Beryllium-7 Analyses in Seawater by Low Background Gamma Spectroscopy

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Oceanographers use the cosmogenic radionuclide $^{7}Be(t_{1/2}$ 53 days) as a tracer for atmospheric input and a conservative tracer of mixing in the open ocean. This paper elucidates a method for improving the analysis of ^{7}Be from seawater. The scavenging efficiency of $Fe(OH)_3$ for each sample is measured by ICP-MS using stable ^{9}Be as a yield monitor. Samples are gamma counted in a large diameter (28mm) well detector. The high purity germanium well detector is coupled with an active anti-coincidence cosmic guard to reduce the spectra background. The improved overall accuracy of the method and lower detection limit of the detector results in a lower volume of seawater needed for analyses. Results will be shown from a study of ^{7}Be in the Sargasso Sea.

Introduction-^{7}Be

^{7}Be is a cosmogenic isotope produced in the stratosphere and troposphere. ^{7}Be has a half-life of 53.4 days and decays to ^{7}Li emitting a 477 keV gamma line with a branching ratio of 0.104. It is predominantly washed out of the atmosphere through wet deposition. It is a tool for oceanographers to study air sea interaction and water mass mixing. Beryllium's largely non-reactive nature in the open ocean makes it an excellent conservative tracer. Its conservative nature and extreme dilution in seawater also makes it difficult to concentrate and analyze. Early experiments at WHOI with $Fe(OH)_3$ cartridges to directly collect ^{7}Be by insitu underwater pumps proved ineffective. Collection efficiencies of the cartridges were too low to be consistently useful. At sea chemistry of whole water samples became the method of choice. The use of stable ^{9}Be as a yield monitor further improved the accuracy of the procedure. The method was optimized at WHOI in 2005 using a seawater line that enters WHOI's coastal research lab. The procedure was then used on an oceanographic cruise on the R/V Oceanus out of Bermuda in the oligotrophic Sargasso Sea.

Introduction-Gamma

In the field of environmental radioactivity, analysis by gamma spectroscopy is advantageous for its non-destructive nature and multiple isotopes lines generated in each spectrum. Well detectors are also advantageous for the improved counting efficiency. Environmental level analyses often involve very low activities. When using a well detector one can increase the sensitivity by either increasing the sample size, using a larger well within the crystal or lower the detector's background thus increasing MDA (the minimum detectable activity). Our hope was to come up with low cost modifications and additions to a commercial HPGe (high purity germanium) well gamma detector to increase its sensitivity by both increasing sample volume and lowering the background.

Experimental-Gamma

We are using a "U" style Canberra high purity germanium closed-ended coaxial gamma detector with a custom well size (28mm diameter, 40mm depth) model #GCW4023S. It is factory specified as having a relative efficiency of 40%. This well is five times larger than the standard Canberra well (34.5cL vs. 6.4cL). This is a significant improvement in itself. There is a slight loss of efficiency for higher energy photons as there is less germanium to interact with.

Cosmic radiation, mostly muons and neutrons, are the main contributors to germanium detector's background.[2] The cosmic radiation interacts with the lead shielding to produce the continuum seen in the germanium gamma spectrum. Increasing the lead shielding thickness does not lower the background past an optimum thickness of 15cm.[4] While additional lead may shield out local sources of gamma background it will increase

the amount of cosmic radiation interactions and the instrument background. The materials that end up on the inside of the shielding must be judiciously chosen. The use of lead depleted in ^{210}Pb, placed adjacent and inside the regular lead shielding is recommended. Also recommended in some applications is a thin layer of pure cadmium and electroplated pure copper. The Cd and Cu absorb lead X-rays, but if these X-rays do not interfere with the researcher's gamma work then lower backgrounds will be achieved by not installing them. These pure Cu, Cd and depleted Pb materials are hard to find in small quantities and expensive, therefore, we did not use them with this instrument.

