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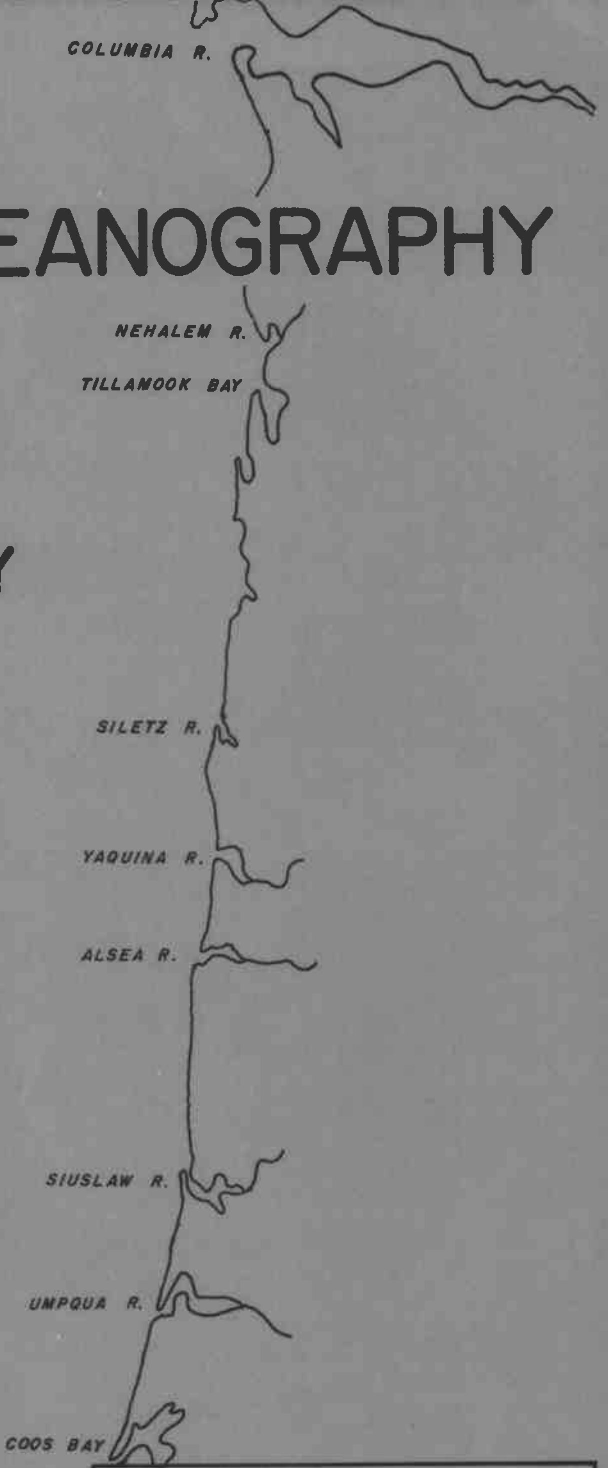

PROGRESS REPORT

# Ecological Studies of Radioactivity in the Columbia River Estuary and Adjacent Pacific Ocean

**Charles L. Osterberg, Principal Investigator**

Compiled and Edited by
**James E. McCauley**

Atomic Energy Commission
Contract AT(45-1)1750
RLO-1750-8

Reference 66-8
**1 July 1965 through 30 June 1966**

# ECOLOGICAL STUDIES OF RADIOACTIVITY IN THE COLUMBIA RIVER AND ADJACENT PACIFIC OCEAN

Compiled and Edited by
James E. McCauley

| | |
|---|---|
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# ACKNOWLEDGEMENT

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# ECOLOGICAL STUDIES OF RADIOACTIVITY IN THE COLUMBIA RIVER ESTUARY AND ADJACENT PACIFIC OCEAN

## I. INTRODUCTION

by Charles L. Osterberg

It is possible to divide our research effort into two parts -- the Columbia River Estuary and the Northeastern Pacific Ocean. The division, though an artificial one, is easy to make since the former investigation is carried out from small boats (up to 32 feet) while the latter requires a full-fledged oceanographic effort. Our report recognizes these two environments. However, it is becoming increasingly apparent that the research efforts in both areas pertain to the same problem and reinforce one another. Thus the radionuclides which are least affected by mechanisms of uptake or removal in the estuary are those which appear in the ocean water at the greatest distance from the river's mouth. Noteworthy examples of these are $^{51}$Cr, which we have successfully measured in surface sea water some 525 km southwest of the mouth of the Columbia (see reprint from Science included in this Progress Report pp. 213), and $^{124}$Sb, which, perhaps, is subject to even fewer losses in the plume. The improvements in $^{51}$Cr yield brought about by refinements in chemical separation by Cutshall et al. (see reprint included herein, pp. 216) offer little hope for higher yields of $^{124}$Sb. However, other steps are being taken to increase our counting sensitivity for this radionuclide.

The possibility of using the known half-life of a gamma emitter as a timing device is also recognized in our oceanic biological studies. For example, Carey hopes to relate the radioactivity of benthic animals to the changes in radioactivity in surface water due to seasonal injections of Columbia River water into the area. If the $^{65}$Zn in benthic animals varies in response to the plume, any lag occurring could be attributed to the time required for the $^{65}$Zn to penetrate to the depth of the animals, thus affording a rate of vertical (downward) transport.

A refinement of this technique is introduced by Pearcy, working with vertically migrating species of nektonic animals. Animals collected from discrete depths are being analyzed for both $^{65}Zn$ (gamma ray spectrometry) and total zinc (atomic absorption spectrometry). Animals in equilibrium (with regard to both $^{65}Zn$ and total Zn) with surface waters should have a maximum specific activity ($^{65}Zn$: total Zn), but this ratio should decrease with time. The lower specific activity of animals taken at depth should give a clue to average time involved in the vertical transport of the $^{65}Zn$. The use of specific activity makes it possible to compare animals with a great affinity for zinc on the same scale as those with a small affinity for zinc.

The work by McCauley on the systematic and ecological structure of benthic populations is essential for the understanding of the role of bottom organisms in the food chains of the sea. The echinoderms constitute a major part of the larger invertebrate epifauna on the ocean floor and systematic and distributional studies on this group are under way with a paper on the Echinoidea almost completed. Studies on the food habits of benthic animals, especially of the fishes, progress slowly because the stomachs of many benthic animals are empty. Careful searching, however, gives some clues to possible diets. In the fish genus Coryphaenoides, which is the dominant fish of the continental slope and adjacent ocean floor, pressure decreases cause most to evert their stomachs when brought to the surface. Yet, careful looking has produced evidence which indicates that these benthic fishes migrate upward to feed on pelagic organisms in the water column. This method of feeding may hasten the passage of radionuclides as well as stable elements to the bottom.

The contributions made to our program by Park will become more apparent after a year or so, since these efforts are of recent origin. The need for a careful measurement of a number of environmental variables possibly affecting estuarine organisms was brought to light by Haertel (AEC Rept. 65-14 p. 3-38, 1965). Changes in population sizes of several orders of magnitude occurred without obvious reasons. Having concurrent nutrient data along with our biological collections should help us sort out the more important variables influencing animals in the estuary.

Our efforts in the estuary have been substantially increased in the past year, largely because more of our graduate students are pursuing theses research there. While each student necessarily chooses a fairly narrow area for study, these "pieces" can be ultimately assembled into a more meaningful whole.

The progress report that follows includes research results ranging from unproved ideas to scientific papers published during the tenure of this contract. The end of the contract year finds the several facets of our work in various states of preparation; therefore, the reader is cautioned that all except the finished papers are subject to revision before being presented for publication.

## R/V SHOSHONE: NEW VESSEL FOR ESTUARINE WORK

In December 1965 the 32-foot towboat SHOSHONE (Fig. 1) was acquired from the U.S. Corps of Engineers, Walla Walla, Washington, and was outfitted for work in the lower Columbia River. This steel boat is powered with twin 250 H.P. Chrysler gasoline engines, and cruises at about 17 knots. It has an 11-foot beam and draws about 30 inches, making it ideal for use in the estuary. The stern working area of 132 square feet has an 8-foot high A-frame for handling sampling gear (Fig. 2). The boat has a hydraulic trawl winch capable of pulling 5 tons and a small 12-volt hydrographic winch (Fig. 3). A 75-watt radiotelephone and Heathkit depth finder have been installed. A galley contains a small plastic sink and stove. The bilge pump was replaced and a gas detector installed for safety. Additional storage compartments are planned for the hold and cabin. At the present time the SHOSHONE is being used in the lower Columbia estuary near Astoria for these AEC sponsored projects: a study of fish populations and hydrography by Norman Kujala, and chemical interactions of river water with sea water by Norman Cutshall.

It is also used in support of theses research for the following students: Lynn Buffo (solvent extraction of Zn); William Renfro (radioecology of a slough of the estuary); C. David Jennings ($^{55}$Fe studies); Ford Cross (benthic amphipods); David Tennant (cycling of $^{51}$Cr and $^{54}$Mn in *Cancer magister*); Lois Haertel (plankton-radioactivity relationship); John Cronin (dissolved organics); Larry Frederick (physical oceanography); and Peter Hanson (sediment-turbidity-radioactivity relationships).

Dr. Osterberg is in charge of the estuarine research. Mr. Kujala is in charge of boat operations and field collections.

Figure 1. R/V SHOSHONE.

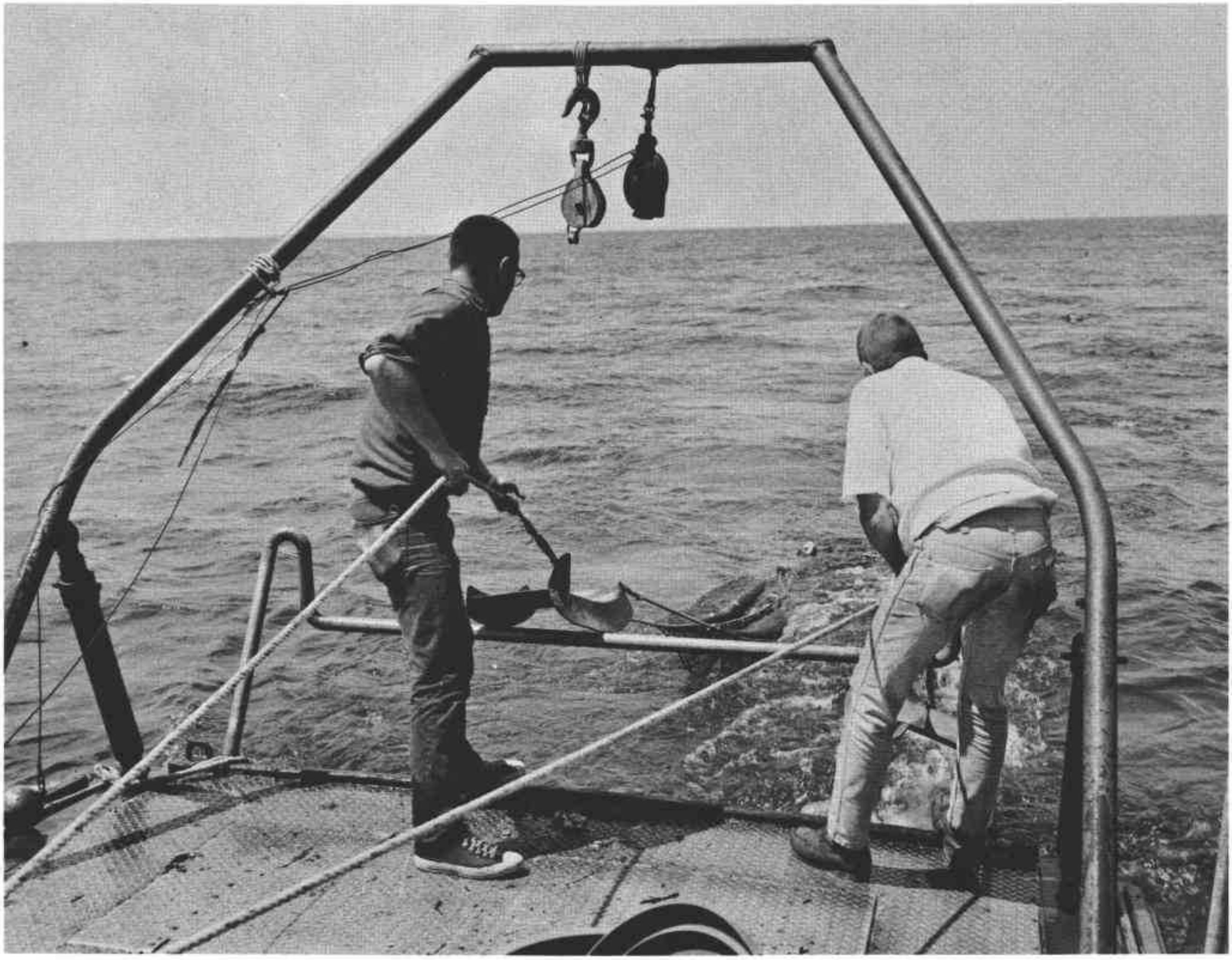

Figure 2. After working deck.

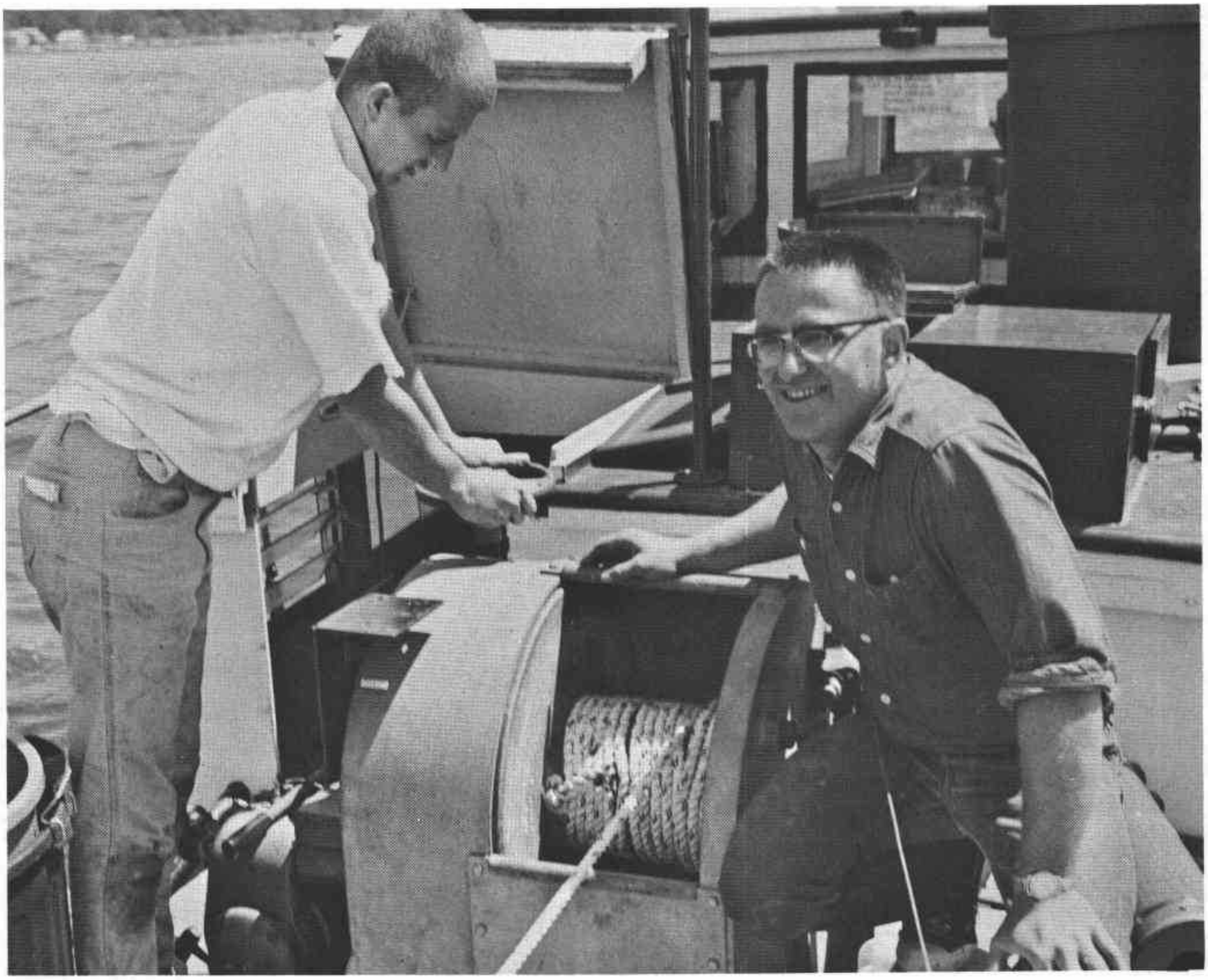

Figure 3. Trawl winch.

# COUNTING PROCEDURES

by Ingvar L. Larsen

During the 11-month period 1 July 1965 to 1 June 1966 approximately 1905 samples were counted. These can be subdivided as follows:

| | |
|---|---|
| Benthic Studies | 355 |
| Nekton Studies | 475 |
| Estuary Studies | 175 |
| Thesis and Experimental Laboratory Studies | 900 * |
| | 1905 |

* (54% 100 min. counts,
19% 400 min. counts,
26% 10 min counts).

Samples were counted in one of two 5 x 5-inch NaI(Tl) well crystals, each connected to a 512 multichannel analyzer (Nuclear Data, series 130). A few samples, because of their large liquid volume, were analyzed on top of a 3 x 5-inch solid NaI(Tl) crystal.

Samples were usually counted for 100 minutes with exceptions made for those that were anticipated to be of lower activity. In this case counting time was extended to 400 minutes. Samples containing tracer radionuclides used in laboratory experiments were of higher activity and were therefore counted for a shorter time interval, usually 10 minutes. Prior to sample counting, the analyzers were checked for drift by using $^{137}$Cs and $^{60}$Co sources. In addition, constant temperature conditions are maintained in order to prevent drift associated with temperature changes.

Readout information obtained from the analyzers consisted of numerical data which were stored on "Tally" paper tape, plotted on graph paper, and printed out by an automatic typewriter. For the Nekton and Benthic studies, information stored on punch tape was transferred to IBM punched cards and computer analyzed by the method of least squares in an IBM 1410 computer (see AEC Prog. Rept. AT(45-1)1750 for 1965, pp. 120-129). Activities in the samples were determined by comparing standard spectra of the known standards to the same spectrum. These samples were routinely analyzed for cobalt-60, potassium-40, zinc-65, manganese-54, cesium-137, and cerium-promethium-144. Radioactive standards also available include: Chromium-51, antimony-124 and 125, ruthenium-rhodium-106, scandium-46, iron-59, selenium-75, and zirconium-niobium-95. Background counts are subtracted from the samples before computations are initiated and activities are corrected to the day of sample collection.

Activities of radionuclides in other studies were determined by comparing the area under the photopeak of the sample to the area under the photopeak of the known standard. Efficiency factors are determined as well as Compton correction factors and computations are done by an IBM 1620 computer.

New standards have been purchased in order to calibrate one of our detectors, which has been repolished and remounted. A plastic counting tube filled to a volume of 12 ml with a solution of $^{65}Zn$ was counted ten consecutive times for 100 minutes each time. Background was subtracted and each analysis was processed by electronic computer. The results are given in Table 1. The activity of each count is listed. The mean of the ten consecutive counts and the error of that mean are also indicated.

TABLE 1. Comparison of 10 replicate 100 minute counts of a $^{65}Zn$ standard.

| Count | PC $^{65}Zn$ |
|---|---|
| A | 966.82 |
| B | 956.88 |
| C | 957.50 |
| D | 970.71 |
| E | 972.29 |
| F | 965.59 |
| G | 967.70 |
| H | 968.42 |
| I | 977.61 |
| J | 966.98 |
| $\bar{X}$ | 967.05 |
| STD. DEV. | 5.93 |

An example of a sample which has been analyzed and computer processed by the least squares method is given below. Figure 1 is a spectrum of the sample as it appears upon completion of its counting time and with the background removed. The spectrum was made by an X-Y recorder connected to the analyzer. The nuclides present are identified on the figure. Figure 2 is the digital information obtained by an IBM electric typewriter also connected to the analyzer. Figure 3 is the information obtained from the computer which uses the least squares method for data reduction. The sample identification number, counting time, sample size, and the elapsed time between collection and counting are included with the digital information given to the computer.

The terms A and corrected A refer to the total activity of the particular nuclide at the time of counting. PC/G represents the activity in picocuries per gram of sample corrected back to the day of collection. STD. DEV. is the error of the activity per gram. Below the indicated activities are several columns of numbers which are the "residual number," that is, the difference between the best least squares fit of the standard radionuclide and the particular radionuclide in the sample. These residuals should be small. Any large or extreme values may indicate the presence of some other radionuclide for which it is not programmed, poor calibration, or drift with respect to the standard radionuclides.

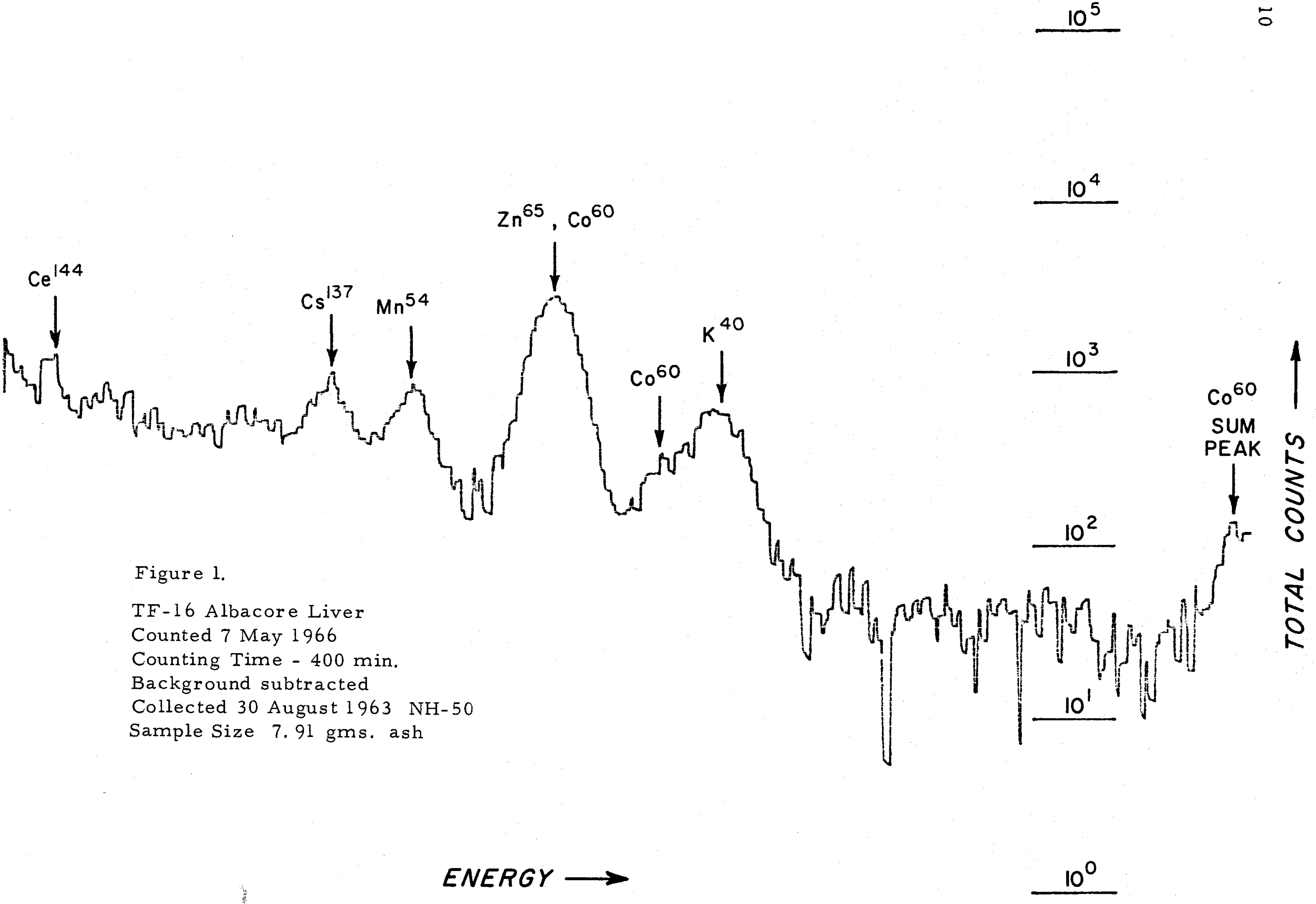

Figure 1.

TF-16 Albacore Liver
Counted 7 May 1966
Counting Time - 400 min.
Background subtracted
Collected 30 August 1963 NH-50
Sample Size 7.91 gms. ash

```
000000 000851 001465 001690 001336 001089 001128 000995
000938 000932 000739 001251 001281 001335 000880 000789
000818 000666 000600 000791 000688 000836 000745 000971
000878 000766 000594 000705 000866 000479 000578 000639
000527 000681 000518 000562 000459 000520 000500 000463
000484 000567 000544 000475 000557 000502 000401 000571
000663 000559 000568 000713 000542 000682 000571 000589
000511 000508 000582 000423 000481 000494 000539 000625
000778 000712 000849 000878 001011 000888 000734 000749
000652 000502 000513 000451 000429 000490 000469 000450
000563 000624 000676 000737 000360 000944 000872 000822
000635 000498 000453 000332 000311 000237 000263 000175
000150 000308 000223 000261 000166 000315 000363 000303
000454 000585 000830 001074 001372 001892 002267 002611
002882 002987 002919 002629 002332 001783 001365 001089
000780 000546 000431 000293 000222 000181 000163 000162
000179 000205 000170 000254 000281 000280 000283 000378
000346 000290 000287 000381 000424 000353 000519 000524
000640 000623 000677 000654 000623 000562 000469 000505
000350 000311 000256 000173 000145 000089 000117 000093
000072 000095 000076 000077 000024 000057 000045 000035
000041 000048 000070 000077 000045 000084 000048 000044
000070 000030 000042 000031 000006 000035 000044 000051
000041 000043 000054 000045 000056 000042 000031 000044
000067 000048 000038 000047 000026 000033 000015 000047
000031 000055 000044 000052 000055 000045 000047 000008
000040 000062 000050 000033 000065 000052 000053 000023
000056 000038 000035 000048 000055 000038 000031 000018
000021 000027 000045 000014 000023 000038 000029 000034
000010 000023 000013 000030 000035 000041 000037 000023
000054 000036 000020 000066 000044 000048 000052 000075
000089 000106 000126 000146 000117 000125 000129 000107
```

Figure 2.

Digital Information

TF-16 Albacore Liver
Counted 7 May 1966
Counting Time - 400 min
Background subtracted
Collected 30 August 1963 NH-50
Sample Size 7.91 gms. ash

Figure 3.

