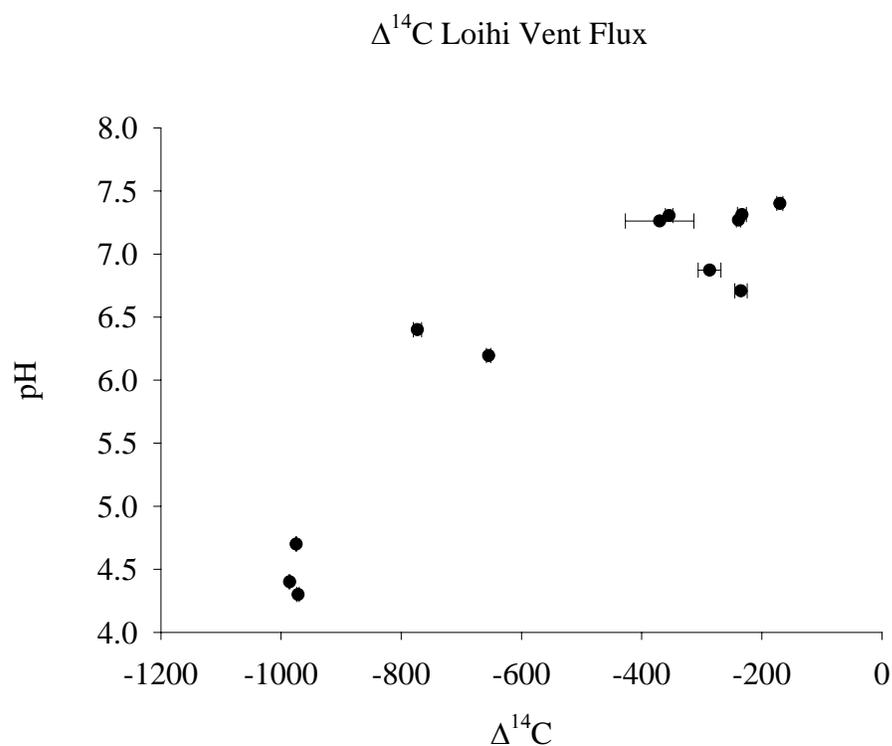


Figure 1: Samples for these data were taken from the mouth of a heat vent on Loihi. This figure compares $\Delta^{14}\text{C}$ relative to the Ph as the *PICSES V* maneuvered vertically from the vent.

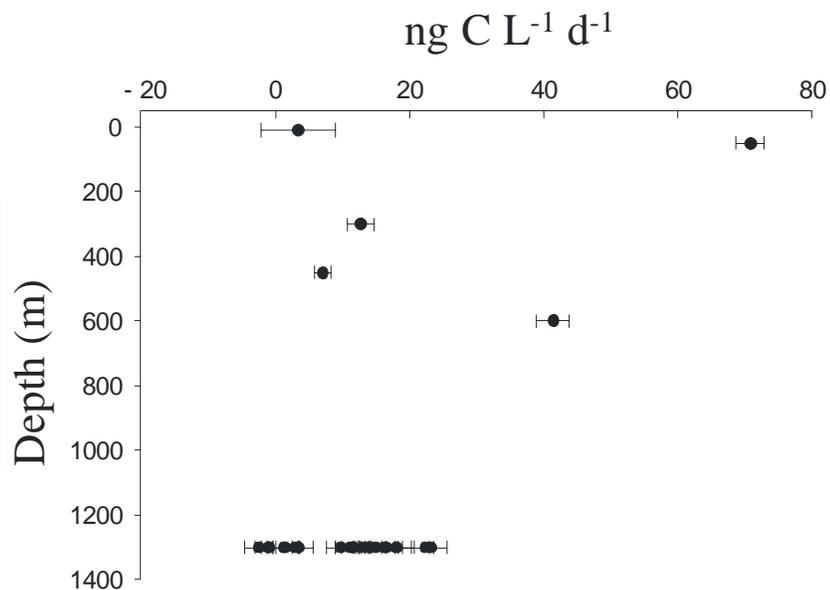


Figure 2: Two vertical profiles of bacterial production and analysis of deep ocean production measured with ^3H -leucine assimilation.

B. pH Influence on Microbial Production

During the *PICSES V* dives water column samples were taken vertically to determine the natural range in bacterial production (Figure 2). In the surface to 400m waters there was a large range in bacterial production from 0 to $70 \text{ ng C l}^{-1} \text{ d}^{-1}$. In the 1300 m water samples the bacterial production ranged from 0 to $22 \text{ ng C l}^{-1} \text{ d}^{-1}$.