Beyond the lead shielding to lower the cosmic radiation induced background there are two basic solutions: increase the overburden above the detector or use an active anti-coincidence guard. The expense of locating a detector system underground is prohibitive for many researchers but it is the most effective. We have located our detector on the ground floor of our research building gaining a small benefit from the three floors of cement above. The best anti-coincidence gamma detectors are surrounded on all sides of the detector and lead shielding with active anti-coincidence units.[4, 5] We assume that more than 1/6th of all cosmic radiation enters the system from above; therefore, we installed a single large fast plastic scintillation shield (80cm x 80cm x 5cm, Bicron BC408 Newbury, Ohio, www.bicron.com) above the gamma detector. This fast plastic scintillation sheet has a few advantages over a proportional detector. There is no counting gas required, it may be lighter, it can be sized easily from the manufacturer to meet the experimental design and it can be purchased with the photo multiplier hardware pre-installed.

Ametek-Ortec supplied the timing design and the timing electronics. The signal from the fast plastic scintillator must be delayed to match the signal from the germanium crystal. Then an appropriate timing window must be experimentally determined which is long enough to veto the errant signal but not so long as to increase the dead time of the detector.

Radon is by far the largest radioactive component in ambient air at a concentration of about 40 Bq m^{3}.[2] Modern germanium detectors can be purchased with a nitrogen gas flushing system. These flushing systems overpressure the detector chamber with nitrogen gas boiled off from the liquid N_2 (LN_2) but each time the chamber is open ambient air is allowed back in. We designed our system with a Plexiglas glove box enclosure around the lead shielding. It has airtight side chambers to introduce and remove samples without opening the whole system to ambient air. The 2 liters of LN which boil off each day from the dewar produces more than 1400 Liters of pure nitrogen gas daily. This nitrogen gas is captured at the top of the dewar and ducted into the Plexiglas box. There are two gloves for manipulating the shield door, changing samples and moving racks of samples in and out of the antechambers. There are also shelves inside to store counted and uncounted samples. Figure 1 shows the Bicron fast plastic anti-cosmic guard sitting on top of the nitrogen gas enclosure. Figure 2 shows the schematic diagram for the detector, the cosmic guard and the timing electronics. This diagram was developed by Ametek-Ortec.

Experimental-^{7}Be

200 liters of unfiltered seawater are collected from niskin bottles, deck hose or ship's clean water intake into a plastic barrel. 1 mL of stable ^{9}Be is added as a yield monitor at a concentration of 10000ppm. This is mixed with the seawater and a 1mL aliquot is taken and stored in a 60mL polybottle. To precipitate both the ^{7}Be and ^{9}Be a 100mL $FeCl_3$ solution (121g of $FeCl_3$ in 500mLs of 1N HCL) is added and mixed with the seawater. A flock of $Fe(OH)_3$ is formed by raising the pH to 8-8.5 with 50% NH_4OH. An aquarium air bubbler mixes and aggregates the $Fe(OH)_3$ overnight, improving the Be scavenging. The seawater is then pumped through a 10" 1μM cutoff polypropylene Hytrex cartridge filter into a second container. A second 1 mL aliquot of filtrate is taken and stored in a second 60ml polybottle. These two aliquots are returned to the lab, weighed, diluted with 50mL 5% HNO_3 and a 1ppb Indium standard, and reweighed. A 2 mL aliquot of this is taken and placed in an ICP-MS autosample vial. After ICP-MS analysis for ^{9}Be, the equation 1-(B/A) gives the collection efficiencies for ^{7}Be with $Fe(OH)_3$ on the Hytrex cartridge. The high throughput and autosampling feature of today's ICP-MS allows a researcher to analyze greater than 50 samples of ^{9}Be in a day.

Experimental results from the cruise gave individual collection efficiencies averaging 79%. Figure 3 plots the collection efficiencies for the Sargasso Sea cruise. Individual analysis of ^{9}Be on the ICP-MS yields a collection efficiency for each sample, thus providing a more accurate ^{7}Be concentration per sample than using an average efficiency.

The ^{7}Be is analyzed after the Hytrex cartridge is ashed in a muffle furnace at 440° C for six hours. This removes the polypropylene and leaves the $Fe(OH)_3$ to be gamma counted for the 477 KeV photon from the decay of ^{7}Be. The large volume germanium

well detector has an efficiency of 10.4% to 15.2% (depending on sample volumes which range between 10mLs and 20mLs) at 477keV.