Computer Analysis Data

TF-16 Albacore Liver
Counted 7 May 1966
Counting Time - 400 min.
Background subtracted
Collected 30 August 1963 NH-50
Sample Size 7. 91 gms. ash

```
TF-16

COUNTING TIME    400. MIN.
SAMPLE SIZE      7.91
ELAPSED TIME     981. DAYS

NUCLIDE           A          CORR A        PC/G        STD DEV
K-40          263.6196     284.7836      36.0030       3.6068
MN-54          11.1203      11.4309      12.9579       2.0954
CO-60          42.2913      34.3856       6.2200       0.5511
ZN-65         169.8346     173.6753     352.3076      16.4052
CS-137          7.9360       8.0825       1.0812       0.2392
CE-144         21.5819      20.5213      28.1393       6.2667
    -1.68     0.03      2.32      1.56      0.91      0.62      0.48      0.21      0.42     -0.24
     0.41    -0.19      0.38      0.19      0.18      0.38     -0.09     -0.26      0.02     -0.24
    -0.03    -0.26      0.42      0.23      0.05     -0.34      0.01      0.48     -0.46     -0.24
    -0.11    -0.25      0.25     -0.27     -0.04     -0.28     -0.08     -0.12     -0.23     -0.12
     0.10    -0.00     -0.10      0.05     -0.11     -0.30      0.01      0.27     -0.01     -0.07
     0.26    -0.14      0.31      0.03      0.20      0.06      0.07      0.23     -0.18     -0.02
    -0.09    -0.08      0.02      0.06     -0.26     -0.07      0.11      0.51      0.39      0.25
     0.51     0.41      0.19      0.15      0.04     -0.03      0.06     -0.06     -0.32     -0.22
    -0.26    -0.31     -0.35      0.01      0.40      0.43      0.62      0.41      0.27      0.31
     0.11     0.13     -0.01      0.09     -0.16     -0.22      0.14     -0.04      0.06     -0.22
    -0.01    -0.06     -0.50     -0.48     -0.63     -0.73     -0.84     -1.04     -0.61     -0.41
    -0.01     0.53      1.01      1.50      1.54      1.67      1.18      0.88      0.79      0.44
     0.19     0.15     -0.02     -0.01     -0.05     -0.07     -0.06     -0.03      0.01     -0.16
    -0.00    -0.05     -0.07     -0.15      0.06      0.02     -0.15     -0.17      0.04      0.16
    -0.08     0.08      0.05      0.24      0.04      0.11      0.07      0.04     -0.01     -0.07
     0.21    -0.02      0.05      0.12     -0.01      0.01     -0.05      0.05      0.04     -0.01
     0.08     0.01      0.03     -0.12     -0.02     -0.05     -0.07     -0.07     -0.04      0.03
     0.05    -0.04      0.07     -0.01     -0.03      0.03     -0.06     -0.03     -0.05     -0.11
    -0.04    -0.02      0.00     -0.02     -0.01      0.01     -0.01      0.01     -0.01     -0.04
    -0.02     0.05     -0.00     -0.03     -0.00     -0.05     -0.03     -0.08     -0.00     -0.04
     0.02    -0.02      0.02      0.02      0.00     -0.01     -0.09     -0.01      0.05      0.01
    -0.03     0.05      0.02      0.03     -0.04      0.03     -0.01     -0.01      0.02      0.03
     0.00    -0.02     -0.04     -0.04     -0.02      0.04     -0.06     -0.01      0.03      0.01
     0.03    -0.03     -0.01     -0.02      0.03      0.03      0.06      0.04      0.00      0.05
     0.01    -0.04      0.05     -0.01     -0.04     -0.05     -0.03     -0.03     -0.00      0.01
     0.06    -0.04     -0.03     -0.01     -0.06
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# RESEARCH IN PROGRESS

## A. ESTUARINE RESEARCH

by Charles L. Osterberg, Leader

The Columbia River provides an excellent opportunity to carry out radioecological studies under natural conditions. The Hanford reactors are a source of several radionuclides ($^{65}$Zn, $^{51}$Cr, $^{54}$Mn, $^{60}$Co, $^{124}$Sb, $^{46}$Sc) which appear regularly in the estuary. Both $^{65}$Zn and $^{51}$Cr are generally found in sediments, water, and biota, while the other radionuclides favor one or another phase. All of these radionuclides behave somewhat differently, depending on their chemistry.

The presence of a "labeled" ecosystem permits a number of studies that would be difficult to carry out elsewhere. Gamma-ray analysis is sensitive, quick, and easy, requiring minimal sample preparation. Processes that would be difficult to follow by conventional techniques are much more straightforward when the system is labeled with several gamma emitters. This advantage becomes apparent when the work of Johnson et al. and Hanson (see pp. 21 and pp. 31) are examined (see also Jenning's thesis submitted in supplement).

Before a study in radioecology of the estuary can be meaningful, it is necessary to study the animals in the estuary, and the environmental variables influencing their abundance. The report on this basic work in ecology by Haertel (abstracted p. 29 ) made up a major portion of last year's progress report and has been submitted for publication. Kujala is continuing the work, with somewhat more emphasis on fishes (see pp. 15), while Haertel has made the study of the plankton of the estuary the topic of her Ph. D. research.

A new and promising study is that started by Renfro (see pp. 37), which will attempt to define the total radionuclide budget of a small slough in the Columbia River estuary. Techniques and instrumentation devised by members of our group (*in situ* sediment probe, large volume precipitation separations, *in situ* measurements of turbidity, salinity, temperature, and suspended and soluble radioactivity) will be employed to measure the radioactivity in the sediments, and soluble and particulate radionuclides in the water. These will be combined quantitatively with a measurement of the radionuclides in the biota to determine the relative abundance of the Hanford-induced radionuclides in the various portions of the slough. These measurements, although necessarily confined to a small part of the estuary, should provide a first approximation of the more important processes in the estuary.

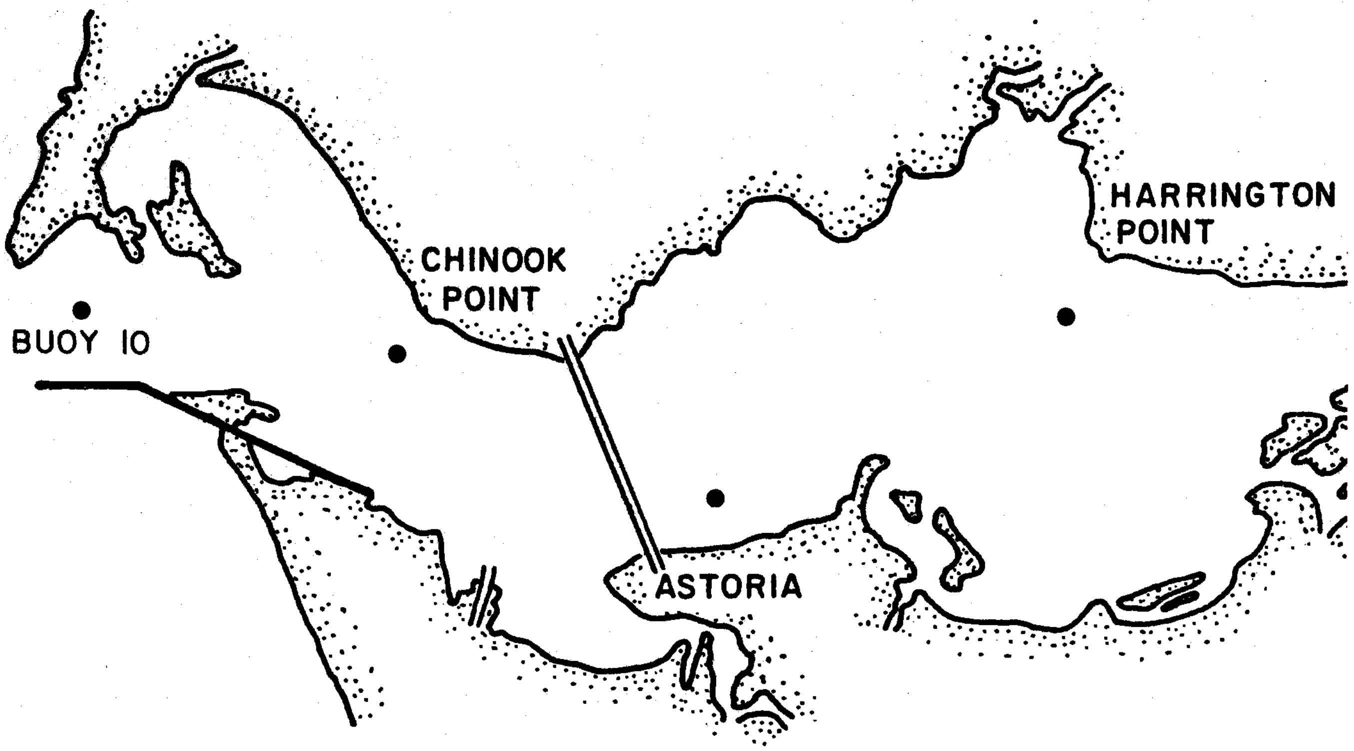

Figure 1. Collection stations in the Columbia River.

# COLUMBIA RIVER SAMPLING PROGRAM

by Norman Kujala

The sampling program in the Columbia River Estuary was started in 1963. Samples continue to be taken at the three original stations (Fig. 1) and an additional station (Buoy 10) has been added at the mouth of the estuary. Monthly collections are obtained with a 22-foot otter trawl and a 1/2-meter plankton net. Secchi disc readings, temperature, salinity, and dissolved oxygen are obtained monthly. Water samples from three depths at each station are analyzed for nutrients by the chemistry group under Dr. Kilho Park. A three-foot Isaacs-Kidd midwater trawl, a 4-foot biological dredge, and a 300-foot monofilament gill net of 1/4" to 4" mesh have been used to supplement the other collecting devices.

Temperature-salinity surveys made during maximum freshwater runoff (June 1965) and minimum runoff (August 31-September 1, 1965) gave information about saltwater encroachment and general water movements. Readings were made with a conductivity temperature and salinity recorder from a depth of 12 meters. The results are shown in Figs. 2, 3, 4, and 5. Figures 2 and 3 show high and low tide conditions during maximum runoff and Figures 4 and 5 show the same for minimum runoff. Comparison between various pairs of figures gives a good idea of the salinity patterns affecting the benthic fauna and the movements of fishes. Otter trawl collections made in the vicinity of each of the four stations are from the bottom near the 12 meter contour.

Data were collected at two stations on each tidal extreme for a 25-hour period during October 1965 in order to study the movements of fishes within the estuary. Animals were collected with otter trawl, gill net and plankton nets, and salinity and temperature measured with conductivity techniques. The salinity and temperature data are shown in Figure 6 and corresponding fish species are listed in Table 1. The results of this study substantiate dividing the estuarine fishes into fresh water, oligohaline, mesohaline, polyhaline and marine groups. Both the large number of marine fishes present upstream (as far as Astoria) and the high salinity values indicated low river runoff, e. g., the marine species Hypomesus pretiosus, Anoplopoma fimbria, Clupea pallasi, and Engraulus mordax were taken at Astoria at high tide when the bottom salinity was more than 20‰.

Monthly samples of meat and bone of each fish species are prepared for radioanalysis but an analysis of the past year's data has not been completed.

Supplemental data on fishes include stomach analyses to determine seasonal feeding habits and age determination by checking both otolith and scale structure.

TABLE I. Catch Results of 25 Hour Tidal Cycle Study at Two Stations on October 14 and 15, 1965.

| | ASTORIA | | | | CHINOOK POINT | | | |
|---|---|---|---|---|---|---|---|---|
| SPECIES CAUGHT | High | Tides | Low | Tides | High | Tides | Low | Tides |
| | 8.3 | 6.1 | -0.7 | 2.7 | 8.3 | 6.1 | -0.7 | 2.7 |
| 1. Starry flounder, Platichthys stellatus | X | X | X | X | X | X | X | X |
| 2. Longfin smelt, Spirinchus dilatus | X | X | X | X | | X | X | X |
| 3. Tom cod, Microgadus proximus | X | X | | X | | X | X | |
| 4. Staghorn sculpin, Leptocottus armatus | X | X | X | X | | | X | X |
| 5. Shrimp, Crangon spp. | X | X | X | X | X | X | X | X |
| 6. Shiner Perch, Cymatogaster aggregatus | X | X | | X | | X | X | |
| 7. Crab, Cancer magister | | | | | X | X | X | X |
| 8. Sand sole, Psettichthys melanostictus | X | X | | X | X | X | X | X |
| 9. Lemon sole, Parophrys vetula | | | | | X | X | X | X |
| 10. Windowtail Poacher, Agonopsis emmelane | | | | | X | | | |
| 11. Snake blenny, Lumpenus sagitta | X | X | | X | | X | | X |
| 12. Anchovy, Engraulis mordax | X | X | X | X | | X | X | |
| 13. Prickly sculpin, Cottus asper | X | | X | X | | | | |
| 14. Chinook salmon, Oncorhynchus tshawytscha | | | | | | | X | X |
| 15. Sable fish, Anoplopoma fimbria | | X | | | | | X | |
| 16. Stickleback, Gasterosteus aculeatus | | | X | | | | | |
| 17. Dogshark, Squalus acanthias | | | | | | X | | |
| 18. Herring, Clupea pallasii | | X | | | X | X | | |
| 19. Surf smelt, Hypomesus pretiosus | | X | | | X | | | X |
| 20. Cutthroat trout, Salmo clarki clarki | | | X | | | | | |
| 21. Shad, Alosa sapidissima | | | X | | | | | |
| 22. Peamouth chub, Mylocheilus caurinus | | | X | X | | | | |
| 23. Toothed smelt, Osmerus dentex | | | | | | X | | |
| 24. Silver salmon, Oncorhynchus Kisutch | X | | | | | | | |

During the past year nine fish species not previously reported in our studies were collected. All are marine species and were taken near the mouth of the estuary at Buoy 10. These species are listed in Table 2.

Table 2. Fish species from the Columbia River not previously reported in this study (AEC Contract AT(45-1)1750).

| | Common Name | Scientific Name |
|---|---|---|
| 1. | Sablefish | *Anoplopoma fimbria* |
| 2. | Windowtail poacher | *Agonopsis emmelane* |
| 3. | Pacific herring | *Clupea pallasii* |
| 4. | Padded sculpin | *Artedius fenenstralis* |
| 5. | Lobefin snailfish | *Polypera greeni* |
| 6. | Ringtail snailfish | *Liparis rutteri* |
| 7. | Warty poacher | *Occa verrucosa* |
| 8. | Tubesnout poacher | *Pallasina barbata aix* |
| 9. | Painted greenling | *Oxylebius pictus* |

Projected studies include continuation of the monthly sampling program, additional 25 hour surveillance of various stations at different seasons, and other collections to determine the population size and characteristics of resident and non-resident fish species.

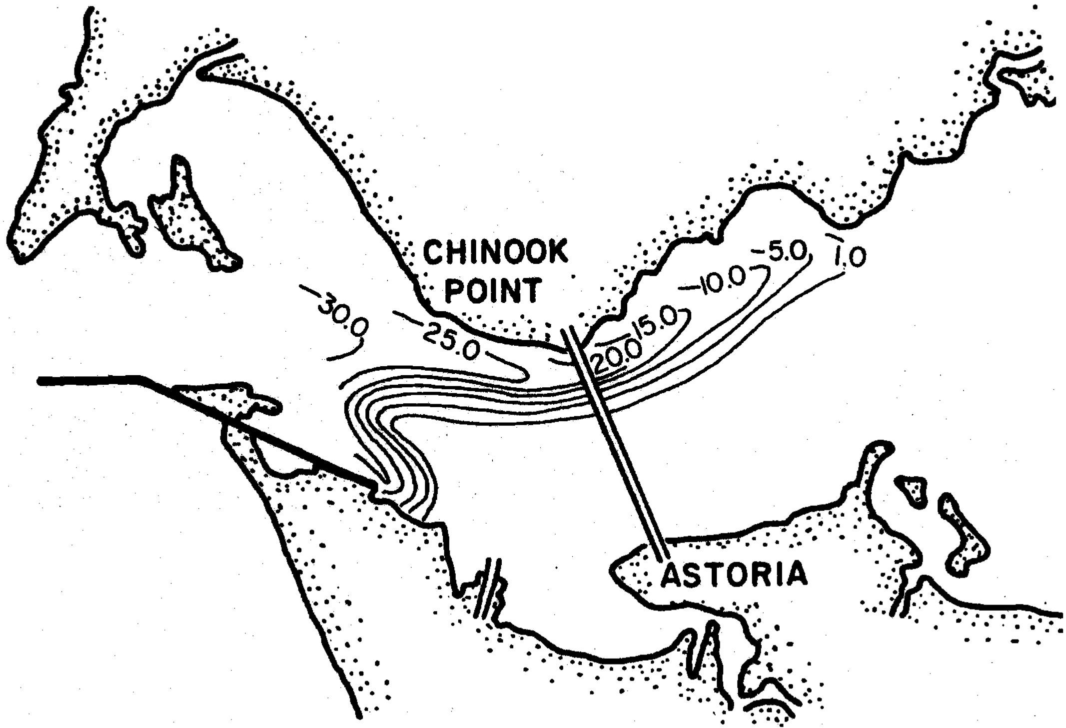

Figure 2. Typical salinities at high water during a period of maximum runoff.

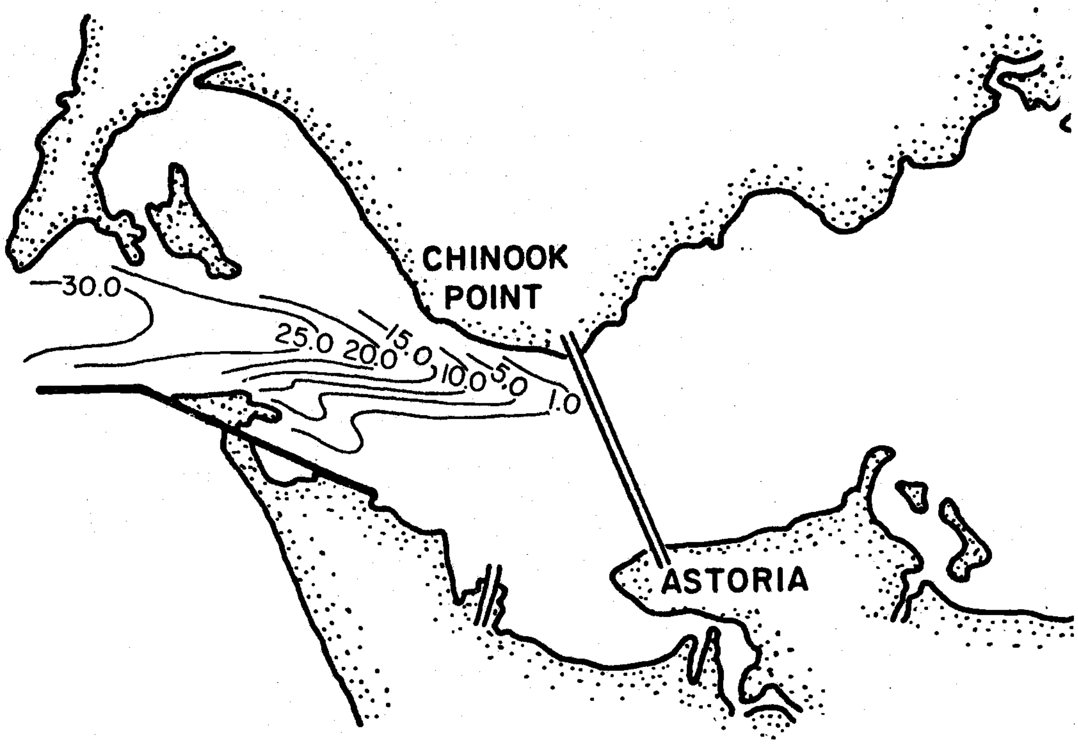

Figure 3. Typical salinities at low water during a period of maximum runoff.

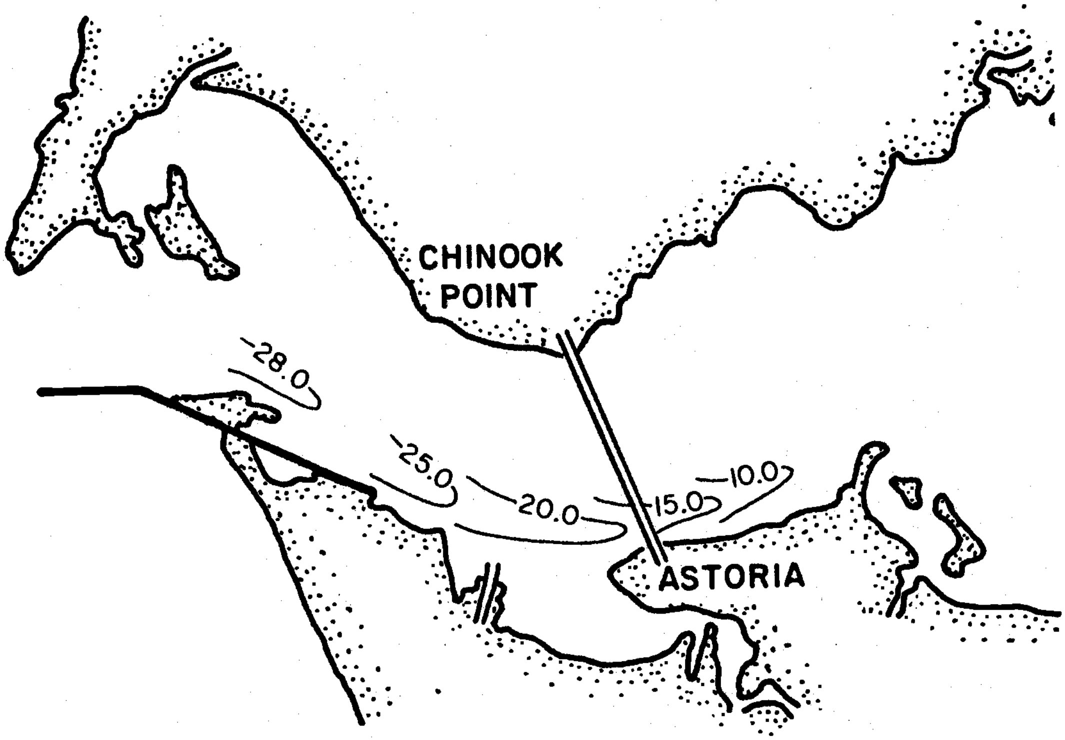

Figure 4. Typical salinities at high water during a period of minimum runoff.

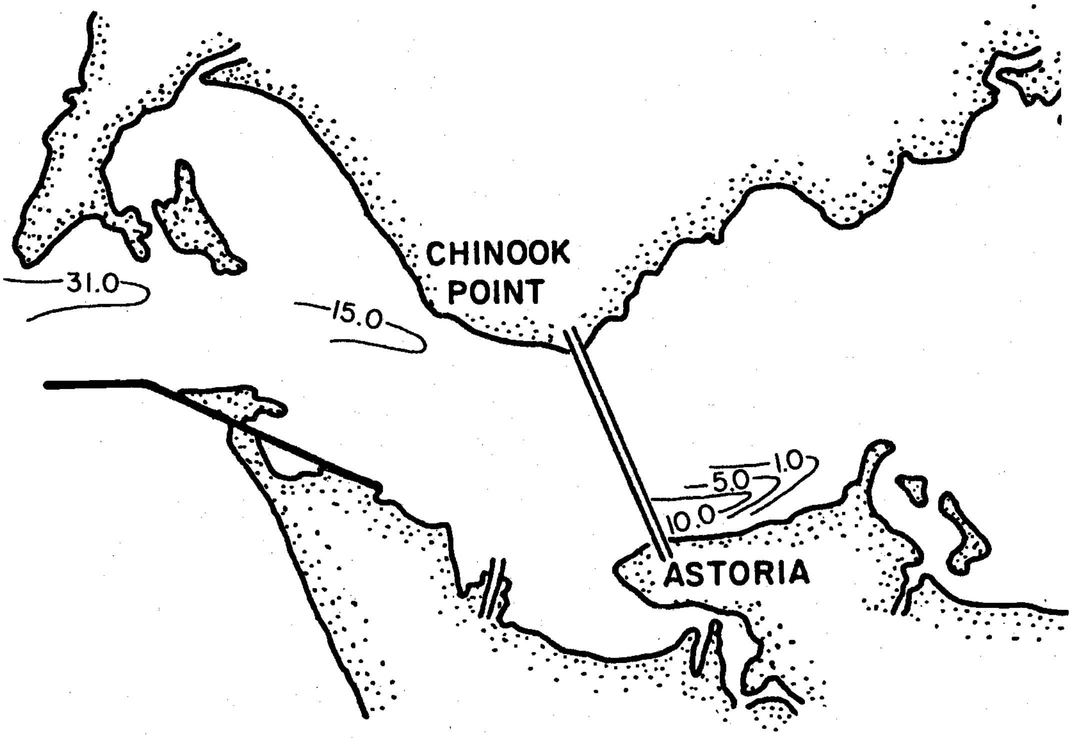

Figure 5. Typical salinities at low water during a period of minimum runoff.

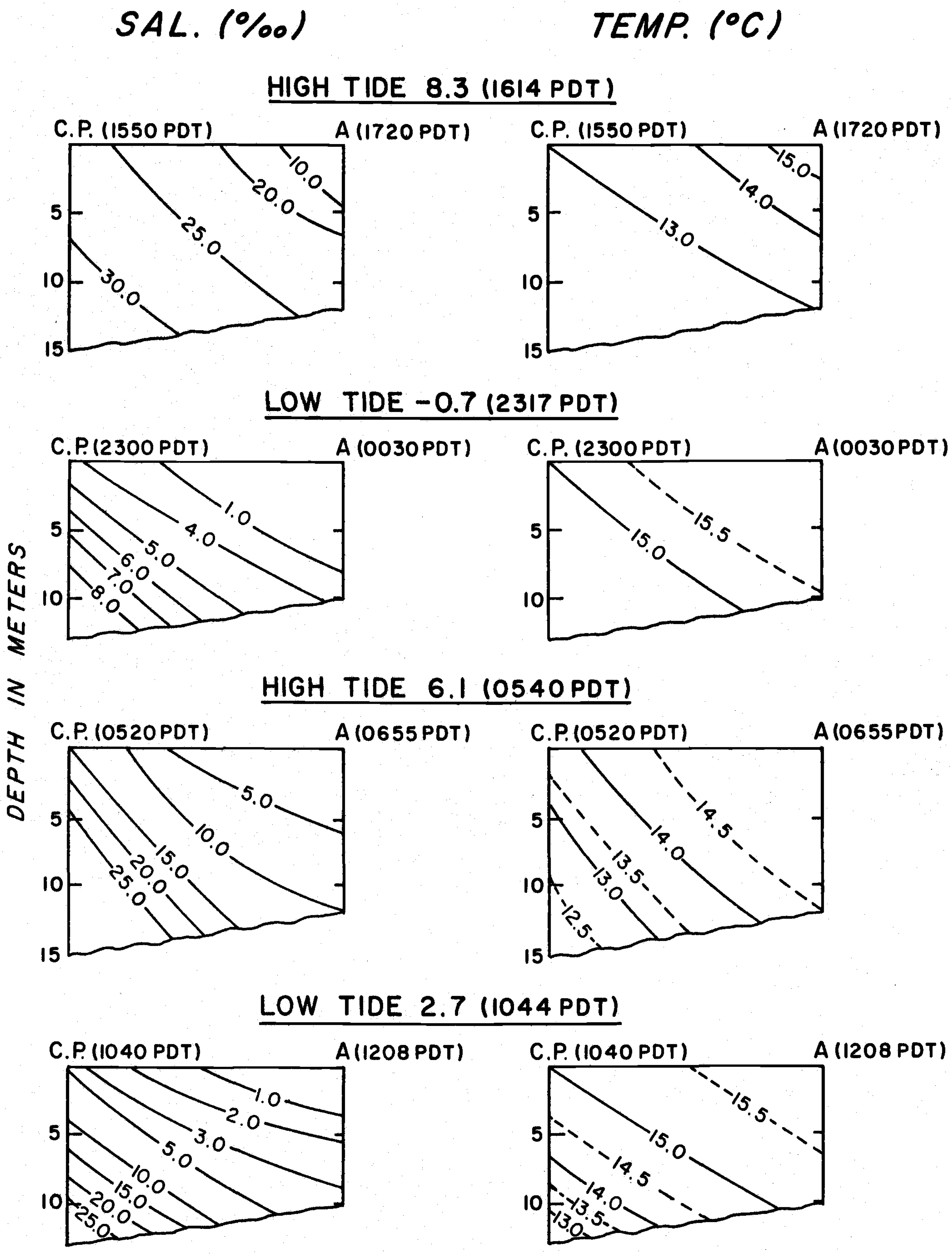

Figure 6. Salinity and temperature data at Chinook Point (C. P.) and Astoria (A) stations during 25 hour tidal cycle study on 14 and 15 October 1965.

# RETENTION OF $^{65}$Zn BY COLUMBIA RIVER SEDIMENT*

by

Vernon Johnson, Norman Cutshall, Charles Osterberg

## ABSTRACT

Ion exchange does not appear to be an important factor in the retention of $^{65}$Zn by Columbia River sediment. There is some evidence for a more specific ion-particle interaction whose exact nature awaits more detailed study.

Cationic $^{65}$Zn in effluent waters from nuclear reactors at Hanford, Washington, becomes predominantly associated with particulate material in the Columbia River (Nelson 1964). Sedimentation of this material carries $^{65}$Zn and other sorbed radionuclides into bottom deposits. The ion-particle interaction responsible for binding and retaining $^{65}$Zn in Columbia River sediments is not well known. We have investigated two types of interaction. The first is cation exchange. The second interaction is an exchange-type reaction in which the nature of the metal ion plays a major role. Several investigators have noted that pure minerals and soils are capable of retaining transition and post-transition metal ions by a more specific mechanism than ordinary cation exchange (Tiller and Hodgson 1962). This reaction has been called "specific sorption" to distinguish it from ordinary cation exchange. Several mechanisms for specific sorption have been proposed (Elgabaly 1960, Tiller and Hodgson 1962, Mortensen 1963). Whatever the mechanism of specific sorption, it is characterized as follows: 1) The metal sorbed cannot be displaced by alkali or alkaline earth ions or by $NH_4^+$, but can be displaced by other transition metals. 2) A general order of displacing power, $Cu^{2+} > Co^{2+} > Zn^{2+} > Mn^{2+}$, prevails.

Our interest in exchange processes was originally prompted by the work of Murata (1939) who showed that seawater displaced $Mn^{2+}$ from ion exchange sites in sediments. Similarly, Fukai (1966) reports that seawater displaces cations of $^{51}$Cr, $^{54}$Mn, $^{65}$Zn and other transition metals from Dowex-50 cation exchange resin. This result is reasonable since cation exchange reactions are subject to the law of mass action. When sediments are carried by a river into the ocean, displacement of exchangeable radiocations should occur. On the other hand, specifically sorbed or insoluble radionuclides should remain bound to the particles.

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* This paper was submitted to Water Resources Research in May 1966.

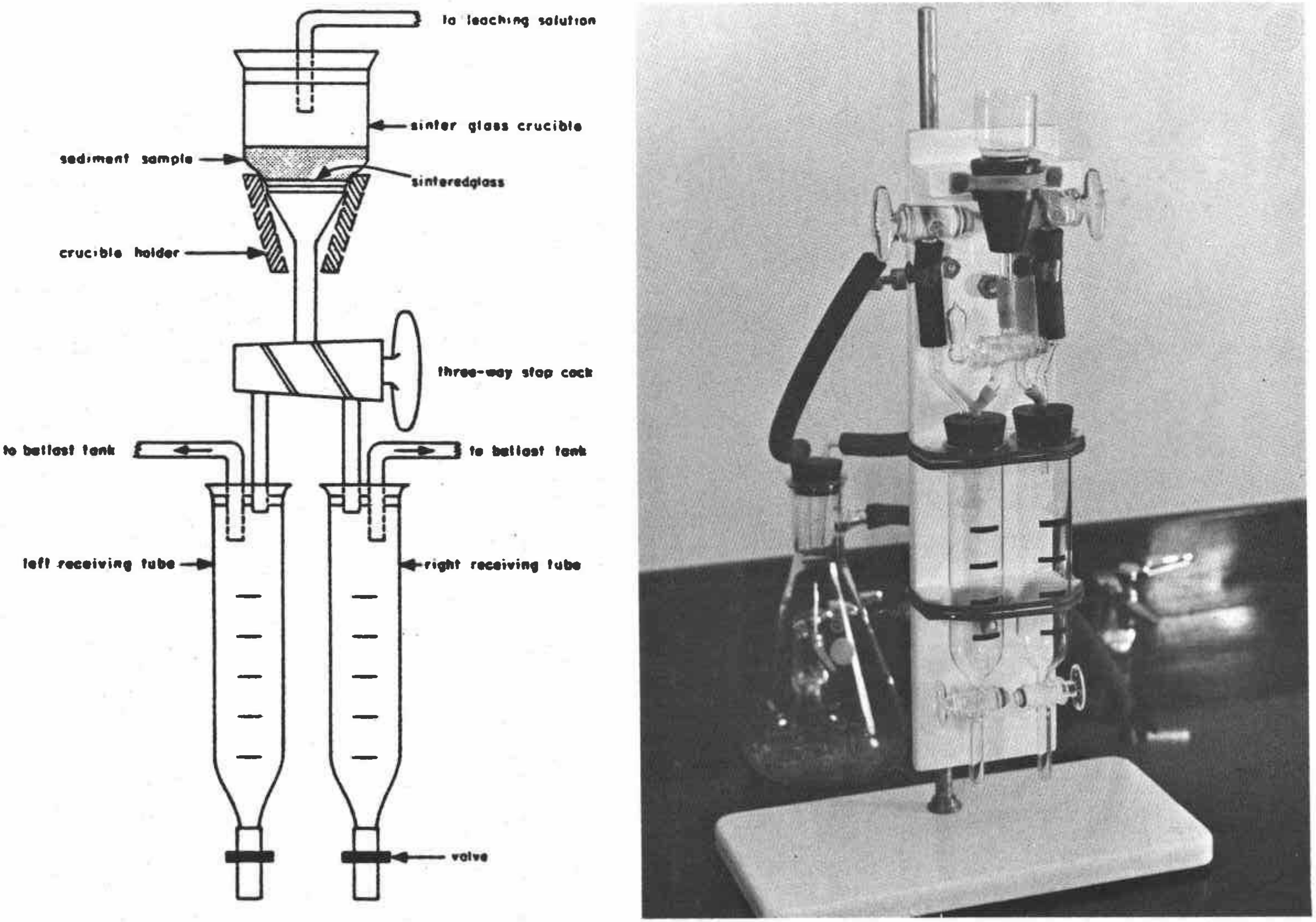

Fig. 1 Device used for eluting sediment under continuous flow conditions.

## METHODS

A portable leaching apparatus was constructed (Johnson,1966) to study exchange processes in sediments from the Columbia River (Figure 1). This device allowed the treatment of sediment samples immediately after collection and thus minimized changes that might occur in the samples during preservation or storage.

Each 10-12 $cm^3$ sediment sample was placed in the sintered glass crucible and the appropriate leaching solution was drawn through the bed. Successive aliquots of leachate could be collected with no interruption of flow. After elution, both the leached sediment and the leachate solution were taken to the laboratory at Corvallis for analysis by gamma-ray spectrometry. Our samples were generally permeable enough to allow the leaching solution to be drawn through at a reasonable rate (1-5 ml/minute). During and after elution the sediment bed was observed carefully to assure that "channeling" did not develop.

Radionuclides held by ion exchange were removed by leaching the sample with synthetic seawater prepared according to Lyman's formula (Sverdrup, et al. 1942). Specifically sorbed $^{65}Zn$ was removed by elution with $CuSO_4$ solution. Some duplicate samples were also treated with $CoCl_2$ or $MnSO_4$ solutions so that the relative effectiveness of different divalent ions in displacing zinc might be observed. The volume of eluant used was selected for seawater and for $CuSO_4$ solution by analyzing successive 25 ml portions of eluate by gamma-ray spectrometry. The displacement by seawater was negligible after the first 100 ml had passed. One-hundred-fifty ml of 0.05 $CuSO_4$ solution were adequate to complete the displacement of specifically sorbed $^{65}Zn$. That is, although some $^{65}Zn$ remained on the sediment, the portion remaining was not displaced by further elution for time periods of approximately one hour. Longer elution times were not attempted. The cobalt and manganese elutions were made with 150 ml of 0.05 M solutions.

## RESULTS

Only a small fraction of the sediment-sorbed $^{65}Zn$ was removed from natural Columbia River sediments by seawater (Table 1). Sample sites are shown in Figure 2. A generally larger but highly variable fraction of the $^{54}Mn$ was displaced. $CuSO_4$ solution removed a considerable fraction of the radiozinc from each of three samples (Table 2). There was an apparent decrease in the fraction of $^{65}Zn$ held by specific sorption for samples collected farther downstream. Although $^{51}Cr$ and $^{46}Sc$ were also present in easily measurable quantities in our samples neither was displaced by seawater or $CuSO_4$ solution.

Table 1. Fractions of $^{65}Zn$ and $^{54}Mn$ displaced from sediment samples by synthetic sea water (percent).

| | Sample Location | Date Mo/Yr | % Sand:[1] % Mud | % $^{65}Zn$[2] Displaced | % $^{54}Mn$[2] Displaced |
|---|---|---|---|---|---|
| 1 | McNary Dam | 8/64 | 5:95 | 0.2±0.03<br>0.4±0.02 | 25.6±0.5<br>21.4±0.5 |
| 2 | Maryhill | 7/64 | 56:44 | 0<br>0.3±0.08 | 22.2±0.8<br>16.1±1.0 |
| 3 | Bonneville Dam | 7/64 | 42:58 | 0.6±0.02<br>1.1±0.07 | 38.1±0.5<br>41.4±1.0 |
| 4 | Puget Island | 3/65 | 44:56 | 2.2±0.4<br>3.3±0.3 | 18.4±4.5<br>18.9±4.0 |
| 5 | Miller Sands | 9/64 | 43:57 | 2.5±0.4<br>2.7±0.2 | 69.5±1.7<br>73.5±1.3 |
| 6 | Tongue Point | 9/64 | 56:41 | 1.5±0.3<br>0 | 30.8±0.9<br>36.5±1.1 |
| 7 | Astoria (upper) | 7/64 | 58:42 | 0<br>0 | 25.2±6.3<br>0 |
| 8 | Astoria (lower) | 9/64 | 58:42 | 0<br>0 | 0<br>0 |

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1. The portion of each sample passing through 0.991 mm screen openings but not through 0.061 mm openings was called sand. That portion passing through the 0.061 mm screen was called mud.

2. ± indicates standard deviations for the leachate count rate. Where the leachate count rate was below 1 cpm for zinc or 1.3 cpm for manganese, ($2\sigma$) a zero was recorded.

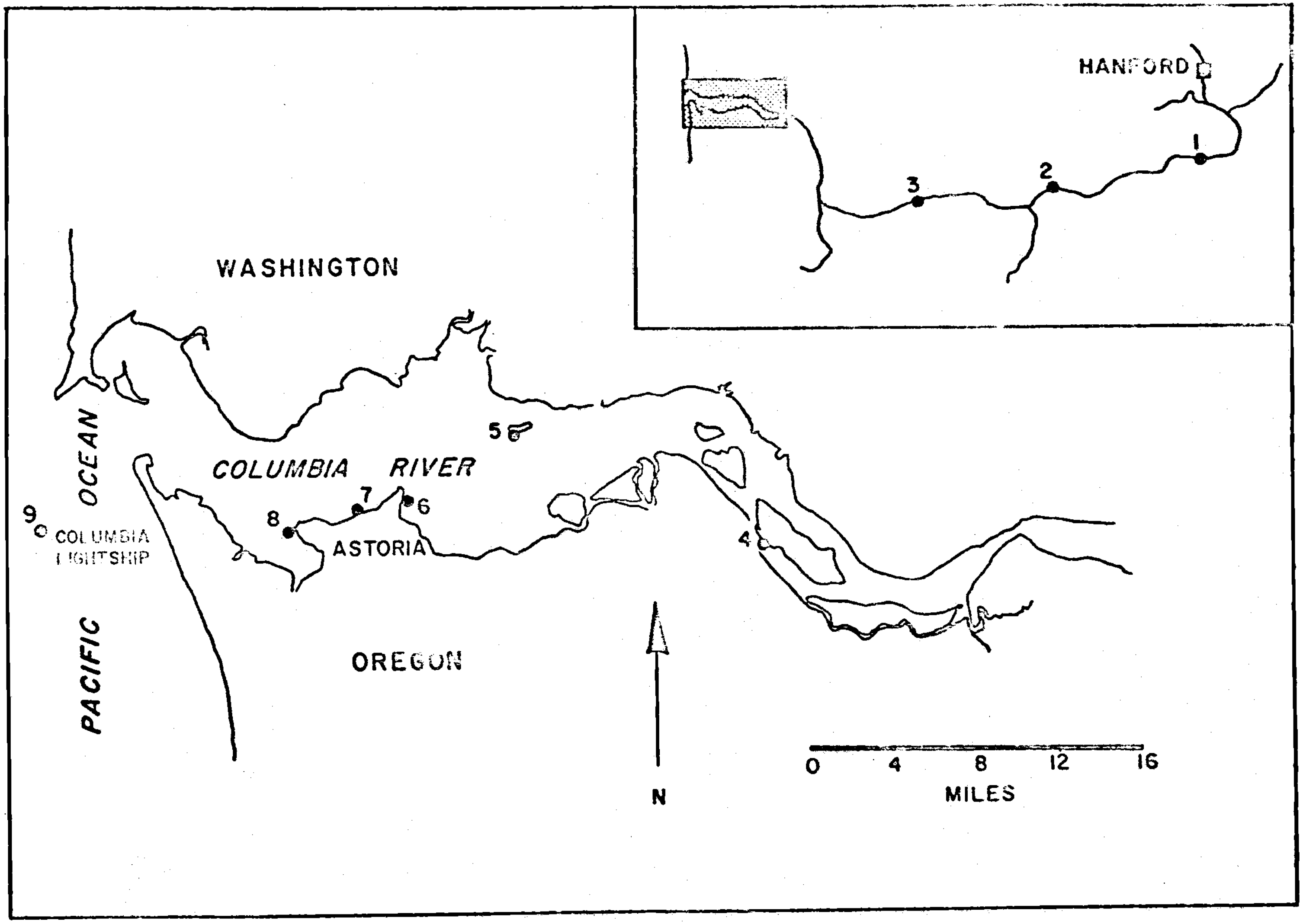

Fig. 2 Sample sites.

Table 2. Fraction of $^{65}Zn$ displaced from sediment samples by 0.05 M copper sulfate solution (percent).

| Sample Location | Date Mo/Yr | % Sand: % Mud[1] | % $^{65}Zn$ Displaced[2] |
|---|---|---|---|
| 4 Puget Island | 3/65 | 44:56 | $50.6 \pm 1.2$<br>$53.9 \pm 1.0$ |
| 7 Astoria (upper) | 7/65 | 28:72 | $43.4 \pm 0.8$ |
| 9 Columbia Lightship | 4/65 | 0:100 | $38.2 \pm 1.2$<br>$34.8 \pm 1.0$ |

1. The portion of each sample passing through 0.991 mm screen openings but not through 0.061 mm openings was called sand. That portion passing through the 0.061 mm screen was called mud.

2. ± indicates standard deviations for the leachate count rate.

When different portions of a sample were leached with $Cu^{2+}$, $Co^{2+}$ and $Mn^{2+}$ the fraction of $^{65}Zn$ removed was 54%, 33%, and 23%, respectively. Since the transition metal salt solutions used are mildly acidic (pH = 5) it was necessary to test for the possibility that $H^+$ was responsible for the release of $^{65}Zn$. Accordingly, a sample was also leached with 150 ml of 0.1 M acetate buffer (pH = 4.9). Less than 5% of the radiozinc was removed from the sediment, probably the same exchangeable $^{65}Zn$ that was subject to cation displacement by seawater. Thus, removal of $^{65}Zn$ by $CuSO_4$ was not due to the acidity of the solution.

## DISCUSSION

A surprisingly small fraction of the $^{65}Zn$ in Columbia River sediment is held on cation exchange sites. A somewhat larger, but variable, fraction of $^{54}Mn$ is apparently so held. Thus, it seems likely that almost all $^{65}Zn$ carried into the sea on suspensoids will remain attached to the particles. Only part of the $^{54}Mn$ would remain on particles. This last conclusion is in agreement with Murata (1939). None of the sediment-sorbed $^{51}Cr$ or $^{46}Sc$ would be removed by the rapid processes we have studied.

A large fraction of the $^{65}Zn$ in Columbia River sediments is specifically sorbed. This fraction can be removed with dilute solutions of transition metals. The apparent decrease in the fraction of $^{65}Zn$ held in this way with distance downstream (thus presumably with age) may indicate that some reaction in the sediment may be acting to change the mode of retention of this nuclide. A larger number of samples is necessary to definitely establish that such a change is occurring. The particle size also decreased in our sample series and this may have some effect.

It is interesting that the apparent order of effectiveness of $Cu^{2+}$, $Co^{2+}$, and $Mn^{2+}$, in displacing specifically sorbed $^{65}Zn$, parallels the order of stability of complexes of divalent metal ions. We must be cautious in interpreting this result, however, since rates of displacement by elution can be affected not only by thermodynamic but also by kinetic factors. Single batch treatments would be more useful for thermodynamic interpretation.

Cation exchange sorption of $^{65}Zn$ is probably even less important in seawater than in freshwater because other cations ($Na^+$, $Mg^{++}$, etc.) are so abundant in the sea. On the other hand, specific sorption may occur in seawater because transition metal ions are generally not abundant in the sea. For this reason it is especially important to distinguish between non-specific cation exchange sorption and specific sorption in seawater.

## ACKNOWLEDGMENT

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## REFERENCES

Elgabaly, M.M. Mechanism of zinc fixation by colloidal clays and related minerals. Soil Science 69:167-173. 1950.

Fukai, R. Fate of some radionuclides fixed on ion-exchange resins in seawater medium. Symposium on the Disposal of Radioactive Wastes into Seas, Oceans, and Surface Waters. Vienna, 16-20 May Abstracts SM-72, 1966.

Johnson, V. Retention of $^{65}$Zn by Columbia River Sediment, M.S. Thesis, Oregon State University, Corvallis, Oregon. 1966.

Mortensen, J. L. The complexing of metals by soil organic matter. Proc. Soil Sci. Soc. Amer. 27:179-186. 1963.

Murata, K. J. Manganese in river and ocean muds. Amer. J. Sci. 237:225-235. 1939.

Nelson, J. L., R. W. Perkins and J. M. Nielsen. Progress in studies of radionuclides in Columbia River sediments. A summary of Hanford achievements in this program under General Electric 1963-1964, U. S. At. Energy Comm. Rept. HW-83614. 1964.

Sverdrup, H. U., M. W. Johnson and R. H. Fleming. The Oceans, Englewood Cliffs, New Jersey, Prentice Hall, p. 186. 1942.

Tiller, K. G. and J. F. Hodgson. The specific sorption of cobalt and zinc by layer silicates, In: Proceedings of the National Conference on Clays and Clay Minerals 9:393-403. 1962.

# ECOLOGY OF THE COLUMBIA RIVER ESTUARY*

by

Lois Haertel and Charles Osterberg

## ABSTRACT

Fauna of the Columbia River Estuary were sampled regularly for 21 months. Analyses of plankton samples indicated that three distinct populations existed in the estuary: a freshwater group, a marine group, and an endemic estuarine group. The latter consisted principally of a large population of Eurytemora hirundoides. Changes in the salinity of the estuary were reflected in the composition of the plankton.

The majority of the fish and benthic invertebrates found in the estuary are euryhaline. The largest numbers of fish species, as well as the largest numbers of individuals, occupy the slightly brackish waters of the central portion of the estuary. The major plankton blooms also occur in this area. Starry flounder (Platichthys stellatus) and sand shrimp (Crangon franciscorum) use the upper estuary as a nursery ground.

Extensive analyses of fish stomach contents confirm that food habits of fishes generally reflect the availability of prey.

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This paper has been submitted to ECOLOGY for consideration.

* A preliminary draft was included in AEC Progress Report AT(45-1)1750 for 1965, pp. 3-38. It has been revised but the information included is largely the same.

Figure 1. Instrument package ready for sampling: (1) Transmissometer underwater sensor; (2) Conductance-Temperature cell; (3) water intake for pumping; (4) Transmissometer unit; (5) Conductance-Temperature unit; (6) stainless steel pump; (7) filter unit; (8) polyethylene storage container.

# VERTICAL DISTRIBUTION OF SOLUBLE AND PARTICULATE RADIONUCLIDES IN THE COLUMBIA RIVER ESTUARY

by Peter J. Hanson

Radioactivity in the Columbia River is distributed throughout the aqueous environment. The biota, bottom sediments and river load, both dissolved and suspended, have been shown to be active sinks for the various radionuclides present in the river. To determine the fate of radionuclides attention must be given to all these areas of distribution. Studies of the radioactivity associated with the biota and the bottom sediments of the river are actively being pursued at this laboratory.

Perkins et al. (1966) have made a study of the behavior and transport of radionuclides in the river between Hanford and Vancouver, Washington. This reach of the Columbia is well upstream from the estuary and, thus, is without seawater influx. The study being conducted at this laboratory will provide knowledge of the fate of radionuclides as they are carried into a salt water environment, and therefore provide a logical extension to the work done upstream.

## METHOD - INSTRUMENT PACKAGE

An instrument package was designed to collect river water samples at any depth while simultaneously recording salinity, temperature and relative turbidity data at the same depth (Fig. 1). Water samples are pumped to the surface and filtered through a 0.45 micron membrane filter. Salinity and temperature data are measured with an induction conductivity-temperature cell mounted on the instrument package. A measure of the turbidity of the river is obtained by an underwater transmissometer, also mounted on the unit.

The instrument package is lowered into the river tethered to a steel cable which is kept vertically taut by means of a 200 pound lead weight. A handwinch is used to raise and lower the instrument package, while an electric winch is used with the tether line and weight. The sampling depth is determined with a depth meter wheel. Power for the pump is supplied by a portable gasoline generator.

Figure 2. Precipitating containers. Precipitates are formed in the calibrated containers. The supernatant liquid is siphoned off and precipitate is washed down into small polyethylene bottles for transport to the laboratory. Air is bubbled through the containers to assure good mixing during precipitation.

## SAMPLE PREPARATION

River water is pumped through the membrane filter (usually 4-15 liters). The filter is then removed from the filter holder, drained of excess water, rolled into a cylindrical shape and placed in a plastic tube for counting. The filtered water is temporarily stored in plastic containers until the dissolved radionuclides can be concentrated by coprecipitation with ferric hydroxide. A system has been developed for carrying out the precipitation in the field (Fig. 2). Filtered water samples are placed in one of the four plastic vats and the precipitate is formed. After settling, the precipitate is removed and stored in a plastic container for transport to the laboratory. In the laboratory the precipitate is filtered onto an 11 cm filter paper, rolled into a cylindrical shape, and placed in a plastic tube for counting. Salinity, temperature, and turbidity data are recorded in situ.

## COUNTING

Plastic tubes containing membrane filters and ferric hydroxide precipitates are each counted for 100 minutes in the well of a ND 130 AT gamma ray spectrometer. Data from each sample are punched on Tally paper tape. The data are transferred from tape to computer cards and spectrum analysis is carried out by means of a computer program developed in this laboratory. (See AEC Prog. Rept., AT(45-1)1750 for 1965, pp. 120-129.) The original computer program has been modified to include the following nuclides: $^{51}$Cr, $^{65}$Zn, $^{46}$Sc, $^{54}$Mn, $^{60}$Co, $^{40}$K, $^{137}$Cs, and $^{144}$Ce.

## SAMPLING TO DATE

Two sampling trips have been carried out to date (Fig. 3). On the first trip, two vertical profiles of the river were made at a location in mid channel off Astoria, Oregon. On the second trip a 24 hour sampling study was carried out on the U. S. Coast Guard dock at Point Adams, Oregon. The effect of tidal salinity changes on the transport and behavior of radionuclides in the lower estuary was the purpose of this study.

The samples are now in the process of being counted and thus no data are yet available (Fig. 4 ).

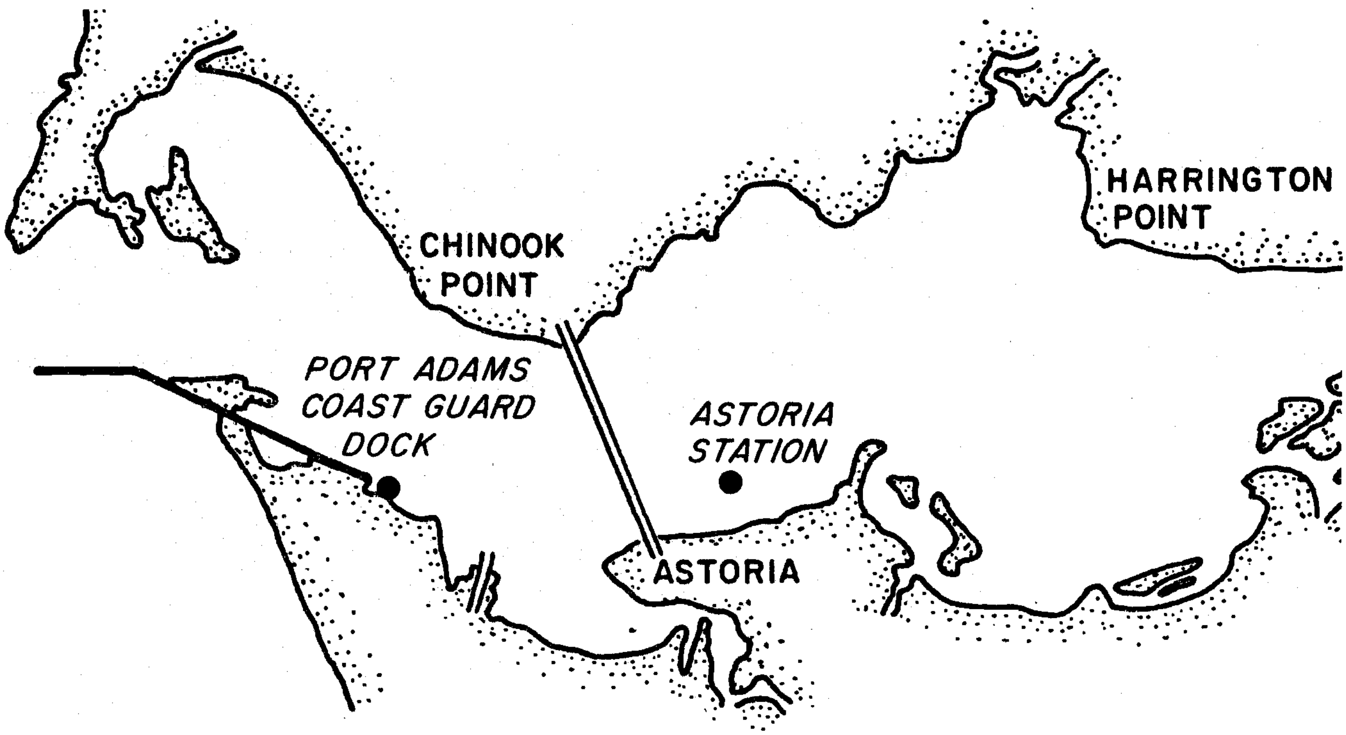

Figure 3. Sampling stations in the Columbia River Estuary.

## WORK TO BE COMPLETED

Until the preliminary data are reduced no definite direction can be given to future sampling.

Experiments are planned to test various aspects of the sampling method. To test the efficiency of the ferric hydroxide coprecipitation method of concentrating soluble cations, laboratory experiments are planned. Radioactive cations in one aliquot of a filtered river water sample will be concentrated by the precipitate method. Another aliquot will be evaporated to dryness, thus concentrating the radioactivity quantitatively in the remaining salts. Efficiency factors for the precipitation of the various cations of interest can then be determined.

Samples taken by pumping will be compared to samples taken by a water sampler of the Van Dorn type. The samples will be used to test the validity of the pumping method with respect to the representativeness of the particulate matter sampled. The water sampler is being specially constructed to fit on the instrument package, thus making it possible to sample by both methods at the same time and depth.

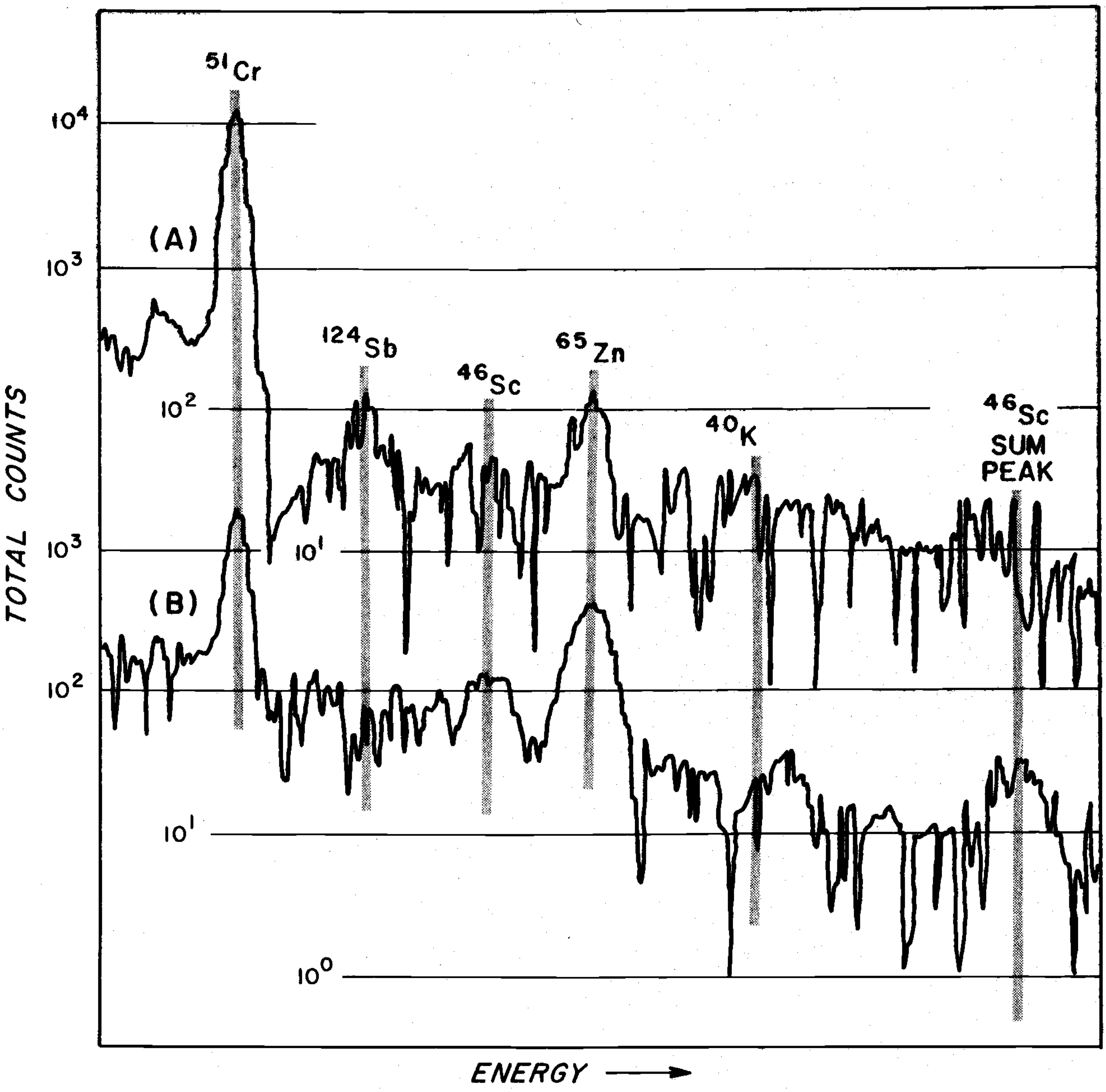

Figure 4. Preliminary spectra - comparison of (A) ferric hydroxide precipitate and (B) membrane filter from same sample - 100 minute counts.

Results of this research will be presented in a thesis, as partial fulfillment of M. S. degree requirements. If the techniques appear sufficiently promising, it is hoped that the research can be extended for use as a Ph. D. problem.

## REFERENCE

Perkins, R. W., J. L. Nelson and W. L. Haushild. 1966. Behavior and Transport of Radionuclides in the Columbia River Between Hanford and Vancouver, Washington. Limnol. Oceanog. 11: 235-248.

# TRANSFER OF RADIONUCLIDES THROUGH ESTUARINE FOOD WEBS

By William C. Renfro

The operations of nuclear reactors may be limited to some extent by the types and amounts of radioactive elements they release to the environment. In some cases, the controlling levels of activity may occur in organisms having the capacity to concentrate radionuclides. For example, the effects of the operations at Windscale are monitored by surveillance of radioactivity levels in edible seaweeds in the adjacent Irish Sea (Dunster, 1958). Clearly, a knowledge of the fate of radionuclides released to the environment is necessary for proper design and operation of nuclear reactors.

This project, presently in early stages of planning, proposes to examine the means by which some radioelements are passed through one or more estuarine food webs. Briefly, the study will entail analyzing the stomach contents of various fishes and invertebrates to determine their places in the estuarine trophic structure. Analyses of selected animals will be made to correlate their body burdens with their positions in the food webs. Finally, laboratory feeding experiments using estuarine animals will be performed in an attempt to quantify the efficiency with which radionuclides are transferred up the food webs.

A small arm of the Columbia River Estuary near Warrenton, Oregon (fig. 1) has been selected as the study site. Roughly 150 meters long, it is "L-shaped" with a mud bottom and dense vegetation along its edges. Trawl and seine collections indicate that it is populated mainly by small fishes and invertebrates.

One aspect of interest in initial phases of the study involves variation in radiozinc concentrations among individuals of the same species: Eight juvenile peamouth chubs (Mylocheilus caurinum) taken in a single seine haul and having nearly equal lengths and weights were analyzed for $^{65}$Zn concentration. Whole bodies were counted after removal of the eyes which have very high $^{65}$Zn concentrations and the viscera which may vary in activity according to the kind and amount of the gut contents. The results are shown in Table 1.

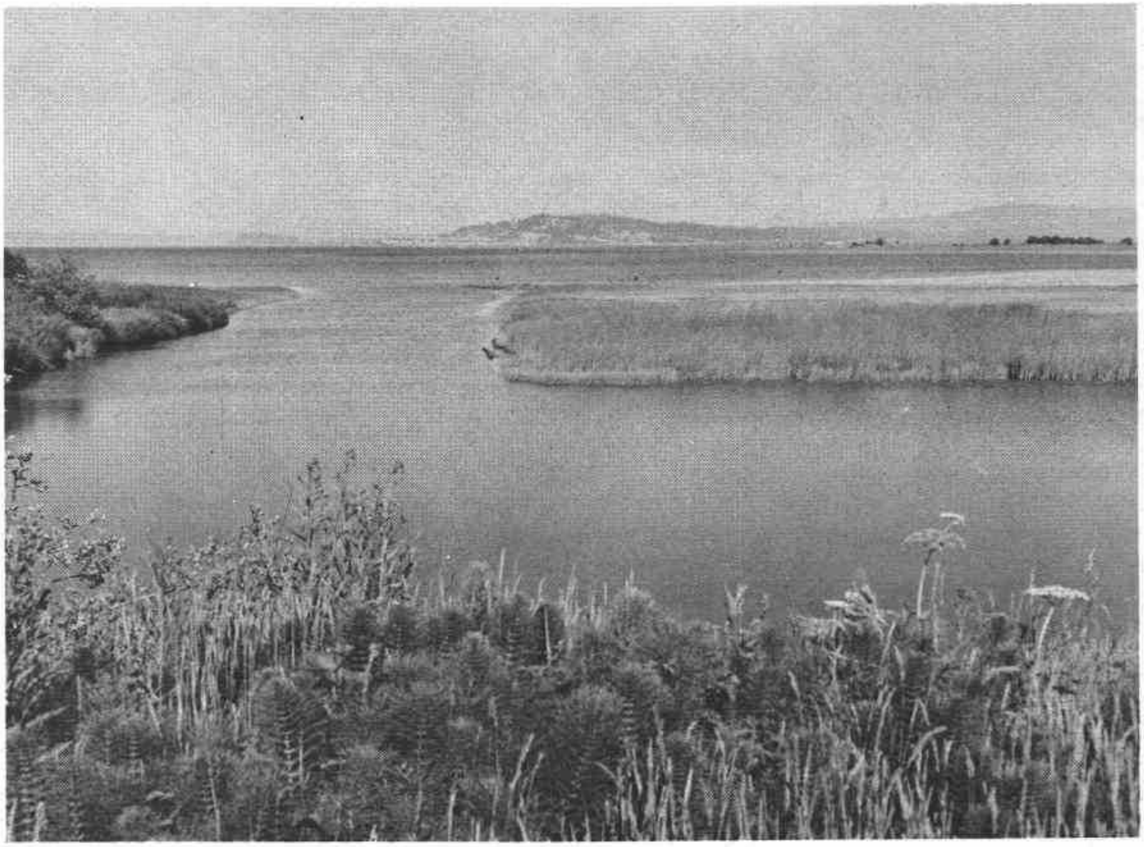

Figure 1. Slough chosen as the sampling site. In the background is the Columbia River and Astoria, Oregon.

Table 1. $^{65}Zn$ concentrations in eight peamouth chubs.

| Number | Standard Length mm. | Wet Weight Gms. | Dry Weight Gms. | Counts Per Minute Per Gm. Dry Weight in $^{65}Zn$ Photopeak | Picocuries $^{65}Zn$ Per Gm. Dry Weight |
|---|---|---|---|---|---|
| 1 | 76 | 5.29 | 1.24 | 34.0 | 118 |
| 2 | 75 | 4.99 | 1.14 | 29.7 | 103 |
| 3 | 80 | 6.32 | 1.41 | 37.2 | 129 |
| 4 | 76 | 5.16 | 1.22 | 26.0 | 90 |
| 5 | 78 | 6.29 | 1.39 | 30.8 | 107 |
| 6 | 82 | 7.62 | 1.70 | 21.6 | 75 |
| 7 | 75 | 5.12 | 1.16 | 43.4 | 150 |
| 8 | 79 | 5.82 | 1.45 | 32.4 | 113 |
| | | | | | Mean = 110.6<br>Std. Dev. = 21.54 |

The range in concentrations of radiozinc (75 to 150 pc/g. dry wt.) seems quite large within a sample of small fishes having otherwise similar characteristics. These results demand further, more detailed examination of individual variation and its consequences for this project.

## REFERENCES

Dunster, H. J. 1958. The disposal of radioactive liquid wastes into coastal waters. In: Second U. D. Intern. Conf. on the Peaceful Uses of Atomic Energy. Geneva, p. 390-399.

# RESEARCH IN PROGRESS

## B. RADIOCHEMISTRY

by Charles L. Osterberg, Leader

The work of Cutshall et al. (1966) has greatly increased the distance to which the plume of the Columbia River can be followed to sea, using $^{51}Cr$ as an indicator of river water. The sensitivity of our measurements offers hope that variations in $^{51}Cr$, when corrected for changes in salinity, can provide a timing device for the plume's movements (see Osterberg, Cutshall, Cronin 1965). (Reprints of both these papers are included, pp. 216 and 213 ).

The modifications by Frederick (see pp. 43) make it possible to obtain excellent data on the $^{51}Cr$ content of seawater on board ship within 4 hours after the sample is collected. With this capability, the cruise plan can be altered to follow the most interesting aspects of the plume.

Perhaps equally useful, if our hopes are realized, is the plan to use $^{51}Cr$: $^{124}Sb$ ratios as a more accurate "clock" than $^{51}Cr$ alone provides. Ultimate success depends on our ability to measure $^{124}Sb$ with something like the same precision that we can now measure $^{51}Cr$. Since we feel that our chemical recovery of $^{124}Sb$ is nearly 100%, the major hope for increased precision must come from an increase in the sensitivity of our counting equipment. To this end a 30-ton press with special carbide dies has been ordered. If the $^{124}Sb$ in the precipitate from 150 gallons of seawater can be concentrated chemically and mechanically into a 12 cc capsule, it can be counted in the well of a 5 x 5-inch detector. The improvement in sensitivity would probably make $^{124}Sb$ data useful for dating purposes. These problems concern Frederick, whose thesis involves a study of the diffusion of the Columbia River water at sea.

Further work with our *in situ* gamma-ray sediment probe has been proceeding rather slowly due to lack of fairly expensive equipment. With the recent delivery of a special winch and new conducting cable (June 1966), this project will begin anew.

# *IN SITU* GAMMA-RAY SEDIMENT PROBE

by C. Osterberg, L. Frederick, N. Cutshall

The *in situ* probe, developed by Jennings et al. (Science *148*: 948-950, 1965) to measure gamma emitters in the sediments of the Columbia River estuary, has been modified for use down to 400 m.

Tests made in April, 1966 off Oregon demonstrate that counts of radionuclides in surface sediments can be made down to 400 m. Although useful data were not obtained on this cruise, the portions of the process which were felt to be most difficult were carried out successfully. That is to say, we were able to determine when the probe was on the bottom, and could keep the ship (R/V YAQUINA) on station long enough to complete a count (10-20 minutes).

Useful data were not obtained due to an intermittent short in the conducting cable. Cable failure resulted from use of a winch with too small a diameter, thus straining the conductors. In laboratory tests, data have been transmitted from the *in situ* detector to the multichannel analyzer through 3000 feet of cable, demonstrating that the technique should work.

A new electrically driven winch (with correct drum size) with slip rings has been received, and will be rigged with new conducting cable. A new terminal device, to avoid strain on the conductors where the cable joins the *in situ* probe, has been ordered. When these new components have been assembled and tested, further field tests will be begun.

# LARGE VOLUME RADIOCHEMISTRY

by Lawrence C. Frederick

The large volume radiochemistry processes were reported in AEC Progress Report AT(45-1)1750 for 1965, pp. 57-63. These processes have been utilized and modified during the past year.

## IMPROVEMENTS IN INSTRUMENTATION

With the utility of the large volume radiochemistry system assured, it was decided to refine the system for increased efficiency in sampling and analysis. The shipboard system to this point consists of a submersible 1 h. p. pump, several hundred feet of hose and electrical line, pump control box, two 170-gallon (640 liter) anchored columns tapered at the base to effect precipitate flow, and necessary plumbing. Water was pumped into one of the 640 liter columns and treated with $FeCl_3$ and $NH_4OH$ to precipitate the dissolved chromium. The water was allowed to settle and the natant siphoned off, then the remainder was drained into 50-liter plastic carboys.

Upon further settling, it was possible to decant, to remove more natant and transfer the concentrate to 5-gallon (19 liter) plastic jerry cans. These cans were then stored until the end of the cruise. By the time the concentrate could be removed to the Corvallis laboratory and analysed for gamma emitters, several days (as many as 10) had elapsed. This is a significant delay in view of the 27.8 day half-life of $^{51}Cr$. It also prevented a cruise plan being altered to follow changing patterns in the Columbia River plume since data were unavailable until some time after the cruise was completed.

These factors indicated that a shipboard gamma ray analysing system should be incorporated and the previous system was drastically modified as follows. Electrical cords to the pump were replaced with a very flexible neoprene-jacketed power cord. This step alone improved the reliability of the pumping system since most failures at sea were attributed to the weak end connections of the former stiff line. The pump was fitted so that it could be raised and lowered over the side with an already existing hydraulic boom and winch on the ship. This eliminated both stresses at the pump coupling points and contact with the side of the ship. As a result, the station could be completed in foul weather.

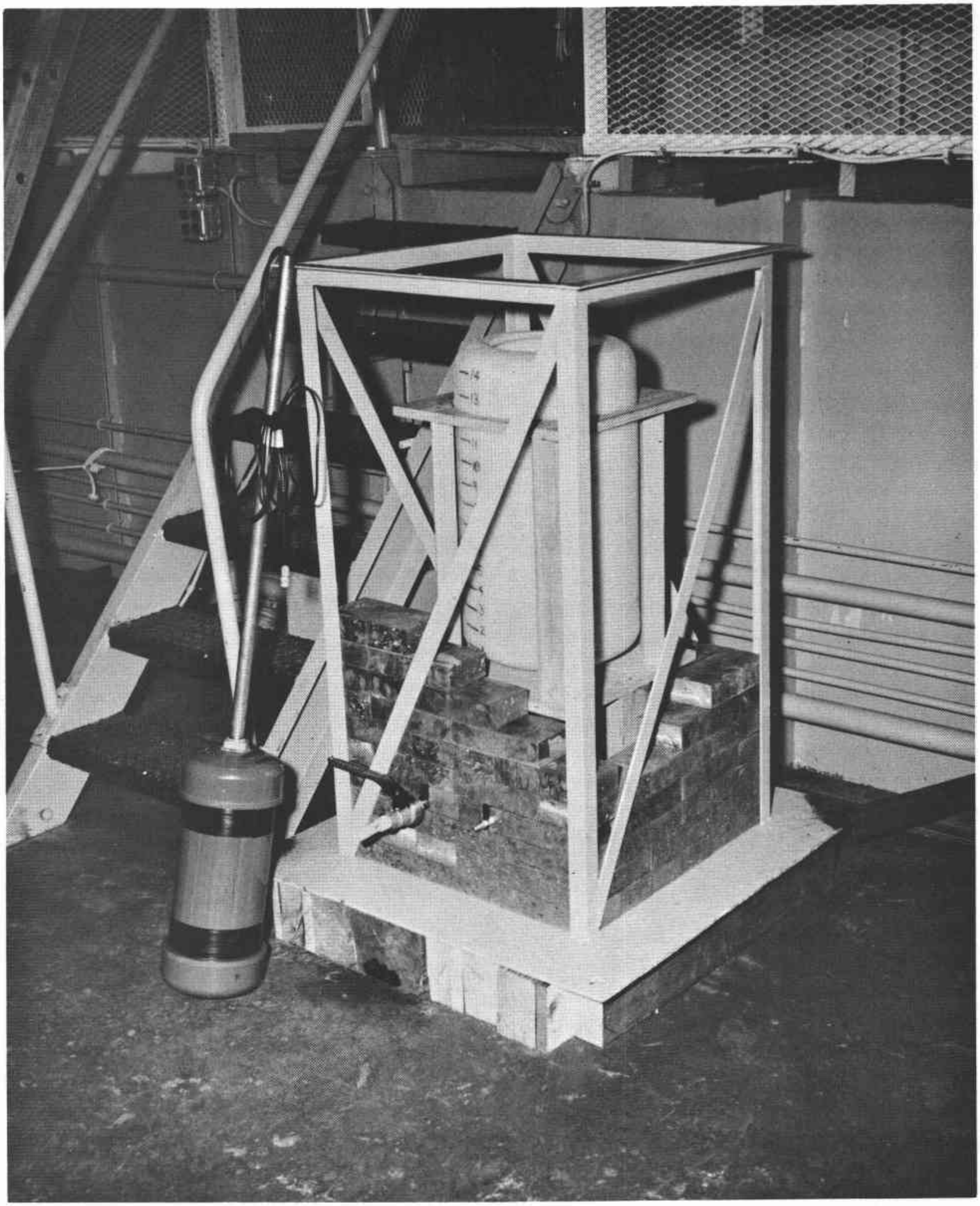

Figure 1. A stage of construction in the shipboard counting chamber. The high purity lead shield is 4 inches thick on the sides and 6 inches thick on top and bottom. Object in left foreground is the scintillator assembly.