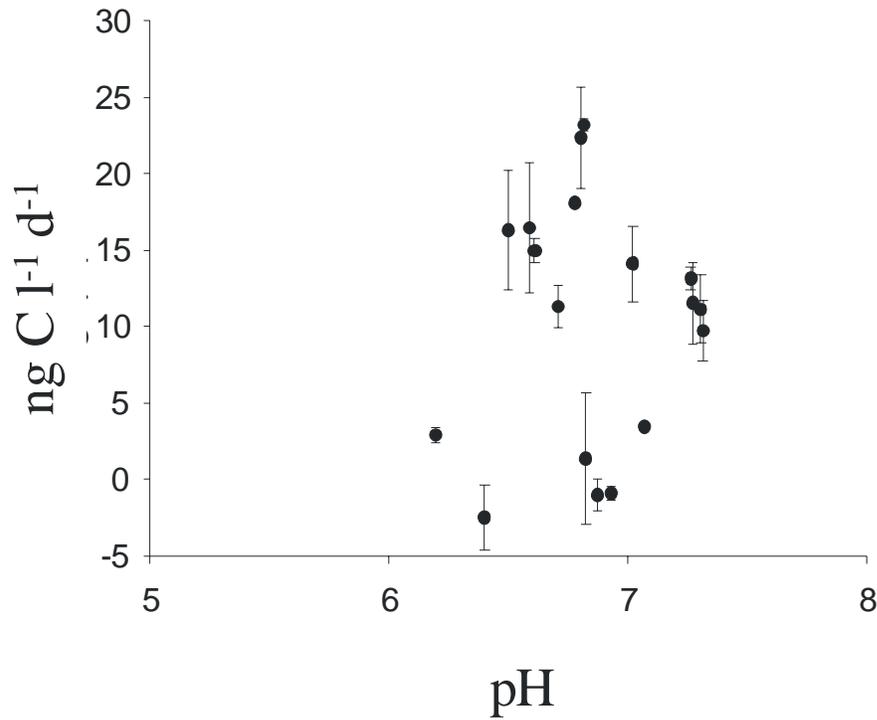


Figure 3: Bacterial production relative to pH for on samples taken as the PICSES V moved vertically from the mouth of the plume.

In the region of the CO₂ vents water samples were taken from the mouth of the plume and through 0.5-1.0 m vertical intervals. These samples were analyzed for pH and the bacterial production (Figure 3). Results indicate a moderate affect of the lower pH on bacterial production. However, similar production rates are observed at the higher pH values of 7.0 to 7.2.

CONCLUSIONS

Application of the $\Delta^{14}\text{C}$ analysis of the DIC in seawater provides valuable information on two research lines. First, the combination of $\Delta^{14}\text{C}$ and pH can provide the technology to map CO_2 release in experimental applications and definitively couple the change in pH to a particular source of CO_2 . With accurate mapping of region influenced by the CO_2 release, there can be a thorough evaluation for the impact to chemical cycles and biological activity. This analysis also shows the need for re-evaluating the mean ocean carbon age. Typically it is thought that the ocean carbon pool turnover is ~6000 years. If input of dead carbon through hydrothermal venting is significant ocean-wide, then the 6000 year turnover time is overestimated. Over the past couple of decades there has been a vast amount of ocean floor exploration. Many active hydrothermal sites have been discovered inputting thermogenic CO_2 . These sources, i.e. hot vents, cold seeps, mud volcanoes, etc., need to be integrated with the ocean carbon model relative to phytoplankton production and lateral terrestrial transport. Results of such an effort will assist in a more thorough analysis of the ocean carbon cycle and the prediction/modeling of global warming.

In the deep ocean bacterial activity is an important factor in the health of the ecosystem. A part of this community is responsible for remineralization of key elements (such as nutrients) needed by other components of the food web. Also in the deep sea environment chemo-autotrophic bacteria can be a key part of the food chain. In many of these systems there are large amounts of reduced compounds (methane, ammonium, and sulfide) that are oxidized by the chemo-autotrophs and result in carbon dioxide fixation. This provides the first step in the food chain for energy. As a result of the importance of the microbial community on ecosystem health we chose to monitor the impact of pH during the dives on Loihi. Results from the bacterial production do not show a strong relationship with the variation in pH (Figure 3). While there was some indication of inhibited production at the lowest pH levels, similar results were observed at a range in pH of 7.0 – 7.2. This variation may be a factor of the growth phase of the sampled bacteria. Studies have shown that a natural bacterial population transitions from a rapid growth until the maximum carrying capacity (K_m) is met. When the growth rate slows at the K_m , bacteriovore grazing reduces the population and the bacterial growth rate accelerates again. Another consideration in this analysis is that with long term low pH the bacterial community at Loihi has adapted and is not inhibited. This work is a valuable study for understanding the impact of carbon sequestration. Future work needs to combine field and laboratory experiments.

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