Results and Discussion-Gamma

Figure 4 shows the comparative background spectra of an HPGe detector without shielding on the 4th floor and ground floor of a cement building at WHOI. The 3+ feet of accumulative reinforced concrete flooring increases the shielding effect of cosmic radiation. Locating HPGe detectors as deep in a building as possible is the least expensive way to lower a detector's background. Figure 5 is a comparative four-day background spectrum of our HPGe with the cosmic guard enabled and disabled. Figure 6 shows the percent improvement over different segments of the gamma spectra using the cosmic guard. An approximate improvement of 35% is shown between 30-1200 keV with no noticeable increase in dead time.

With the use of a N_2 radon reduction box, a small but noticeable reduction in the background was observed. This small change matches the data from a 500m water equivalent depth instrument where testing showed only 3% of background comes from Rn and daughters.[3]

Conclusions-Gamma

The results from this experimental setup lead to the following conclusions:

1) Relocation of HPGe detectors to the lowest floor possible results in a cheap and easy reduction in background.

2) If a new well detector is to be purchased and samples of more than 5 mLs are to be analyzed, a larger well will greatly increase the signal and have a minimal effect on low energy efficiency.

3) For $10,000 to $15000 the cosmic guard and associated timing electronics can be purchased to lower the background further by 35%.

4) Reductions in radon and daughter's backgrounds are too low to be worth making a significant investment on or our experimental setup was insufficient to realize more substantial reductions in background.

Results and Discussion-^{7}Be

Figure 7 shows an expected ^{7}Be gradient in seawater and the processes that impact its vertical distribution. Figure 8 shows a vertical four-point profile taken 22 July 2005 in the Sargasso Sea where the mixed layer was approximately 2 to 5 meters. The samples were collected and processed from the CTD rosette niskins the same day. The total errors reflect eight to eighteen-hour counts done 23 to 25 days post-sampling. This figure demonstrates this methods accuracy in open ocean ^{7}Be measurements below the mixed layer. To test whether or not ^{7}Be is associated with marine particles, approximately 1000L of seawater was pumped through a 1μm Hytrex filter from a depth of three meters, to collect particulate matter. The ashed sample had a ^{7}Be activity below the detection limit of the gamma detector, indicating that ^{7}Be remains in the dissolved phase while in the oligotrophic waters in the Sargasso Sea and can therefore be used as a conservative tracer.

Conclusions-^{7}Be

^{7}Be can be used as a conservative tracer because it does not have a strong affinity for particulate matter in oligotrophic waters. ^{7}Be activities can be used to determine the vertical diffusivity (Figure 7). Due to the short half-life of 53.3 days it can be used to determine vertical diffusivity over a seasonal timescale. The values of K_z can help

determine whether the diapyncal diffusivity of nutrients is a significant source of nutrients to the euphotic zone. The diapyncal flux of nutrients into the euphotic zone is determined by multiplying the vertical diffusivity values obtained from the ^{7}Be profiles by the nutrient gradient (Figure 7).

The volume of seawater sample necessary for this method can be 200 liters, which is considerably less than prior studies.[1] As such, the typical oceanographic ship's CTD rosette can be used to collect seawater from a single depth in one cast. The use of stable Be as a yield monitor also saves one from radiological usage issues at sea or in the lab. The deck sample collection and processing only requires some basic reagents and a simple filtration rig.

The sample preparation for the ICP-MS is straight forward in this method. The aliquot must be diluted by weight so the salts do not interfere with the introduction of the sample to the ICP-MS and Indium is added as a secondary yield monitor. There are no chemistry or purification steps necessary. It takes one day of sample preparation and one day on the ICP-MS to analyze more than 50 ^{9}Be samples for final yield, which is a key step in the accurate determination of ^{7}Be in seawater by this new method.