Corrosion resistant lever-type ball valves and clear vinyl tubing were placed on the system for reliability and to speed transfer operations. The natant siphon tubing was modified to maintain a uniform position, thereby insuring removal of a consistent amount of residual water after coprecipitation of the trace radionuclides.

A 6-inch thick lead brick shield was constructed around a specially prepared plastic tank inside the ship hold below the main tank columns (Fig. 1 and 2). The brickwork was supported by a metal frame constructed out of pre-World War II angle iron and sheet steel. The tank was made by removing the base of a 50-liter carboy, inverting it in a wooden frame and porting the cap to accept plumbing. Provision was made to place a sealed scintillator detector through the opening in the top of the tank. The level of the detector was made adjustable by a slide clamp arrangement for optimizing counter geometry. The detector was packaged in a watertight plastic container that allowed room for a .5-inch thick thermal insulating layer. Electrical leads were carried out through the support standpipe in the top of the container to a field-adapted multi-channel analyzer. This analyzer and detection system included all the electronic components necessary for gamma ray spectrometry. The concentrate from the settling columns could now be adjusted to a fixed volume, placed in the shielded plastic counting tank and analyzed. After analysis, the concentrate could be drained from the tank, any residue flushed out by means of a circular flush ring mounted around the top inner rim of the tank (see Fig. 6, p.189) and then be stored in a container for further analysis after the cruise.

For long counting times, constant geometry of the sample was maintained by gently bubbling air through a one-way valve in the bottom of the tank. Otherwise precipitate settling during the count would introduce variable counting geometry and make interpretation of the readout impossible.

To adjust the concentrate to constant volume for counting it was necessary to construct two secondary tanks, one for each of the main columns (Fig. 3). These were made from 50-liter carboys which had the bases removed and the caps ported for draining. These tanks were inverted and mounted above the counter assembly in the hold and just beneath the main columns. The tanks were calibrated in gallons and the sides were ported at several gallon capacity levels. At this point, it was decided that these tanks should also be used to elevate the temperature to the ambient temperature of the ship compartment in order to protect the crystal detector from any thermal shock. For this, a stainless-steel clad electrical heating ring was mounted inside the

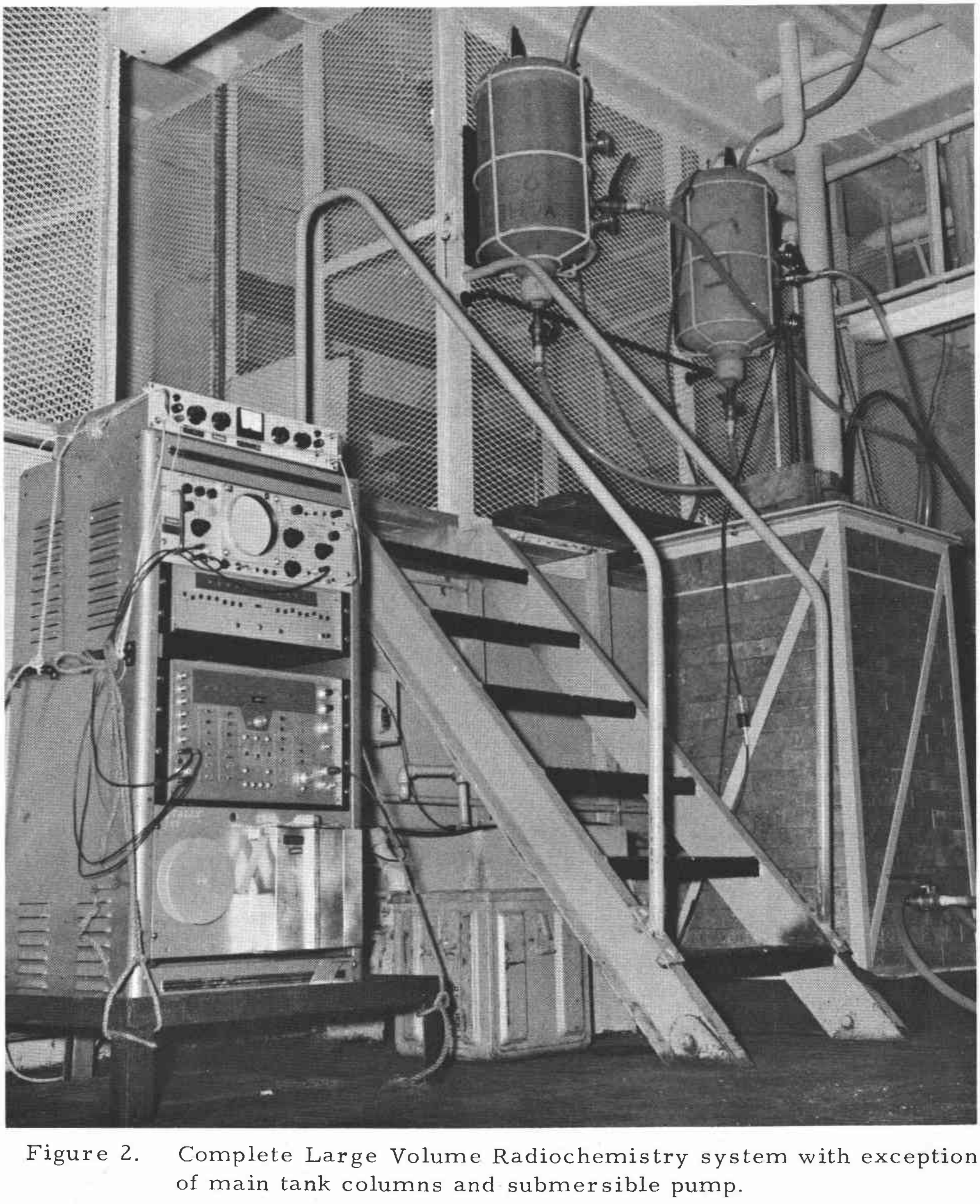

Figure 2. Complete Large Volume Radiochemistry system with exception of main tank columns and submersible pump.

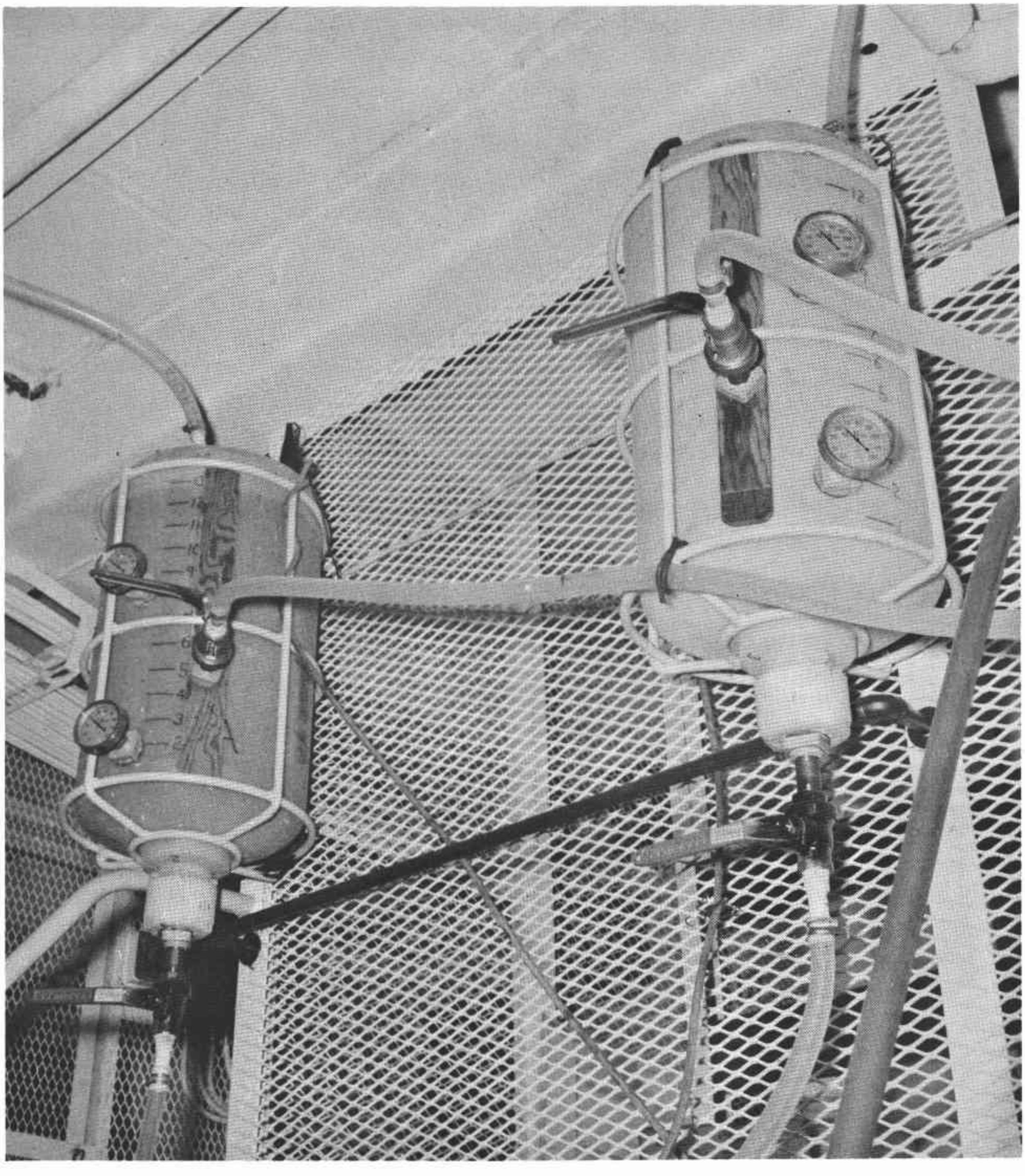

Figure 3. Secondary tanks mounted on wall of ship's hold. The left tank has been warmed to ambient temperature and the precipitate is settling. Right tank is empty.

tank near the bottom. Each ring was controlled by a transformer in order to deliver power without exceeding shipboard line ratings. Dial thermometers were mounted in the side of each tank to monitor temperature, and air bubbling was provided through glass wands in the tanks to speed thermal circulation and assure homogeneous temperature distribution.

A typical sampling procedure now entailed the following. After arriving on station, the pump was lowered over the side and one of the main columns was filled. A water sample was removed during the process so that salinity could be determined. As soon as the tank was filled to the 150-gallon (568 liter) mark the pump was secured and the ship moved to the next planned station. Meanwhile, suitable chemicals were added in a definite timed sequence to the column (see AEC Prog. Rept. AT(45-1)1750 for 1965, pp. 57-59) to form the precipitate, mixing all the while by bubbling air gently through a one-way valve at the base of the column. Then the bubbling was stopped and precipitate allowed to settle until the natant was clear. The natant was then siphoned to the 12-gallon (46.22 liter) level. Precipitate and remaining natant were allowed to pass into the secondary tank. The main tank was then flushed with one gallon (3.78 liter) of clear natant water that was retained prior to siphoning. This too passed into the secondary tank below deck.

In the secondary tank, the heating and air bubbling process was immediately started. When the ambient temperature was reached, the bubbling and heating were stopped, allowing the precipitate to settle. When the precipitate level (observed through the translucent plastic tank) reached a point safely below the side valve, the valve was opened and the natant above the valve level was allowed to drain out. This side port had a tube extension that reached to the center axis of the tank, thereby assuring drainage to the desired level regardless of ship pitch and roll. The amount left in the tank was fixed at 5.0 gallons (19 liter). This included a small amount of clear natant which formed a buffer to prevent accidental loss of precipitate in the turbulence of the tapping process. The 5-gallon sample was allowed to pass into the counting tank through the drain in the cap of the secondary tank.

The secondary tank was then flushed out with .5 gallons (1.9 liter) of clear natant that was retained in the tapping process. This, too, passed into the counting tank, increasing the sample volume to 5.5 gallons (20.8 liter). This volume was not chosen randomly. The I.D. of the counter tank and the O.D. of the detector container are of such a form that with this volume, a maximum counting rate occurs. This was determined by trial and error. Gentle air bubbling in the counter tank was started and the spectrum analyzer was set for live time counting of 100 minutes. After readout of the analyzer, bubbling was stopped and the concentrate was allowed to drain out of the bottom of the counting tank into a plastic carboy. The counting tank was flushed out with fresh water using the flush ring. This, too, passed into the same carboy. This carboy was then stored aboard ship for further analysis in the Corvallis laboratory.

The time lapse from arrival at station to readout of the sample was in every case 4 hours with negligible deviation. This permitted us to make any changes immediately in the cruise plan that would permit a more advantageous study of the plume. A further advantage was that 5 samples could be in stages of process at any one time since the system has 5 separate tanks (2 640-liter precipitation tanks, 2 50- liter secondary settling tanks, and 1 counting chamber).

The data, as read out by the analyzer, may be used for absolute measures of isotope activity only after the system has been calibrated and the percent recovery of the system has been measured for that isotope. For the purposes of the investigations now underway, the system has been calibrated for $^{51}Cr$, and all work with the system has been done with mainly this isotope in mind.

## Modifications Now Underway

The successful functioning of the present shipboard system so far does not leave much room for improvement. There is, however, one situation that will be changed before it presents a problem. Presently, the main tank columns are formed from 55 gallon (208 liter) drums end welded together with three drums making a column. In addition, each column has a 10 inch (25.4 cm) long, full cone at the bottom with a standard iron pipe coupling for a drain connection. The inside of both tanks has been coated with several layers of epoxy paint. There is evidence that this coating is not going to last. Accordingly, conventional polyethylene tank liners have been made and will be installed to eliminate a potential source of corrosion trouble. The liners will conform to the tanks and have a conical bottom with a plastic pipe coupling as a drain connection.

## New Considerations for LVC Sample Analysis

In the past, concentrates that have been brought back to the Corvallis laboratory for complete radioanalysis were subjected to the following process. After settling and decanting to a volume of 1 gallon (3.78 liters) a precipitate was re-dissolved in nitric acid and evaporated down to 800 ml volume in a steam bath. This reduced volume was placed in a heavy wall polythylene cylinder and tightly capped. The cylinder was then placed on a scintillator in a counting chamber and analyzed for 800 minutes ( live time). The counting assembly had been previously calibrated against a $^{51}$Cr solution of known activity. After counting, the sample was usually stored for reference in a glass bottle. The long time that lapsed until the last sample could be counted, the short half-life (27. 8 days) of $^{51}$Cr, the nuisance of calibration for isotopes of interest and the bulk storage of fairly large volumes led us to look for more efficient ways to process the precipitate.

It was postulated that a fractional part of a well mixed precipitate would have an activity in direct proportion to the total activity of the sample. This fraction could then be vacuum oven dried and placed in the conventional plastic test tube that we use routinely in conjunction with our two well-type gamma ray spectrometers. The major advantage of this is that these spectrometers have been calibrated for up to 14 radio-isotopes of interest to us. The digital paper-tape readout of spectra from these instruments can be submitted to computer reduction by means of a least square program we have developed and currently use (see AEC Prog. Rept. AT(45-1)1750 for 1965, pp. 120-130). Furthermore, because of higher geometry, live time counting could be significantly decreased. Sample storage would be reduced by a bulk volume factor of better than 10, since we could safely dispose of the remaining unused precipitate.

This idea was put to trial successfully in the most recent cruise for large volume radiochemistry of the Columbia River plume and the results will be mentioned in the discussion of this cruise below (see page 51).

Another method was also tried. In this, an entire precipitate was vacuum oven dried, placed in counting tubes and analyzed. The precipitate was then gathered back together and the soluble salts were leached out by two successive elutions with distilled water. The elutants were evaporated completely to recover the salts which were then vacuum dried, placed in counting tubes, and counted. The insoluble solid left after leaching was also vacuum dried, placed in counting tubes, and counted. At no time was the vacuum oven temperature allowed to approach boiling since it was feared that such violent action would result in permanent loss of activity in the vapor.

Results of activities before and after leaching showed that less than 5% of the activity in the total precipitate before leaching was tied up in the soluble salts whereas the dried volume (~50 ml weighing ~50 gr. ) of insoluble salts was 40 to 45% of the original dried volume. This lead us to believe that suitable compression of this loose mass of insoluble salts in a pellet forming die under at least 30 ton pressure would yield a pellet that could be placed in a single counting tube. The advantages of such reduction are obvious. Extremely low levels of activity in a precipitate could be detected. The limit of sensitivity of our well-type spectrometers is in the neighborhood of ~4 pc above background in a counting tube.

This idea has provoked enough interest so that plans are underway to obtain a 30 ton hydraulic laboratory press and also a pellet forming die that will make a pellet conforming to the internal dimensions of our counting tubes with a volume of 12 ml. This volume is that for which the spectrometers have been calibrated. The self shielding of the iron (density 7.7) in the high density pellet (density ~4) may be a factor to contend with, but could well prove negligible.

At one time it was thought that subjecting the insoluble salts to high temperature in a muffle furnace would dehydrate the iron hydroxide thus decreasing the volume still further $Fe(OH)_3 \rightarrow 1/2\ Fe_2O_3 + 1\text{-}1/2\ H_2O\uparrow$). This idea was bypassed when it was realized that the temperature necessary to accomplish this (~500°C) is too close to the melting point of antimony (630.5°C) and above that of zinc (419.5°C). Their loss could not be tolerated since their unstable isotopes $^{124}Sb$, $^{125}Sb$ and $^{65}Zn$ are of great importance in the study of the Columbia River plume.

## Application of the Modified Large Volume Radiochemistry System

The large-volume radiochemistry modified shipboard system mentioned above has been used twice to date. A trial cruise conducted in early December of 1965 allowed us to correct any possible system failures and also familiarize assistants with the system. The main purpose of the cruise was to collect benthic specimens and the cruise plan was such that we did not enter the plume so data taken during this trip with the LVC system were not pertinent to the plume study.

The first actual use of the system was in an investigation of the flow of the Columbia River plume in the winter. This cruise was made during the period of 21-27 February on the R/V YAQUINA. The pattern of horizontal extent of the plume was determined by analyzing both surface salinity and $^{51}Cr$ activity in the upper two meters of the mixed layer. Since this was the first extensive investigation of this phenomenon, the original cruise plan was a simple matrix of stations on 20 n. mi. (37 km) intervals along the coast of Washington from the Columbia River lightship to Cape Alava and thence out to sea 40 n. mi. (74 km). This matrix was based on the theory that the prevailing southerly longshore winds in the winter would force the Columbia effluent north close along the coast. Such was the case.

The shipboard system's rapid measuring capability allowed us to make extensive changes from the original cruise plan several times in succession. Because of this we were able to place our sampling stations along the plume at will. As a result we were able to follow the Columbia River effluent to Cape Flattery at the entrance to the Strait of Juan de Fuca, a distance of 140 n. mi. (260 km). Depletion of our supply of chemical reagents prevented us from tracking further, but 39 stations were completed. Since background measurements were made and the system was calibrated, measurements could be converted from cpm to picocuries. This was unnecessary, however, and could be done at any time with the permanent paper tape readout. Only the integrated photo-peak area for $^{51}$Cr was needed for relative comparisons of activity between stations. The minimum detectable activity of the system at a 100 minute live time count was calculated to be 2 cpm per sample. This sensitivity is thought to be more than sufficient for outlining the plume and amounts to less than 940 picocuries of $^{51}$Cr per 150 gallon (568 liters) sample of seawater. For comparison, at the mouth of the Columbia River the activity of $^{51}$Cr per 150 gallon sample was 0.233 microcuries (233,000 picocuries).

At the conclusion of the cruise, the precipitates were removed to the Corvallis laboratory. Here they were prepared as outlined in the section on New Considerations for LVC Sample Analysis above (see page 49). The dried fractional amount of a 1 gallon (3.78 liter) precipitate necessary to fill a counting tube was estimated. This consistent amount, 250 ml, was withdrawn and weighed from each sample after vigorous agitation to assure a homogeneous mixture. After vacuum oven drying the fractions were weighed and placed in counting tubes. Fractions short of the necessary 12 ml dry volume had the balance made up with sugar, which was mixed in well to give a homogenous sample. No fraction ever exceeded 12 ml. These fractions were then counted for 400 minutes each in one or the other of two well-type gamma ray spectrometers. Due to delay in standardizing these spectrometers for antimony-124, the readout spectra from this process have not yet been broken down by computer analysis. We expect to be able to finish this shortly.

With the computer analysis, we hope to be able to use the change in ratios of two apparently conservative trace elements, $^{51}$Cr and $^{124}$Sb to determine the plume's transport velocity and diffusion rate in a horizontal plane.

# CHEMISTRY OF CHROMIUM-51

by Norman Cutshall

In our 1965 progress report we stated that the addition of trivalent antimony to sea water samples increased the yield of $^{51}Cr$ in subsequent ferric hydroxide precipitates. We suggested that $^{51}Cr$ from the Columbia River remained in the hexavalent state after entering the sea and that Sb(III) reduced Cr(VI) to Cr(III) which was removed more effectively by $Fe(OH)_3$. Further experiments in the laboratory and at sea confirmed our beliefs. The results of these experiments were published in Science (Vol. 52, pp. 202-203). A copy of that paper is included in this report.

# RESEARCH IN PROGRESS

## C. CHEMISTRY

by Charles L. Osterberg, Leader

A major accomplishment during the past year was the successful operation of a pulse jet reverse flow column aboard a research vessel at sea. This pioneering feat was made possible because of the experience of Battelle-Northwest Laboratories in this area. A group of four from Battelle, led by Dr. Lee Burger, went to sea with the apparatus. This is part of the thesis research of John Cronin, in progress, on dissolved organics in seawater (see pp.56).

Further gains in analysis of stable zinc in seawater were made, as reported by Buffo (see pp. 64). Major change over the techniques used last year was the incorporation of another step--back extraction of the zinc from the organic solution into dilute HCl. This step gives an increase in concentration, but a major consideration is that the solution is stable, and can be stored at sea for subsequent analysis.

Perhaps most significant has been the "debugging" of our atomic absorption spectrometer. Tennant (see pp.67) has perfected the sample preparation process essential to the technique, and induced the instrument to perform somewhat closer to our original expectations.

# SOLVENT EXTRACTION OF ORGANICS FROM SEA WATER WITH A PULSE COLUMN

By J. Cronin*, L. L. Burger°, E. C. Martin°, C. L. Osterberg*

Organic compounds are found in sea water in very low concentration (ca. 10 mg/l total carbon); thus chemical analysis is very complicated. The sensitivity of conventional analytical methods is also limited still more by the presence of large quantities of inorganic salts. Either more sensitive instrumentation is required or larger quantities of water must be processed to obtain sufficient amounts of organic matter for analysis.

Solvent extraction was chosen as a suitable procedure for obtaining the necessary quantity. Earlier work, in the authors' laboratories, utilized two different solvent extraction procedures (1). Limited results obtained from these procedures can probably be attributed to low extraction efficiency.

For improved efficiency of extraction, a pulse column similar to those designed at the Hanford Laboratories (2), was adapted for use aboard the Research Vessel YAQUINA. The pulse column has already proven to be an efficient device for the separation of trans-uranium elements. An important factor in its application to the extraction of organic compounds is choice of solvent. The ideal solvent would have high extraction coefficients for the various organic molecules, optimum vapor pressure, ease of purification, stability and low cost. Based on these criteria, hexone (4-methyl-2-pentanone) was chosen as the solvent. The decision was supported by previous experience using hexone in solvent extraction technology. A total of 817 liters of reagent grade hexone was purchased and redistilled at a pressure of 260 mm Hg. A portion of the redistilled solvent was chromatographed ("Aerograph Model A-700" gas chromatograph). Also portions of the head and heel (which were collected and analyzed separately) were chromatographed for reference.

Because of the low flash point (30° C) of hexone, explosion-proof equipment was used throughout. Vent lines connected all feed and receiving vessels and an additional exhaust fan was provided in the laboratory.

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* Oregon State University, Department of Oceanography, Corvallis, Oregon.
° Battelle-Northwest Laboratories, Richland, Washington.

The sea water to be extracted was taken in through a sea-cock forward of the ship's waste disposal and located about 2 m below the surface. The sea-cock was opened as needed while the ship was underway. The extractions were carried out over an 82 hr. period during which time the vessel covered the route shown in Figure 1.

A constant monitoring of the water with a CTI instrument (conductance-temperature indicator) indicated the salinity of the water to be 31.65-32.60% and the temperature to be 11° C ± 0.5° C. The temperature of the extraction system was 14° C.

Tests made at sea with the apparatus described were completely satisfactory from the operative point of view. The water was pumped (Jacuzzi, 1 hp. submersible) through a 0.45μ membrane filter and glass fiber prefilter (26.7 cm PVC filter holder from Gelman Instruments). The water was then introduced into the pulse column for extraction. The pulse column schematic is shown in Figure 2 and Figures 3 and 4 show the equipment in place aboard the R/V YAQUINA. The flow rates and operating conditions are found in Table I.

## TABLE I

## Operating Conditions of Pulse Column

| | |
|---|---|
| Column Size | 3-inch diameter--4-foot length with two 1-foot T joints. |
| Cartridge | 2-inch spacings, Fluorothene sieve plates 3/16" hole, 23% free area separated by five stainless steel nozzle plates 3/16" holes, 23% free area. |
| Flow Rates | Aqueous - 3000-3760 ml/min.<br>Solvent - 300-350 ml/min. |
| Pulse | Frequency - 64 to 80 cps with 80 cps majority of time<br>amplitude - 1 to 1.5 inches. |
| Holdup | 5 aqueous to 1 organic solvent. |

Both aqueous continuous and organic continuous operation were tried, the latter appeared to give a better dispersion and was used during the experiments.

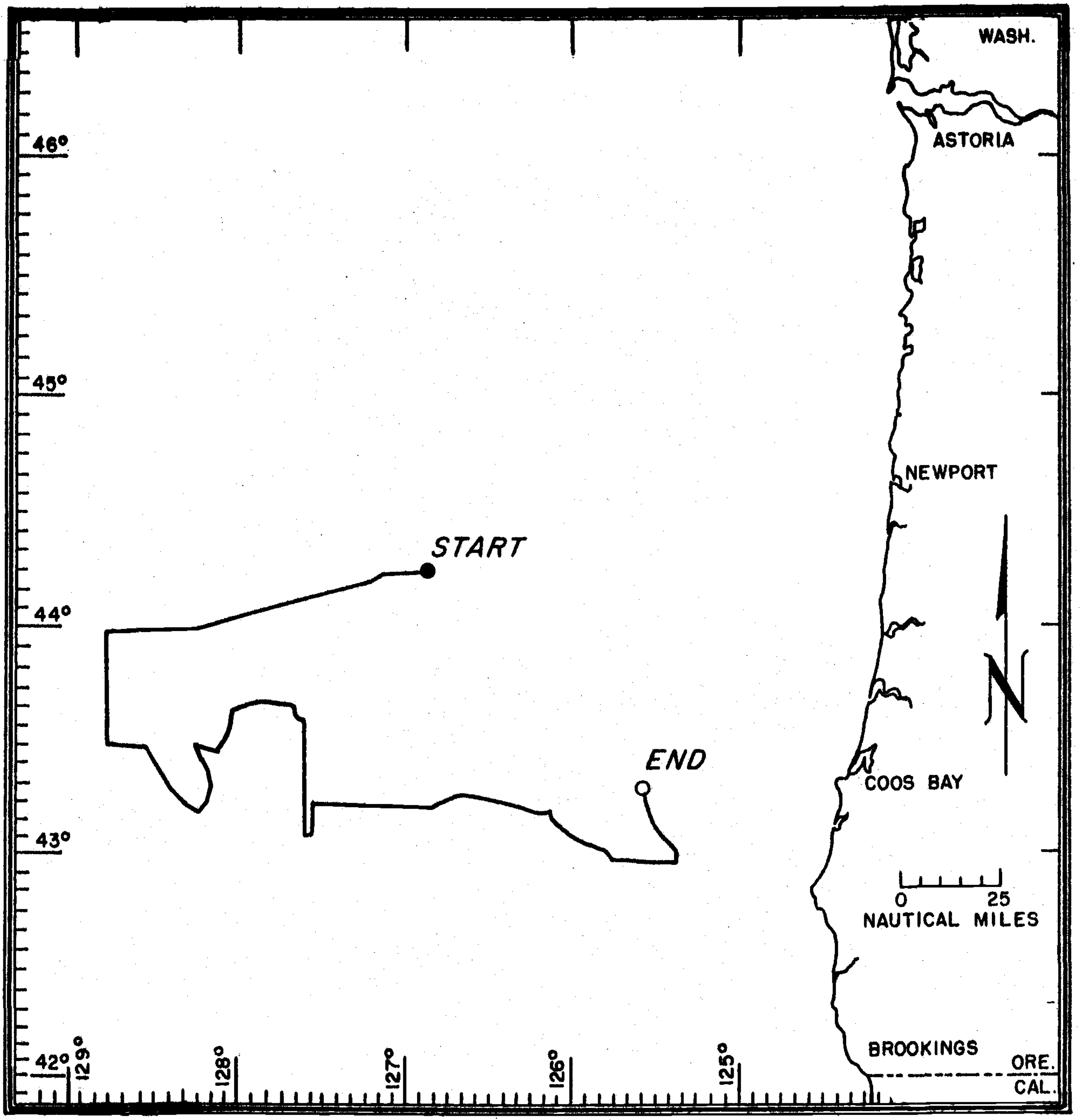

Figure 1. Track-line of R/V YAQUINA during extraction period.

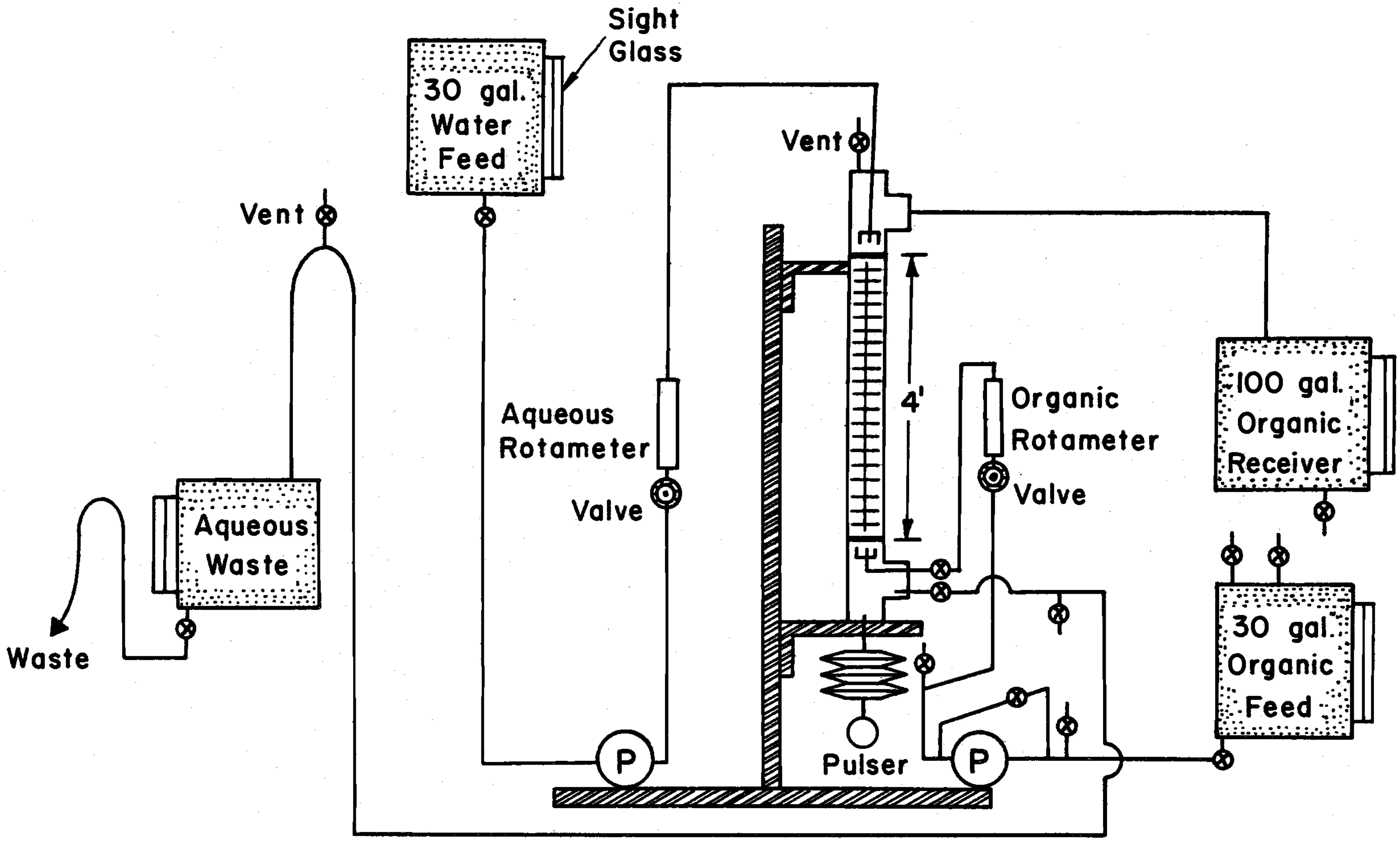

Figure 2. Schematic drawing of pulse column.

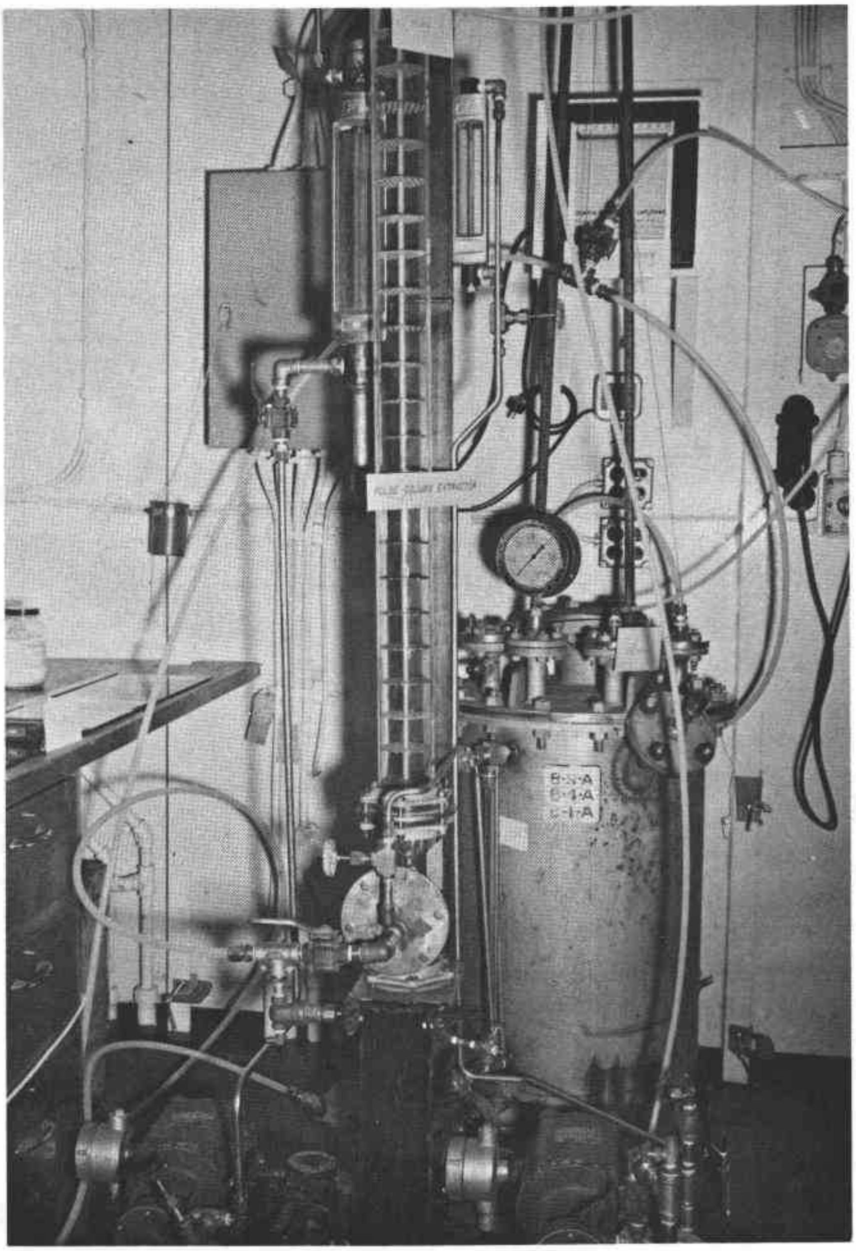

Figure 3. The pulse-column apparatus as installed on the R/V YAQUINA.

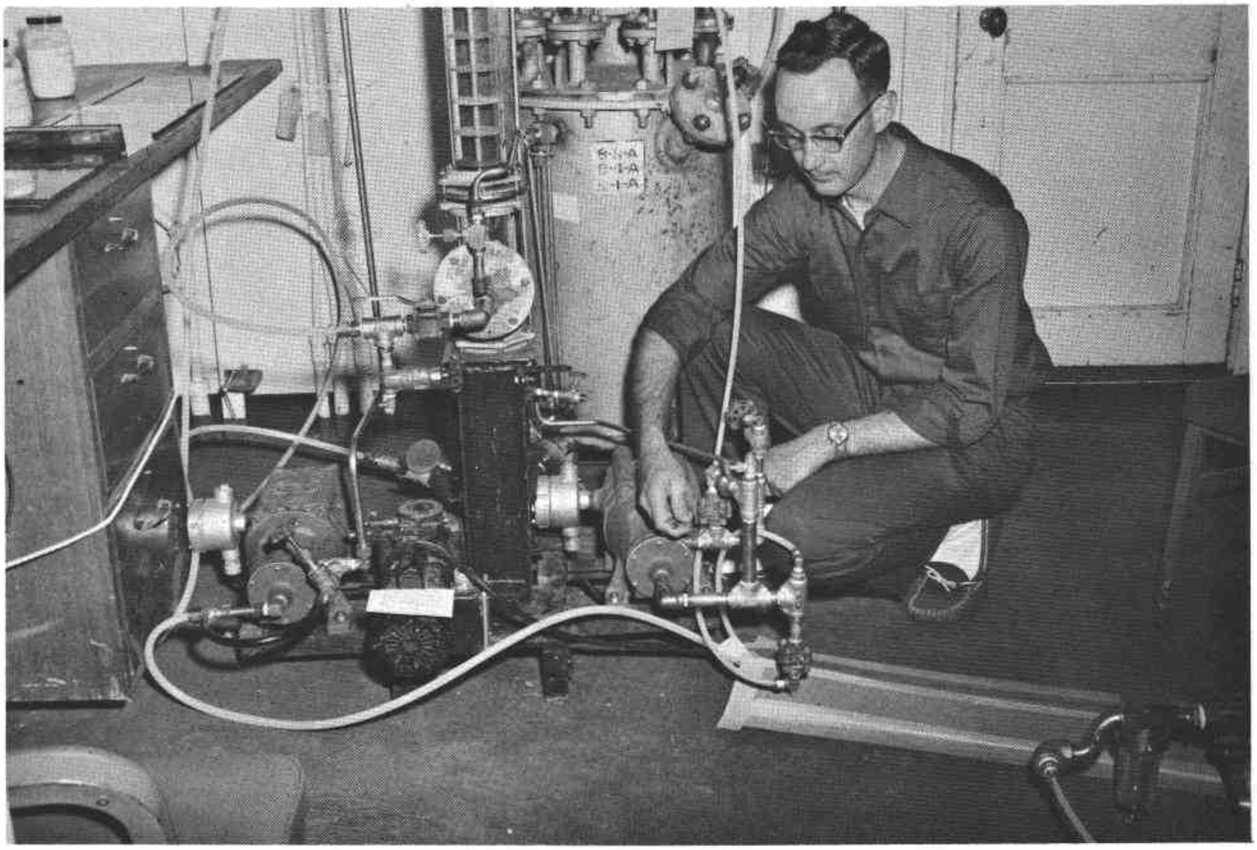

Figure 4. The base of the pulse-column apparatus.

Preliminary evaporations of the product solvent indicated that organic matter was being recovered from the sea water. The procedure was varied with each experiment as follows:

| | |
|---|---|
| Experiment 1 | 4600 liters of sea water at pH $\sim$ 8.2 -- 379 liters of solvent used with 265 liters recovered. A 300 ml portion of the product solvent yielded 17.1 mg of organic material. |
| Experiment 2 | 6927 liters of sea water adjusted to pH = $\sim$ 3.5 with conc. HCl -- 341 liters of solvent were used and recycled with 189 liters recovered. Two 300 ml portions of the product solvent yielded 29.0 and 15.0 mg of organic matter. |
| Experiment 3 | 700 liters of sea water adjusted to pH = $\sim$ 3.5 with HCl -- 389 liters of solvent used for one cycle only yielded 30 liters product solvent. A 300 ml portion of the product solvent contained 13.3 mg of organic material. |
| Experiment 4 | 511 liters of sea water adjusted to pH = $\sim$ 3.5 with HCl -- 57 liters of solvent from Experiment 3 was continually recycled until flooding* occurred. 15 liters of solvent were recovered. This hexone was assumed to be near equilibrium with the sea water. A 300 ml portion of the product solvent contained 24.7 mg of organic material.<br>* Flooding, lack of phase separation, apparently resulted from the changed physical properties of the solvent after extensive extraction. |
| Experiment 5 | 7.5 liters of reagent grade amyl acetate (not redistilled) was introduced into the column and water (pH = $\sim$ 3.5) pumped through at a reduced rate, when flooding occurred 322 liters of water had been extracted.<br>Because of the small volumes, the interface samples and the amyl acetate were not evaporated to determine solid organic matter. |

On return to shore facilities the product solvent was redistilled at a pressure of 70 mm Hg (65° C) with water (4° C) used to cool the condenser and a dry ice trap for collection of volatile material.

Further analysis utilizing gas-liquid, column and thin layer chromatography as well as mass spectroscopy, IR, UV, and visible spectrometry will be completed in the summer of 1966 at Battelle-Northwest Laboratories, Richland, Washington.

The preliminary results noted indicate that pulse column extraction can be utilized successfully at sea for the extraction of organic matter from sea water.

## REFERENCES

Cronin, John T., Ph. D. Thesis, Oregon State University, Corvallis, Oregon. In preparation.

Reactor Handbook, 2nd Edition, Vol. II, Fuel Reprocessing, Interscience Publishers, N. Y. (1961), pp. 566-78.

# SOLVENT EXTRACTION OF STABLE ZINC

By Lynn Buffo

In the previous progress report a concentration and analysis procedure for the determination of trace zinc in sea water was described (See AEC Prog. Rept. AT(45-1)1750 for 1965 p. 65). The variable and unexplained results when the procedure was taken to sea prompted the following laboratory study and consequent modification of the concentration process. Final analysis by the Atomic Absorption Spectrometer is still carried out as previously described.

The working procedures described by Cronin consisted of filtering 500 ml of sea water through a 0.45μ glass membrane filter and buffering to a pH of 6.8-7.0 using 0.5M citric acid buffer. Following the addition of two milliliters of 2% chelating agent (NaDEDTC), the sea water was shaken periodically for one hour, and the chelated zinc was extracted into the organic solvent MIBK. This was shaken similarly for another half hour and separated. Analysis on the Perkin Elmer Model 303 Atomic Absorption Spectrometer completed the determination.

The initial effort was to carry out the mechanization suggested in the '65 report so that results would be independent of personnel. A shaking machine with a timing device was modified to handle eight 1000-ml separatory funnels; thus, the interminable (when done by hand) shaking periods were made uniform in time and in efficiency of mixing.

Zinc-65 tracers were used to follow the steps in the extraction process and to evaluate the extent of extraction. A known amount of zinc-65 was transferred quantitatively to 500 ml of sea water in a separatory funnel. The extraction procedure as described above was then carried out with the exception that the organic layer was drained into a 100-ml volumetric flask and diluted to the mark. The percent recovery was then determined by gamma ray spectrometry. In the campus laboratory the process gave a recovery of 97 ± 2 %, but was found inadequate for shipboard use due to the instability of the extracted sample. Apparently, adsorption onto the container walls resulted in drastic reductions in the recoveries of aliquots taken from the original extracted sample and counted. Other evidence was the increased count rate of the counting tubes with time due to the changing geometry within the tubes.

A back-extraction into HCl was then attempted and proved to be highly successful. The solution was very stable with time, and the back-extraction gave an additional concentration factor soon to be needed. The extraction procedure was studied to determine minimum time periods required for shaking and reagent volumes needed for successful extraction. The following is the procedure in its present form: Measure carefully 750 ml of sea water into a 1000-ml separatory funnel. No buffer is needed. Chelate with two milliliters of 2% NaDEDTC and shake mechanically for 35 minutes. Add about 100 ml of MIBK and shake another 35 minutes. Drain off the lower aqueous layer and add about 25 ml of 0.36 NHCl to the organic phase in the separatory funnel and shake for 20 minutes. Since some of the aqueous phase will have dissolved into the MIBK, drain the HCl layer into a 25-ml volumetric flask and dilute to the mark. In this way a known concentration factor of 30-fold is realized. During study, a 5-ml aliquot is analyzed in multichannel spectrometer for recovery of zinc-65. For actual sea water analysis (unspiked), the sample is simply measured on the AAS directly from the volumetric flask.

The percent recovery with the back-extraction process was shown by tracer experiments to be 97 ± 2%. The reproducibility on the AAS was very good. Four simultaneously-run duplicate samples from an unfiltered sea water source gave a standard deviation of 1.2%, all four samples falling within 1.2 standard deviations.

An interesting experiment was performed using samples taken at sea from four different stations--two duplicates per station. One of each duplicate was spiked and buffered, the other merely spiked. The samples were allowed to come to equilibrium for a couple months. When analyzed, the four buffered samples gave results of 0.7-4% recovery, while the unbuffered samples gave 93-94% recovery. It would appear that the citrate buffer competes with the NaDEDTC for the zinc and, in this case, had sufficient time to do so effectively. The NaDEDTC apparently did not have sufficient time in the analysis process to displace the citrate chelate, and the end result was very slight recovery. This could have strong implications as to the soundness of using citrate to buffer this type of solution.

The most recent step has been to take the process to sea to check out the equipment, the personnel, and hopefully the sample storage possibilities. Sampling was done with a 3-gallon PVC-formica Van Dorn bottle and analysis followed immediately. Duplicate samples were kept in polyethylene bottles for periodic sampling back at the lab. The results are shown in Table 1.

Table 1. Zinc in parts per billion of sea water from four collections (four subsamples of each).

| | | 1st Run (4/12-4/14) | 2nd Run (4. 20) | 3rd Run (5/17) |
|---|---|---|---|---|
| Sample | Location | ppb Zn | ppb Zn | ppb Zn |
| 1. a | NH 15 | 39. 0 | 72. 0 | 69. 4 |
| b | surface | 46. 7 | 71. 4 | 69. 4 |
| c | | 52. 7 | | |
| d | | 60. 7 | | |
| | | av. 49. 8 | 71. 7 | 69. 4 |
| 2. a | NH 65 | 54. 0 | 80. 0 | 80. 4 |
| b | surface | 52. 7 | 80. 0 | 82. 6 |
| c | | 41. 0 | | |
| d | | 45. 4 | | |
| | | av. 48. 3 | 80. 0 | 81. 5 |
| 3. a | NH 65 | 14. 0 | 23. 0 | 20. 7 |
| b | 100 m | 14. 0 | 23. 0 | 20. 7 |
| c | | 15. 8 | | |
| d | | 16. 0 | | |
| | | av. 15. 0 | 23. 0 | 20. 7 |
| 4. a | NH 65 | 14. 0 | 13. 0 | 16. 3 |
| b | 300 m | 13. 3 | 16. 0 | 16. 3 |
| c | | 15. 3 | | |
| d | | 16. 7 | | |
| | | av. 14. 8 | 14. 5 | 16. 3 |

The results are evidence of the need for shipboard extractions. With time, three of the samples increased in extracted zinc by considerable amounts--up to 70%. The variation in duplicate samples of fresh sea water, particularly surface samples, is probably due to actual variation in the sample since surface waters are actively contaminated by land run-off and need not be homogeneous. The deeper samples show less deviation, and all duplicate samples become consistent with time.

Immediate plans call for more shipboard experimentation as to the length of time (in terms of hours) a fresh sea water sample can wait prior to analysis, and as to possible means of storing samples for a few hours, e. g. freezing. Either alternative would allow a delay in analysis following the sampling. This will be important, if not necessary, for extensive vertical sampling or for near-synoptic surface data. The actual data collecting will then follow. Both the Columbia River estuary and the coastal waters will be sampled.

# TRACE ELEMENT ANALYSES

by David A. Tennant

## INTRODUCTION

The work presented describes the procedures used to determine the concentrations of certain trace elements found in oceanic animals. To date, the trace elements of most interest to us have been zinc and manganese, since radioisotopes of both are very prevalent in our sampling area.

Since only Zn and Mn determinations will be described herein, procedures and applications reported here should not be necessarily applied to other trace elements.

A Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer (Fig. 1) was used for all measurements.

### Preparation of Standards

Aqueous solutions containing known amounts of the trace element of interest are used as standards to obtain a working curve.

Because metals are more free of contaminants than their salts, standard solutions are made up from high purity metal. The metal is washed with approximately 2% nitric acid, rinsed three times with distilled water, and dried at 60° C to constant weight. Any distilled water used for trace metal analysis must be absolutely free of contamination. After weighing the metal is dissolved in 1 : 1 nitric acid, and diluted with distilled water to a known volume. Working standards can be obtained by dilution.

Standard concentrations are as follows:

| Zinc | | Manganese | |
|---|---|---|---|
| Stock solution | 511 ppm | Stock solution | 1,303 ppm |
| Working standards | 1.02 ppm | Working standards | 0.26 ppm |
| | 2.04 ppm | | 0.52 ppm |
| | 3.06 ppm | | 0.78 ppm |
| | 5.11 ppm | | 1.30 ppm |

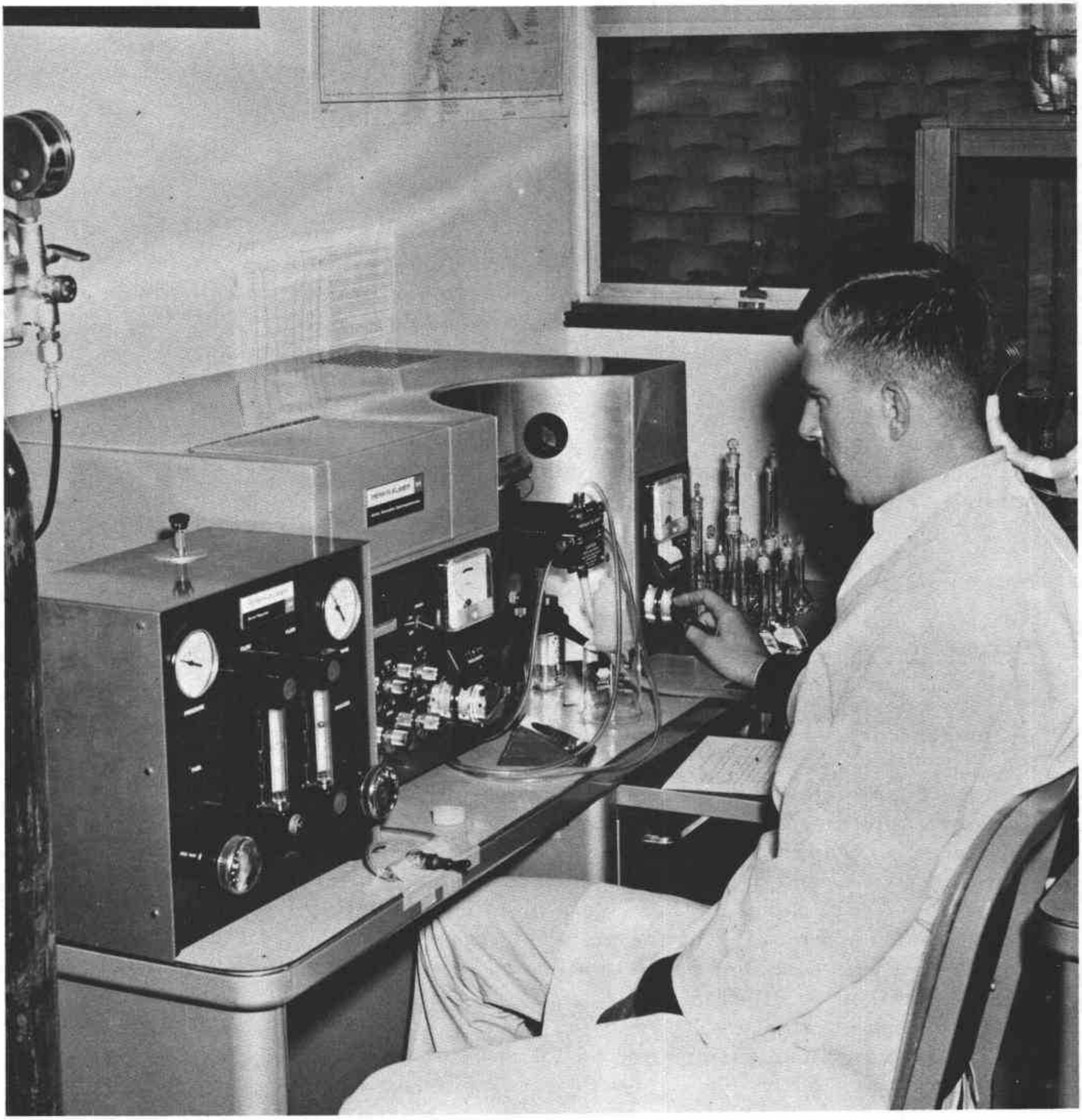

Figure 1. The Perkin-Elmer Model 303 atomic absorption spectrophotometer used for trace element determinations.

## Sample Treatment and Preparation

Since zinc and manganese occur in relatively low concentrations, contamination or losses must be prevented.

Formalin has been shown to be an unsuitable preservative. This is apparent (Fig. 2) from a comparison of formalin in which fish were preserved ("dirty formalin") with a fresh solution of preservative ("clean formalin"). "Clean formalin" was used as a blank from which the base line is obtained. The peaks represent approximately 0. 2 ppm and 0. 3 ppm zinc from left to right. Zinc was obviously leached from the fish tissue into the formalin.

Therefore, samples taken aboard ship are kept frozen in polyethylene bags, until prepared for analysis.

The samples are dried at 60°C to constant weight, then ashed in a muffle furnace at 450° C. Ashing time and temperature are very critical steps. Above 450° C zinc may be volatilized, at too low a temperature or insufficient time a black charred ash is obtained. A correctly ashed sample will be white to grey and powdery.

A portion of the ash is weighed, digested, and diluted to volume.

During our preliminary work, the trace element was leached from the ash with 0. 36 N HCl in accordance with the instructions in the Perkin Elmer Analytical Methods manual, but all of the metal was not being extracted from the ash. We found that 90% fuming nitric acid worked well, so an experiment was run to compare the effectiveness of leaching vs. digestion. Results of the experiment are shown in Table 1.

Complete digestion of the ash is very difficult. To digest the ash, about 10 ml. of 90% fuming $HNO_3$ or red fuming $HNO_3$ is added to the flask and boiled until dry. Temperature does not seem to be critical as long as the mixture does not bump.

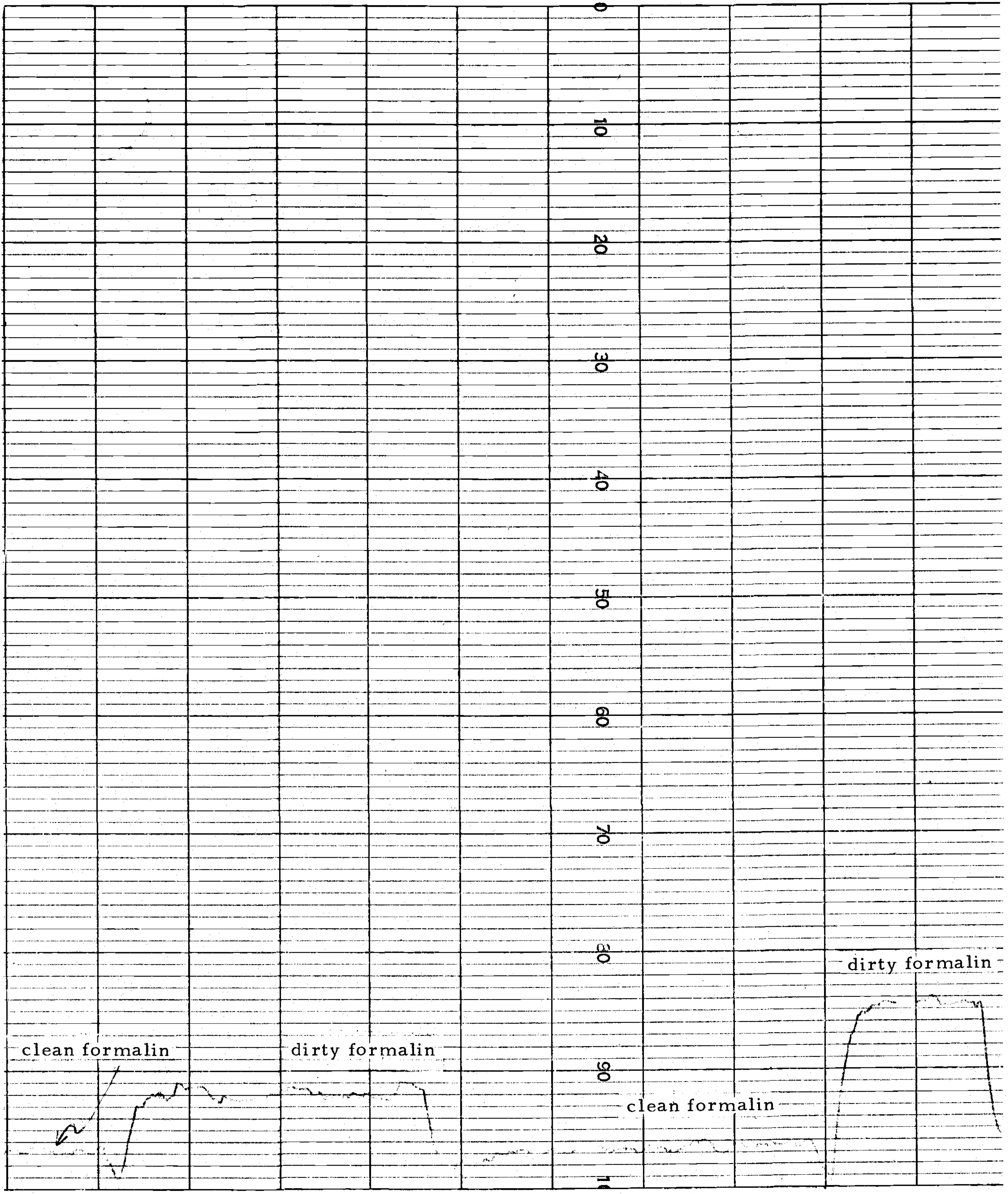

Figure 2. Strip chart recording of "clean" and "dirty" formalin.

Table 1. Zinc concentrations obtained in experiments to show effectiveness of leaching vs. digestion.

| | Micrograms Zn/gm ash | |
|---|---|---|
| Sample No. | Leaching | Digestion |
| 151-1 | 570 | 581 |
| 2 | 558 | 569 |
| 3 | 546 | 585 |
| 4 | 559 | 596 |
| average | 558 | 583 |
| 100-1 | 228 | 385 |
| 2 | 236 | 401 |
| 3 | 234 | 403 |
| 4 | 241 | 415 |
| 5 | 206 | --- |
| average | 229 | 401 |
| 709-1 | 914 | 1274 |
| 2 | 919 | 1183 |
| 3 | 1017 | 1210 |
| 4 | 948 | 1301 |
| average | 950 | 1242 |

If the dry residue is black, indicating much unoxidized organic matter, an additional 10 ml of fuming nitric acid is added and boiled to dryness again. The second addition of acid may result in a finely divided yellow precipitate which causes severe bumping. A few ml. of concentrated HCl dissolves this precipitate. This procedure is repeated until a white to reddish-brown crust of residue is left on the bottom of the flask. Minute amounts of silicious and carboniferous material remaining in the samples are ignored. The residue is taken up in acid (0.36 N HCl), cooled, and diluted to volume.

The samples and standards are aspirated into the flame of the spectrometer via capillary tubing, taking care to avoid undigested particulate matter which might clog or slow the flow of the sample through the capillary tube because the flow rate for standards and samples must be the same.

An air-acetylene mixture is currently used in our spectrometer burner. The air-propane mixture previously used gave 150 to 250% greater absorption, but overall data were more variable because of the tendency for the weak flame to deflect in minor drafts. The air-acetylene flame is hotter, stronger, and less subject to "flickering." It is important that optimum burner conditions be maintained, since smaller ash samples are then required for analysis. Ashing and digestion of small samples of organic material is considerably easier than for large amounts.

## Data Processing

The readout of trace element concentration, indicated by percent adsorption, is recorded on a 10 mv. potentiometric strip chart recorder. Since the chart is graduated from one to one hundred, percent absorption can be read directly if the base line is kept on zero (Fig. 3).

Absorbance of the samples is read from the strip chart readout and concentration determined from a standard curve derived by plotting absorbance against concentration of a known (Fig. 4). A least squares fit is programmed for the standard curve on a digital computer. IBM cards need only to be punched with sample number, percent absorption and sample weight (ash) and the computer reads out corresponding trace element concentration expressed in micrograms of Zn per gram ash. The computer program and readout are shown in Fig. 5 and 6. An analysis was made to determine how the computer readout values compared to manual graphing values (Table 2). The differences observed reflect the least squares fit in the computer program. It can be observed from Fig. 4 that the plot of the standards vs. absorbance does not give a perfectly straight line which is characteristic of deviation from Beer's Law at higher absorption,e. g. concentration.

In the immediate future, the computer program will be revised to readout micrograms (zinc) per gram ash free dry wt. and specific activity, e. g. picocuries $Zn^{65}$ per microgram stable zinc.

To date, our main concern using atomic absorption has been reproducibility. An extensive experimental program has been carried out to determine what variations can be expected. A series of samples was analyzed and the series repeated after an elapsed time. Thus the analysis would proceed: Sample #1, Sample #2, Sample #3 . . .

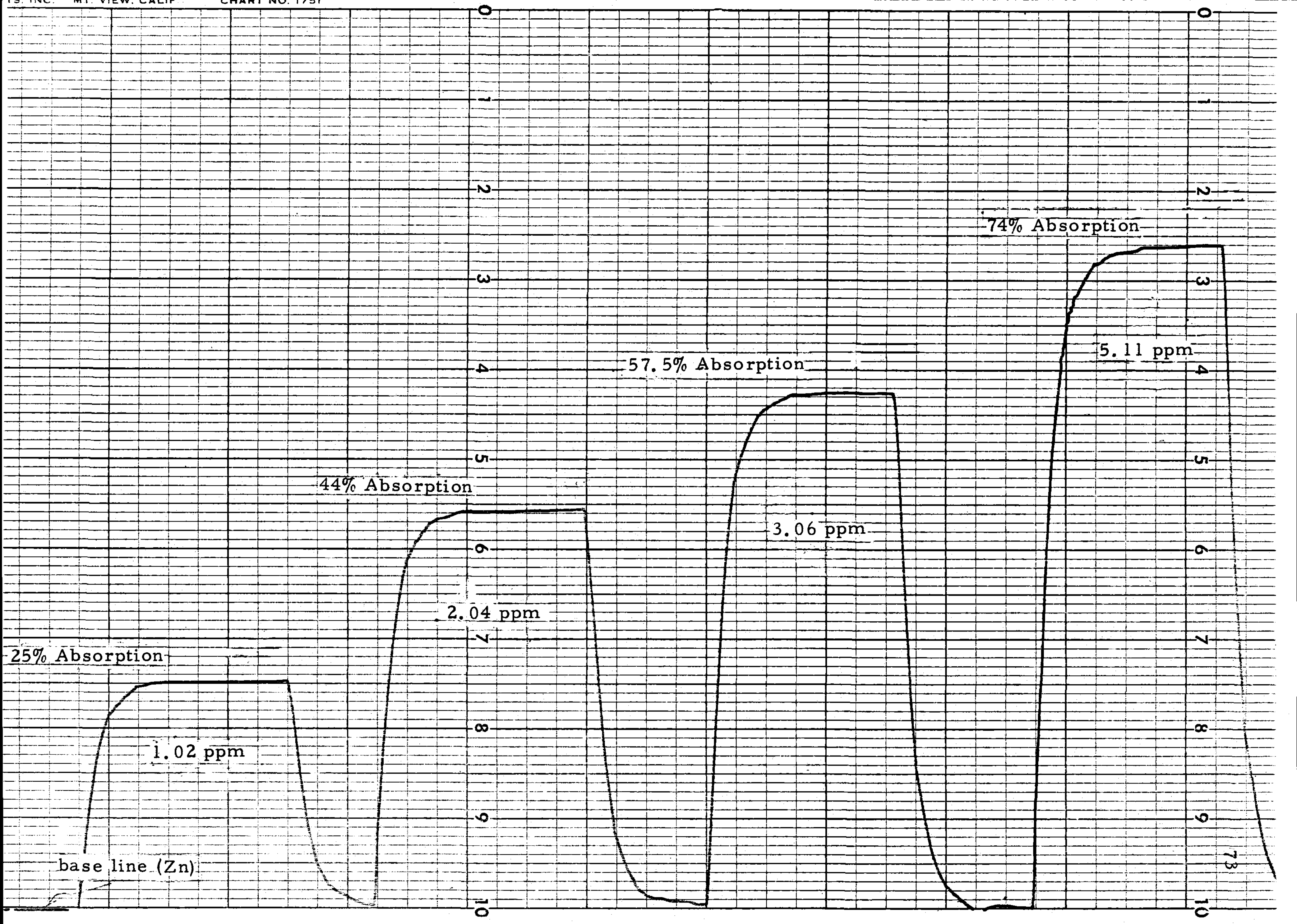

Figure 3. Strip chart readout showing base line and percent absorption.

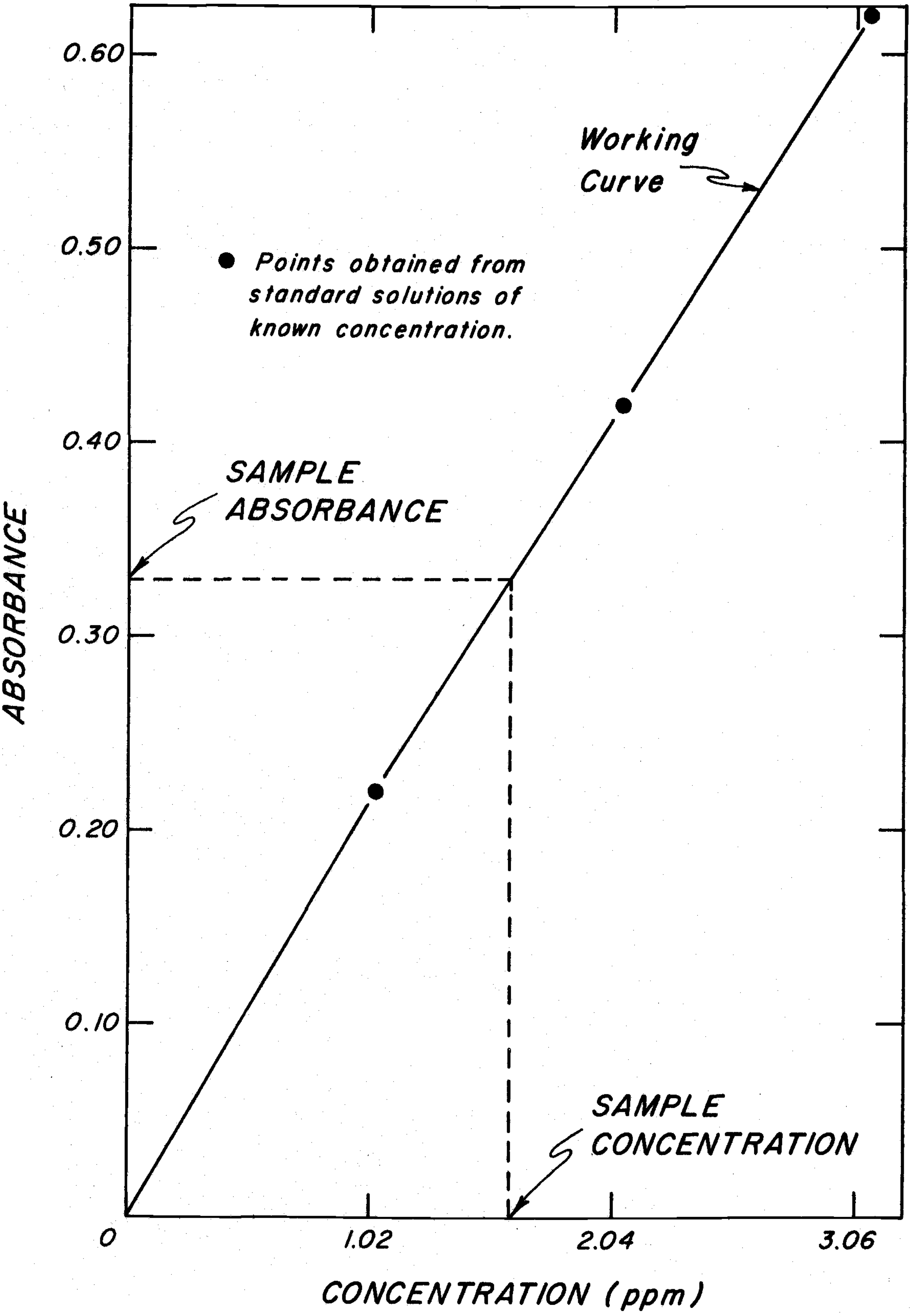

Figure 4. Standard curve from which unknown sample concentrations are determined.

Table 2. Comparison of computer readout values to values obtained by manual calculation (μgm Zn/gm ash).

| Sample No. | Computer | Std. Graph |
|---|---|---|
| 474-1 | 252.2064 | 239 |
| 474-2 | 270.6793 | 270 |
| 474-3 | 268.8783 | 270 |
| 474-4 | 254.4557 | 253 |
| 694 | 470.2810 | 469 |
| 698A | 329.3078 | 328 |
| 508 | 435.6935 | 433 |
| 526 | 492.7592 | 489 |
| 629 | 483.7305 | 480 |
| 617A | 291.1863 | 283 |
| 617B | 293.8950 | 281 |
| 617C | 299.0174 | 284 |
| 617D | 297.4167 | 285 |
| 617E | 295.4957 | 284 |
| 617F | 293.9850 | 284 |
| 617-1 | 302.0636 | 289 |
| 617-2 | 296.0919 | 293 |
| 617-3 | 300.1123 | 290 |
| 617-4 | 288.7253 | 284 |
| 617-5 | 331.1897 | 316 |
| 617-6 | 296.1755 | 297 |