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References

1. D. Kadko and D.Olson, Deep Sea Research I, 43, (1996) 89-116

2. G. Heusser, Annu.Rev.Nucl. Sci. 45 (1995)543-590

3. R. Wordel et al. Appl. Radiat. Isot. Vol. 47 9/10 (1996) 1061-1067

4. P.Povinec et al. MARC V Journal of Radioanalytical and Nuclear Chemistry Vol. 3 248(2001) 713-719

5. J. Laurec et al. Nuclear Instruments and Methods in Physical Research A369 (1996) 566-571

Figure Page

Figure 1. Front view and side view of cosmic guard, N_2 box and detector. The two upper circles on the front view are the glove ports. The nitrogen gas line connecting the dewar and the detector chamber in the side view.

Figure 2. Diagram of delay timing.

Figure 3. Collection efficiencies for ^{7}Be in seawater on R/V Oceanus cruise July 2005.

Figure 4. Comparison one-hour spectra of unshielded HPGe on the 4th floor and ground floor of WHOI building.

Figure 5. Comparison spectra of four-day background count with cosmic guard disabled (upper) and enabled (lower).

Figure 6. Spectral comparisons broken into energy regions.

Figure 7. Steady State conditions assumed, ^{7}Be atmospheric input is from the top down and is lost only by decay, therefore ^{7}Be can be used as a conservative tracer. The vertical diffusivity diagram is shown along with the nutrient flux. By determining the K_z value and multiplying it by the nutrient gradient, the nutrient flux to the euphotic zone can be determined.

Figure 8. ^{7}Be depth profile, 22 July 2005, R/V Oceanus

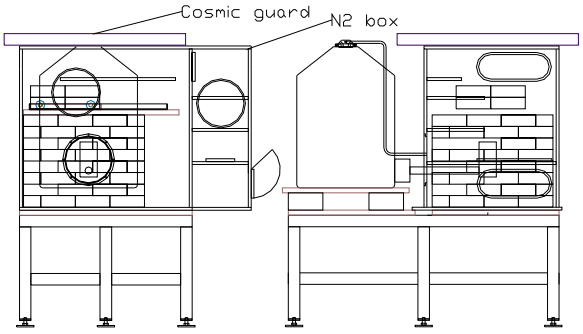

Figure 1.

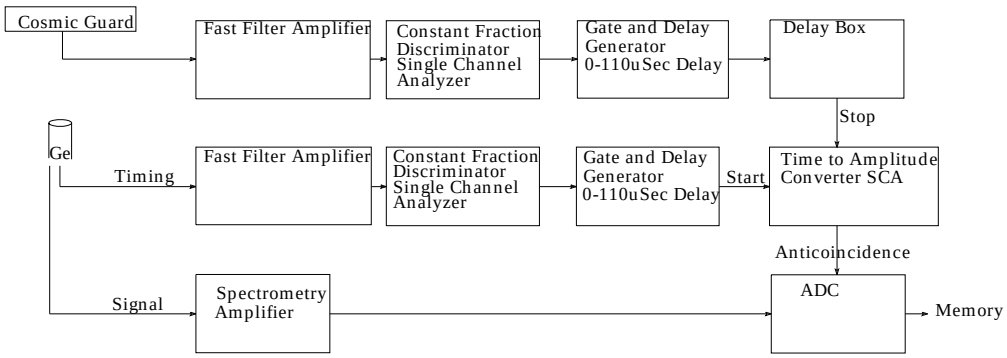
Cosmic Guard
Fast Filter Amplifier
Constant Fraction Discriminator Single Channel Analyzer
Gate and Delay Generator 0-110uSec Delay
Delay Box
Stop
Ge
Timing
Fast Filter Amplifier
Constant Fraction Discriminator Single Channel Analyzer
Gate and Delay Generator 0-110uSec Delay
Start
Time to Amplitude Converter SCA
Anticoincidence
Signal
Spectrometry Amplifier
ADC
Memory

Figure 2.