```
                                   3200  FORTRAN  (2.1.0)/(RTS)      07/01/66
       PROGRAM TENNANT
C      PROGRAM TENNANT FOR JOB 1067 BY SUE BORDEN.
       REAL NSAM
       DIMENSION AB(900),X(9),Y(9)
    11 FORMAT(2I5/(8F10.0))
    10 FORMAT(20F4.4)
    12 FORMAT(A5,F10.1,F10.4)
    13 FORMAT(1H ,A5,4F10.4)
       READ(1,10)(AB(I),I=1,900)
   100 READ(1,11)M,NSCAL,(X(I),Y(I),I=1,M)
       GOTO (30000,30006) EOFCKF(01)
 30006 IF(M.EQ.0) 30000,30001
 30000 STOP
 30001 SUMX=0.
       SUMY=0.
       SUMXS=0.
       SUMYS=0.
       SUMXY=0.
       DO 1 I=1,M
       IF(NSCAL.GE.5) 2,30002
 30002 N=X(I)*10.+1.
       N=X(I)*10. +1.
       X(I)=AB(N)
     2 SUMX=SUMX+X(I)
       SUMY=SUMY+Y(I)
       SUMXS=SUMXS+X(I)*X(I)
       SUMYS=SUMYS+Y(I)*Y(I)
     1 SUMXY=SUMXY+X(I)*Y(I)
       R=M
       Q=1./(R *SUMXS-SUMX*SUMX)
       A=(R *SUMXY-SUMX*SUMY)*Q
       B=(SUMY*SUMXS-SUMX*SUMXY)*Q
    99 READ(1,12)NSAM,PCT,WT
       GOTO(30000,30005) EOFCKF(1)
 30005 Q=PCT
       IF(WT.EQ.0) 100,30003
 30003 IF(NSCAL.GE.5) 3,30004
 30004 NPCT=PCT*10.+1.
       Q=AB(NPCT)
     3 PPM=(A*Q+B)*25.
       ZN=PPM/WT
       WRITE(3,13)NSAM,PCT,PPM,WT,ZN
       GO TO 99
       END

         3200 FORTRAN DIAGNOSTIC RESULTS - FOR  TENNANT


NO ERRORS
LOAD,56
RUN,005
```

```
SUBP
 67074  Q8QERROR     67352  FIXF         67421  Q1QADRI      67602  Q8QCUTTB
 70423  EOFCHK       70510  FORMAT       71051  BCDOUT       72607  BCDINP

ENTR
 67352  IFIX         67352  XFIXF        67352  FIXF         67544  Q1QSTRX
 67437  Q1QADXR      67515  Q1QSBRX      67475  Q1QADRX      67472  Q1QDVIR
 67437  Q1QADIR      67460  Q1QDVRI      67454  Q1QMURI      67421  Q1QADRI
 67603  Q8QENTRY     67632  Q8QEXITS     70357  Q8QPAUSE     70423  EOFCK
 71152  Q8QLGOTC     71152  Q8QLGOTI     70510  Q8QIFRMT     70541  Q8QFORMT
 70101  Q8QEDITS     67074  Q8QERROR     70265  PWRTBLO      67760  Q8QIOERR
 71157  Q8QLGOTR     71051  Q8QINGOT     67450  Q1QSBRI      67521  Q1QSTIR
 72706  Q8QLGINI     73261  Q8QENGIN     72712  Q8QLGINR     72607  Q8QINGIN
 03761  FDPBOXS      05615  RIO          01174  EINT.        01160  DINT.
 00536  CIT.RTM      05657  RDCKSUM      05730  START2       05375  ACCOUNTS
 03761  ABNORMAL     01235  CIO          05434  MEMORY       04603  MIBUF
 05135  EST          05236  UST          05276  CST          05355  BRHT
 05307  AET

COMM
    NONE

DATA
    NONE

EXTA
    NONE




EQUENCE,042, NO CHARGE.
OB,1067,JOHN,010,ND
QUIP,56=MT,55=MT
QUIP,01=60,03=61
ORTRAN,X,L,P
```

Figure 5. Computer program for trace element concentration determination.

```
SEQUENCE,067
JOB,1067,SHEB,010,ND
EQUIP,01=60,03=61
RUN,005,NM
851C     25.5000   26.1124    .0578  451.7717
303      36.0000   39.8885    .001039888.5235
304      51.8000   65.6039    .0138 4753.9094
596C     49.0000   60.4692    .0182 3322.4842
907      57.5000   77.7725    .0307 2533.3067
TF19     66.3000  102.9234    .0247 4166.9410
509C     65.3000   99.7546    .0289 3451.7171
983      54.5000   65.3870    .1026  637.3003
771      28.5000   27.7490    .1121  247.5382
785       5.0000    4.0887    .0067  610.2503
1027     41.6000   44.6027    .1057  421.9746
781      22.8000   21.3642    .1174  181.9777
764      32.0000   31.9289    .0909  351.2530
933      33.5000   33.7887    .1237  273.1507
819      29.0000   28.3242    .0787  359.9014
766      25.1000   23.8759    .0563  424.0842
713       8.0000    6.7538    .0309  218.5703
753      41.5000   44.4493    .0654  679.6533
758      58.9000   73.8618    .0471 1568.1909
829      21.7000   20.1754    .0893  225.9285
986      61.5000   81.7459    .1011  808.5646
TF19     65.0000   91.1885    .0229 3982.0294
963      24.3000   23.1872    .0615  377.0273
961      24.8000   23.7510    .0248  957.7019
772      24.5000   23.4205    .0562  416.7346
765      35.0000   36.0581    .0634  568.7393
827      25.0000   23.9649    .0967  247.8270
768      22.0000   20.6597    .0788  262.1784
962      17.5000   15.9157    .0681  233.7108
964      36.0000   37.3607    .0565  661.2516
851C     14.8000   13.2132    .0301  438.9769
767      13.7000   12.1244    .0401  302.3548
763      19.8000   18.3071    .0721  253.9129
959      12.0000   10.4718    .0427  245.2417
770      18.0000   16.4406    .1057  155.5407
333      49.0000   56.5310    .0101 5597.1249
715      72.5000  113.5000    .1315  863.1179
TF16     14.7000    5.8896    .1906   30.9003
TF5      13.0000    5.5995    .2358   23.7467
TF7      19.6000    6.7532    .2572   26.2566
876      21.1000    7.0298    .2800   25.1064
851C      8.0000    4.7797    .2951   16.1970
851B     13.5000    5.6838    .3547   16.0243
841      19.5000    6.7363    .1688   39.9071
303      27.2000    8.2105    .1730   47.4595
TF20     12.8000    5.5657    .2009   27.7041
907      24.2000   21.5025    .2216   97.0329
828      24.9000   22.0986    .0431  512.7277