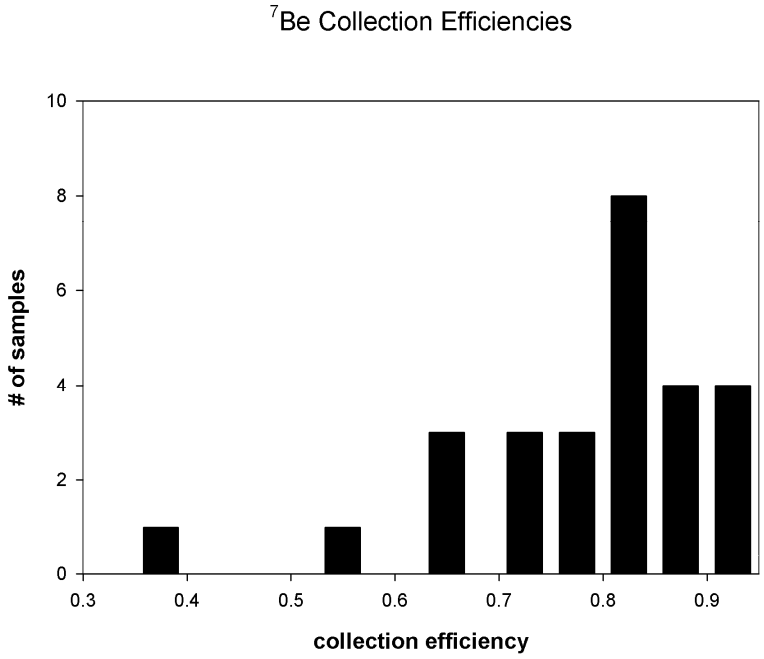
^{7}Be Collection Efficiencies
# of samples
collection efficiency
0
2
4
6
8
10
0.3
0.4
0.5
0.6
0.7
0.8
0.9

Figure 3.

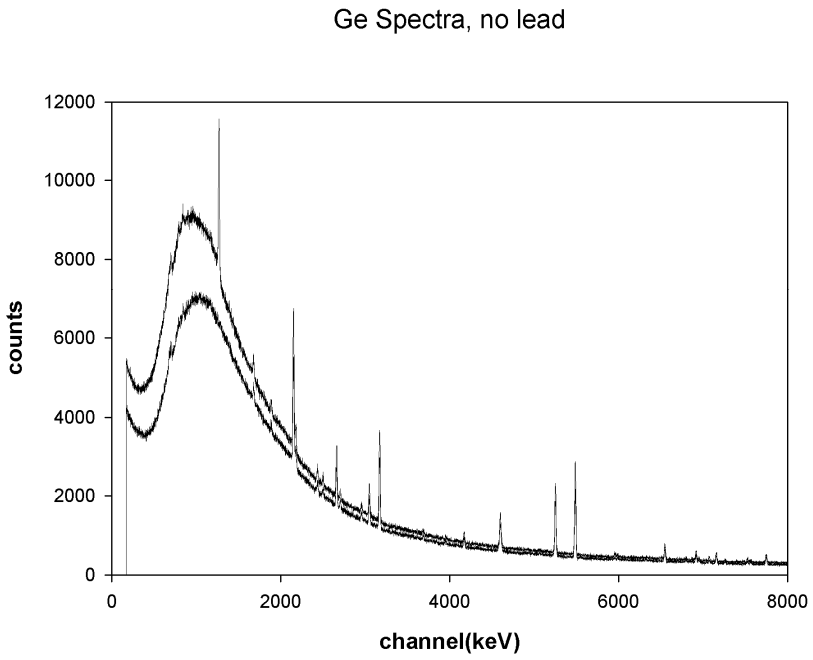
Ge Spectra, no lead
12000
10000
8000
6000
4000
2000
0
counts
0
2000
4000
6000
8000
channel(keV)

Figure 4.

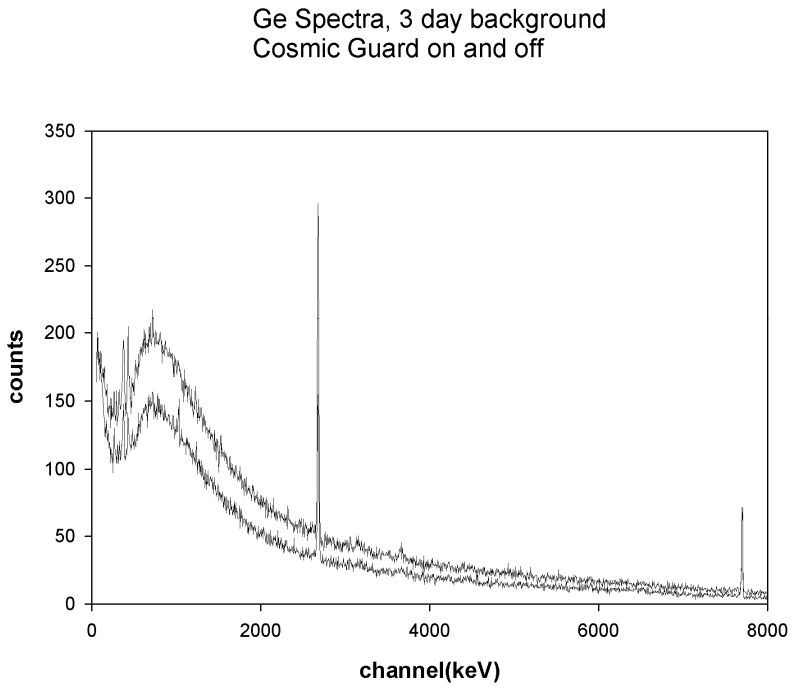
Ge Spectra, 3 day background
Cosmic Guard on and off
350
300
250
200
150
100
50
0
counts
0
2000
4000
6000
8000
channel(keV)

Figure 5.

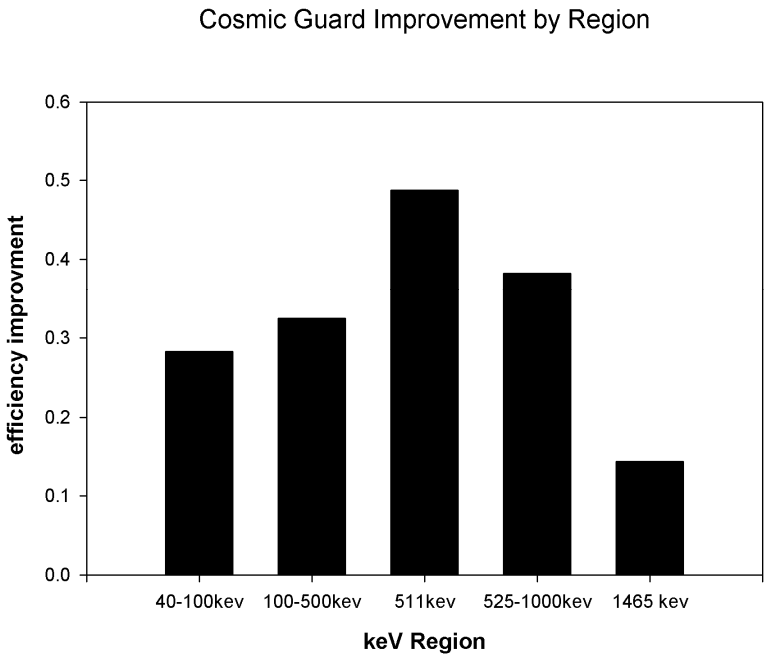
Cosmic Guard Improvement by Region
efficiency improvment
0.6
0.5
0.4
0.3
0.2
0.1
0.0
40-100kev
100-500kev
511kev
525-1000kev
1465 kev
keV Region

Figure 6.