ELAPSED TIME     000.58 MINUTES
```

Figure 6. Computer readout of Zn concentration (μg Zn/gm ash).

sample #n, sample #1, sample #2, sample #3 . . . sample #n. Each sample was analyzed three times. Table 3 shows the results using aqueous zinc solutions of various concentrations. A propane-air fuel mixture was used for the above analysis. Standard deviations and coefficients of variation were calculated for each absorption value from the average absorption value.

For the next analysis of variability, replicate subsamples of ash were used. Each subsample was prepared and anlyzed separately and its respective concentrations calculated. Zn concentrations should be identical for all subsamples provided the main ash sample is homogeneous. Table 4 gives the absorption readings of these analyses, which were also run with propane-air.

The two variation analyses were then carried out in the same manner using acetylene-air as a carrier fuel mixture. Instead of using an aqueous zinc solution for determining reproducability of absorbance readings, sub-aliquots of an ash-digestion solution were used (Table 5). Ash subsamples were used to determine variation in the ash (Table 6). Variations of absorption readings were calculated for this determination also. The samples used in the last two analyses were prepared by our lab technician and were run on the spectrometer by a Perkin-Elmer employee who is a specialist in atomic absorption.

The next test of reproducibility was done on many individuals of one species. They were put through the entire procedure as separate individuals and in most cases analyzed several days apart using different standard curves. Results of the analysis are shown in Table 7.

A brief analysis of reproducibility, carried out for manganese determinations, involved reproducibility of absorption readings (Table 8). Aqueous manganese solutions were used.

In a second experiment four replicate ash subsamples were weighed and digested separately and analyzed. Reproducibility between ash subsamples were therefore determined (Table 9). A more extensive analysis of variation of Mn concentrations will be carried out in the near future.

Table 3. Replicate absorbance values of aqueous zinc solutions.

| Solution Number | | | Absorption | | | |
|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | Ave. | $\sigma$ | $\bar{x}$ |
| 1 | 56.90 | 56.80 | 56.80 | 56.83 | 0.06 | 0.10% |
| 2 | 72.00 | 71.70 | 71.60 | 71.77 | 0.22 | 0.30% |
| 3 | 74.60 | 75.50 | 74.50 | 74.87 | 0.55 | 0.74% |
| 4 | 82.60 | 82.70 | 82.50 | 82.60 | 0.10 | 0.12% |
| 5 | 63.20 | 63.80 | 62.90 | 63.30 | 0.46 | 0.73% |
| 6 | 75.50 | 75.70 | 75.90 | 75.70 | 6.20 | 0.26% |
| 7 | 84.90 | 85.00 | 84.90 | 84.93 | 0.06 | 0.07% |
| 8 | 76.80 | 77.50 | 77.00 | 77.10 | 0.36 | 0.47% |

Table 4. Analysis of reproducibility of ash subsamples from *Coryphaenoides* sp. using acetylene - air (Zn).

| Replicate Ash | Replicate Absorbance Values | | | | | | µg Zn/ |
|---|---|---|---|---|---|---|---|
| Subsamples | 1 | 2 | 3 | Ave. | $\sigma$ | $\bar{x}$ | gm Ash |
| 1 | .1878 | .1938 | .1871 | .1896 | .004 | 1.9% | 236 |
| 2 | .1746 | .1818 | .1851 | .1805 | .005 | 2.9% | 228 |
| 3 | .1726 | .1838 | .1726 | .1763 | .004 | 2.3% | 226 |
| 4 | .2000 | .2007 | .1884 | .1965 | .007 | 3.5% | 221 |
| 5 | | | | | | | |
| 6 | .1824 | .1838 | .1624 | .1762 | .012 | 6.8% | 227 |
| 7 | .1568 | .1500 | .1415 | .1494 | .008 | 5.2% | 237 |
| | | | | | | $\mu$ = | 230 |
| | | | | | | $\sigma$ = | 6.05 |
| | | | | | | $\bar{x}$ = | 2.60% |

Table 5. Analysis of reproducibility of absorption readouts using acetylene - air (Zn).

| | Absorption | | | µg Zn/gm |
|---|---|---|---|---|
| Aliquot | 1 | 2 | Ave. | Ash |
| 1 | 19.6 | 19.5 | 19.5 | 283 |
| 2 | 19.6 | 19.4 | 19.5 | 282 |
| 3 | 20.0 | 19.7 | 19.8 | 285 |
| 4 | 19.6 | 19.8 | 19.7 | 285 |
| 5 | 19.6 | 19.6 | 19.6 | 285 |
| 6 | 19.5 | 19.6 | 19.5 | 285 |
| | | | Mean = | 284.08 |
| | | | $\sigma$ = | 1.22 |
| | | | C = | 0.43% |

Table 6. Analysis of reproducibility of ash subsamples from *Pasiphaea pacifica* using acetylene - air (Zn).

| Sample Number | Absorption 1 | 2 | 3 | Ave. | $\sigma$ | C | µg Zn/ gm Ash |
|---|---|---|---|---|---|---|---|
| 617-1 | 16.7 | 17.2 | 16.6 | 16.8 | 0.3 | 1.9% | 292.8 |
| -2 | 15.7 | 15.8 | 15.8 | 15.8 | 0.1 | .44% | 289.5 |
| -3 | 26.9 | 27.4 | 27.5 | 27.3 | 0.2 | .73% | 293.0 |
| -4 | 21.5 | 21.2 | 20.5 | 21.2 | 0.5 | 2.4 % | 290.1 |
| -5 | 31.7 | 31.5 | 32.2 | 31.8 | 0.4 | 1.3 % | 284.9 |
| -6 | 19.5 | 19.3 | 19.5 | 19.4 | 0.1 | 0.52% | 316.2 |
| -7 | 34.9 | 34.7 | 35.4 | 35.0 | 0.4 | 1.0 | 297.0 |
| | | | | | | Mean = | 294.78 |
| | | | | | | $\sigma$ = | 10.15 |
| | | | | | | C = | 3.44% |

Table 7. Analysis of reproducibility of separate individuals within one species (Zn).

*Tactostoma macropus*

| Sample No. | μg Zn/gm Ash |
|---|---|
| 780 | 277 |
| 504 | 219 |
| 531 | 181 |
| 659 | 357 |
| 825 | 228 |
| | $\mu$ = 252 |
| | $\sigma$ = 67.6 |
| | $\bar{x}$ = 27% |

*Diaphus theta*

| Sample No. | μg Zn/gm Ash |
|---|---|
| 506 | 549 |
| 773 | 538 |
| 776 | 342 |
| 772 | 416 |
| 824 | 494 |
| | $\mu$ = 467 |
| | $\sigma$ = 87.8 |
| | $\bar{x}$ = 19% |

*Lampanyctus leucopsaurus*

| Sample No. | μg Zn/gm Ash |
|---|---|
| 507 | 484 |
| 508 | 377 |
| 526 | 485 |
| 530 | 340 |
| 789 | 572 |
| | $\mu$ = 452 |
| | $\sigma$ = 92.7 |
| | $\bar{x}$ = 20% |

*Euphausia pacifica*

| Sample No. | μg Zn/gm Ash |
|---|---|
| 525 | 300 |
| 629 | 509 |
| 694 | 490 |
| 700 | 354 |
| 843 | 454 |
| | $\mu$ = 421 |
| | $\sigma$ = 88.2 |
| | $x$ = 21% |

Table 8. Analysis of reproducibility of ash subsamples from *Thunnus alalunga* (Mn).

| | Replicate Absorbance Readings | | | | | |
|---|---|---|---|---|---|---|
| Sample | 1 | 2 | 3 | Ave. | $\sigma$ | $\bar{x}$ |
| 0.26 | 10.8 | 10.3 | 10.7 | 10.6 | .265 | 2.50% |
| 0.52 | 23.0 | 23.7 | 23.3 | 23.3 | .354 | 1.52% |
| 0.78 | 35.8 | 35.0 | 33.5 | 34.8 | 1.17 | 3.36% |
| 1.30 | 56.0 | 56.0 | 56.6 | 56.2 | 0.347 | 0.62% |

Table 9. Analysis of reproducibility of absorption readouts (Mn).

| Sample | Ave. Absorption | μg Zn/gm Ash |
|---|---|---|
| 851c-1 | 3.6 | 19.2830 |
| -2 | 6.0 | 19.6350 |
| -3 | 8.4 | 22.7167 |
| -4 | 8.8 | 24.5072 |
| | | $\mu$ = 21.5355 |
| | | $\sigma$ = 2.5107 |
| | | $\bar{x}$ = 11.65% |

## Discussion

Our ability to reproduce the same result from one ash sample at one time is reliable, and while not what we had hoped for, is well within workable limits. Variation from subsample to subsample can be explained but is not easily corrected.

Little need be said about quantitative and volumetric measurements--they must be exact. It is very important to obtain as nearly the same ash consistency as is possible from sample to sample. Digestion should be thorough. Perhaps perchloric acid digestion may be a better solvent than fuming $HNO_3$; unfortunately we do not have the facilities to afford its use.

Precautions are taken to avoid contamination. With such low concentrations, homogeneity of the ash is very crucial but not always easy to insure. There is the possibility that a "loaded" particle will be taken with one subsample and not the next.

The greatest problem yet to be solved is to reduce the variation which occurs from individual to individual within a species. It seems reasonable to assume that the zinc concentration of different individuals within one species would be very nearly the same, but as can be seen from Table 10, this is not always the case, at least by our analytical methods.

Causes for variation in this case can be many. While contamination is possible from aboard ship until the ash reaches the digestion flask, tests have shown that this could hardly cause the variation observed. Variations in sample drying and ashing cause variations in calculated concentrations since values are claculated on a weight basis. If individual samples of the same species do not lose weight proportionately the corresponding concentrations values will differ accordingly. An analysis of this correlation will be carried out in the immediate future. Table 10 shows relative weight losses in individuals of the same species during ashing and drying. Variation of samples of the same species can show up if the same ash consistency is not produced from them. If the ash consistency is greatly different, i.e., some samples are not ashed completely, digestion will not be complete. Zinc may be left within undigested organic particles.

Table 10. Variation of weight lost during drying and ashing of fish sample (*Tactostoma macropus*).

| Sample No. | µg Zn/ gm Ash | Wet wt. | Dry wt. | $\frac{\text{D. W.}}{\text{W. W.}}$ x100 | Ash wt. | $\frac{\text{A. W.}}{\text{D. W.}}$ x100 | $\frac{\text{A. W.}}{\text{W. W.}}$ x100 |
|---|---|---|---|---|---|---|---|
| 780 | 276 | 49.20 | 7.04 | 14% | 1.33 | 19% | 2.6% |
| 504 | 219 | 81.20 | 8.60 | 11% | 1.84 | 21% | 2.3% |
| 181 | 181 | 117.10 | 14.55 | 12% | 3.06 | 21% | 2.6% |
| 357 | 357 | 41.47 | 5.33 | 13% | 0.87 | 17% | 2.1% |
| 228 | 228 | 76.08 | 8.49 | 11% | 1.53 | 18% | 2.0% |
| $\mu$ = | 252 | | | 12% | | 19% | 2.3% |
| $\sigma$ = | 67.6 | | | 1.33 | | 1.80 | 0.28 |
| $\bar{x}$ = | 27% | | | 11% | | 9.47% | 12% |

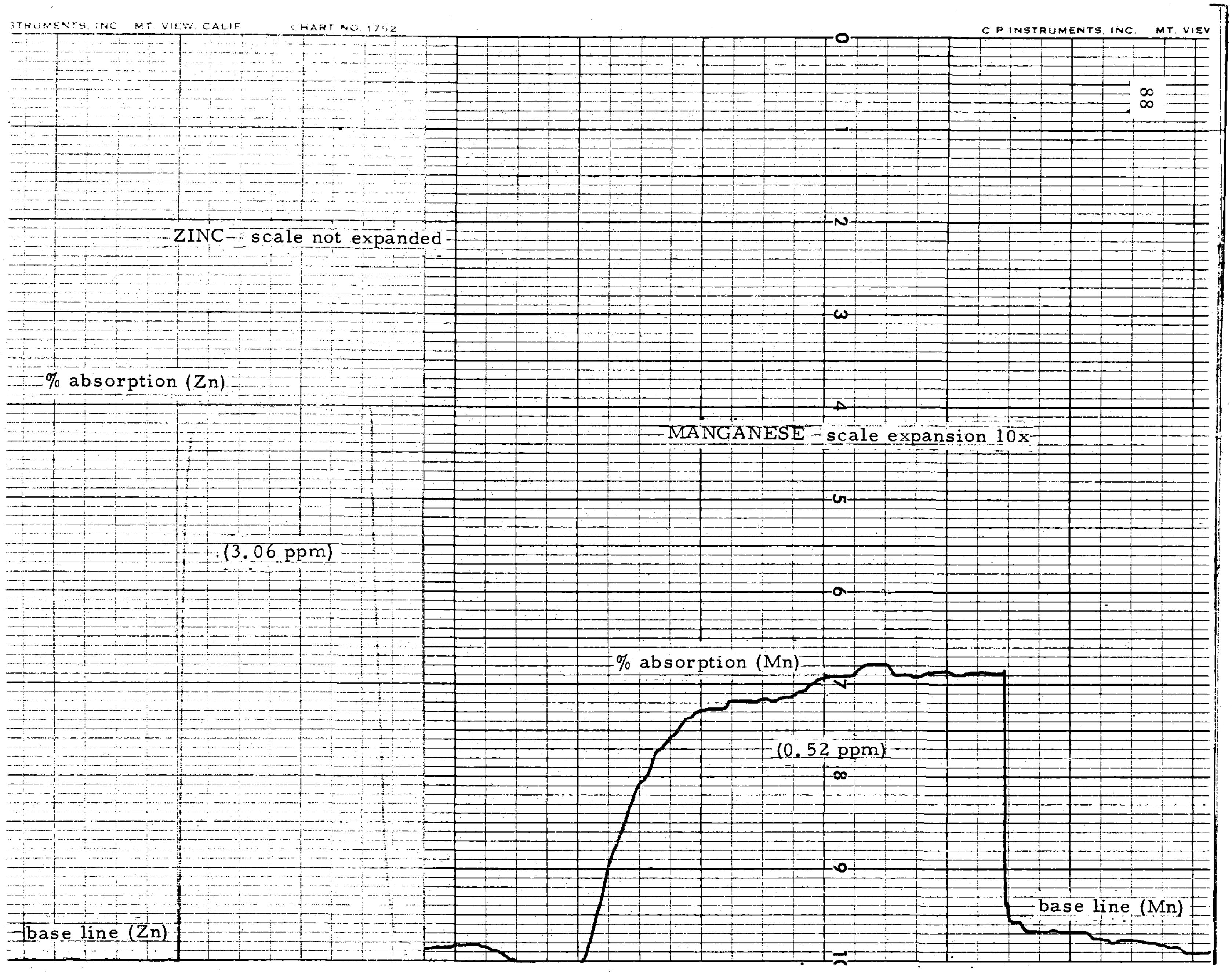

Figure 7. Strip chart recordings of Mn as compared to that of Zn.

The ashing and drying precautions refer both to our zinc and manganese determinations.

The reproducibility of ash subsamples analyzed for Mn (Table 10) can be seen to be poorer than those for Zn (Table 5). The main reason for this is that the Mn determinations are run at a scale expansion of 10 times that of zinc due to relatively low Mn levels. The scale expansion increases the electronic noise level considerably. Consequently the strip chart readout is increasingly difficult to interpret accurately (Fig. 7).

In the coming year much time will be used to understand more about the causes of the variation observed in our analyses and methods which can be employed to overcome them.

# RESEARCH IN PROGRESS

## D. CHEMICAL STUDIES*

Kilho Park, M. Catalfomo, C. Osterberg

Major effort has been devoted to modifying a technique to measure phosphorus - 32 in estuarine water samples. This method, developed elsewhere for measurement of $^{32}$P in blood samples, converts the phosphorus to a gas (phosphine) which is collected on a specially treated filter. The filter is readily counted for $^{32}$P activity. It is hoped that the method will free the samples from other beta emitters known to be present in the estuary, and avoid the problem of self absorption. The great affinity of organisms for $^{32}$P makes some knowledge of its behavior in the environment desirable. Phosphorus-32 is perhaps the most biologically important radionuclide present in the river from the Hanford reactors.

Routine monthly measurement of nutrients at three, and later four, stations at three depths is well underway. This program has tremendous significance in our overall study of the radioecology of the estuary. It is hoped that these factors can be related to the sudden fluctuations in populations (particularly the copepod Eurytemora hirundoides; see Haertel) observed in the estuary. All of the nutrient factors currently measured are of ecological importance, particularly since they are measured in water collected concurrently with our biological collections.

The data, because of their sparcity, have not yet been examined critically. A summary sheet, chosen at random, shows the scope of our analyses (Fig. 1). The same information is entered into the "Astoria Chemical Data" from (Fig. 2), and contour lines are drawn.

It is hoped that having the "nutrient data" in this format will be useful to ecologists working in the estuary.

Methods of analysis are as follows:

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*Dr. Kilho Park devoted a small portion of his efforts (10% for six months) toward problems related to our contract. Since he is at sea on an extended cruise (May, June, July, 1966), only a brief summary of this work can be presented.

## CHEMICAL SUMMARY SHEET

**Kilho Park**
Department of Oceanography
Oregon State University
Corvallis, Oregon

Date: Jan. 22, 1966, ~~Low Tide, 7:30AM~~ Compiled by:

½ Tide Low Tide, 7:30AM

| Station | Depth (m) | Temp. (°C) | Salinity (‰) | Oxygen (ml/L) | pH | Alkalinity (meq) | Inorganic Phosphate (μM) | Silicate (μM) | Nitrate (μM) | $CO_2$ (μM) | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. Chinook P. | 0 | 5.7 | 6.60 | 7.82 | 7.80 | 1.13 | 0.75 | 171.77 | 23.03 | 0.96 | |
| 2. Chinook Point | 6 | 6.1 | 9.00 | 7.52 | 7.89 | 1.16 | 0.88 | 156.14 | 21.82 | 1.02 | |
| 3. Chinook Point | 11 | 8.3 | 11.40 | 7.27 | 7.91 | 1.27 | 0.94 | 140.74 | 18.18 | 1.04 | |
| 4. Astoria | 0 | 5.0 | 0.35 | 8.11 | 7.68 | 0.90 | 0.87 | 239.09 | 31.51 | 0.82 | |
| 5. Astoria | 5 | 4.9 | 0.36 | 8.06 | 7.78 | 0.92 | 0.97 | 238.25 | 28.61 | 0.81 | |
| 6. Astoria | 10 | 5.1 | 0.60 | 8.16 | 7.70 | 0.91 | 0.93 | 182.88 | 23.76 | 0.80 | |
| 7. Harrington Point | 0 | 5.0 | 0.15 | 8.10 | 7.78 | 1.02 | 1.02 | 247.48 | 28.85 | 0.89 | |
| 8. Harrington Point | 6 | 5.0 | 0.15 | 8.06 | 7.78 | 1.04 | 0.97 | 223.99 | 19.64 | 0.91 | |
| 9. Harrington Point | 12 | 5.0 | 0.10 | 8.01 | 7.79 | 1.03 | 0.97 | 239.93 | 29.07 | 0.91 | |
| 10. | | | | | | | | | | | |
| 11. | | | | | | | | | | | |
| 12. | | | | | | | | | | | |
| 13. | | | | | | | | | | | |
| 14. | | | | | | | | | | | |

Figure 1. Specimen "Chemical Summary Sheet".

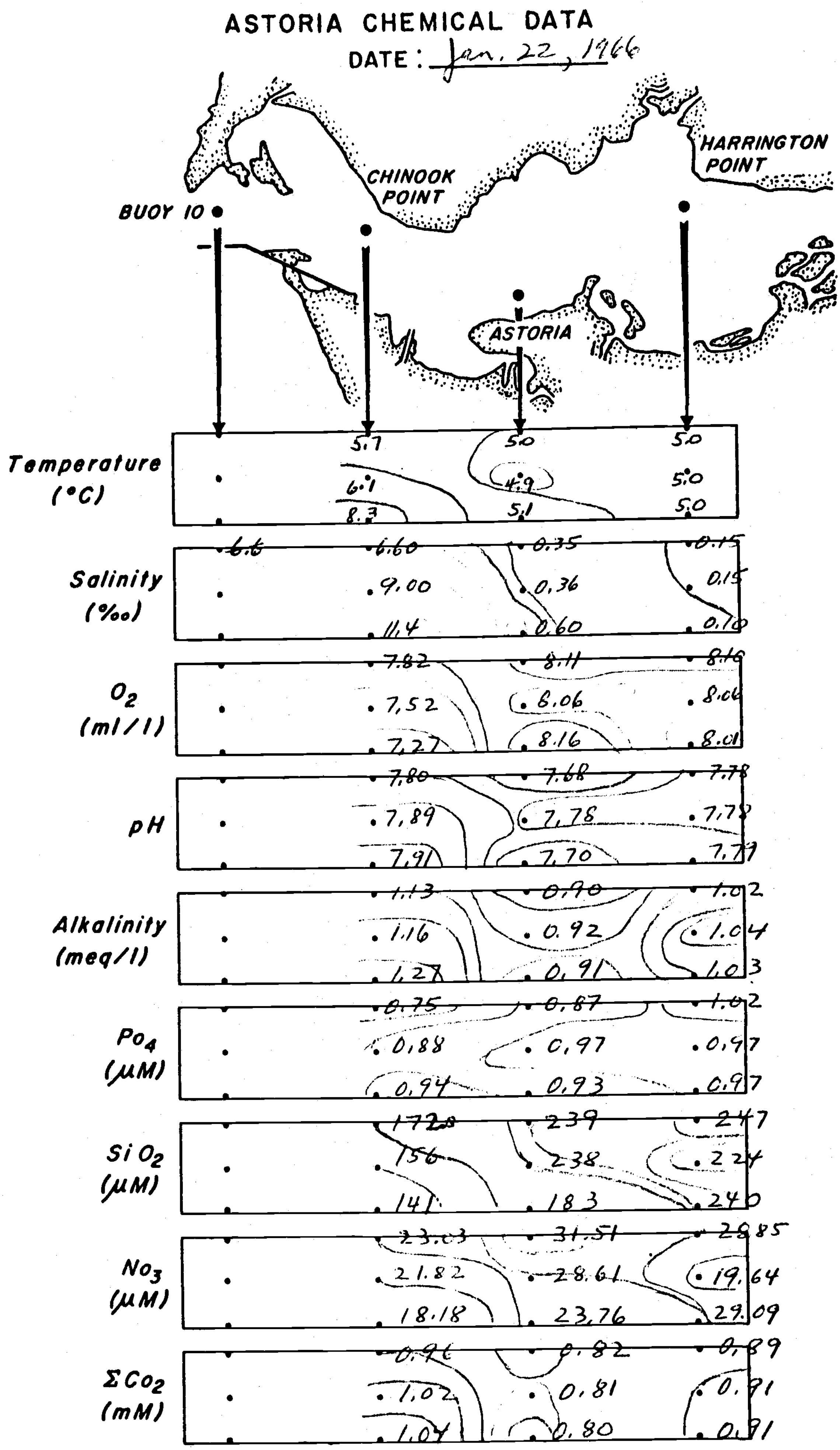

Figure 2. Specimen "Astoria Chemical Data".

1) Salinity: Salinometer (Hytech)

2) Oxygen: Winkler titration

3) pH: Beckman pH meter

4) Alkalinity: Beckman pH meter for buffer-curve, 100 ml sample is titrated with 0.1 N HCl.

5) Phosphate: Beckman DU modified ascorbic acid reduction method (U. of Washington).

6) Silicate: Beckman DU Mullin Riley method, (same as used by U. of Washington)

7) Nitrate: Beckman DU (same as used by U. of Washington)

8) $CO_2$: by gas partitioner

The samples for measurements 3 through 8 are kept in the icebox and analyzed as soon as possible after collection (usually within five days). (pH and buffer curves for alkalinity are usually run in within two days.)

A third portion of this work, the specific alkalinity of the Columbia River water, did not originally appear closely related to our radioecology work (and is, in fact, entirely supported by other funds). However, it has been proved to be a completely independent measurement of the Columbia River plume at sea (see Park, Limnol. Oceanog. 11: 118-120, 1966). An interesting result of the comparison of differences of specific alkalinity of seawater, rain water and Columbia River water indicates that surface water off Oregon in the winter is a mixture of water from the three sources. In other words, even though the plume of the river goes northward (away from Oregon) in the winter, plume water from the previous summer appears to remain and exert its effect on the specific alkalinity of the seawater. The observation is particularly interesting since it seems to verify the measurements made of radioactivity in marine organisms. That is, levels of $Zn^{65}$ in marine animals taken off Oregon in the winter are much higher than those from off southern California or Alaska. Apparently Columbia River water, which flows as far south as central California in the summer, mixes and moves back off Oregon in the winter. At this time it is free to move inshore, since there is no upwelling to isolate it from the coast, as occurs in summer.

# RESEARCH IN PROGRESS

## E. RADIOBIOLOGY

by Charles L. Osterberg, Leader

USPHS funds have been used to set up facilities for laboratory studies of uptake and loss of radionuclides of experimental animals (see Fig. 2 , p. 103). Cross, who had an AEC-Battelle Northwest fellowship to learn experimental techniques from Doctors Dean and Nakatani, is using the equipment to complete his Ph. D. research on $^{65}Zn$ in an amphipod (see pp. 98-104).

Holton, whose interest is radiation genetics, is considering using brine shrimp as experimental animals (see p. 112). He has bred his test animals through many generations, meanwhile devoting most of his time to the completion of course requirements.

As in former years, the bulk of our data is from field studies. Phase one of our study on the radioactivity in salmon has been completed (see Kujala, thesis, included in supplement). We have since obtained 36 samples of salmon from Japan, and these data plus other "loose ends" will be incorporated into a final paper which should be presented for publication within several months.

Johnson's work on the clam (see pp.105 -111) was a sideline of of his sediment work. Although we were not aware that the clams were present in the river, he and Cutshall found them to be quite plentiful and easily collected them while diving for surface sediments.

The note by Mellinger (see pp. 113 -118) is in a different category. It was assigned as a research problem and included here because of its pertinence.

# ZINC-65 METABOLISM IN A MARINE BENTHIC AMPHIPOD*

by Ford A. Cross

## INTRODUCTION

Johnson (1966) has concluded that the major portion of zinc-65 transported to the Pacific Ocean via the Columbia River should be in particulate form and subject to sedimentation. His conclusion is based on data showing sediment-sorbed zinc-65 to be bound by an ion-particle interaction more specific than ion exchange and not easily displaced upon entering sea water.

As a result much radiozinc is concentrated in the sediments and thus much less available to pelagic organisms than if it were in ionic form (Mauchline and Templeton, 1964). Benthic populations in these areas are therefore subjected to an increased amount of radiozinc activity. The ability of benthic organisms to take up and retain sediment-sorbed zinc-65 and thus to recycle this contaminant from the sediment back into the food web now becomes important. Parker (1962), working in a Texas bay, found a large reservoir of zinc in the top few centimeters of sediment and also found that organisms associated with the sediment show relatively high zinc values. Thus one would suspect that there is some interchange of zinc between the sediment and benthic organisms.

A trapping technique developed at Scripps Institute of Oceanography enables us to trap a benthic gammarid amphipod in fairly large numbers. This organism, plentiful in 80 meters of water off the Oregon coast, is apparently a new species of _Anonyx_ and is being described by Dr. J. Laurens Barnhard of the U. S. National Museum, using specimens which we provided. _Anonyx_ species burrows into very sandy sediments during the day, and emerges to feed at night. At least this is our conclusion as we have been unable to trap this organism during the daylight hours. _Anonyx_ sp. apparently is a very efficient scavenger of dead and dying matter because the dead herring used as bait are rapidly consumed.

_Anonyx_ sp. is extremely hardy and has been kept for as long as two months in the laboratory. They average 21-22 mm in length and over 200 mg in wet weight.

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* The results presented in this paper were obtained at the AEC Battelle Northwest Laboratories in Richland, Washington, under the Richland Graduate Fellowship Program. This work, sponsored by the Ecology section, was under the guidance of Dr. R. L. Nakatani and Dr. J. M. Dean; their assistance and encouragement is gratefully appreciated.

The purpose of this study is to examine the zinc-65 metabolism in this organism as affected by contaminated water, food, and sediment. We are also utilizing autoradiography to examine the tissue localization of radiozinc.

Test animals were collected by means of baited traps at a depth of 80 meters off Depoe Bay, Oregon. These traps consisted of one gallon paint cans with lids modified to allow the amphipods to enter, but, once inside, not easily to escape. The traps were baited with dead herring, placed on the bottom, attached by rope to a surface buoy, and left for several hours. Retrieved traps contain numerous amphipods, and no other animals. Thus, sorting is no problem. Once collected, these amphipods were placed in glass jars in a refrigeration case and transported 400 miles inland to the Battelle Laboratories. Upon arrival in Richland, the organisms were maintained in fish troughs and allowed to acclimate to three temperatures (3°, 7°, and 12° C.). Portable refrigeration units were employed for thermal regulation.

## EXPERIMENTAL RESULTS

Temperature effects on $^{65}Zn$ uptake were studied by serially killing of amphipods acclimated to the temperatures listed above and held in sea water filtered through 0.45 $\mu$ milipore membrane and containing 25 $\mu$Ci/l of carrier-free $^{65}Zn$. Figure 1 shows the uptake curves for each of the temperature treatment groups. Each point represents the average of six animals. The increase in uptake with higher temperature was expected. However, differences between the 7° and 12° C groups are of special interest because these temperatures approximate the range of seasonal change in their environment. Longer experiments are clearly needed to determine maximal uptake levels. Concentration factors (on a wet weight basis) after 96 hours were approximately 73, 55, and 12 for the 12°, 7°, and 3° C groups respectively.

To determine the effect of temperature on zinc retention, three groups of amphipods (24 animals/group) were placed in filtered sea water contaminated with 25 $\mu$Ci $^{65}Zn$/l at 3°, 7°, and 12° C for a period of 8-10 days. Each amphipod was then weighed, counted for radioactivity and returned to individual containers in $^{65}Zn$ free sea water of the same experimental temperature. Twelve animals from each temperature group were placed in containers with ocean sediments and twelve animals were placed in containers without sediment. Thus we were able to look at not only the effect of temperature upon retention, but also the effect of sediment upon the retention of $^{65}Zn$. Sea water was replaced weekly to prevent the buildup of $^{65}Zn$ in the containers.

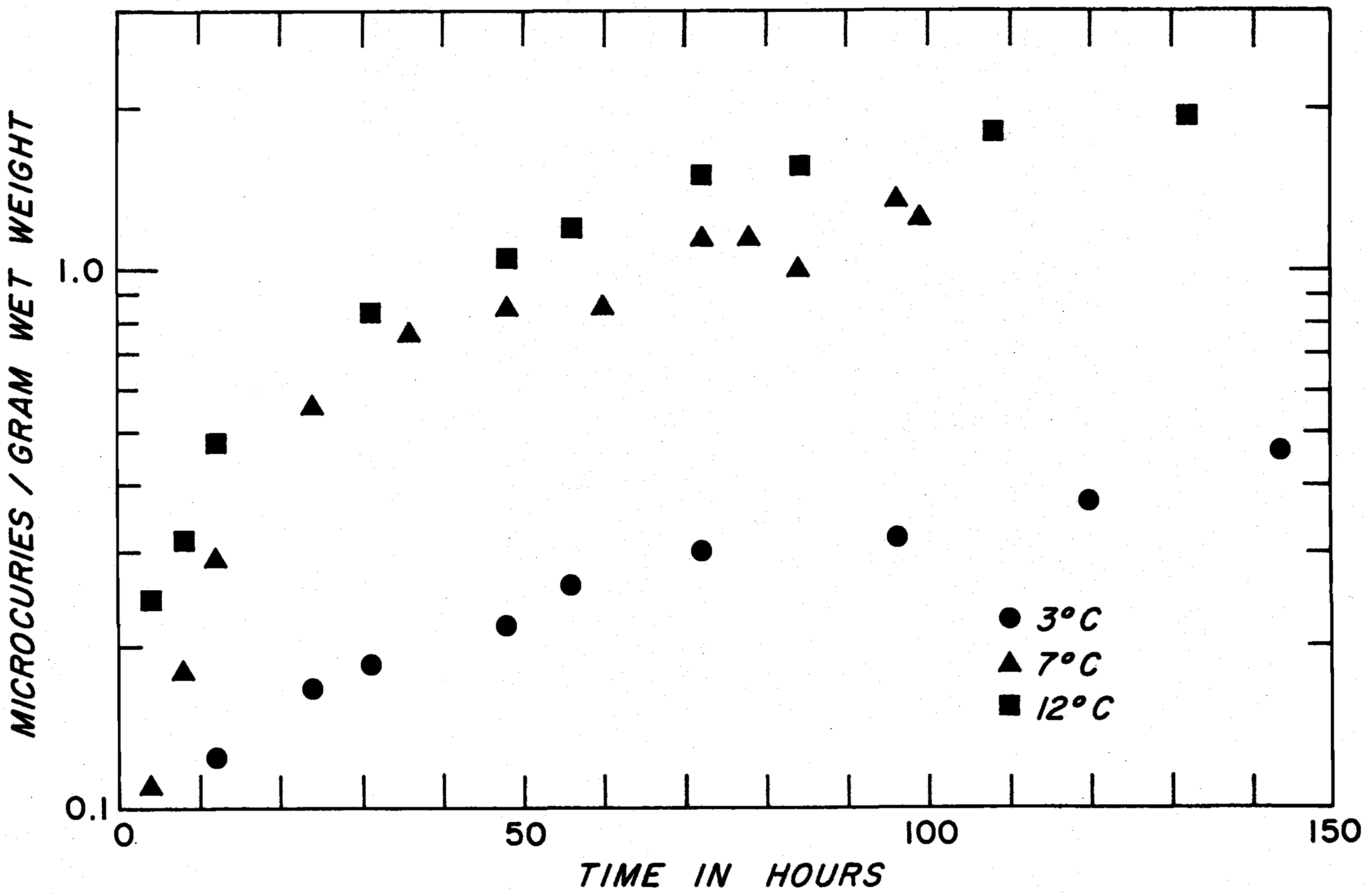

Figure 1. Uptake curves of $^{65}$Zn from filtered sea water for Anonyx sp. as a function of temperature. Each point represents the average of six animals.

Periodically each amphipod was removed from its individual container, placed in a test tube containing 2 ml of sea water, counted in a single channel analyzer for two minutes, and then returned to its container. This procedure was carried out for a period of 29 days. The data for each group were then averaged and plotted on semilog paper in terms of percent activity retained per unit time. The straight line portion of the graph was then extrapolated back to the ordinate and the biological half-life would be the time needed for the levels in the organisms to fall to 50% of this assimilated value. These data are presented in Table 1. Since no correction was made for physical decay, the results are given in terms of effective half-life. (Effective half-life may be defined as the time needed for an organism to lose 50% of its assimilated radioactivity as a result of losses from both biological turnover or elimination and physical decay of the particular nuclide involved.)

Table 1. A comparison of the effective half-lives of Anonyx sp. as a function of temperature and the influence of sediment.

| Temperature | Water Only* | Sediment and Water* |
|---|---|---|
| 3° C | 100d | 85d |
| 7° C | 81d | 72d |
| 12° C | 64d | 68d |

* Effective half-life

For all three temperatures used there is less variability in the organisms which were exposed to sediment than those which were not. When comparing the non-sediment group to the sediment group for any particular temperature, one finds that the sediment groups exhibit a lower effective half-life for 3° and 7° C than the non-sediment group. However, at 12° C the effective half-life is very nearly the same for both groups. From these data it appears that the presence of sediment may influence the effective half-life of $^{65}$Zn in Anonyx sp. at lower temperatures. However, no significant nor consistent trends are apparent for all three temperatures involved. One conclusion may be drawn, however. Because these amphipods show a relatively long retention time, they may form significant reservoirs of $^{65}$Zn for benthic feeding fishes.

Because Anonyx sp. are benthic, feed on detritus and burrow into the sediment, it might be assumed that they remove and incorporate $^{65}$Zn which has become bound to the sediment. An experiment was performed to determine how the three major components of the sediments, i. e., bacteria, organic detritus and inorganic fraction contribute to the labeling of the amphipods. Each of three groups of amphipods was exposed to one of three differently treated sediments for seven days at 7° C. The experimental sediments, originally collected at 180 meters, were untreated, sterilized by autoclaving or oxidized with hydrogen peroxide. The sediments were labeled with $^{65}$Zn and rinsed with sea water overnight to remove the loosely bound zinc before presentation to the animals. Radioanalysis showed only slight labeling of the serially killed animals and little difference among the groups. The $^{65}$Zn incorporation into the amphipods could probably be attributed entirely to the small amount of $^{65}$Zn leached from the sediment by the sea water. These data indicate that Anonyx sp. apparently cannot readily remove $^{65}$Zn which has been subject to sedimentation and recycle it into the biosphere.

Once $^{65}$Zn has become incorporated into a crustacean, it is important to localize the site of radioactivity. If the activity is bound to the external surface of the exoskeleton or within the internal tissues, then a major portion of the radioactivity will probably be available for assimilation by the next trophic level. However, if the $^{65}$Zn is bound within the exoskeleton material, assimilation becomes difficult as chitin, being an acetyglucosamine, is not easily broken down and assimilated. Fowler (1966) has postulated that the molting of euphasiids may significantly affect the redistribution of $^{65}$Zn in the biosphere. His data indicate that approximately 25% of the euphasiid's radiozinc activity is associated with the cast-off exoskeleton. The possible sinking and utilization of these exoskeletons by bacteria and other marine organisms would offer an alternate pathway for $^{65}$Zn accumulation in marine food webs. Anonyx sp. also loses approximately 25% of its $^{65}$Zn activity upon molting although its molting cycle appears to be much less frequent than that of Euphausia pacifica (the common pelagic euphausiid off Oregon).

In order to localize $^{65}$Zn activity within Anonyx sp. autoradiographs were prepared by the biological analysis section of the Biology division of the Battelle Laboratories. Cross sections of $^{65}$Zn labelled amphipods show exoskeleton and muscle tissue as the predominant sites of radiozinc localization.

A large amount of activity associated with the exoskeleton appears to be incorporated into exoskeletal material. Activity is seen both in the cracks and fissures of the outermost layer and incorporated within the exoskeleton itself in areas that appear protected from surface contamination. This intra-skeletal incorporation was quite surprising to us as we had expected outer surface adsorption to be the most important mode of exoskeletal contamination. The activity is not very diffuse but arranged in rows parallel to the outer surface. We are in the process of looking at this phenomenon more closely in order to offer a plausible explanation for its existence.

The radiozinc activity associated with muscle tissue appears to be confined mainly to the interstitial areas rather than within the cells. A small amount of activity is associated with the hepatopancreas and little if any activity is associated with the digestive tract and gonadal tissues. No cross sections were available for the gill area. Organisms used for these sections incorporated $^{65}$Zn from filtered sea water and no feeding took place during the experiment. Autoradiographs will soon be prepared from amphipods fed $^{65}$Zn labelled brine shrimp and a comparison will then be made of the tissue distribution of radiozinc acquired from two external sources, i. e. food and water.

The $^{65}$Zn metabolism work is now being pursued at Oregon State University. For this purpose a Fisher Isotherm refrigerated bath and an eight foot fiberglass fish trough were purchased (Fig. 2).

Figure 2. A refrigeration unit, fish trough, and temperature recorder which will be used to study radionuclide metabolism in marine organisms.

The coolant from the bath is circulated through the trough via aluminum tubing. A temperature recorder is used to obtain permanent temperature records.

A feeding experiment is planned in which both $^{51}$Cr and $^{65}$Zn will be fed to Anonyx sp. via brine shrimp. The experiment is designed so that uptake data can be obtained from food, from water and from both food and water. Because two nuclides will be employed, the gamma-ray spectrometer will be used for counting.

Additional feeding experiments may involve $^{46}$Sc and $^{141}$Ce and possibly other radionuclide pairs.

Finally, other trawls will be taken at the depths where Anonyx sp. is most abundant. Stomachs of the organisms taken will be analyzed in order to ascertain which fishes and invertebrates might be utilizing Anonyx sp. as a source of energy.

## BIBLIOGRAPHY

Fowler, S. 1966. 'Uptake and retention of $^{65}$Zn by Euphausicea pacifica. M.S. thesis. Oregon State University. 58 p.

Johnson, V. E. 1966. Retention of Zinc-65 by Columbia River sediment. M.S. thesis. Oregon State University. 56 p.

Mauchline, J., and W. J. Templeton. 1964. Artificial and natural radioisotopes in the marine environment. Oceanogr. Mar. Biol. Ann. Rev. 2: 229-279.

Parker, P. U. 1962. Zinc in a Texas bay. Publ. of the Instit. of Marine Science 8: 75-79.

# DISTRIBUTION OF HANFORD INDUCED GAMMA EMITTERS IN A FRESH WATER MOLLUSC: ANODONTA WAHLAMATENSIS

V. Johnson, N. Cutshall, C. Osterberg

The recent appearance in the literature of a report on the distribution of stable manganese in molluscs from some fresh water lakes in Italy has prompted us to examine the distribution of Hanford induced radiotransition elements in a fresh water bivalve inhabiting the lower Columbia River. The Italian workers Merlini, Girardi, Pietra and Brazzelli (1965) found, for example, that stable manganese in soft parts of _Anodonta cygnea_ and _Unio mancus elongotulus_ varied in the following order:

gills > mantle > viscera > muscle

In order to make a similar comparison for _Anodonta wahlamatensis_ from the Columbia River, specimens from three different sites were dissected into the above tissue groups. The tissues were rinsed, blotted on paper towels to remove excess moisture, and then packed into 13 cc counting tubes for radioanalysis. Data from our deep well counter were reduced by a computer-programmed least squares method of spectral analysis (Frederick, et al. 1965). The program was set up for determination of $^{51}$Cr, $^{54}$Mn, $^{65}$Zn, $^{46}$Sc and $^{60}$Co. All of these, with the exception of $^{46}$Sc, are known to be present in _Anodonta_ from the Columbia; however, too long a period of time lapsed between collection and analysis of most of the specimens taken for this study to permit determination of the relatively short-lived $^{51}$Cr. Results for $^{54}$Mn, $^{65}$Zn and $^{60}$Co are shown in Table 1.

The first point of interest to be noted from Table 1 is the rather striking agreement in the order of distribution of $^{54}$Mn in _A. wahlamatensis_ from all three sites and the order of stable manganese concentrations in the same tissues reported for the Italian _Anodonta._ Merlini, et al. found, for example, average manganese levels in sorted parts of _A. cygnea_ were as follows: gills, 18,699 ppm; mantle, 5,092 ppm; visceral sac, 1,164 ppm; and muscle, 212 ppm. It is furthermore noteworthy that $^{65}$Zn exhibits this same trend. Firm conclusions for $^{60}$Co cannot be drawn since only one of the sets of data in Table 1 can be used due to the relatively low activity and

Table 1. $^{65}$Zn, $^{54}$Mn, and $^{60}$Co levels in soft parts of *Anodonta wahlamatensis* collected from three different sites on the lower Columbia River. Data are given as picocuries per gram wet weight.

| | Puget Island pCi/g | | | Harrington Point pCi/g | | | Astoria pCi/g | | |
|---|---|---|---|---|---|---|---|---|---|
| | $^{65}$Zn | $^{54}$Mn | $^{60}$Co | $^{65}$Zn | $^{54}$Mn | $^{60}$Co | $^{65}$Zn | $^{54}$Mn | $^{60}$Co |
| Gills | 484.2±25.7 | 29.2±4.2 | 1.4±0.7 | 316.0±13.1 | 21.2±2.2 | 6.8±0.9 | 569.0±44.4 | 40.8±10.5 | 2.1±3.9 |
| Mantle | 347.6±12.9 | 14.0±1.9 | 1.2±0.4 | 169.2±6.5 | 5.0±0.9 | 2.8±0.5 | 352.1±23.0 | 21.9±4.8 | 1.7±1.8 |
| Viscera | 102.2±11.5 | 0.9±1.6 | 1.4±0.5 | 42.2±1.4 | 1.4±0.2 | 1.6±0.1 | 57.5±4.5 | 3.6±0.9 | 0.7±0.4 |
| Muscle | 61.9±1.9 | 2.1±0.2 | 0.9±0.1 | 3.7±0.4 | 1.7±0.3 | 0.9±0.1 | 23.6±0.9 | 0.7±0.2 | 1.3±0.3 |

high counting error of this nuclide in the tissues comprising the other two sets. It is interesting however, that $^{60}Co$ does exhibit the same trend as $^{54}Mn$ and $^{65}Zn$ in the one set (Harrington Point) for which the counting error is sufficiently low.

After observing the above orders of distribution the question arose as to whether this observation might be due to some physiological or biochemical phenomena, or perhaps due to greater retention of particulate material by the mantle and gills. Brooks and Rumsby (1965), for example, felt that contamination of tissues such as the gills by sediment particles was a significant factor contributing to the incongruous results they obtained for the relative concentration levels of a number of transition metals in some New Zealand shellfish (scallops, oysters and mussels). This point was resolved for our samples by comparing gamma ray spectra of Anodonta tissue and environmental sediment (see Fig. 1). The rather conspicuous absence of $^{46}Sc$, which is largely particulate in the river, in the Anodonta tissue strongly suggests that particulate contamination is an unlikely explanation for the distribution of the radiotransition metals in our samples.

Further question was raised concerning the use of wet weights rather than dry weights in our study. It was felt that the viscera, for example, might retain more moisture than other tissues thereby yielding relatively lower levels of activity. This possibility was investigated by comparing the levels of activity of one of the sets of data in Table 1 on both a wet and dry weight basis. Results, Table 2, show that the use of wet weights had no effect on the order of distribution.

Table 2. Comparison of the order of distribution on a wet and dry weight basis (dry weights were obtained by oven drying at 80° C for five days).

| | $^{65}Zn$, pCi/g | |
|---|---|---|
| Tissue | Wet Weight | Dry Weight |
| Gill | 569.0±44.4 | 2845.1±222.0 |
| Mantle | 352.1±23.0 | 1247.7± 82.2 |
| Viscera | 57.5± 4.5 | 285.4± 22.5 |
| Muscle | 23.6± 0.9 | |

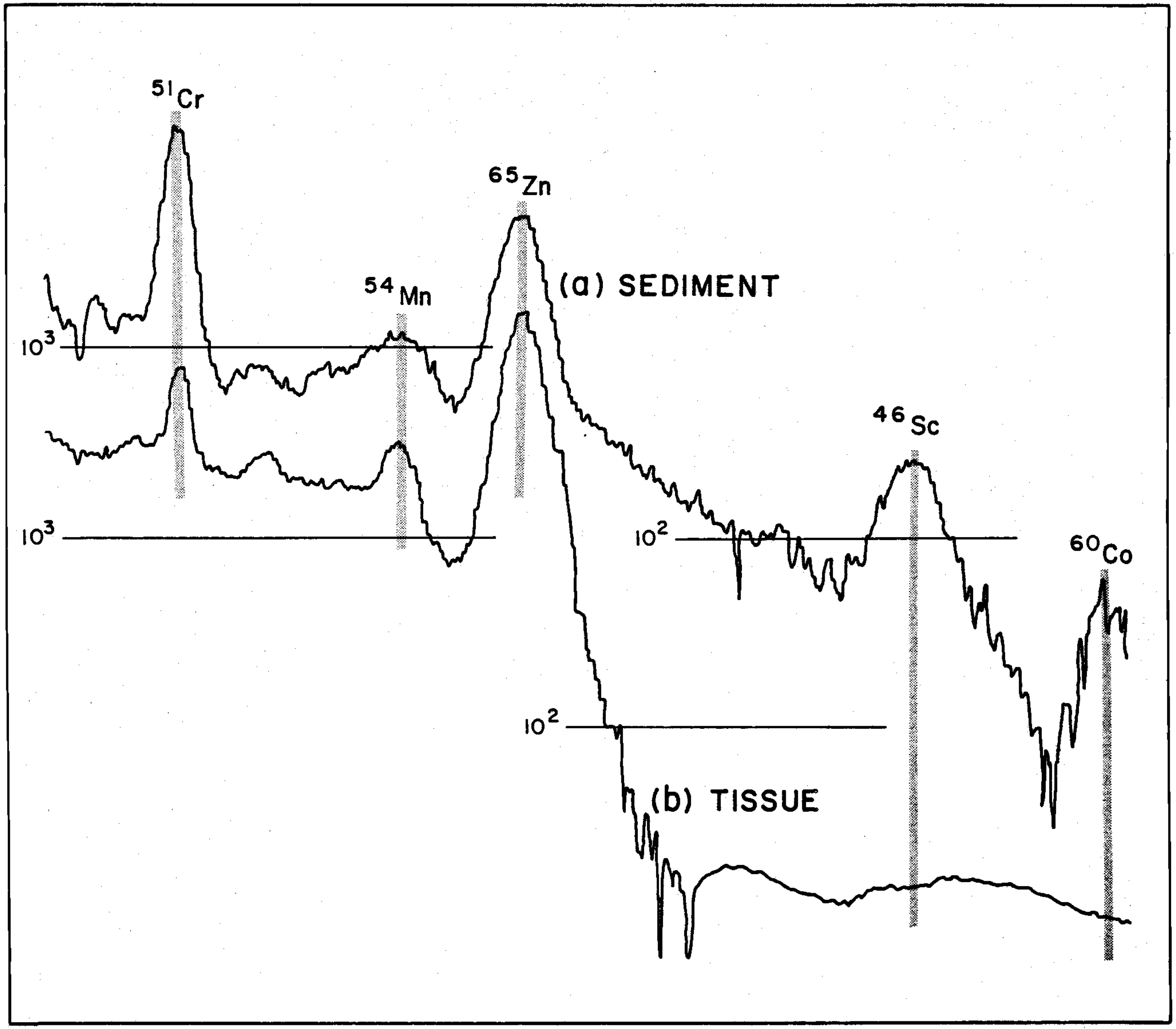

Figure 1. Gamma-ray spectra of *Anodonta wahlamatensis* soft tissue (b) and environmental sediment (a). Note the absence of $^{46}$Sc in the tissue and the prominent $^{46}$Sc photopeak in the sediment.

We conclude that the order of distribution of $^{54}$Mn, $^{65}$Zn and possibly $^{60}$Co in Anodonta wahlamatensis is not due to particulate contamination nor due to the method of sample preparation used, but rather, reflects a biochemical specificity of certain tissues or their constituents for transition metals. It appears that the relative concentration of radionuclides in different tissues of A. wahlamatensis is the same as was reported for stable elements in A. cygnea and U. mancus elongatulus. This tends to confirm our hopes that the chemical forms of these trace radionuclides from the Hanford reactors are the same as their stable counterparts in the environment.

## REFERENCES

Brooks, Robert R., and Martin G. Rumsby. 1965. The biogeochemistry of trace element uptake by some New Zealand bivalves. Limnol. Oceanog. 10: 521-527.

Frederick, Lawrence C., I. Lauren Larsen, and Susan Borden. 1965. Radionuclide spectrum analysis. In: Ecological studies of radioactivity in the Columbia River and adjacent Pacific Ocean, C. Osterberg, Ed. (Oregon State University Prog. Rep. 65-14, Corvallis, 1965) 255 pages, mimeographed.

Merlini, M., F. Girardi, R. Pietra, and A. Brazzelli. 1965. The stable manganese content of molluscs from Lake Maggiore determined by activation analysis. Limnol. Oceanog., 10: 371-378.

# BENTHOS-NEKTON-RADIOCHEMISTRY CRUISE

by Norman Cutshall

Following our successful tracing of the Columbia River plume using $^{51}$Cr in June, 1965 (as reported last year), we made a study of the plume cross-section in late August, 1965. During the week 20-28 August, surface waters were sampled along an east-west line of stations at 44°39' N. At one station (NH-85) we also took samples at depths of 5, 10, 20, 50 and 100 meters. The results are shown in Table 1.

The well-defined plume that had been present in June was no longer apparent. Traces of $^{51}$Cr were found in most of the samples from NH-5 (5 nautical miles, 9.27 kilometers, west of Newport) to NH-305 (305 nautical miles, 565.22 kilometers, west of Newport). None of the samples taken on the outbound leg (Table 1a) contained more than 6 pc/liter of $^{51}$Cr. Less than a week later, on the return trip, considerably higher concentrations (and lower salinities) were found (Table 1b). These results indicate that there are rather rapid changes in the internal structure of the plume itself.

The set of vertical samples taken at NH-85 show that $^{51}$Cr had penetrated to a depth of at least 20 meters but not to 50 meters (Table 1c). The concentration of $^{51}$Cr at 10 meters depth was approximately one-half the surface concentration. Further sampling of this kind is needed to establish vertical mixing rates of Columbia River water.

Table 1. Results of BNR Cruise. All Stations are at Latitude 44°39'N.

| Station | Distance offshore km | Date | Salinity, ‰ | $^{51}$Cr, pc/liter |
|---|---|---|---|---|
| 1a) seaward leg | | | | |
| NH-5 | 9 | 20 Aug | 32.6 | 1.61 |
| NH-25 | 46 | 21 Aug | 32.0 | 5.65 |
| NH-45 | 83 | 21 Aug | 32.2 | 2.60 |
| NH-65 | 120 | 21 Aug | 32.4 | 0.25 |
| NH-120 | 222 | 22 Aug | 32.1 | 0.66 |
| NH-165 | 306 | 23 Aug | 32.0 | 1.43 |
| NH-215 | 398 | 23 Aug | 32.2 | 0 |
| NH-255 | 473 | 23 Aug | 31.4 | 3.81 |
| NH-305 | 562 | 24 Aug | 31.6 | 2.88 |
| 1b) landward leg | | | | |
| NH-85 | 158 | 26 Aug | 31.8 | 4.33 |
| NH-65 | 120 | 26 Aug | 31.6 | 10.71 |
| NH-39 | 72 | 27 Aug | 30.8 | 23.53 |
| NH-24 | 44 | 27 Aug | 31.8 | 8.78 |

1c) vertical station at NH-85 158 km offshore

| Depth, meters | Date | Salinity, ‰ | $^{51}$Cr, pc/liter |
|---|---|---|---|
| 0 | 26 Aug | 31.8 | 4.33 |
| 5 | 26 Aug | 31.8 | 4.07 |
| 10 | 26 Aug | 32.1 | 2.20 |
| 20 | 26 Aug | 32.2 | 0.37 |
| 50 | 26 Aug | 32.5 | 0 |
| 100 | 26 Aug | 33.2 | 0 |

# EFFECTS OF IRRADIATION ON VARIOUS STRAINS OF *ARTEMUS*

by Robert L. Holton

Brine shrimps, *Artemia spp.*, will be used in a study of the effects of irradiation on the ability of a population of animals to maintain and/or increase the size of the population.

*Artemia* spp. from various locations are being collected and one aspect of the study will be to determine how different populations of *Artemia* will respond to the same doses of ionizing radiation. The populations to be used will include sexual diploid and tetraploid populations as well as parthenogenetic diploid and tetraploid strains.

A second aspect of the study will be to determine how a given population of *Artemia* will respond to irradiation from different sources, including externally administered X-rays and incorporated nuclides such as $^{32}P$ and $^{65}Zn$ which are important in the Columbia River estuary.

# THE CONCENTRATION OF ZINC-65 IN MYTILUS CALIFORNIANUS AS A FUNCTION OF DISTANCE FROM THE COLUMBIA RIVER*

by Peter J. Mellinger

## INTRODUCTION

Hanford Atomic Products Operations in Richland, Washington, uses Columbia River water to cool its nuclear reactors. When this coolant is exposed to a high neutron flux, trace element impurities are converted into radioactive isotopes (Osterberg, Pattullo, and Pearcy 1964). As this water is returned to the river and transported toward the ocean its radioactivity is subject to biological, chemical and physical alterations. Of some 60 radionuclides leaving Hanford for this three week journey to the Pacific only a few reach the ocean in significant amounts due to short half lives.

As the Columbia enters the ocean, a low salinity surface lens is created which extends north of the river entrance during the winter months due to onshore southwesterly winds and prevailing ocean currents.

Of the radionuclides reaching the ocean, $^{65}Zn$, which is converted from $^{64}Zn$ by radiative capture, $^{64}Zn\ (n,\gamma)\ ^{65}Zn$, is found in every type of animal collected, although in highly varying amounts (Osterberg, Pearcy, and Curl 1964).

The objective of this study was to examine the variation in $^{65}Zn$ concentration in the mussel Mytilus californianus with distance from the mouth of the Columbia River.

## METHODS

Mussels were collected in the intertidal zone by hand. They were preserved in formalin for later processing in the laboratory. After dissecting into three fractions; the posterior adductor muscle,

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*This paper is a term paper done under the direction of Dr. Osterberg. The author was a graduate student in General Science at Oregon State University, presently employed by the USAEC, Richland, Washington.

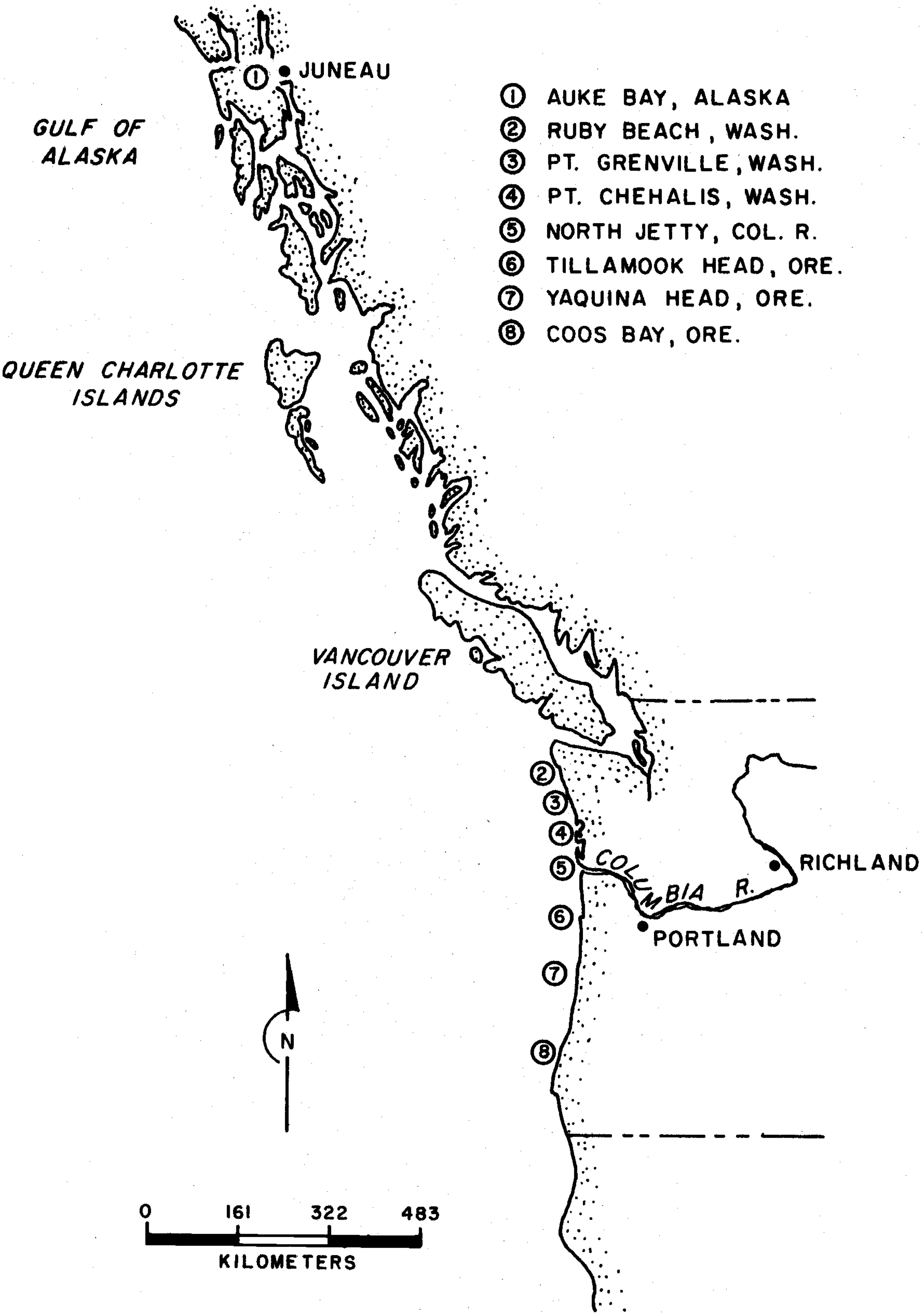

Figure 1. Collection sites.

the foot, and the remaining soft parts making up the third and largest fraction, the sub-samples were dried, ground, and packed into 15 cc plastic counting tubes.

The range of collecting stations (Fig. 1) extended from Coos Bay, Oregon, northward to Auke Bay, Alaska. Eight stations were sampled during low tides of late January 1966 except for the Alaskan sample which was collected in the last week of February. Total shoreline distance was about 1675 kilometers.

The samples were counted for 400 minutes in a 12.7 x 12.7 cm NaI(Tl) well-type scintillation crystal in conjunction with a 512 channel Nuclear Data 130 AT multichannel analyzer. Because 0.0119% of all naturally occurring potassium is radioactive $^{40}$K, a KI standard was made and counted to determine the percentage of counts in the $^{65}$Zn photopeak which were due to $^{40}$K compton interactions. A zinc standard was used to compute the efficiency factor of the system so that counts per minute could be converted into picocuries.

## RESULTS AND DISCUSSION

Concentrations of $^{65}$Zn in all body parts exhibited a definite pattern (Fig. 2). The highest values were found at the mouth of the Columbia River with decreasing amounts as distance increased. The largest sub-sample, the remaining soft parts, showed a higher $^{65}$Zn concentration than did the muscle or the foot in all cases but one. A rapid decline in accumulated zinc-65 was observed with distance north and south of the Columbia River mouth as was expected. The decrease with distance was more rapid toward the south than toward the north. The distance north and south at which the $^{65}$Zn in these mussels diminished to one-half their river activity was noted. Fig. 2 shows this half value distance to be 24 km to the south and 96.5 km to the north. These data agree closely with the observations made by Seymour, and Lewis (1964). They show distances at which the river activity reaches one-half to be 32.2 km south and 64.4 km north of the river entrance. The difference in our data probably lies in that I collected during the winter when the Columbia River plume was in the north and onshore. Seymour's conclusions covered an average of the radioactivity over a two year period.

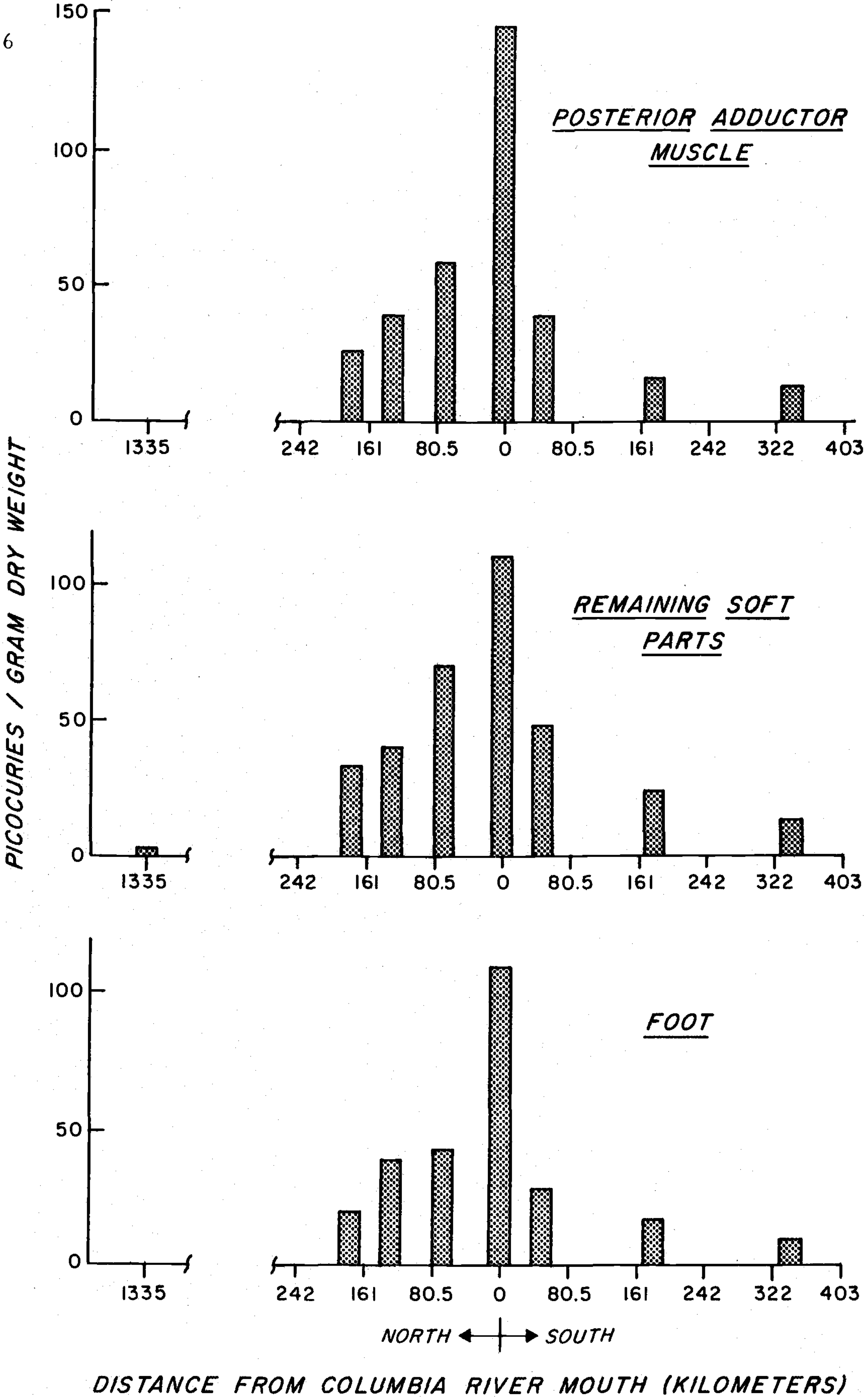

Figure 2. Variations in concentrations of $^{65}Zn$ with distance from the Columbia River.

The faster decrease toward the south, Seymour feels, occurs because Columbia River water when transported northward in the winter is closer to the coast than when it is transported southward in the summer.

Watson, Davis, and Hanson (1961) found that mussels from locations 161 km from the river mouth contained less than 10% of the $^{65}Zn$ found in mussels at the mouth. As can be seen in Fig. 2, 10% of the value at the mouth was still not reached at distances greater than 322 km distant. Watson points out that there was an increase in activity since their first measurement in 1957 up to 1960 when their paper was published.

## SUMMARY

The zinc-65 concentration in mussels from the Washington and Oregon coast were measured in a 512 channel gamma ray spectrometer. The activity of $^{65}Zn$ from the samples decreased rapidly with increasing distance from the Columbia River mouth. The activity decreased faster with distance south of the river indicating the seasonal effect of the Columbia River plume which is onshore in the winter north and offshore in the summer south of the river mouth.

Data represented in Figure 2.

| Location | Post. adductor muscle | Foot | Remaining soft pts. |
|---|---|---|---|
| Auke Bay, Alaska | 0* | 0 | 0.82 |
| Ruby Beach, Wash. | 23.97 | 19.49 | 31.35 |
| Pt. Grenville, Wash. | 37.21 | 37.69 | 39.84 |
| Pt. Chehalis, Wash. | 59.28 | 42.85 | 70.78 |
| North Jetty, Astoria | 143.72 | 109.59 | 110.15 |
| Tillamook Head, Ore. | 39.58 | 27.16 | 49.27 |
| Yaquina Head, Ore. | 15.88 | 14.50 | 21.15 |
| Coos Bay, Ore. | 11.72 | 8.20 | 12.24 |

* All computations are based on picocuries/gm. dry wt.

# REFERENCES

Watson, D. G., J. J. Davis, and W. C. Hanson. 1961. Zinc-65 in marine organisms along the Oregon and Washington coasts. Science, 133: 1826-1828.

Osterberg, C., June G. Pattullo, and W. G. Pearcy. 1964. Zinc-65 in euphausiids as related to Columbia River water off the Oregon coast. Limnol. and Oceanogr. 9 (2): 249-257.

Osterberg, C., W. G. Pearcy, and H. Curl, Jr. 1964. Radioactivity and its relationships to the oceanic food chain. J. Mar. Res. 22 (1): 2-12.

Seymour, A. H., G. B. Lewis. 1964. Radionuclides of Columbia River origin in marine organisms, sediments, and water collected from the coastal and offshore waters of Washington and Oregon 1961-1963. UWFL-86.

# RESEARCH IN PROGRESS

## F. RADIOECOLOGY AND ECOLOGY OF BENTHIC ANIMALS

A. G. Carey, Jr. and J. E. McCauley

Benthic research for the AEC includes: (1) the study of the distribution and abundance of benthic invertebrates, particularly the large epifauna, as related to various aspects of the marine environment; and (2) the study of the role played by the bottom fauna in the cycling, transport, and concentration of certain trace elements in the sea. The northeast Pacific Ocean off the coast of Oregon is well suited for these studies, as artificial radionuclides are introduced into the oceanic environment from the Columbia River.

### Sampling and Instrumentation

Benthic samples were collected on nine cruises during the report period. Sixty-eight Smith-McIntyre 0.1 $m^2$ bottom grab and 47 23-foot otter trawl samples were collected for radioanalysis for gamma-emitters throughout the year. A major effort was made to sample standard stations on the Newport station line on a seasonal basis and to sample off Tillamook Head, a short distance from the Columbia River. The latter sampling line was initiated to provide significant levels of radioactivity in both the sediment and fauna for food chain research.

The design and construction of a quantitative 3-meter beam trawl for use at standard AEC trawling stations is still in progress. Several models of the trawl have been built and tested at sea, but its present form is too unstable to produce satisfactory results. A major redesign is in progress, and it is planned to have the trawl operational by next winter.

### Radioecology

Four hundred and seventy-three samples have been radioanalyzed for gamma-emitters in the benthic program during the last year. Sixty-one species of animals were represented. Sediment was analyzed from forty stations.

A summary of the results to date was prepared (Carey, Pearcy, and Osterberg, 1966) for the IAEA Symposium in Vienna, Austria, May 1966, and is included in this progress report (see pp. 192-209) Highest concentrations of zinc-65 in the benthic organisms were found near the Columbia River and on the continental shelf. The amount of radiozinc rapidly decreased beyond 400 meters depth. Zinc-65 was demonstrated through several steps of a benthic food chain, e. g. from sediment through an ophiuran (brittle star) to a carnivorous asteroid (starfish).

Reduction of all significant data by computer is underway. All spectra from radioanalysis of the benthic fauna must be carefully examined for the presence of natural radioactivity, e. g. the uranium decay series; the computer program is unable to handle these data at present. Radioanalysis data for all groups of bottom organisms is presently being compiled and studied; detailed results will be available at a later date.

Samples at the standard AEC trawling stations have been collected for radioanalysis on a seasonal basis. There are indications that a yearly pattern is present, and that it may lag behind seasonal maxima in radioisotope concentrations in the nekton.

Stable Zinc

A program to determine the total amount of zinc in the bottom invertebrates was initiated this year to provide data for use in calculating specific activities for $^{65}$Zn. Such information is necessary for a complete understanding of concentration factors for radionuclides by the fauna, and it may prove valuable in determining rates and routes of organic material in the food web.

Analysis for total zinc with a Perkin-Elmer Model 303 atomic absorption spectrometer (See Tennant this progress report pp. 67-89) has been completed for 48 individual samples of benthic invertebrates. Values range from 27.9 $\mu$g/g ash wt. to 1624.9$\mu$g/g ash wt. with an average of 638.6$\mu$g/g ash wt. The largest amount of zinc was found in Hymenaster (whole animal), a genus of abyssal starfish, and the lowest in the test of Allocentrotus fragilis, a sea urchin.

Table 1 presents some of the data on specific activities for $^{65}$Zn. There is a general trend toward a decrease in the specific activity with increasing depth and distance from the Columbia River though there are still inconsistencies in the data. Further work needs to be done to fully define the pattern in the oceanic environment.

Table 1. Specific Activities for Zn$^{65}$

| Species | Common Name | Depth (m) | Distance from Columbia (km) | pc $^{65}$Zn/g ash-free dry wt. | μg Zn/g ash-free dry wt. | Specific Activity |
|---|---|---|---|---|---|---|
| A. 200 m Contour Southward of Columbia | | | | | | |
| Allocentrotus fragilis (gut) | sea urchin | 200 | 81 | 89. 86 | 416. 11 | 0. 18 |
| Pandalus jordani | shrimp | 200 | 81 | 23. 70 | 96. 89 | 0. 24 |
| Stichopus californicus | sea cucmber | 200 | 81 | 8. 31 | 84. 28 | 0. 10 |
| Pandalus jordani | shrimp | 200 | 115 | 28. 18 | 72. 09 | 0. 39 |
| Allocentrotus fragilis (gut) | sea urchin | 200 | 115 | 119. 24 | 619. 66 | 0. 19 |
| Allocentrotus fragilis (gut) | sea urchin | 200 | 139 | 48. 30 | 564. 80 | 0. 09 |
| Pandalus jordani | shrimp | 200 | 139 | 24. 12 | 83. 01 | 0. 29 |
| B. 44° 39. 1' Latitude | | | | | | |
| Pisaster brevispinus | starfish | 50 | 178 | 11. 99 | 277. 23 | 0. 04 |
| Leioptilus quadrangularis | sea pen | 50 | 178 | 50. 89 | 257. 36 | 0. 20 |
| Neptunea sp. | snail | 885 | 191 | 7. 74 | 716. 61 | 0. 01 |
| Hymenaster sp. | starfish | 2926 | 213 | 0. 75 | 2710. 67 | 0. 0003 |
| Hymenaster sp. | starfish | 2833 | 213 | 1. 73 | 2789. 58 | 0. 001 |
| Paelopatides sp. | sea cucumber | 2926 | 213 | 0. 74 | 237. 31 | 0. 003 |
| | sea anenome | 2790 | 318 | 0. 93 | 161. 16 | 0. 01 |

## Joint Radioecology Cruises

Two cruises were undertaken during the summer of 1965 to obtain information on the distribution of radionuclides in the a) environment, (water and sediment) and b) organisms (pelagic, mesopelagic, and benthic). Final analysis of these data is underway. A brief report on the information to be available for the bottom invertebrates is presented:

Cruise A (6507) Coos Bay to Tillamook Head

Station 1 (Coos Bay) 285 km from Columbia River
July 27, 1965 123 km from Cape Arago, Oregon
3050 m deep

23 animal samples radioanalyzed (20 species of invertebrates represented); stable zinc analysis on nine species; one sediment sample radioanalyzed.

Station 2 (Newport) 228 km from Columbia River
July 29, 1965 129 km from Newport, Oregon
2975 m deep

15 samples radioanalyzed (11 species of invertebrates represented), stable zinc analysis on one species; one sediment sample radioanalyzed.

Station 3 (Astoria) 132 km from Columbia River
August 1, 1965 72 km from Tillamook Head, Oregon
2540 m deep

11 samples radioanalyzed (10 species of invertebrates represented), stable zinc analysis on five species, one sediment sample radioanalyzed.

Cruise B (6508) Newport line

Station 4 223 km from Columbia River
August 21, 1965 142 km from Newport, Oregon
2880 m deep

19 samples radioanalyzed (14 species invertebrates represented), stable zinc analysis on six species; one sediment sample radioanalyzed.

| Station 5 | 286 km from Columbia River |
|---|---|
| August 22, 1965 | 277 km from Newport, Oregon |
| | 2840 m deep |

16 samples radioanalyzed (11 species of invertebrates represented); stable zinc analysis on four species; one sediment sample radioanalyzed.

| Station 6 | 429 km from Columbia River |
|---|---|
| August 24,1965 | 370 km from Newport, Oregon |
| | 2750 m deep |

13 samples radioanalyzed, (nine species of invertebrates represented); stable zinc analysis on three species; one sediment sample radioanalyzed.

## Distribution, Abundance, Systematics, and Ecology of Benthic Invertebrates

Continued collections of benthic fauna from the Newport station line as well as from the Tillamook line and others have added to our understanding of the distribution of the fauna with depth and distance from shore.

Studies on the food of the asteroids have been undertaken during the past year. Generally, the predators become proportionately less and deposit feeders more with increasing depth (Table 2). The starfish have been dissected and gut contents removed and enumerated. In many cases the food source still remains uncertain even though fairly many individuals may have been examined. Continued research along these lines should clear up some of these problems. Some species, however, may feed on detritus, extrude their stomachs for exterior digestion, or feed in some other manner that cannot be ascertained by laboratory stomach contents analysis. The use of a deep sea camera may provide information on the attitude and general behavior of the asteroids that may aid in the interpretation of the laboratory analyses. A camera has been scheduled for use in September, 1966, as part of the complementary ecological research sponsored by the National Science Foundation (NSF Grant GB-4629).

Table 2. Food Source of Asteroids.

| Species | Number Dissected | No. with Significant Material in Gut | Food Source |  |  | Literature | Depth (m) | Stomach Contents |
|---|---|---|---|---|---|---|---|---|
|  |  |  | Predator | Deposit Feeder | ? |  |  |  |
| Mediaster aequalis | 5 | 0 |  |  | X | ----- | 45-800 | Few sand grains. |
| Pisaster brevispinus | 2 | 2 |  |  | X | predator | 50 | Small amount of sediment. |
| Luidia foliolata | 25 | 23 | X |  |  | predator | 100-200 | Ophiuroids, echinoids, holothurian. |
| Thrissacanthias penicillatus | 31 | 26 | X |  |  | ----- | 125-600 | Mollusks, Ophiurans, small amount of sediment. |
| Stylasterias forreri | 1 | 1 | X |  |  | ----- | 200 | Gastrods (5). |
| Pseudarchaster parelii alascensis | 9 | 6 | X | X |  | ----- | 200 | Gastropods, some to much sediment. |
| Diplopteraster multipes | 1 | 1 |  |  | X | ----- | 400 | Some sand, stomach partly everted. |
| Dipsacaster anoplus | 44 | 41 | X |  |  | ----- | 600-1250 | Pelecypods, gastropods, echiuroids, much sediment. |
| Solaster borealis | 11 | 6 |  | X |  | ----- | 600-1600 | Some sediment. |
| Hippasteria spinosa | 1 | 1 |  | X |  | ----- | 800 | Small amount of sediment. |
| Ampheraster marianus | 3 | 3 |  |  | X | ----- | 800 | Some sediment, crustacean, mouth open. |
| Heterozonias alternatus | 14 | 10 |  | X |  | ----- | 800-1200 | Some sediment. |
| Nearchaster aciculosus | 22 | 14 | X | X |  | ----- | 1200-2090 | Small amount of sediment, ophiuroid arms. |
| Lophaster purcilliger | 15 | 4 |  |  | X | ----- | 1250-2090 | Traces of sediment. |
| Ctenodiscus crispatus | 23 | 21 |  | X |  | deposit | 1335-1425 | Large amount of sediment. |
| Psilaster pectinatus | 5 | 4 | X | X |  | predator | 1800-2000 | Small to large amount of sediment, polychaetes, scaphopod. |
| Hymenaster quadrispinosus | 27 | 12 |  | X |  | ----- | 2600-2800 | Some sediment, stomach partially everted. |
| Dytaster gilberti | 17 | 6 |  | X |  | deposit | 2600-2860 | Small to large amount of sediment. |
| Pseudarchaster dissonus | 6 | 3 |  | X |  | ----- | 2700-2820 | Some sediment, ophiuran fragments. |
| Benthopelten sp. | 33 | 6 |  |  | X | ----- | 2735-2850 | Trace of sediment, isopod, mouth open |
| Eremicaster pacificus | 6 | 6 |  | X |  | ----- | 2770-2850 | Large amount of sediment. |
| Mediaster elegans (?) | 5 | 0 |  |  | X | ----- | 2820-2830 | Trace of sediment. |

A study of the feeding habits of Coryphaenoides spp. (pp. 134-135) dominant fish species of the lower continental slope and ocean floor, has suggested that benthic fishes may feed higher in the water column and thereby contribute to a more rapid transport of radioactive materials to the ocean floor through the food cycles.

The identification of the fauna continues; publications on the systematics of echinoderms collected during the AEC research will be forthcoming.

## Complementary Programs

Research (NSF Grant GB-4629) on the smaller benthic fauna, particularly the infauna, has continued and further information on the distribution and abundance of these fauna has been gathered. The data substantiate the preliminary results presented a year ago (see reprint included herein, pp. 251-261). The overall distribution picture of the fauna is one of layering with areas of marked faunal change that appear to be associated with sediment changes and depth. Further sampling, and analysis of animals and sediment are underway. Sixteen anchor-box dredge (see reprint included herein, pp. 262-265) samples have been collected during this report period.

# RADIONUCLIDES IN SEDIMENTS

by Andrew G. Carey, Jr.

An attempt has been made to define the artificial radionuclides in the sedimentary environment of benthic organisms. The major purposes of this phase of the program are: (1) to determine the quantity of radionuclides in the sediment in order to provide an estimate of the concentration factors of the sediment-ingesting fauna, and (2) to explain further the fate of zinc, especially $^{65}Zn$, at sea.

## METHODS

Sediment samples have been collected from a variety of areas off the Oregon coast (see Figure 1 and Table I for a partial list) with a 0.1 $m^2$ Smith-McIntyre bottom grab. Top flaps were added to the grab to minimize the possibility of washing the sample during retrieval. Upon removal of the screen lids and flaps, the top 1 cm of sediment was carefully lifted off and frozen at sea. Upon return to the laboratory these samples were dried to constant weight at 65° C. One hundred mls of dried sediment were placed in a 15 cm plastic petri dish and counted on top of a 12.7 x 12.7 cm Harshaw NaI(Tl) crystal. Gamma-ray emissions were counted with a 512 channel Nuclear Data ND-130 Gamma-ray spectrometer for 400 minutes.

Spectra were plotted on an X-Y recorder and compared visually. The predominance of natural radioactivity (see Figures 2, 3, 4) precluded further reduction of these data by computer and other conventional methods. It was initially hoped that spectra of sediments collected beyond the influence of the Columbia River plume might be used as a background to subtract out most of the suites of natural radioactivity. However, the mineralogy was probably different enough to prevent meaningful results by this technique. Standardization methods are presently under development.

## RESULTS

Three series of sediment spectra have been compiled from three station lines and are shown in Figures 2, 3, 4. Upon inspection, the zinc-65 energy level per unit volume of sediment appears significantly higher at 150 m and possibly 200 m depth off Tillamook Head than at the other depths (Figure 2) along a line of stations to the west of Tillamook Head (46° 00' N).

Along the 200 m contour to the south of the river mouth zinc-65 appears in the bottom sediments to a distance of about 115 km. Beyond this point radiozinc could not be detected in the sediments by the above methods (Figure 3).

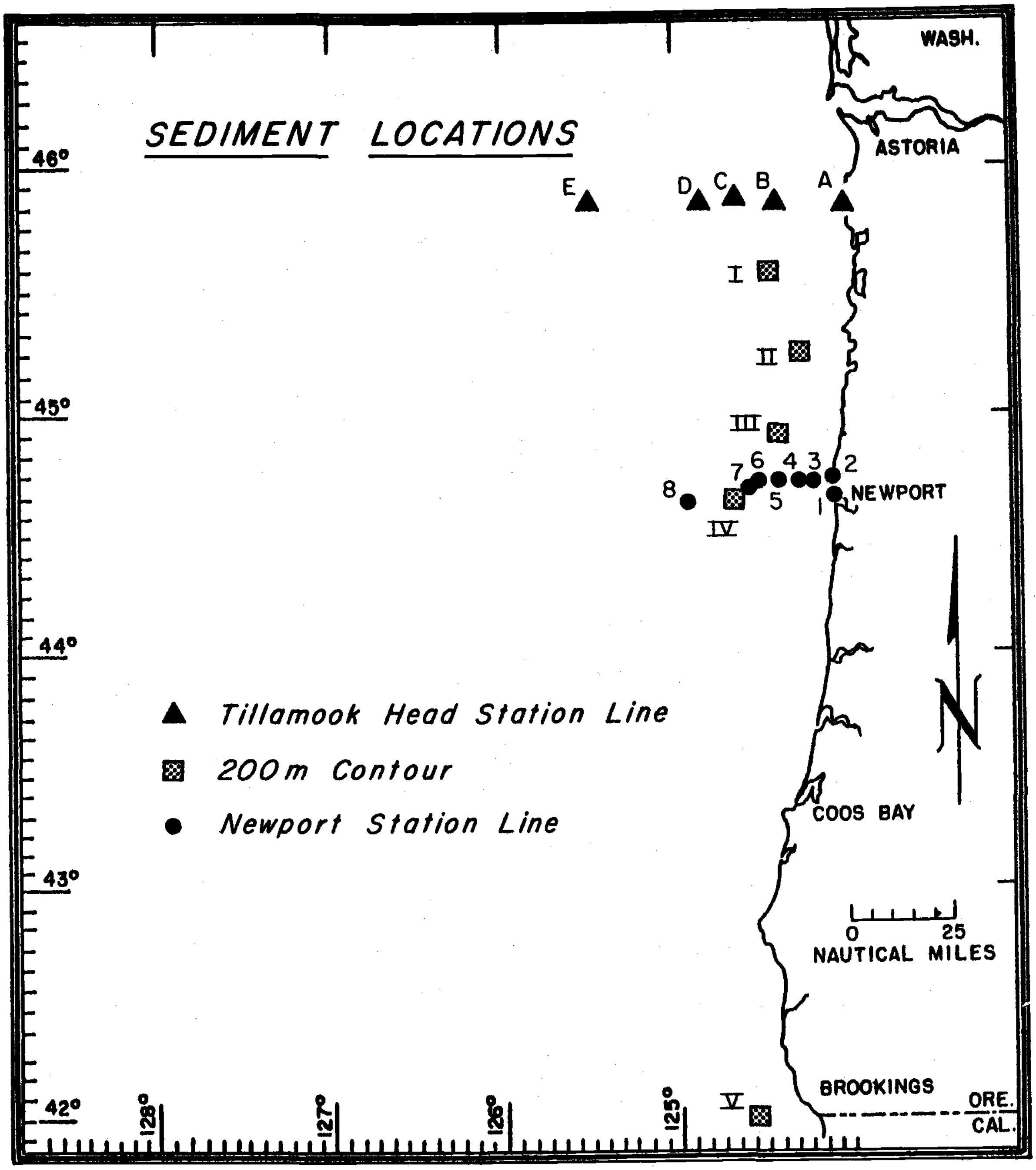

Figure 1. Station locations for radioanalyzed sediment samples. Station designations pertain to the respective gamma-ray spectra.

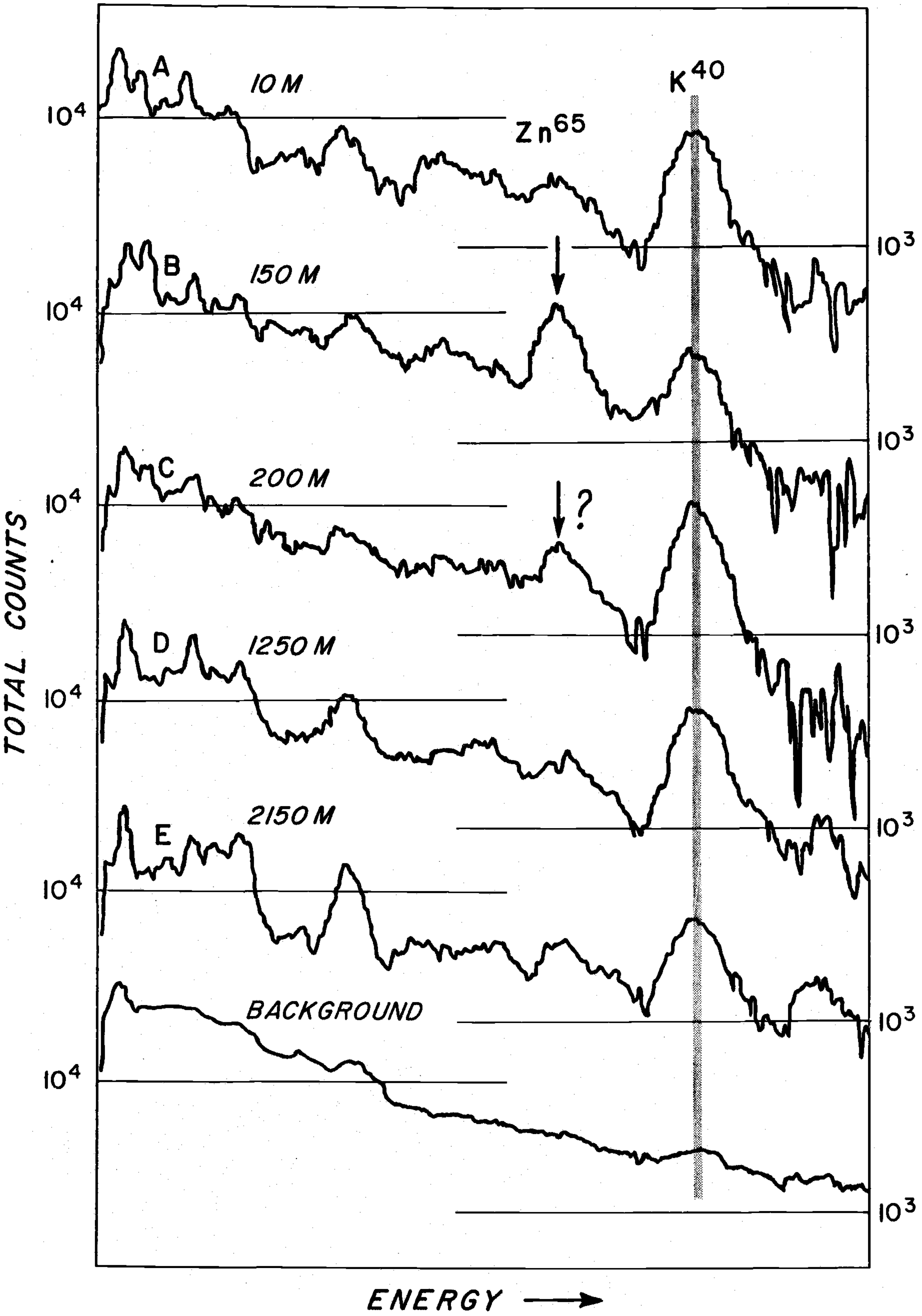

Figure 2. Gamma-ray spectra of sediment samples from the Tillamook Head station line. Note the prominent peak in the $Zn^{65}$ energy region. A trace of $Zn^{65}$ may be present at the 200 meter station.

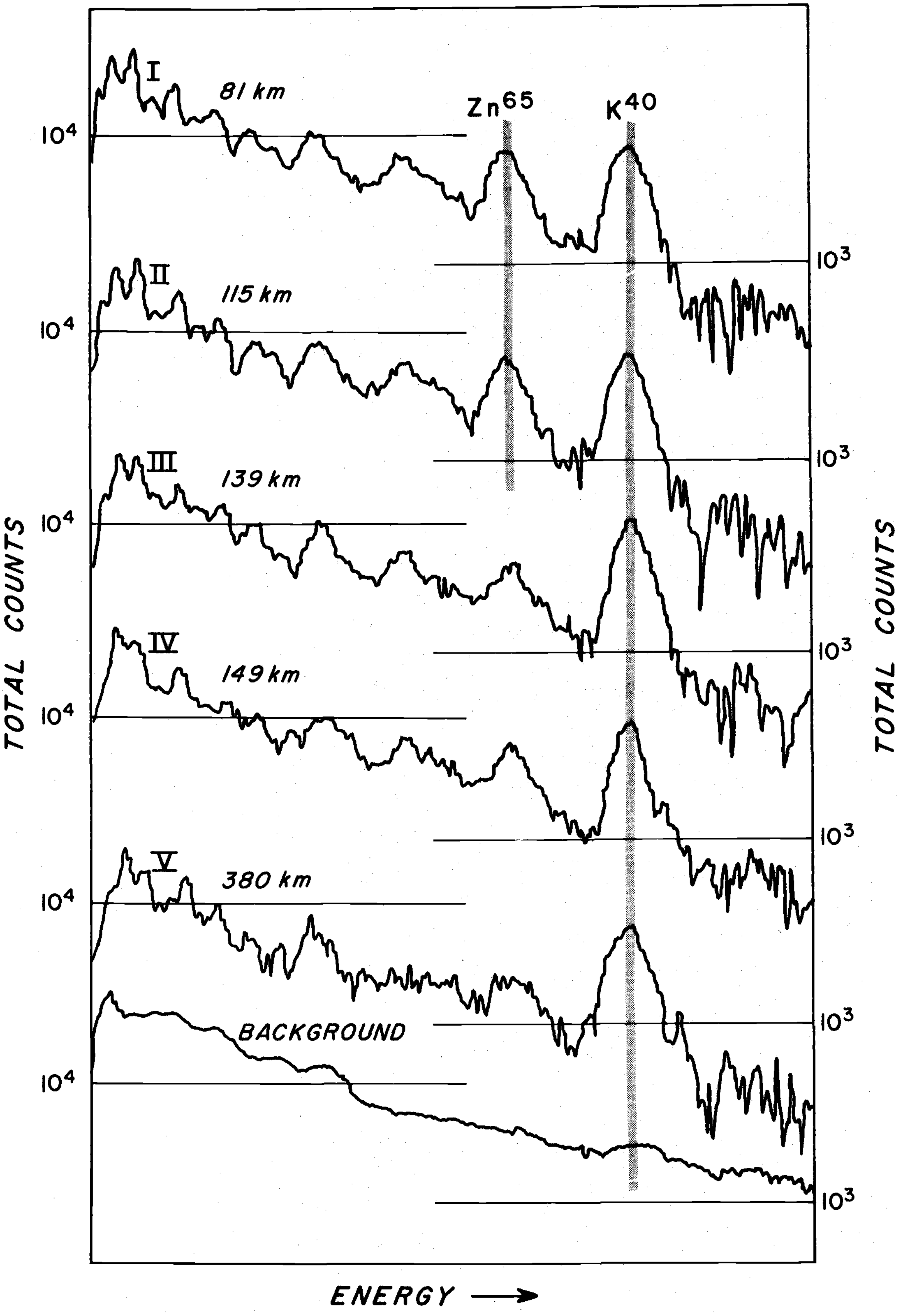

Figure 3. Gamma-ray spectra of sediment samples from the 200 meter countout southward from the Columbia River. Note the prominent $Zn^{65}$ peak at 81 and 115 km.

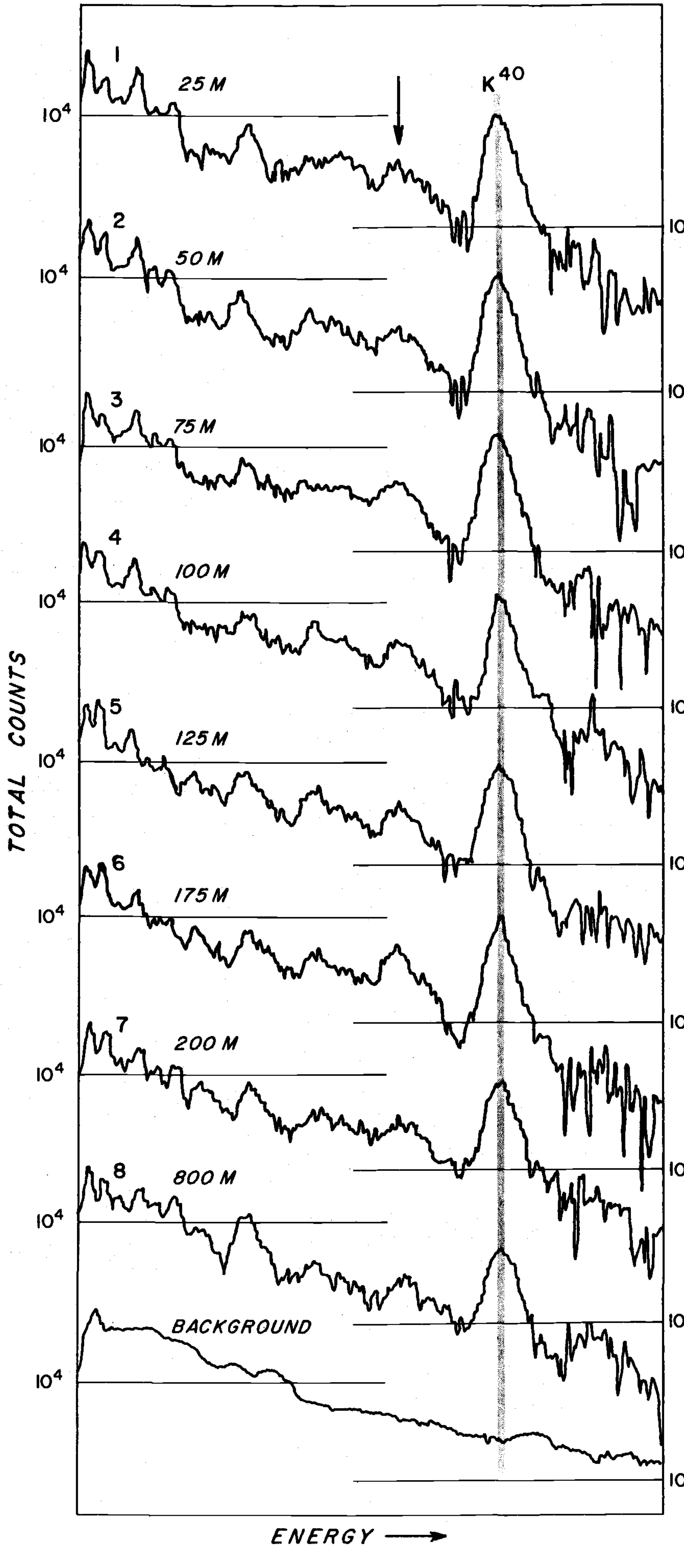

Figure 4. Gamma-ray spectra of sediment samples from the Newport station line. Note the lack of a prominent peak in the Zn$^{65}$ energy region (marked with arrow).

Off Newport, (44° 39' N) Oregon, no $^{65}Zn$ has been detected in depths of 25 to 2800 m and to a distance of 472 km from shore. Spectra of sediments from 25 to 800 m along the east-west station line off Newport are presented in Figure 4. Beyond 800 m spectra show increasing amounts of natural radioactivity, leveling off at about 305 km from shore.

## DISCUSSION

The natural radioactivity in these sediment samples, particularly the uranium series, obscures the detection of radiozinc by visual examination of the spectra, as a sum peak from this series is present in the spectra in the zinc energy levels. In spite of this, zinc-65 from the Columbia River is present in detectable quantities in the sediment only in shallow water near the Columbia. Spectra of sediment from areas beyond the direct influence of the Columbia River are very similar to those of sediments from the Newport stations; there appears to be no difference in the photopeak in the zinc-65 energy channels.

The present methods cannot give absolute values for the amount of radiozinc present in the sediments. A more fruitful approach may be to separate the zinc from the sediment chemically. Future use of an in situ gamma-ray probe will aid in the interpretation of these data.

Though zinc-65 cannot be demonstrated in the sediments off Newport, Oregon, it is readily detected in the benthic fauna on the continental shelf and upper continental slope in this area. The fauna, then, are important in concentrating $^{65}Zn$. Further research is necessary to define the environmental levels of zinc-65 before concentration factors can be determined.

## TABLE I

## SEDIMENT RADIOANALYSIS STATION DATA

| | Station | Date of Collection | Depth (m) | Distance From Columbia River (km) | Distance From Shore (km) |
|---|---|---|---|---|---|
| (Along 200 m contour south from mouth of Columbia River) | I | 27 August 1965 | 200 | 81 | 35 |
| | II | 27 August 1965 | 200 | 115 | 32 |
| | III | 27 August 1965 | 215 | 139 | 46 |
| | IV | 27 August 1965 | 190 | 149 | 30 |
| | V | 16 November 1965 | 180 | 380 | 25 |
| (46° 00' N) | A | 23 March 1966 | 50 | 44 | 4 |
| | B | 24 March 1966 | 150 | 50 | 36 |
| | C | 24 March 1966 | 200 | 64 | 55 |
| | D | 24 March 1966 | 1250 | 73 | 69 |
| | E | 25 March 1966 | 2150 | 121 | 120 |
| (44° 39' N) | 1 | 3 June 1965 | 25 | 178 | 3 |
| | 2 | 3 June 1965 | 50 | 168 | 6 |
| | 3 | 3 June 1965 | 75 | 171 | 15 |
| | 4 | 4 June 1965 | 100 | 172 | 21 |
| | 5 | 4 June 1965 | 125 | 174 | 29 |
| | 6 | 4 June 1965 | 175 | 174 | 39 |
| | 7 | 15 January 1965 | 200 | 181 | 42 |
| | 8 | 14 January 1965 | 800 | 191 | 70 |

# PRELIMINARY NOTES ON THE OCCURRENCE AND ACTIVITY OF RADIOISOTOPES IN MARINE BENTHOS OFF OREGON

Andrew G. Carey, Jr. and Charles L. Osterberg

In a preliminary manuscript on the radioecology of the benthos off Oregon (Progress Report AT(45-1)1750 for 1965, pp. 174-187) Carey and Osterberg reported data on the distribution of artificial gamma-emitting radionuclides as effected by depth, distance from shore, taxonomic group, and season of the year. Data on fallout radionuclides from atomic testing and induced radionuclides, from the Hanford Reactors at Richland, Washington, were presented. It was shown that all groups of animals studied contained zinc-65, though some groups had more activity per unit weight than others. The concentration of radiozinc rapidly decreases below about 400 meters depth. Though readily detected in the bottom fauna off Newport, Oregon, on the continental shelf and slope, $^{65}$Zn has not been detected in the sedimentary environment. Before decaying away after cessation of atmospheric atomic testing in 1963, zirconium-95 - niobium-95 were found in deposit-feeding benthos from all depths in about equal amounts; but the higher trophic levels, the carnivores and scavengers, contained little or no $^{95}$Zr - $^{95}$Nb.

Further data on radionuclides, particularly seasonal, sediment, and taxonomic information, have been collected during the past year and will allow us to expand our report and to draw firmer conclusions. It is apparent that the concentrations of radionuclides in the bottom organisms and the sediments decrease with distance from the mouth of the Columbia River. Detectable quantities of $^{65}$Zn are not found in the sediments at a depth of 200 meters beyond 115 km from the river mouth. The falloff of $^{65}$Zn in the fauna is much less rapid than in the sediment.

# FEEDING HABITS OF *CORYPHAENOIDES* SPP.

by James E. McCauley

A study of the food habits of macrourid fishes of the genus *Coryphaenoides* is under way. *Coryphaenoides* is the dominant fish genus in the benthic fauna of the lower continental slope and adjacent ocean floor. These species are taken in relatively large numbers and a survey of stomach contents has been made where possible. This group of fishes contains an air bladder which expands as the fish are brought to the surface and usually forces the stomach to evert through the mouth. Several hundred fishes have been sorted but only 21 were found with normal or only partially everted stomachs. These fish were examined very carefully for stomach contents.

In addition to stomach analyses, the intestines of about 35 fish were examined. These, of course, do not provide as much information as stomach analyses because the soft parts of animals are usually digested beyond recognition, but many hard parts remain.

Among the animal fragments collected, many are undoubtedly from benthic animals as was expected and include fragments from:

Solenogasters
Snail
Sponges
Pogonophoran
Foraminifera
Sea Urchin (including *Urechinus*)
Calcareous tubes
Brittle Stars
Clam
Sea Cucumber (probably *Chirodota* sp.)
Annelids - many, includes maldanids, *Travisia* sp.

This assemblage of animal fragments suggests that these fishes probably feed selectively from the surface of the bottom and do not dig in the sediments even though the nose appears well constructed for digging.

But other food fragments are more probably of pelagic origin suggesting that these fishes at times swim up into the water column to feed. These include fragments from:

Shrimp - many eyes, carapace fragments, and appendages,
Squid beaks
Fish - bones, many ctenoid scales (possibly from *Corphaenoides*), cycloid scales, some flesh fragments, and lenses.

Copepod - carapace and egg sacs
Ellobiopsid parasite on shrimp
Octopus - probably Gonatotropsis borealis, a pelagic form.

The shrimp constituted a major portion of the identifiable mass in the stomach and intestine, implying at least a short excursion of the fish into the water column to feed. Pearcy has taken an occasional Coryphaenoides sp. in the midwater trawl, establishing some vertical movement of this benthic fish.

Such vertical movement for feeding must be influential in transporting materials downward in nutrient cycles, and it would appear that radionuclides also could be carried down in this manner.

In addition to the food from the stomachs a number of parasitic trematode worms were recovered from the stomachs. These parasites are being studied in an NSF supported project (Grant GB-5136).

# ECHINOIDS OFF OREGON

By James E. McCauley and Andrew G. Carey, Jr.

In a preliminary manuscript on the Echinoids off Oregon (A. E. C. Prog. Rept. AT(45-1)1750 for 1965, pp. 190-198) McCauley and Carey reported eight species off the coast of Oregon. Additional collections and further study have revealed the presence of two other species, Aëropsis fulva and Urechinus loveni; also, the taxonomic status of Brisaster townsendi and B. latifrons is being restudied.

## Aëropsis fulva (A. Agassiz, 1898)

Order: Spatangoida Family: Aëropsidae

Alexander Agassiz (1898) described this species from five "Albatross" collections made off the Pacific Coast of Columbia in 1175-1772 fathoms (2148-3181 m). Clark (1944) reported four examples from Peruvian waters in about 5200 m and fragments from the Bering Sea in 3228 m. Mortensen (1950) was reluctant to accept the species from the Bering Sea on the basis of fragments only, but recently Baranova (1957) confirmed the presence in the Bering Sea with 20 specimens from depths of 3300-3040 m. Baranova also added some details to the morphological description of the species, especially with respect to the fine structure of the spines and pedicellaria.