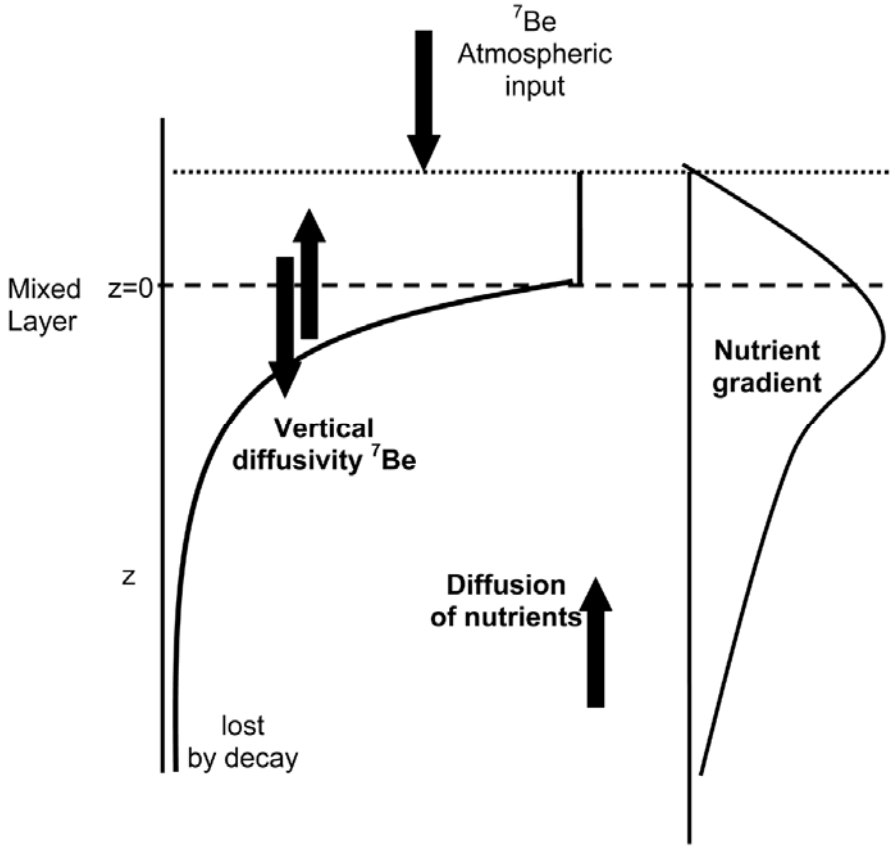
^{7}Be
Atmospheric
input
Mixed
Layer
z=0
Vertical
diffusivity ^{7}Be
Nutrient
gradient
z
Diffusion
of nutrients
lost
by decay

Figure 7.

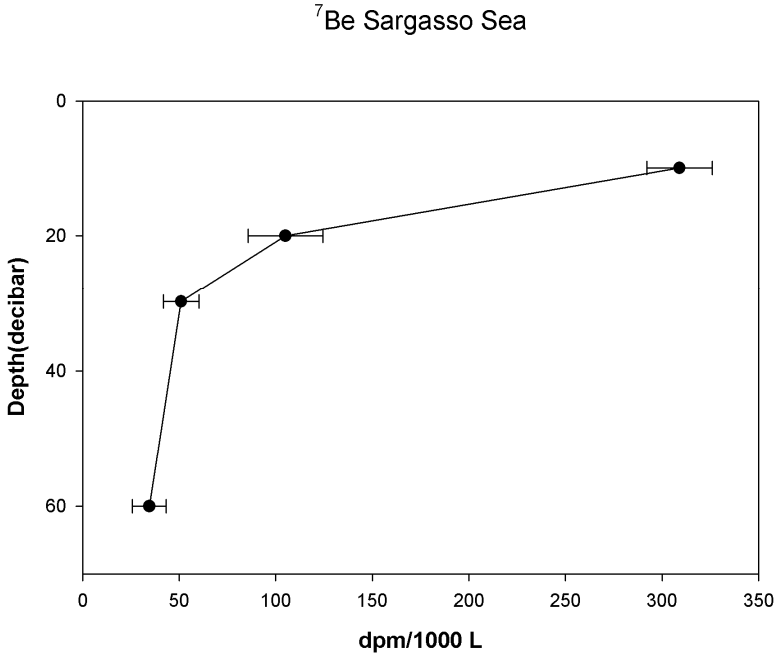
^{7}Be Sargasso Sea
Depth(decibar)
0
20
40
60
0
50
100
150
200
250
300
350
dpm/1000 L

Figure 8.