We collected specimens from seven stations on the Cascadia Abyssal Plain off Oregon in depths of 2600-2806 m. These specimens, while largely fragments, agree completely with the published descriptions and supply a distributional record between the tropics and the arctic.

Geographical distribution: Pacific Coast of American from Peru to the Bering Sea.

Bathymetric distribution: 2148-5200 m.

Substrate: Terriginous green-gray muds.

## Urechinus loveni (A. Agassiz, 1898)

Order: Spatangoida Family: Urechinidae

This species was first reported by Alexander Agassiz from "Albatross" collections in 1898 but was not fully described until 1904 (Agassiz, 1904). His specimens came from 1877 fathoms (3345 m) off Acalpulco, Mexico. Clark (1917) later reported it from the Bering Sea and Sea of Okhotsk from depths of 3230-3608 m. Agassiz's (1904) is quite complete and no new details can be supplied.

We collected fragments of this fragile urchin from 2600-2833 m on the Cascadia Abyssal Plain off Oregon where it occurred in ten samples from seven stations. It appeared to be fairly common at these depths as fragments of several individuals were frequently present in each sample. Only one specimen has been reasonably intact. This specimen measured 83 mm long, 74 mm wide, and 59 mm high; its color was lavender. Agassiz (1904) does not give measurements in his text, but his figures, which are stated to be natural size, have the same dimensions.

Our collections are from shallower waters than previously reported and fill a distributional gap between the Mexican and Arctic collections.

Geographical distribution: North Pacific Ocean, as far south along the North American Coast as Acapulco, Mexico

Bathymetric distribution: 2600-3608 m.

Substrate: Terriginous green-grey muds.

## *BRISASTER LATIFRONS* AND *BRISASTER TOWNSENDI*

*Brisaster latifrons* (Agassiz, 1898) and *B. townsendi* (Agassiz, 1898) were described from "Albatross" specimens collected off Central America. Many specimens have been collected subsequently from the west coast of North America, the Bering Sea, and the east coast of Asia down into Japanese waters. Criteria for separating the two species are not well defined, and it may well be that there are not two species but rather variants of a single species showing environmental effects.

Most of the Asiatic specimens have been called *B. latifrons* but Mortensen (1951) believes that they probably belong to *B. owstoni*. The American specimens have been called both *B. latifrons* and *B. townsendi* but by far the most seem to be *B. townsendi*. Almost all the figures of American specimens are of *B. townsendi*. Most of the recent workers in the group express doubt about the validity of two species, but no one has settled the problem.

We have more than 300 specimens in our collection and have borrowed much of the "Albatross" material from the U. S. National Museum. We also have a small collection from the Zoology Department of the University of Washington and are negotiating to borrow the collection from the California Academy of Sciences. A new collection from off Oregon has been made to fill a bathymetric gap.

We are now studying these collections and hope that the taxonomic problem of these two species can be solved either by synonymizing the two or by redescribing them on a more realistic basis.

An amended bathymetric range of the Echinoid species off Oregon is given in Table 1.

Table 1. Bathymetric range of Echinoidea in the Eastern Pacific Ocean off Oregon.

| Species | Depth (meters) |
|---|---|
| *Dendraster excentricus* | 0-52 |
| *Strongylocentrotus purpuratus* | 0-64 |
| *Strongylocentrotus franciscanus* | 0-64 |
| *Strongylocentrotus echinoides* | 80-110 |
| *Allocentrotus fragilis* | 80-800 |
| *Brisaster* (?)*townsendi* | 100-800 |
| *Aeropsis fulva* | 2600-2870 |
| *Urechinus loveni* | 2600-2830 |
| *Sperosoma giganteum* | 2090-3000 |
| *Ceratophysa rosea* | 2600-2830 |

# REFERENCES

Agassiz, A. 1898. Preliminary Report on the Echini-Albatross Report. Bull. Mus. Comp. Zool., Harvard 32: 71-86.

---------- 1904. Panamic Deep Sea Echini. Mem. Mus. Comp. Zool., Harvard 31: 1-246.

Baranova, Z. I. 1957. Echinoderms of the Bering Sea. Investigations of the Far Eastern Seas. U.S.S.R. 4: 149-266.

Clark, H. L. 1914. Hawaiian and other Pacific Echini. Mem. Mus. Comp. Zool., Harvard 46: 5-78.

------------ 1917. Hawaiian and other Pacific Echini. Mem. Mus. Comp. Zool., Harvard 46: 85-28 .

Mortensen, T. 1950. A Monograph of the Echinoidea. 5(1): 432.

------------ 1951. A Monograph of the Echinoidea. 5(2): 593.

# RESEARCH IN PROGRESS

## G. ECOLOGY AND RADIOECOLOGY OF OCEANIC ANIMALS

by William G. Pearcy, Leader

The major objective of our studies on oceanic animals is to learn more about the ecology of vertically migrating and deep-sea animals and their role in the transport and distribution of trace elements in the ocean. Using these organisms and the isotopes they have accumulated, we hope to further our knowledge of the open-ocean ecosystem, particularly the dynamic interrelationships between animals occupying different depths, from the sea surface to the deep-sea floor.

Progress during the past year related to the objectives is included under three categories: radioecology, vertical distribution and ecology, and sampling methods.

### Radioecology

The $^{65}Zn$ content of mixed-species catches of pelagic animals displayed seasonal, depth, and day-night variations (see pp. 143 and pp. 144). Moreover, this study provided evidence for the movement of $^{65}Zn$ through the halocline and for the accumulation of significant amounts of $^{65}Zn$ by vertical migrants. The proportion of radiozinc to total zinc (specific activity) also decreased with increasing depth (see pp. 145-147).

Radioanalysis of albacore tuna showed that $^{65}Zn$ and the $^{65}Zn/^{54}Mn$ ratio, but not $^{54}Mn$, were decidedly lower off California than Oregon and Washington. As the summer progressed, the zinc-65 content of albacore livers clearly increased off southern Oregon (see pp. 148-152).

### Vertical Distribution and Ecology

The gross features of vertical distribution and migration have been described for mesopelagic fishes by Pearcy (see enclosed reprint, pp. 268-280) for oceanic shrimps by Pearcy and Forss (see abstract, p. 168). Papers on the general distributional ecology of other groups of animals include papers on cephalopods (see enclosed reprint by Pearcy, pp. 281-286) a medusa (see enclosed reprint by Renshaw, pp. 287-297) chaetognaths (see Renshaw manuscript, pp. 160-167) and shrimps (see Forss and Pearcy manuscript, pp. 212).

Feeding and trophic level relationships are an important aspect of ecological studies. Certain relationships between radioactivity and food chains were interpreted by Osterberg, Pearcy, and Curl (Journal of Marine Research 22(1): 2-12, 1964). The paper on the feeding habits of two species of common shrimps by Renfro and Pearcy (see pp. 153-159) provides further information on the oceanic food web.

## Sampling Methods

Knowledge of the behavior and distribution of organisms is an essential prerequisite to meanful interpretation of radioecological data, yet this knowledge can be no better than our sampling techniques. For example, avoidance of trawls during daylight hours by some animals confounds accurate estimates of vertical migration or movement of radioisotopes. Since all of our basic ecological data come from samples, we continally attempt to improve our methods (see Pearcy and Hubbard, Deep Sea Research 11: 263-264, 1964; other sampling method papers included in this Progress Report are on pp. 266-267.

# RADIOECOLOGY OF VERTICALLY MIGRATING PELAGIC ANIMALS*

by William G. Pearcy

## ABSTRACT

Quantitative midwater trawl samples from discrete depth strata provided data on seasonal, depth, geographic, and diel variations in the zinc-65 activity of mixed macroplankton and micronekton collections. Pronounced seasonal variations with summer maxima were evident in zinc-65 per unit of wet weight, in the upper 150 m. These variations are damped in the 150-500 m stratum, and were absent in deeper water, 500-1000 m. The zinc-65 concentrations were notably higher in night than day collections from 0-150, suggesting that vertically migrating animals may actually accumulate more radionuclides than surface, non-migratory species.

The zinc-65 contained in animals collected per unit volume of water also displayed seasonal and day-night variations, peak radioactivity being found in nocturnal samples from the summer from near-surface waters. The location of the Columbia River plume undoubtedly influenced the seasonal fluctuations of zinc-65 content off Oregon.

Night-time collections consistently captured more biomass in the 0-1000 m water column than daytime samples, indicating that both differential avoidance and vertical migration affect the estimates of variation of zinc-65 off Oregon. If it is assumed that vertical migration explains all the increased biomass in surface waters at night, then the difference between zinc-65 contained in animals in the upper 150 meters in the daytime and at night constitutes about 80% of the total zinc in animals collected from the entire 1000 meter water column in the nighttime, suggesting that 80% of the radioactive zinc is in vertical migrating animals. This is the first time that an estimation of diel vertical movement of radiozinc has been attempted for oceanic animals. Since euphausiids were dominant animals only from nocturnal and not diurnal catches, they are implicated as being important organisms in influencing both day-night and seasonal variations of zinc-65.

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* A large portion of this material was included in AEC Prog. Rept. AT(45-1)1750 pp. 137-146. A paper is in preparation for publication.

To determine if the winter, 0-150 m levels of zinc-65, or the deep-water levels, were significantly above background for the northeastern Pacific, winter samples from up to 1850 km off Oregon were radioanalyzed. All were appreciably lower than samples near shore, indicating that even in winter levels of zinc-65 off Oregon are relatively high. This is probably due to the high percentage of residual Columbia River water found off Oregon during that season.

Samples of pelagic animals from the Central Pacific Water Mass had higher zinc-65 and higher manganese-54 levels than samples several hundred miles off Oregon, but lower zinc-65 than near-shore collections.

# SPECIFIC ACTIVITIES OF OCEANIC ANIMALS

by William G. Pearcy

During the past year 282 samples of oceanic animals, each sample consisting of whole individuals of one single species, have been radioanalyzed for gamma emitters, and 299 samples have been analyzed by atomic absorption spectrometry. Principal emphasis has been on zinc, to enable calculation of specific activities.

Two special cruises were made during the summer of 1965 to learn how zinc-65 content was related to specific activities of oceanic animals from different depths and different geographic locations off Oregon. These cruises alone provided samples for 163 estimates of specific activities from 50 different species of animals, including fishes, crustaceans, cephalopods, and coelenterates. Since most species were analyzed three or four times, specific activities of the same species could be compared from different localities. A summary of the general trends is presented at this time; a detailed analysis is in progress.

## Variations Related to Depth Distribution

When species are grouped by depth distributions, based on the depth range of actual capture and our previous knowledge from opening-closing nets, several trends are evident in the zinc-65 and specific activities of zinc. Table 1 gives an example of the data for the fishes at one station. In general, both $^{65}Zn$ per gram ash-free dry weight of tissue and the specific activities (pc/μg) decrease with depth. Highest values were found in near surface species and lowest values in deep-sea fishes.

Differences between lower mesopelagic fishes (500-1000 m) and abysso-benthic fishes (2800 m) were not apparent despite the large depth separation. The high specific activity and zinc-65 content of *Tarletonbeania crenularis* is of interest. This is undoubtedly related to the migration of this species of lantern fish to the surface at night, whereas the other vertical migrants are usually deeper, and beneath plume waters.

Table I. Specific Activities of Zinc From Fishes Collected at Various Depths at NH-65, July 29 and 30, 1965.

| | pc | µg | pc/µg |
|---|---|---|---|
| Epipelagic Fishes (0-10 m) | | | |
| Cololabis saira | 27.7 | 64.2 | .432 |
| Anoplopoma fimbria (juveniles) | 62.3 | 93.2 | .668 |
| Upper Mesopelagic Fishes Vertical Migrants (0-500 m) | | | |
| Tarletonbeania crenularis | 25.4 | 87.4 | .290 |
| Symbolophorus | 5.06 | 33.4 | .152 |
| Lampanyctus leucopsarus | 3.63 | 25.2 | .144 |
| Tactostoma macropus | 2.20 | 49.4 | .044 |
| Diaphus theta | 7.54 | 59.9 | .126 |
| Lower Mesopelagic Fishes (500-1000 m) | | | |
| Bathylagus spp. | 2.56 | 53.0 | .048 |
| Cyclothone pacifica | 0.10 | 61.3 | .002 |
| Lampanyctus nannochir | .20 | 23.2 | .009 |
| L. regalis | 4.53 | 50.7 | .089 |
| Poromitra crassiceps | 4.52 | 69.7 | .065 |
| Abyssal Benthic Fishes (2800 m) | | | |
| Coryphaenoides spp. | 1.29 | 79.0 | .016 |
| | 0.90 | 114.7 | .008 |

Considerable variation was noted in the specific activities of different species presumably from comparable depths. In some cases, the zinc-65 was several times higher in one of two individuals of the same species from the same station. In other instances the stable element concentrations for a single species were variable. Some of these variations may be related to the feeding habits of the animals and their gut contents at the time of analysis; others may be related to the size or maturity of individuals. Further study is needed, but in any case, specific activities may be a very useful indication of differences in the ecology and distribution of these animals.

### North-South Variations

Collections made at three stations 121 km offshore (off the Columbia River, off Newport, and off Coos Bay, Oregon) provided information on latitudinal variations of the zinc concentrations. Again, levels appeared to be related to the depth distribution of the species. For example, the epipelagic saury (*Cololabis saira*) had the highest specific activity off Newport. The specific activities of the upper mesopelagic fishes *Tarletonbeania crenularis* and *Lampanyctus leucopsarus* were about the same at all three stations. But five species of lower mesopelagic fishes all had the lowest specific activities at the northern station off the Columbia River.

### East-West Variations

The specific activities of shallow water species, including *Cololabis saira* and *Tarletonbeania crenularis* as well as the benthic *Microstomus pacificus*, were highest inshore, 46 km off Newport. In general, mesopelagic fishes, not usually captured inshore where depth is shallow, had higher specific activities at the 121 or 157 km station off Newport than farther offshore.

Thus, bathymetric, north-south and east-west trends were found in zinc-65 and specific activities.

# RADIOECOLOGY OF ALBACORE (THUNNUS ALALUNGA) FROM THE NORTHEASTERN PACIFIC

By William G. Pearcy

Livers from 136 albacore tuna collected during 1962-1965 off Washington, Oregon, southern California, and Baja, California, were radioanalyzed by means of gamma-ray spectrometry. Twenty-three samples were also analyzed by atomic absorption spectrometry, providing data on specific activities of zinc and manganese.

Most of the livers were preserved with formaldehyde and dried, ashed, and radioanalyzed within several weeks after capture. Some livers were frozen. A comparison of 10 frozen and 10 preserved livers taken from albacore collected at the same time and location indicated no difference for $^{54}$Mn (t=0.59). On the other hand, formalin preserved livers contained significantly higher quantities of $^{65}$Zn (t=2.61) than frozen livers. The reason for this is not clear, but it does not indicate extraction or leaching of $^{65}$Zn by the preservative, such as was found in a liver preserved for one year.

Geographic and seasonal variations in $^{65}$Zn and $^{54}$Mn per gram of liver ash and the $^{65}$Zn:$^{54}$Mn ratios are shown in Figs. 1, 2, 3.

## ZINC-65

The zinc-65 content of albacore livers (Fig. 1) is not the same in all areas of the northeastern Pacific. Albacore livers off southern California contained low amounts of $^{65}$Zn per gram of ash compared to those off Oregon and Washington. Moreover, $^{65}$Zn during the summer period was much less variable off California.

Off southern Oregon (415-555 km south of the mouth of the Columbia River) there was an obvious trend for the $^{65}$Zn content of tuna livers to increase from July through October (mid-section, Fig. 1). This trend was found during both 1963 and 1964. During early July the values are approximately the same as those of tuna taken off southern California, but they increased markedly during the summer so that by September they were about an order of magnitude higher than in early July and those taken off southern California in September. The enhancement of $^{65}$Zn during this period I attribute to the association and feeding of albacore in Columbia River plume waters.

Off northern Oregon and Washington, only 45-305 km north of the mouth of the Columbia River, the accumulation of $^{65}$Zn during summer months is not readily apparent, although the values for 1965 suggest

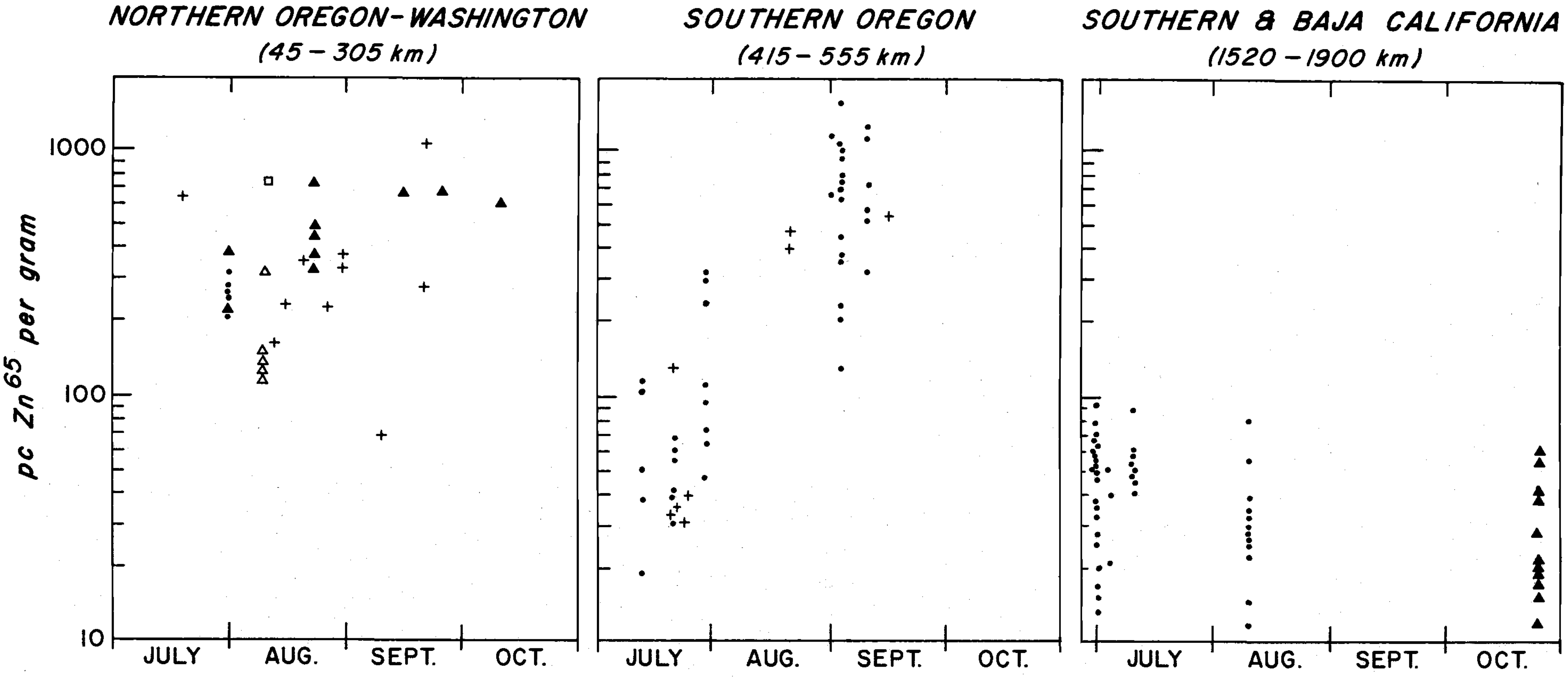

Figure 1. Zinc-65 per gram of ash of albacore livers for three regions of the northeastern Pacific. Measurements in parentheses beneath areas are distances from the mouth of the Columbia River. 1962 = □ ; 1963 = +; 1964 = ● ; 1965 = ▲; 1965 off Washington = △ .

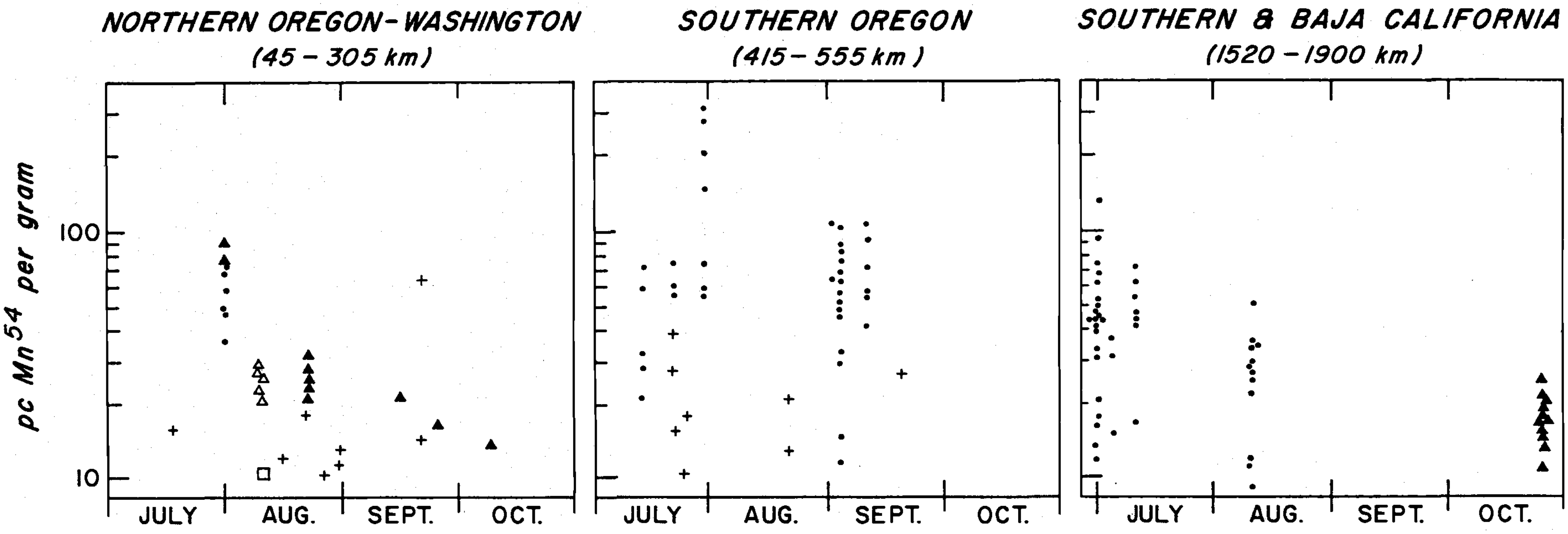

Figure 2. Manganese -54 per gram of ash of albacore livers from three regions from the northeastern Pacific. Measurements in parentheses beneath areas are distances from the mouth of the Columbia River. 1962 = □, 1963 = +, 1964 = •, 1965 = ▲, 1965 off Washington = △.

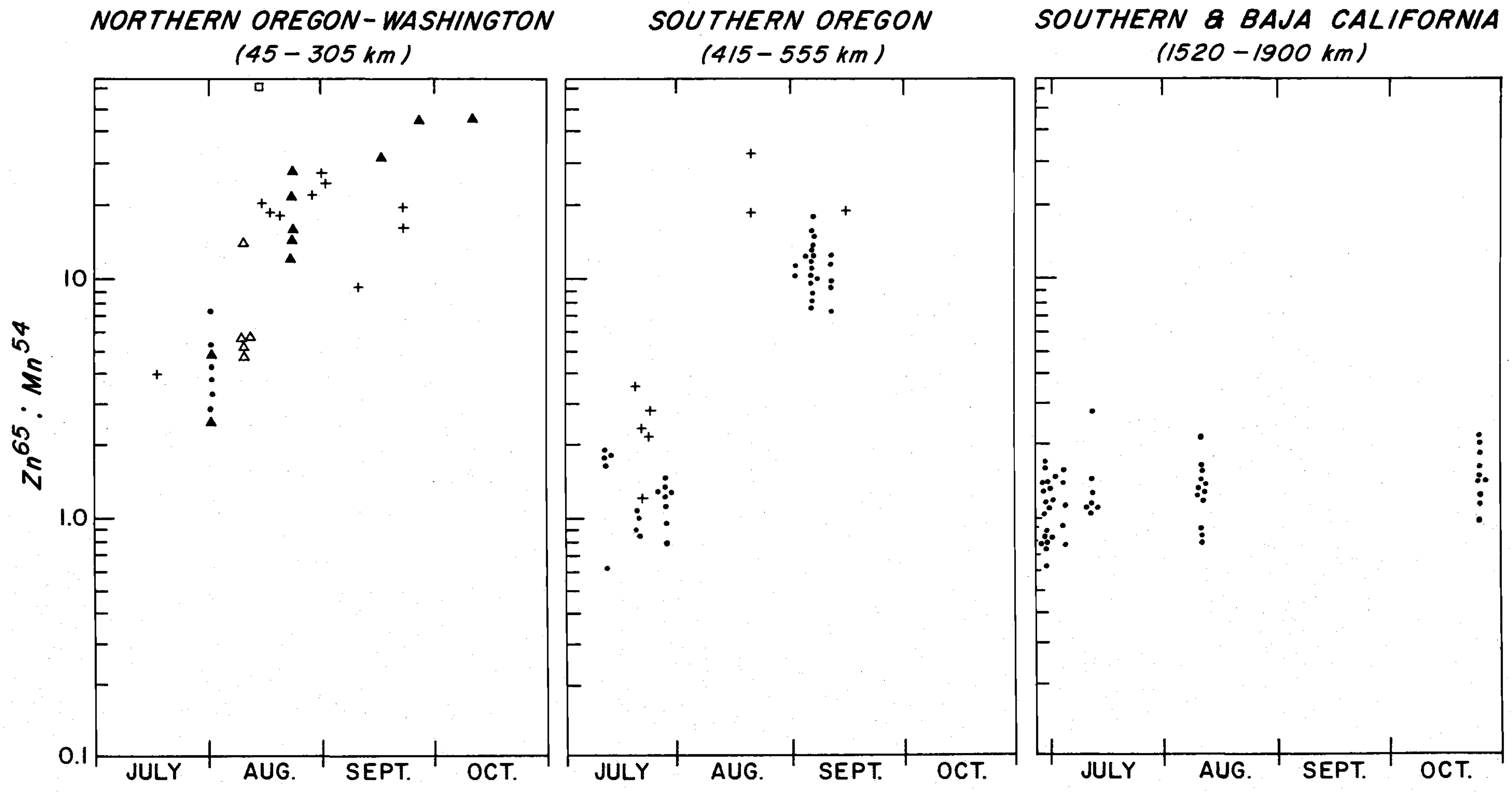

Figure 3. The $^{65}$Zn:$^{54}$Mn ratio of albacore livers from three regions of the northeastern Pacific. Measurements in parentheses beneath areas are distances from the mouth of the Columbia River. 1962 = □, 1963 = +, 1964 = ●, 1965 = ▲, 1965 off Washington = △.

such a trend. Albacore which migrate northward during early summer were not collected this far north in July, hence the absence of early and probably low July values. The first albacore collected off northern Oregon have probably accumulated significant amounts of $^{65}Zn$ above their offshore values. If this is the case, it indicates migration of fish through plume waters, probably off southern Oregon, before their arrival off northern Oregon.

The highest $^{65}Zn$ values found from albacore livers were not from the area nearest the Columbia River, presumably the main source of $^{65}Zn$, but off southern Oregon in 1964. This may be explained by the time lag for incorporation and accumulation of $^{65}Zn$ through several trophic levels of the food chain. A similar explanation was given by Kujala (M.S. thesis, 1966, see appendix volume), who found more $^{65}Zn$ in salmon taken at Eureka, California, than the same species collected at Astoria, near the mouth of the Columbia River. Osterberg, Pattullo, and Pearcy (Limnology and Oceanography 9(2): 249-257, 1964) noted a somewhat smaller time lag in euphausiids. Those off Newport were higher than those off Astoria.

## MANGANESE-54

Regional variations in $^{54}Mn$ in albacore liver ash were not nearly as pronounced as those found for $^{65}Zn$ (Fig. 2). In general, the levels in all areas from Washington to southern California were about the same. Annual variations were not obvious. Values for 1963, however, appeared to be lower than either those for 1964 or 1965 off Oregon.

Off northern Oregon a decrease in $^{54}Mn$ content during the summer of 1965 was evident, but was not evident for 1963 and 1964; yet the highest $^{54}Mn$ values were found early in the summer in all three areas.

## $^{65}Zn$:$^{54}Mn$ RATIO

Off both northern and southern Oregon the $^{65}Zn$:$^{54}Mn$ ratios increased drastically during the summer. This was primarily due to the increase in $^{65}Zn$, at least off southern Oregon. But the decrease in $^{54}Mn$ must also be a contributing factor off northern Oregon because this trend is not evident from either the $^{65}Zn$ or $^{54}Mn$ values alone (Fig. 1 and 2). Off southern California the $^{65}Zn$:$^{54}Mn$ ratios are similar to those found off northern Oregon early in the season. No seasonal variations in the ratios were apparent off California.

# FOOD AND FEEDING APPARATUS OF TWO PELAGIC SHRIMPS*

by William C. Renfro and William G. Pearcy

## ABSTRACT

The stomach contents and digestive apparatus of Pasiphaea pacifica and Sergestes similis were studied. Both are carnivores. Large pieces of euphausiids and whole copepods were found in the stomachs of S. similis. Small pieces of crustaceans, mainly euphausiids, and chaetognath spines were found in the stomachs of P. pacifica. These differences in the size of ingested food particles are closely related to the structure of the mouth parts and the stomach musculature.

## INTRODUCTION

This report describes the feeding apparatus and stomach contents of two shrimp species found off the Oregon coast. The shrimps, a carid, Pasiphaea pacifica Rathbun, and a penaeid, Sergestes similis Hansen, are abundant in epipelagic waters at night (Pearcy and Forss, in press) and are thought to be important intermediate organisms in the oceanic food web. Despite this, little is known about the food habits or trophic ecology of these species in the marine ecosystem.

## METHODS AND MATERIALS

The specimens examined were captured with a 2-meter (6-foot.) Isaacs-Kidd midwater trawl in depths from 200 meters to the surface, 28 to 83 kilometers from shore (Pearcy, 1964). All samples were collected at night. Trawl towing times averaged less than one hour each. Preserved specimens from several seasons were selected to avoid bias caused by seasonal changes in food habits. After measurement of carapace length (distance from orbital notch to the median posterior edge of the cephalothorax), an incision was made in the carapace of each shrimp, and its pharynx, stomach, and the anterior portion of its intestine were extracted with small forceps. Next, the digestive tract was opened and its contents examined under a dissecting microscope. Finally, the mouth parts were drawn to scale with the aid of an ocular micrometer.

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* This paper was submitted to the Journal of the Fisheries Research Board of Canada in March 1966.

## RESULTS

### Pasiphaea pacifica

Most specimens (about 80%) had empty stomachs. The stomach contents of 25 P. pacifica which contained food are listed in Table 1. Crustaceans chopped into many pieces comprised the bulk of the diet. The size and general appearance, particularly the eye shape, of the crustaceans found in the stomachs indicated that most were Euphausia pacifica, a species which is abundant off Oregon. Although only one copepod was definitely recognized, some of the items listed as crustacean fragments may have been copepod remains.

The frequent occurrence of arrow-worm (Chaetognatha) grasping spines in full as well as otherwise empty stomachs (Table 1) poses a

Table 1. Stomach contents of Pasiphaea pacifica.

| Date of Capture | Carapace Length mm | Contents | Number of Arrow-worm Spines |
|---|---|---|---|
| Dec. '62 | 21 | One copepod | 60 |
| Feb. '63 | 22 | One small crustacean | 0 |
| Feb. '63 | 20 | Fragments of small crustacean | 7 |
| Feb. '63 | 20 | Fragments of small crustacean | 0 |
| Apr. '63 | 18 | One small crustacean | 0 |
| Apr. '63 | 20 | Fragments of small crustacean | 0 |
| May '63 | 12 | Appendages of small crustacean | 0 |
| May '63 | 20 | One small crustacean | 0 |
| May '63 | 25 | One small crustacean | 6 |
| May '63 | 22 | One small crustacean | 2 |
| May '63 | 24 | One small crustacean | 1 |
| May '63 | 15 | Fragments of small crustacean | 0 |
| May '63 | 11 | One euphausiid | 0 |
| May '63 | 22 | One euphausiid | 5 |
| May '63 | 13 | One euphausiid | 0 |
| May '63 | 20 | One euphausiid | 47 |
| Jul. '63 | 21 | One small crustacean | 0 |
| Jul. '63 | 22 | One euphausiid | 0 |
| Jul. '63 | 19 | One euphausiid | 0 |
| Jul. '63 | 18 | One euphausiid | 0 |
| Jul. '63 | 15 | One or two small crustaceans | 0 |
| Feb. '64 | 18 | One euphausiid | 4 |
| Feb. '64 | 15 | One euphausiid | 26 |
| Feb. '64 | 17 | One euphausiid | 18 |
| Feb. '64 | 11 | Fragments of small crustacean | 0 |

problem in interpretation. On one hand, the presence of these 1 to 2 mm long spines may indicate only that arrow-worms are occasionally eaten, with a few indigestible spines remaining for days or even weeks as evidence of the meal. On the other hand, some shrimp stomachs yielded 26 to 60 spines, proving that three or more arrow-worms (each with a maximum of about 12 spines) had been consumed.

The mouth parts of P. pacifica (Figure 1A) appear to be better adapted for manipulating relatively large prey than for capturing minute organisms. The maxillae and maxillipeds are comparatively short, stout, and lack setae necessary to form an effective filter. There are no mandibular palps, and absence of grinding surfaces on the median faces of the mandibles indicates that this species probably could not crush pteropod shells or other shelled organisms. Each mandible possesses a long cutting edge with sharp teeth, accounting for the well chopped condition of food items in the stomach.

The stomach is a long, thin-walled sac with few exterior muscle attachments. At its posterior end a small gastric mill with toothed medial surfaces probably grinds food passing into the intestine. When empty, the stomach is so transparent that it is possible to see through the carapace and stomach walls to the floor of the body cavity.

### Sergestes similis

Again, approximately 80% of the stomachs examined were empty. Small crustaceans, calanoid copepods, and euphausiids form the diet of S. similis (Table 2). Food items in this penaeid had been swallowed in larger pieces than P. pacifica. Copepods were swallowed whole. Apparently small oil globules from the copepod bodies were released and remained in the stomach after the flesh and exoskeleton had been digested and passed into the intestine. No evidence of arrow-worms was found.

Mouth parts of S. similis are longer and more setose than those of P. pacifica (Figure 1B). The mandibles have sharp, toothless, cutting edges, small molar processes, and long palps. In addition to these feeding appendages, the last two pairs of thoracic legs possess long setae which in turn bear closely spaced setules (tiny hair-like bristles) forming a fine-meshed structure possibly used to capture or hold prey. With these feeding devices S. similis can utilize food in a wide range of sizes. Indeed, laboratory experiments show that it can capture and consume living Euphausia pacifica half its own length as well as Artemia salina nauplii less than 1 mm long.

A short esophagus leads from the mouth to a small, heavily sclerotized stomach. The stomach is very muscular and is attached to the surrounding body walls by numerous muscle bands. It is equipped posteriorly with an efficient gastric mill insuring that large food items swallowed are properly reduced.

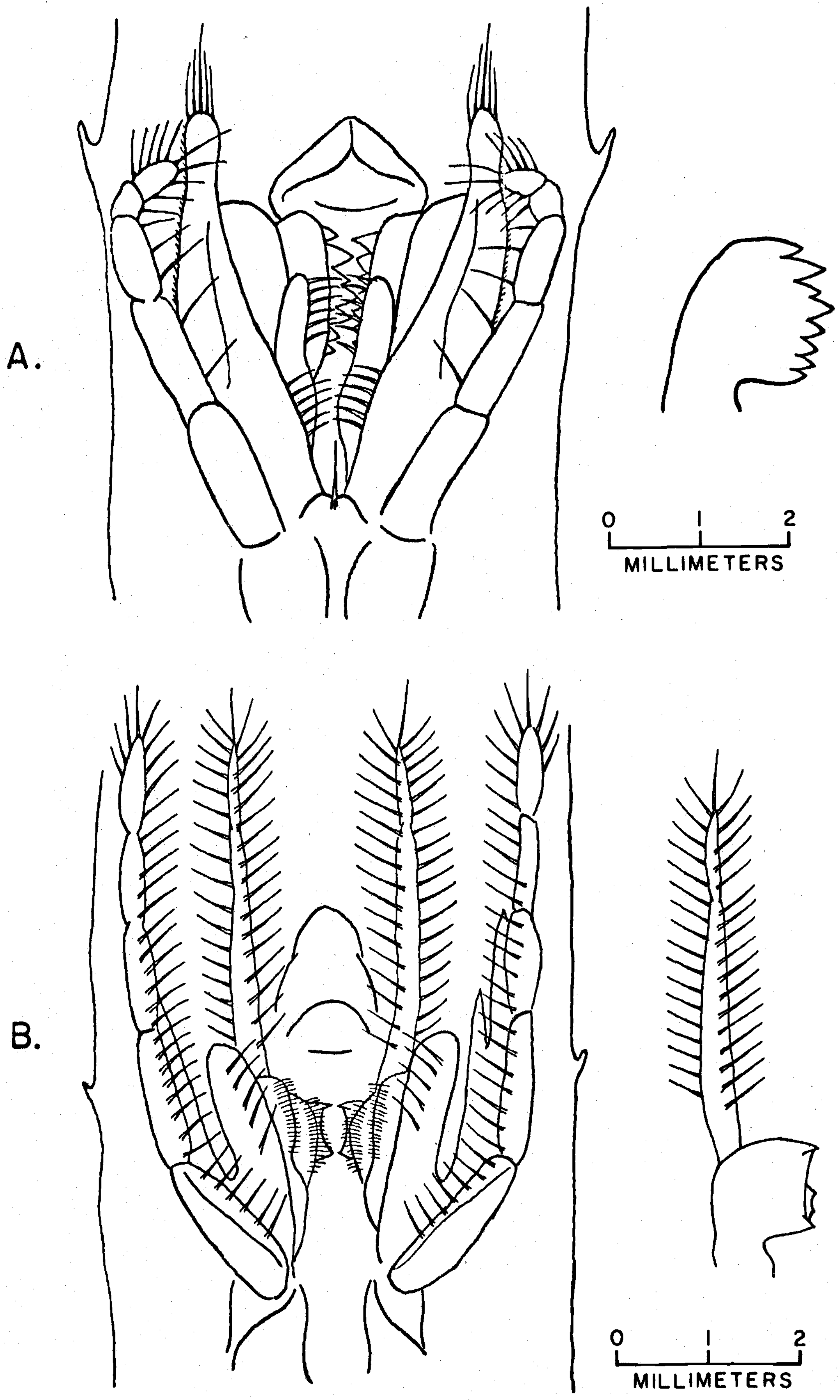

Figure 1. Mouth parts and right mandibles of A) Sergestes similis (carapace length 18 mm) and B) Pasiphaea pacifica (carapace length 11 mm). Ventral views.

## DISCUSSION

Both the shrimps are carnivores. Despite a careful search, no diatom frustules or other traces of plant material were found in their stomachs. The contribution of arrow-worms to the diet of P. pacifica may be relatively small, although this point is not resolved. These observations agree closely with those of Osterberg, Pearcy, and Curl (1964), who placed both these shrimps in trophic level III. Tchindonova (1959) examined a few stomachs of S. similis collected in the northwestern Pacific and found primarily copepods.

It is instructive to contrast the function and anatomy of the mouth parts and stomachs of these shrimps. The thin-walled, non-muscular stomach and small gastric mill of P. pacifica are poorly adapted for reducing large pieces of food, but its mandibles bear sharp teeth which incise the prey into manageable pieces before ingestion. Sergestes similis, on the other hand, has a strongly sclerotized, well-muscled stomach and a gastric mill capable of breaking down larger food items, but its mandibles are correspondingly smaller and presumably less efficient than those of P. pacifica. Tchindonova (1959) also noted this correlation between feeding appendages and size of food items in the stomachs of various Decapods. She stated that Sergestes similis, S. japonicus, and Hymenodora glacialis eat small prey whole, while small specimens of H. glacialis, H. frontalis, and Gennadas borealis grind their food.

In summary, both P. pacifica and S. similis feed primarily on euphausiids, but mechanically degrade them in different ways. Pasiphaea pacifica apparently supplements its diet with carnivorous arrow-worms and S. similis with copepods. Euphausia pacifica has been shown to consume animals as well as plants (Ponomareva, 1954). Consequently, both shrimps might best be placed partly in trophic level III (carnivores which prey on herbivores) and partly in trophic level IV (carnivores which eat trophic level III carnivores).

## ACKNOWLEDGMENTS

We thank Dr. James E. McCauley for suggestions and review of the manuscript. The material examined came from research collections for National Science Foundation Grant GB-1588.

Table 2. Stomach contents of <u>Sergestes similis</u>.

| Date of Capture | Carapace Length mm | Contents |
|---|---|---|
| Dec. '63 | 9 | One small crustacean |
| Dec. '63 | 10 | Fragments of small crustacean |
| Dec. '63 | 13 | One euphausiid |
| Dec. '63 | 8 | Fragments of small crustacean |
| Apr. '64 | 12 | Fragments of small crustacean(s) |
| Apr. '64 | 11 | Fragments of small crustacean(s) |
| Apr. '64 | 11 | One euphausiid |
| Apr. '64 | 10 | Fragments of small crustacean(s) |
| Jul. '64 | 13 | 6 calanoid copepods |
| Jul. '64 | 7 | 2 calanoid copepods plus fragments of one small crustacean |
| Jul. '64 | 8 | 3 calanoid copepods plus one 0.25 mm diameter egg |
| Jul. '64 | 9 | Several oil globules (copepods) |
| Jul. '64 | 12 | Several oil globules (copepods) |
| Jul. '64 | 8 | Several oil globules (copepods) |
| Jul. '64 | 8 | Several oil globules (copepods) |
| Oct. '64 | 12 | Two euphausiids |
| Oct. '64 | 10 | One euphausiid |
| Oct. '64 | 10 | Unidentifiable animal fragments |
| Oct. '64 | 9 | Fragments of crustacean(s) |
| Oct. '64 | 8 | One euphausiid |
| Jan. '65 | 11 | One euphausiid |
| Jan. '65 | 11 | Two euphausiids |
| Jan. '65 | 15 | Two euphausiids |
| Jan. '65 | 15 | Three calanoid copepods |
| Jan. '65 | 11 | One calanoid copepod |

# REFERENCES

Osterberg, C., W. G. Pearcy, and H. Curl, Jr. 1964. Radioactivity and its relationship to oceanic food chains. J. Mar. Res. 22: 2-12

Pearcy, W. G. 1964. Some distributional features of mesopelagic fishes off Oregon. J. Mar. Res. 22: 83-102.

Pearcy, W. G., and C. A. Forss. In press. Depth distribution of oceanic shrimps off Oregon. J. Fish. Res. Bd. Canada.

Ponomareva, L. A. 1954. Euphausiids of the Sea of Japan feeding on Copepods. Rep. Acad. Sci. U.S.S.R. (Doklady), Zool. 98: 153-154. (Translated by V. O. Pahn).

Tchindonova, J. G. 1959. Feeding of some groups of macroplankton in the northwestern Pacific. Trudy Instit. Okeanol., Acad. Sci. U.S.S.R. 30: 166-189.

# POPULATIONS OF CHAETOGNATHS OFF THE OREGON COAST, THEIR AGE, STRUCTURE, AND VERTICAL AND SEASONAL DISTRIBUTIONS

by R. Ward Renshaw

## INTRODUCTION

The investigations by Brinton (1962), Trebble (1962), Fager and McGowan (1963), and Alvarino (1961, 1962, and 1964) have contributed much to the knowledge of various groups of plankton and their occurrence in the Northeast Pacific Ocean. However, opening-closing nets to sample discrete depths have seldom been used. Moreover, few samples have been taken off the Oregon coast. The present investigation was undertaken to sample the plankton off the Oregon coast at discrete depths using opening-closing nets and to obtain estimates of seasonal variation in abundance of the major planktonic groups or species. The following is the preliminary report on seasonal variation of the chaetognaths off the Oregon coast.

## METHODS

From February 1963 to December 1964 plankton samples were collected at one station approximately 92 km off the Oregon coast (44° 39' N 125° 14' W). The method of collection is referred to as opening-closing multiple meter nets. On a single plankton tow three to five nets were placed on the cable at the same time. Each net sampled a different depth. The depths are as follows:

0- 150 m
150- 250
250- 500
500- 600
600-1000

Yentsch et al. (1962) described the piston cutters which were used for opening and closing the nets. Although he did not field test the method it proved to be reliable (better than 80%) after some alterations, one of which was described by Renshaw and Pearcy (1964).

In the laboratory the collected samples were split in half. One half of the sample was then completely sorted into major taxonomic groups. The chaetognaths from the sorted samples provided data for this study on vertical distribution, seasonal distribution, and size frequency distribution.

# RESULTS

The chaetognaths off the Oregon coast are an abundant planktonic group. They are represented in the samples by two genera and 12 species. The number of species present at any one time depends upon the depth sampled and the season of the year. The 12 species are as follows:

*Sagitta bierii*
*S. elegans*
*S. euneritica*
*S. decipiens*
*S. maxima*
*S. minima*
*S. macrocephala*
*S. scrippsae*
*S. zetesios*
*Eukrohnia hamata*
*E. bathypelagica*
*E. fowleri*

The six most abundant species, *Sagitta bierii*, *S. euneritica*, *S. decipiens*, *S. minima*, *S. scrippsae*, and *Eukrohnia hamata*, are found in the upper 150 m.

## VERTICAL DISTRIBUTION

In general, the number of species and abundance of chaetognaths decrease with depth. Fig. 1 gives the vertical distribution of the 12 species off the Oregon coast. Some exceptions to previously recorded vertical distributions are apparent. *Sagitta scrippsae* was found as deep as 600 m, although it was rare between 500 and 600 m. *Eukrohnia bathypelagica* was found as shallow as 500 m, although Alvarino (1964) gives its distribution below 1000 m. *Sagitta decipiens* is generally found below 150 m, but in Oregon waters it was also constantly found above 150 m, although maximum abundance below 150 m. The other species conform to their previously reported depth distributions.

## VERTICAL MIGRATION

The evidence for diurnal vertical migrations is largely based on the variations in the number of individuals caught at different times

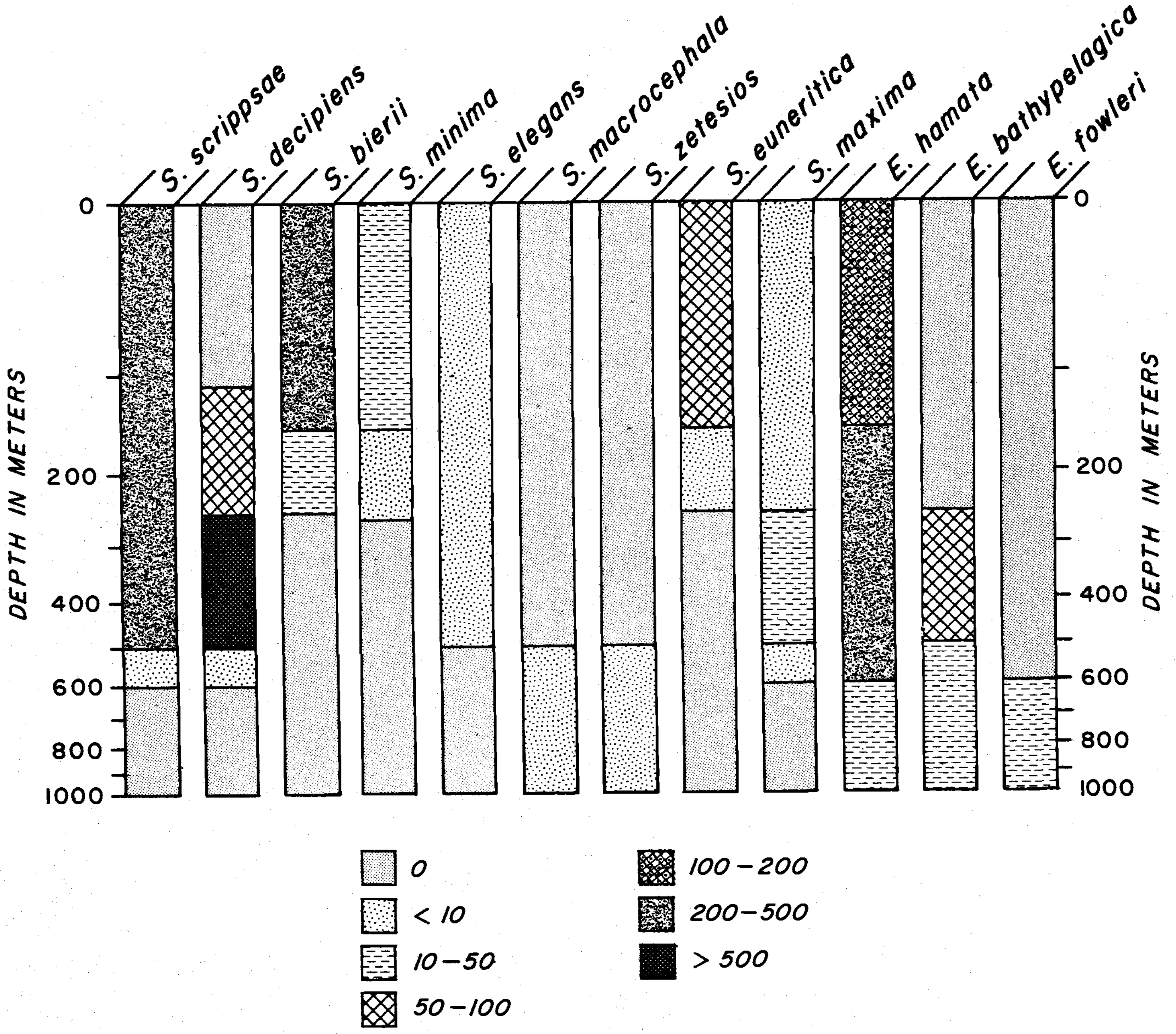

Figure 1. The vertical distribution of chaetognaths off the Oregon coast.

and depths. Several factors are believed to contribute to vertical migrations. Among them, light intensity is usually considered important. However, Clarke, Pierce, and Bumpus (1943) considered the variations in depth and numbers as seasonal variations, related to size and maturity. David (1955) found a similar situation in the southern ocean. Data from the present study tend to support these views.

Of the numerically abundant species that inhabit the upper 500 m, there was no evidence of diurnal vertical migrations based on differences between day and night catches at various strata. But a definite seasonal change in the size distribution for *S. scrippsae*, *S. macrocephala*, *S. zetesios*, and *Eukrohnia hamata* with depth was apparent. Pre-adults or small individuals occurred nearer the surface than the larger, more mature individuals; consequently, during the breeding periods of the species, the upper water layers contained more individuals than the deeper layers.

Catches of more large individuals of *S. scrippsae* in night than day in 0-150 m tows indicated either net avoidance or vertical migration (Fig. 2). Since there was no evidence for an influx from deeper depths and there is a vertical size stratification this is thought to be caused by better avoidance of the net during daylight periods.

## SEASONAL DISTRIBUTION

Seasonal distribution is given for only the four most abundant species. Table 1 summarizes the minimum and maximum periods of abundance.

Table 1. The four most abundant species and their periods of maximum and minimum distributions in the upper 500 m. Periods of maximum abundance are indicated by XX and minimum abundance by ---.

| | J | F | M | A | M | J | J | A | S | O | N | D |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Eukrohnia hamata* | --- | --- | XX | XX | XX | XX | --- | --- | --- | --- | --- | --- |
| *Sagitta scrippsae* | --- | XX | XX | XX | --- | --- | --- | XX | XX | XX | XX | --- |
| *Sagitta bierii* | XX | XX | XX | --- | --- | --- | --- | --- | --- | --- | XX | XX |
| *Sagitta decipiens* | --- | --- | --- | XX | XX | XX | XX | XX | XX | XX | --- | --- |

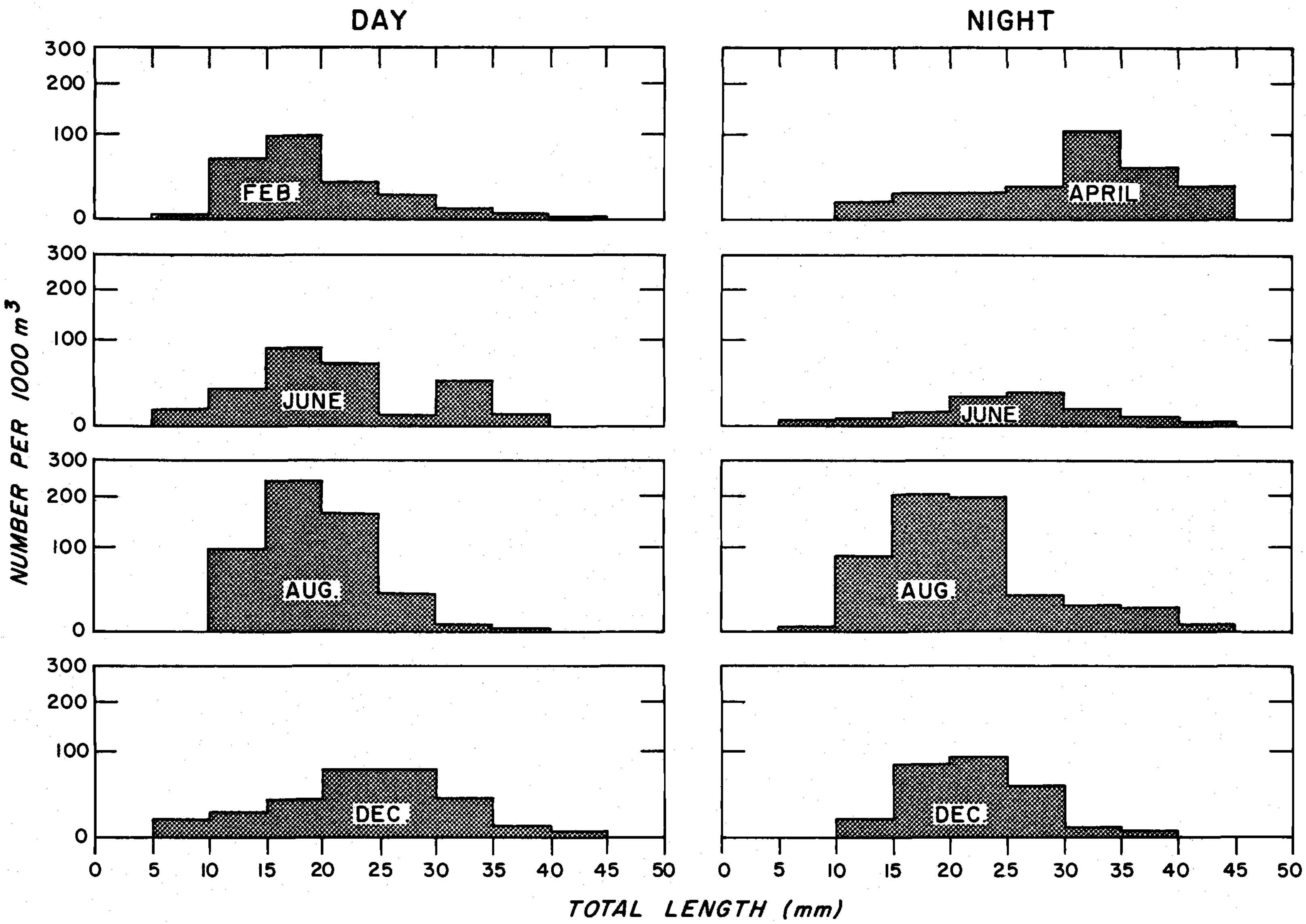

Figure 2. Size frequency distributions of *Sagitta scrippsae* in the upper 150 m for day and night tows.

*Sagitta bierii* is an epipelagic species taken in the upper 250 m. During the two years of sampling it was abundant only during the winter months (December and February) when its numbers increased to more than 0.5/m$^3$. This increase is due to mature individuals, indicating a breeding population during the winter months. A sharp decrease in numbers occurred in spring and summer months.

*Sagitta decipiens*, the third most abundant species in the samples, was most abundant below 150 m during the summer and fall months, when its numbers reached more than 1.0/m$^3$. This summer population was comprised of both mature and immature individuals, while the winter population was composed almost entirely of non-breeding individuals. Apparently *Sagitta decipiens* breeds only in the spring and summer.

*Eukrohnia hamata* is most abundant in the spring to summer (April-July) and less abundant during the winter months. Preliminary results indicate that E. *hamata* breeds throughout the year. The increase in numbers in the spring is due to small immature individuals in the upper 150 m. The larger, more mature ones are in deeper water.

*Sagitta scrippsae* is the species that has the highest average throughout the year, although *S. decipiens* and *Eukrohnia hamata* have peaks of greater numbers. *Sagitta scrippsae* has two periods of maximum abundance. The first and largest (greater than 1.0/m$^3$) occurred in the later winter (February-April). From May through July its numbers decrease before reaching a second peak of abundance in August. Table 2 shows that the first peak of abundance is mainly due to the larger, more mature individuals, and the second peak is due to

Table 2. Seasonal distribution of *Sagitta scrippsae* to show composition as to life stages. Numbers indicate percent of the total number of this species captured in the upper 150 m. Intermediate individuals show evidence of gonadal development but are not yet mature.

| | J | F | M | A | M | J | J | A | S | O | N | D |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mature | -- | 10 | 40 | 50 | -- | 20 | 15 | 5 | -- | -- | -- | 5 |
| Immature | -- | 50 | 40 | 20 | -- | 70 | 75 | 85 | -- | -- | -- | 60 |
| Intermediate | -- | 40 | 40 | 30 | -- | 10 | 10 | 10 | -- | -- | -- | 35 |

immature ones. Thus, a seasonal cycle is inferred. In early spring the population of *S. scrippsae* is spread throughout the upper 500 m (Table 1). Both large and small individuals are in the upper 150 m. As spring progresses to summer, the population becomes stratified, with the small ones in the upper 150 m and the larger individuals in deeper water. The second peak of abundance in August does not have as many numbers per m$^3$ as the first peak and is composed almost entirely of small animals. However, Table 2 gives the data for the upper 150 m only. Below 150 m the larger, mature individuals are present. As fall and winter approach there is a decrease in numbers of the large individuals below 150 m. The decrease in number in the upper 150 m is attributed to the population spreading vertically in the water and to the mortality of the young. It is presumed that the larger individuals in the deeper water breed and die and the small immature individuals in the upper 150 m spread vertically and obtain a mixed population throughout the winter. Then in spring the population is not as stratified as in summer when breeding occurs.

By comparing the four species in Table 1, it can be noted that the periods of maximum abundance do not directly coincide with each other. This indicates each species has a different breeding period. *Sagitta decipiens* and *S. bierii* have similar vertical distributions and may reduce species competition for food by breeding at different times of the year. The breeding periods of *S. scrippsae* and *Eukrohnia hamata* are not distinctly different but competition for food may be reduced by the greater vertical distributions, and also by the fact that small individuals of *S. scrippsae* appear in larger numbers later in the summer relative to *Eukrohnia hamata*.

# REFERENCES

Alvarino, A., 1961. Two new chaetognaths from the Pacific. Pacific Science, 15 (1): 67-77.

Alvarino, A., 1962. Two new Pacific chaetognaths, their distribution and relationships to allied species. Bull. Scripps Inst. Oceanogr., 8 (1): 1-50.

Alvarino, A., 1964. Bathymetric distribution of chaetognaths. Pacific Science, 18 (1): 64-82.

Brinton, E., 1962. The distribution of Pacific euphausiids. Bull. Scripps Inst. Oceanogr., 8 (2): 51-270.

Clarke, G. L., E. L. Pierce, and D. Bumpus, 1943. The distribution and reproduction of Sagitta elegans on Georges Bank in relation to the hydrographical conditions. Biol. Bull., 85 (3): 201-226.

Fager, E. W., and J. McGowan, 1963. Zooplankton species groups in the North Pacific. Science, 140 (3566): 453-460.

Renshaw, W., and W. Pearcy, 1964. A new swivel cable clamp for towing large plankton nets at different depths. Deep-Sea Res., 11: 933-934.

Trebble, N., 1962. Distribution of pelagic polychaetes in the North Pacific Ocean. British Museum (Nat. Hist.) Bull. Zool., 7 (9): 25-492.

Yentsch, C., G. Grice, and A. Hart, 1962. Some opening-closing devices for plankton nets operated by pressure, electrical and mechanical action. Rapp. Proc. Verbaux Reunions. 153: 59-65.

# DEPTH DISTRIBUTION OF OCEANIC SHRIMPS (DECAPODA-NATANTIA) OFF OREGON*

by

William G. Pearcy and Carl A. Forss

## ABSTRACT

Sixteen species of oceanic shrimps, seven Penaeidea and nine Caridea, were collected in 244 collections within the upper 1500 m at one station in the northeast Pacific off Oregon. Most of the species were primarily mesopelagic in distribution.

The dominant species, Sergestes similis, was the only shrimp common in epipelagic waters at night and the only species clearly demonstrating diel vertical migrations. Night catches exceeded day catches in near-surface waters, while day catches exceeded night catches at mid-depths. S. similis migrated into the upper 50 m at night and on one occasion was collected at the surface.

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* This paper has been accepted for publication in the Proceedings of the Fisheries Research Board of Canada.

A preliminary draft was included in AEC Progress Report AT(45-1)1750 for 1965, pp. 147-157. It has been revised and the reference section expanded.

## STUDENT PARTICIPATION

Part of the success of our research program has been a result of participation by graduate students. Many of these students have written portions of this progress report and contributed to the research on other parts. Four have earned master's degrees during this report period. Some information on each student is presented below.

Ph. D. Candidates:

| | |
|---|---|
| John T. Cronin | AEC - Battelle Northwest, Richland Graduate Fellow |

John received and M. S. in biochemistry at Texas A & M and has been at Oregon State about two years. He has been working with Dr. Burger and Mr. Martin at Hanford to develop a pulse column for use at sea to extract organics from sea water. He has completed his course work and languages and plans to take his preliminary examinations soon.

| | |
|---|---|
| Ford A. Cross | AEC - Battelle Northwest, Richland Graduate Fellow and later USPHS Trainee |

"Bud" came to us with a B. S. from Mount Union College and earned his M. S. at Oregon State. He spent six months at Hanford working with Dr. Dean on the retention of $^{65}$Zn by a marine amphipod. He has completed all requirements for the Ph. D. except writing his dissertation.

| | |
|---|---|
| Lawrence C. Frederick | USPHS Trainee |

Larry has both B. S. and M. S. degrees in physics from the University of New Hampshire. He is working with the large volume radiochemistry project and is responsible for many of the successful modifications. His research is involved with the correlation of $^{51}$Cr and salinity in the Columbia River Plume. He has completed his course work, languages, and preliminary examinations.

| | |
|---|---|
| Lois Haertel | USPHS Predoctoral Fellow |

Mrs. Haertel came to us with both B. S. and M. S. from the University of Illinois. She was in charge of the Columbia River ecology program for more than a year then resigned to become a full-time graduate student last September. She is currently involved in course work and language study.

Robert L. Holton USPHS Predoctoral Fellow

Bob came to us with a B. A. from the University of Montana and M.S. degrees from both Oregon State and the University of Minnesota. He has been a secondary school teacher for 13 years and has done work at the Oregon Regional Primate Research Laboratory. He has completed his course work requirements.

David Jennings USPHS Trainee

Dave completed his B. A. from Northwest Nazarene College in Idaho in 1961 and his M. S. at Oregon State in March 1966. His thesis is abstracted in the following section. He circumnavigated the globe as an instructor on The University of the Seven Seas, Chapman College, and returned in June to start work on his Ph. D.

R. Ward Renshaw AEC Assistantship

Ward came to us with a M.S. from the University of the Pacific. He has been working on the vertical distribution of zooplankton and has completed his thesis research. He has discontinued his studies to accept a teaching appointment at Long Beach State College.

William C. Renfro PHS Pre-Doctoral Fellow

Bill came to us with B. A. and M. A. degrees from the University of Texas and more than five years experience as a Fishery Research Biologist with the U.S. Bureau of Commercial Fisheries. He is working on the transfer of radionuclides in the food web in a small area of the Columbia River estuary. His course work and languages are completed and he expects to take preliminary examinations soon.

## M. S. Candidates

Lynn K. Buffo USPHS Trainee

Miss Buffo came to us last fall with a B. A. from Carleton College. She is working on a solvent extraction process for stable zinc. She expects to complete her master's degree by January 1967.

Peter J. Hanson USPHS Trainee

Pete came to us with B. S. degrees in both chemistry and geology from Fresno State College. He has been working on the vertical distribution of radionuclides in the Columbia River estuary. Requirements for his master's degree are almost completed and he has already started to fulfill requirements for his Ph. D.

The following students have been supported by funds other than AEC and are included herein because their research complements AEC sponsored ecological research.

Henry A. Donaldson (ONR)

Henry is working on seasonal and bathymetric distribution in the sonic scatering layer. He is a master's student of Dr. Pearcy.

Frank J. Hebard (NSF)

Frank completed his Ph. D. under Dr. Pearcy in June 1966 on the distribution of euphausiids and copepods to various oceanographic conditions. He is now employed at the Auke Bay Laboratory of the U. S. Fish and Wildlife Service.

Gary Hufford (NSF)

Gary is a master's student of Dr. Carey. He is working on the reproductive ecology of echinoderms of the outer shelf and abyssal plain.

R. Michael Laurs (NSF)

Mike is working on the ecological effects of upwelling in the ocean. He has completed his doctoral preliminary examinations under Dr. Pearcy and will complete his degree requirements in the next few months. He will join the U. S. Fish and Wildlife Service and will lead the biological investigations for the Bureau of Commercial Fisheries on the EASTROPAC expedition.

Ronald C. Tipper (USN)

Ron, a Lt. j. g. in the regular Navy, has been assigned to duty with this department to study deep-sea fouling. He is working on a Ph. D. with Dr. McCauley.

Harriet VanArsdale (NSF)

Miss VanArsdale is studying for a M. S. with Dr. Pearcy on the distribution of pelagic hyperiid amphipods. She should complete degree requirements by September 1966.

## THESES

Four students have earned advanced degrees during the period of this Progress Report. An abstract of each thesis is included below and a copy of each complete thesis is being submitted separately.

## RETENTION OF ZINC-65 BY COLUMBIA RIVER SEDIMENT

by Vernon Gene Johnson*

### Abstract of Thesis

The relative importance of ion-exchange and specific sorption as mechanisms of retention of zinc-65 by Columbia River sediment have been investigated using an elution technique.

The exchangeable $^{65}Zn$ fraction and the effect of seawater _per se_ on sediment sorbed gamma emitters were determined simultaneously by elution with synthetic seawater in the field immediately upon collection of the samples using a portable lab designed especially for this study.

Specifically sorbed radiozinc was determined by elution with a dilute solution of copper sulfate. Sediment samples in this phase of the study were frozen upon collection and the elution carried out in the lab on defrosted portions of the frozen sample.

Less than 5% of the sediment sorbed zinc-65 was found to be exchangeable while from 35 to 54% was displaceable with $CuSO_4$. The large amount of copper displaceable radiozinc was shown _not_ to be simply an ion-exchange displacement nor a pH effect, but rather, replacement of $^{65}Zn$ by Cu II appears to be due to the greater affinity of the latter for the specific sorption sites.

It was concluded that ion-exchange is unimportant in retention of $^{65}Zn$ by Columbia River sediment and that a considerable portion of the sediment sorbed radiozinc is bound by a more specific ion-particle interaction than ion-exchange. It was furthermore concluded that seawater should have a negligible effect on sediment sorbed gamma emitters in the Columbia.

Implications of the results are discussed with respect to radioactive waste disposal.

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* Mr. Johnson completed his requirements for the M.S. Degree in December 1965, and is now employed in radiological physics by Phillips Petroleum Company, Idaho Falls, Idaho. Dr. Osterberg was the major professor. He received full support from the Atomic Energy Commission.

## AN INVESTIGATION OF THE DISTRIBUTION OF <u>NEPHTYS</u> <u>CAECOIDES</u> IN YAQUINA BAY

by George Edwin Morrison*

### Abstract of Thesis

A study was undertaken in Yaquina Bay, Oregon during the summer of 1964 to determine the distribution and the factors affecting the distribution of the polychaete worm, *Nephtys caecoides*, Hartman, 1938, in the estuary.

This organism has a continuous distribution from offshore to a point approximately eight kilometers into the bay.

Environmental factors considered were salinity, temperature, and sediment composition.

The results of this study do not single out a factor as the one limiting the distribution of *N. caecoides* in Yaquina Bay. During summer months, it is possible that sediment porosity, organic content and temperature operate together to form an unfavorable environment.

## RADIOACTIVITY OF SEDIMENTS IN THE COLUMBIA RIVER ESTUARY

by Charles David Jennings**

Sediment radioactivity was measured in the Columbia River by use of an *in situ* gamma-ray detector, calibrated to give activity in pc/cm$^2$. The probe has several advantages over methods which couple collection of sediments with which field measurements can be made.

Sediments concentrate radioactivity and in the Columbia River the level of radiation is about an order of magnitude higher in the sediments than in the water above it. Benthic organisms which live in the sediments are constantly exposed to this higher radiation level.

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* Mr. Morrison completed his requirements for the M. S. Degree in December 1965 and is now employed as a biologist with the USPHS at the Taft Sanitary Engineering Center, Cincinnati, Ohio. Dr. Carey was the major Professor. He received partial support from the Atomic Energy Commission.

** Mr. Jennings completed his requirements for the M. S. Degree in March 1966. He was employed as an instructor on the University of the Seven Seas, Chapman College, Orange, California from March through June and circumnavigated the globe. He returned to this department the end of June to start work on a Ph. D. program. Dr. Osterberg was his major Professor. He received partial support from the Atomic Energy Commission.

Chromium-51 and $^{65}$Zn were the two man-made radionuclides present in greatest abundance in the Columbia River. The $^{51}$Cr/$^{65}$Zn ratio in the sediments varied, but $^{51}$Cr activity was about ten times as high as the Zn activity. Also identified in the Columbia River sediments, but with lower activities were $^{40}$K, $^{60}$Co, and $^{54}$Mn.

## ARTIFICIAL RADIONUCLIDES IN PACIFIC SALMON

by Norman Frederick Kujala*

### Abstract of Thesis

Pacific salmon, Oncorhynchus, concentrate certain gamma-emitting radionuclides (zinc-65, manganese-54, potassium-40, and cesium-137) in their viscera. In some cases the pattern of concentration of radionuclides seems related to the position of the fresh water plume of the Columbia River, a well known source of $^{65}$Zn in the northeast Pacific Ocean. Fishes whose migratory paths are far south of the river have more $^{65}$Zn, but less $^{54}$Mn.

In other cases concentrations can be at least partially explained by differences in feeding habits. The more carnivorous chinook and coho salmon accumulate the highest concentrations of $^{65}$Zn, $^{54}$Mn, and $^{137}$Cs. On the other hand, the sockeye, a plankton feeder, has low radioactivity, with $^{54}$Mn the dominant radionuclide, some $^{65}$Zn, but no $^{137}$Cs. The few chum and pink salmon examined most nearly resembled the sockeye in radioactivity.

In southeastern Alaskan waters there is a distinct difference in relative abundance of $^{65}$Zn and $^{54}$Mn in salmon. Manganese-54 is the dominant isotope in salmon of northern Alaskan waters, and $^{65}$Zn is more prominent in the spectra of fishes from Canadian and contingent United States waters. The Columbia River plume undoubtedly accounts for this increase in $^{65}$Zn.

To learn the effects of diet on concentration of radioactivity in salmon, stomach contents were removed and analyzed separately. Megalops crab larva concentrated $^{54}$Mn and $^{65}$Zn, whereas euphausiids concentrated only $^{65}$Zn. Spectra of herring and anchovies were similar to those of the salmon.

Separated visceral organs, shellfish, and steelhead trout were also analyzed. The same gamma emitters were present, but in differing amounts.

The radioactivity of salmon viscera clearly indicates that the influence of the Columbia River is widespread. There is some possibility that $^{65}$Zn and $^{54}$Mn may serve as ecological tools, complimenting tag studies as a means of tracing migrations.

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* Mr. Kujala completed the requirements for his M. S. Degree in June 1966 and then joined the staff of the Department ot Oceanography at Oregon State University. He will be the director of the field sampling program in the Columbia River estuary replacing Lois Haertel who is now devoting full time to a Ph. D. program in radioecology. He received full support from the Atomic Energy Commission.

# PAPERS PRESENTED AND MEETINGS ATTENDED

**CHARLES L. OSTERBERG**

AAAS - Berkeley, California
December 26-31, 1965

International Atomic Energy Agency Symposium on Disposal of Radioactive Wastes into the Seas, Oceans, and Surface Waters.
Vienna, Austria.
May 16-20, 1966
Title: "Some Aspects of Columbia River Radioactivity"

Second International Oceanographic Congress. Moscow, U. S. S. R.
May 30 - June 9, 1966
Title: "Artificial Radionuclides in Marine Organisms in the Northeast Pacific Ocean off Oregon, U. S. A."

Pacific Division AAAS - ASLO - Seattle, Washington
June 14-17, 1966

**ANDREW G. CAREY, JR.**

Pacific Division AAAS - ASLO- Seattle, Washington
June 13-18, 1966

**NORMAN H. CUTSHALL**

American Chemical Society, Pittsburg, Pennsylvania
March 22-24, 1966

Pacific Division AAAS - ASLO - Seattle, Washington
June 13-18, 1966

JAMES E. McCAULEY

Pacific Division AAAS - ASLO - Seattle, Washington
June 13-18, 1966

Visiting Lecturer - Pacific Northwest College and University
Association for Improvement in the Teaching of Sciences.
Title: "The Ocean Floor as a Habitat"
Mt Angel College - 21 April 1966
Oregon College of Education - 27 April 1966

WILLIAM G. PEARCY

Pacific Division AAAS - ASLO - Seattle, Washington
June 13-18, 1966
Title: "The Distribution and Biology of the Pelagic Shrimp
*Sergestes similis* off the Oregon Coast" (with Carl Forss)

Pacific Northwest Oceanographers - Vancouver, B. C.
February 17-19, 1966
Title: "Biological Oceanography at Oregon State University"

AAAS - Berkeley, California
December 26-31, 1965

# SOME NON-BIOLOGICAL ASPECTS OF COLUMBIA RIVER RADIOACTIVITY*

Charles Osterberg, Norman Cutshall, Vernon Johnson,
John Cronin, David Jennings, Lawrence Frederick

The nuclear facility at Hanford, Washington, about 350 miles upstream from the mouth of the Columbia River, is a major contributor of artificial radionuclides to the northeastern Pacific Ocean. The production of artificial radionuclides by these reactors makes it possible to use the Columbia River, its estuary, and the adjacent ocean as a radioecology laboratory. This is especially true since radioisotopes introduced through the use of Columbia River water as a coolant include neutron-induced isotopes of metals in the first transition series, some of which are biologically important. The relationship of neutron-induced radionuclides to the biota is a phase of our laboratory's work included in a separate paper prepared for this symposium by Carey *et al.*

Partitioning occurs when radionuclides are added to natural waters. Some of the radioactivity remains in the water, some becomes associated with the sediment, and some is removed by plants and animals living in the water. With modern techniques, it is a simple matter to detect radioactivity in the sediment, biota, and water of the Columbia River. However, levels of radioactivity are low, particularly in the water, and long counting times are required (Fig. 1).

At sea, after dilution of Columbia River water occurs, measurements of radioactivity become more difficult. Marine organisms have been used as biological monitors or indicators of radioactivity. Oysters (*Crassostrea gigas*), for example, were recognized as concentrators of $^{65}$Zn in estuaries [1], and euphausiids (*Euphausia pacifica*) were used to follow the same isotope at sea [2].

Because of their ability to concentrate certain elements, marine organisms are generally more radioactive than the water and are relatively easy to analyze. Sediments are more difficult to analyze than the organisms and the resulting spectra are complicated by natural radioisotopes present therein. Measurements of radioactivity remaining in the water require the most sensitive techniques.

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* This paper was presented by Dr. Charles L. Osterberg in the *Symposium on Disposal of Radioactive Wastes in the Seas, Oceans, and Surface Waters*, International Atomic Agency, Vienna, Austria, 16-20 June 1966, and will be included in the proceedings.

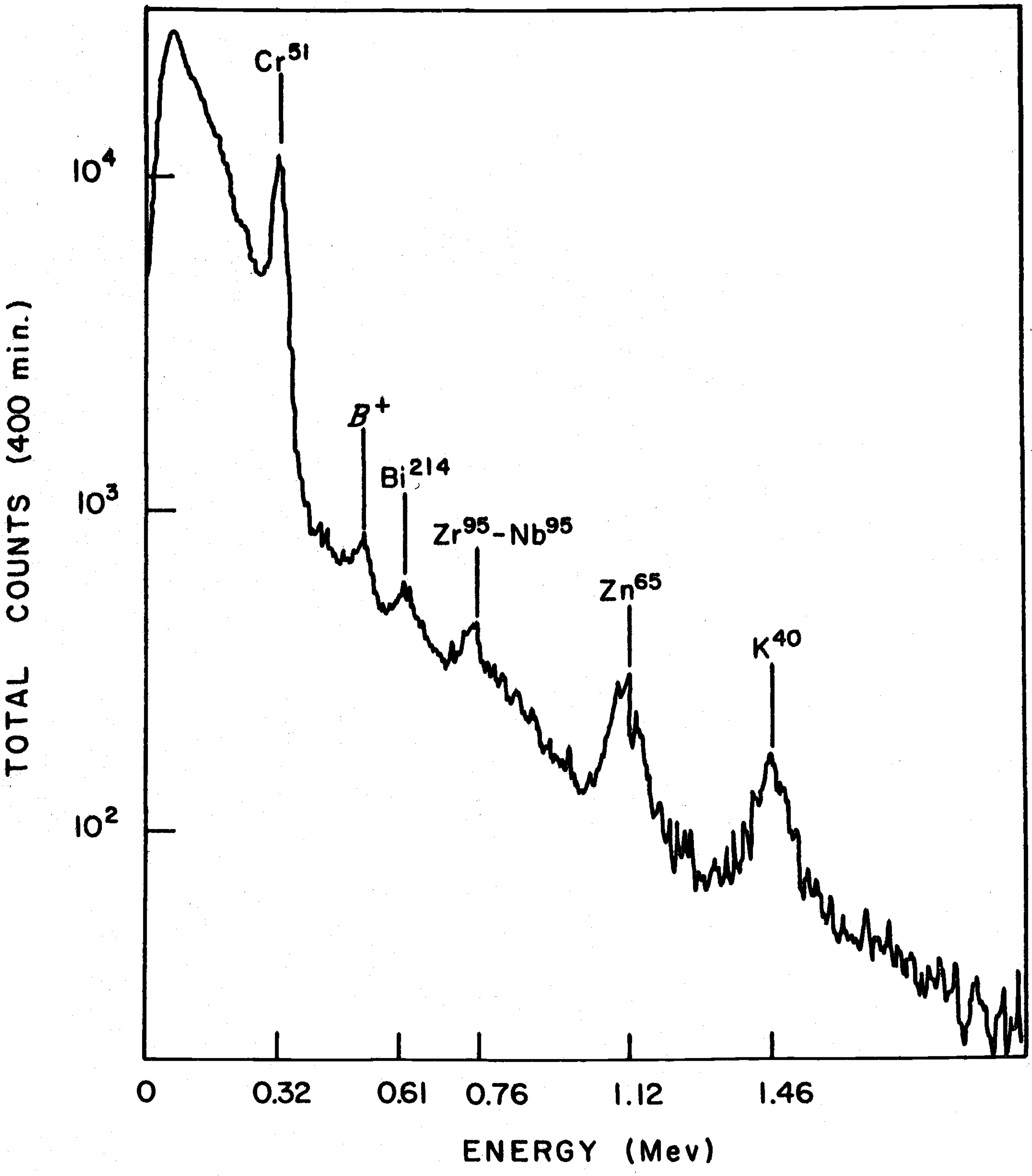

Fig. 1 Gamma ray spectrum of Columbia River water made near Vancouver, Washington, December 1963. Counting time was 400 minutes, with a 3 x 3-inch NaI(Tl) detector in an *in situ* probe, held 1 meter beneath the surface. Since no background was subtracted, it is possible that some of the $^{40}$K and $^{214}$Bi are in the detector. $^{51}$Cr and $^{65}$Zn are from the Hanford reactors, while $^{95}$Zr-$^{95}$Nb is probably fallout.

We usually assume that radionuclides which are associated with filterable particles in seawater will eventually reach bottom, and become associated with sediment. This settling in response to gravity is important in the ocean since there are no opposing forces of comparable magnitude to counteract it.

In a river, however, the faster currents can hold more suspended particles in the water. Because of active mixing and the large ratio of bottom area to water volume in the river, the affinity of the sediment surface for dissolved radionuclides becomes important. The manner in which the radionuclides are bound to the sediment is not completely clear, but the paper by Nelson et al. [3], and perhaps others given in this symposium, should provide interesting data in this regard.

Whatever the mechanism, the surface of the sediment layer is more radioactive than the water immediately above it. This difference in radioactivity was demonstrated when Gross et al. [4], measured several radionuclides directly in seawater using a gamma ray probe in situ. In tests carried out in the Columbia River estuary in 1963, the probe was lowered until it touched bottom. At this point there was a large increase in the counting rate, occurring within an interval of only a few centimeters.

Geologists work on the premise that younger sediments overlay older ones, and in the absence of a mechanism for stirring the sediments, this argument is tenable. Although the burrowing by marine organisms in certain areas confuses this somewhat, it still is a good overall approximation. No large amounts of artificial radionuclides were released to the environment before 1944 -- a short period of time indeed, on a geological time scale. It seems reasonable to assume that man-made radioactivity is confined to a thin layer of the marine sediments at the water-sediment interface. To measure the artificial radionuclides associated with sediment, therefore, it is necessary to analyze this thin layer. However, we need fairly large samples to successfully measure low levels of radionuclides and collection of sufficient material poses somewhat of a problem. As much of this thin layer as possible must be removed from the bottom and brought to the surface through the water column with minimum loss and with minimum disturbance of the sample. If the sediment layers in the samples are mixed in unknown proportions, interpretation of their gamma ray spectra is difficult, if not impossible.

Gross et al. [5] were able to measure $^{65}Zn$ and $^{51}Cr$ in surface sediments from core samples collected up to 180 miles from the mouth of the Columbia River. They reported that these two radionuclides decrease by a factor of 10 within 100 miles of the mouth. We, too, tried this technique, but confined our sampling to the upper end of Astoria Canyon, near the mouth of the Columbia River. Our data also showed $^{65}Zn$ and $^{51}Cr$ to be present in larger amounts near the mouth than farther offshore [6].

The behavior of the *in situ* probe of Gross *et al.* [4], when it touched the bottom, led us to design a gamma ray probe specially suited to measure radioactivity in sediment *in situ*. Our probe differed from that used by Gross *et al.* in one major detail; it incorporated a tripod into the design so that the gamma ray probe would maintain an upright position on the bottom, thus more nearly assuring constant geometry. The instrument, which could work only to depths of about 30 m due to the short conducting cable, was described in a recent article [7]. It has since been modified and used to a depth of 400 m. However, this probe seems most useful for carrying out a rapid survey of radiological conditions on the bottom of an estuary or harbor.

Some radioactive sediments are deposited in the Columbia River estuary. Judging from measurements of transparency (made with Secchi disk and underwater telescope), part of the suspended materials settles out rapidly. Haertel and Osterberg[8] report that the transparency of river water increased appreciably where it mixed with salt water. We found that much of the $^{65}Zn$ is associated with filterable particulate matter in the water whereas most of the $^{51}Cr$ is in solution. That is, when the water was filtered through a membrane filter (0.45 μm), most of the $^{65}Zn$ remained on the filter while most of the $^{51}Cr$ passes through. Whether or not seawater releases the $^{65}Zn$ from the suspended particles, putting it back into solution, seems to be an important question. If $^{65}Zn$ is not so displaced, much of it should settle out with particulate material near the river's mouth. Our probe data show that the ratio of $^{65}Zn$ to $^{51}Cr$ is higher in the sediments than in the water.

Zinc-65 enters the Columbia River in cationic form and is rapidly taken up by suspended material[9]. Bachmann [10] thought that ion exchange on sediments might be involved in the behavior of zinc. If ion exchange were an important mechanism, $Mg^{++}$, $Na^{+}$, and $Ca^{++}$ in seawater should displace much of the $^{65}Zn$ from suspended sediments. Displacement by ion-exchange should occur quickly. Bear[11] stated, "Others have shown that the rate of cation-exchange in soils is generally rapid, requiring only a few minutes for equilibrium. The exchange is a surface reaction and proceeds just as fast as ions from solution are supplied to the exchanger surface . . . " (p. 183).

Johnson [12] collected fresh surface sediments from the river and estuary. Using a portable continuous flow device set up in the field, he collected five successive 50 ml samples of seawater which had been filtered through 10 $cm^3$ of fresh surface sediment. Although $^{51}Cr$, $^{65}Zn$, $^{54}Mn$, and $^{46}Sc$ (from the Hanford reactors) were found in the sediment samples, the leachate contained less than 5% of the $^{65}Zn$ from the sediment and about 33% of the $^{54}Mn$. Since this technique had succeeded previously in removing 100% of the $^{65}Zn$ added to a Dowex-50 cation exchange resin, the conclusion was that less than 5% of the $^{65}$Zn on Columbia River sediments was subject to displacement by ion exchange (Fig. 2). On the other hand, the higher efficiency of $^{54}$Mn extraction seems to corroborate the work of Murata [13] who found that an appreciable fraction of the manganese in muds from several rivers was removed by $NH_4Ac$.

Many investigators have observed that pure minerals and soils are capable of retaining transition metals by a more specific interaction than cation exchange [14]. For example, $Co^{++}$ sorbed on montmorillonite in the presence of 0.1 M $CaCl_2$ could be displaced by other transition elements, but not by $Mg^{++}$, $Ca^{++}$, or $NH_4^+$. Hodgson [15] noted the following order of effectiveness in displacing ability for some doubly charged transition metals:

$$Cu^{++} > Co^{++} > Zn^{++} > Fe^{++} > Ni^{++} = Mn^{++}$$

This, of course, is similar to the stability orders of the complexes formed by metal ions and a variety of ligands which appear throughout the literature (for example, see Goldberg [16]), suggesting that the $^{65}$Zn may be complexed to something in or on the sediment. Nelson and Cutshall [17] showed that over 80% of the $^{65}$Zn associated with bottom sediment from the Columbia River (behind McNary Dam) appeared in the organic fraction.

To distinguish the exchangeable $^{65}$Zn (i.e., displaceable by seawater) from that fraction which was not displaceable, Johnson [12] called the latter "specifically sorbed." He found that 35 to 54% of the "specifically sorbed" $^{65}$Zn could be removed from 10 $cm^3$ of sediment by eluting with 150 mls of 0.05 M $CuSO_4$, at 2.5 ml/minute flow rate. $Cu^{++}$ was more effective than either $Co^{++}$ or $Mn^{++}$, but Johnson reminds us that the stability order generally given in the literature was established from equilibria data, while his results were based on elution data. The important conclusion to be drawn is that only a minor part of the $^{65}$Zn on Columbia River sediments is displaced by ion exchange, while a much larger portion appears to be bound in a complex, perhaps with organic matter.

It might be appropriate to comment briefly on the organic fraction in water, since presumably it is, at least in part, related to the dissolved organics in the sediments. Cronin and Osterberg [18] processed more than 2000 liters of Columbia River water at Astoria, Oregon, by solvent extraction. Twenty liters of petroleum ether were used to extract dissolved organics from each 160-liter portion of filtered estuarine water. Samples were treated three times using fresh ether and the volume of the dissolved organic sample was eventually reduced to 2 liters by distillation. A low temperature vacuum distillation followed. Then 10 grams

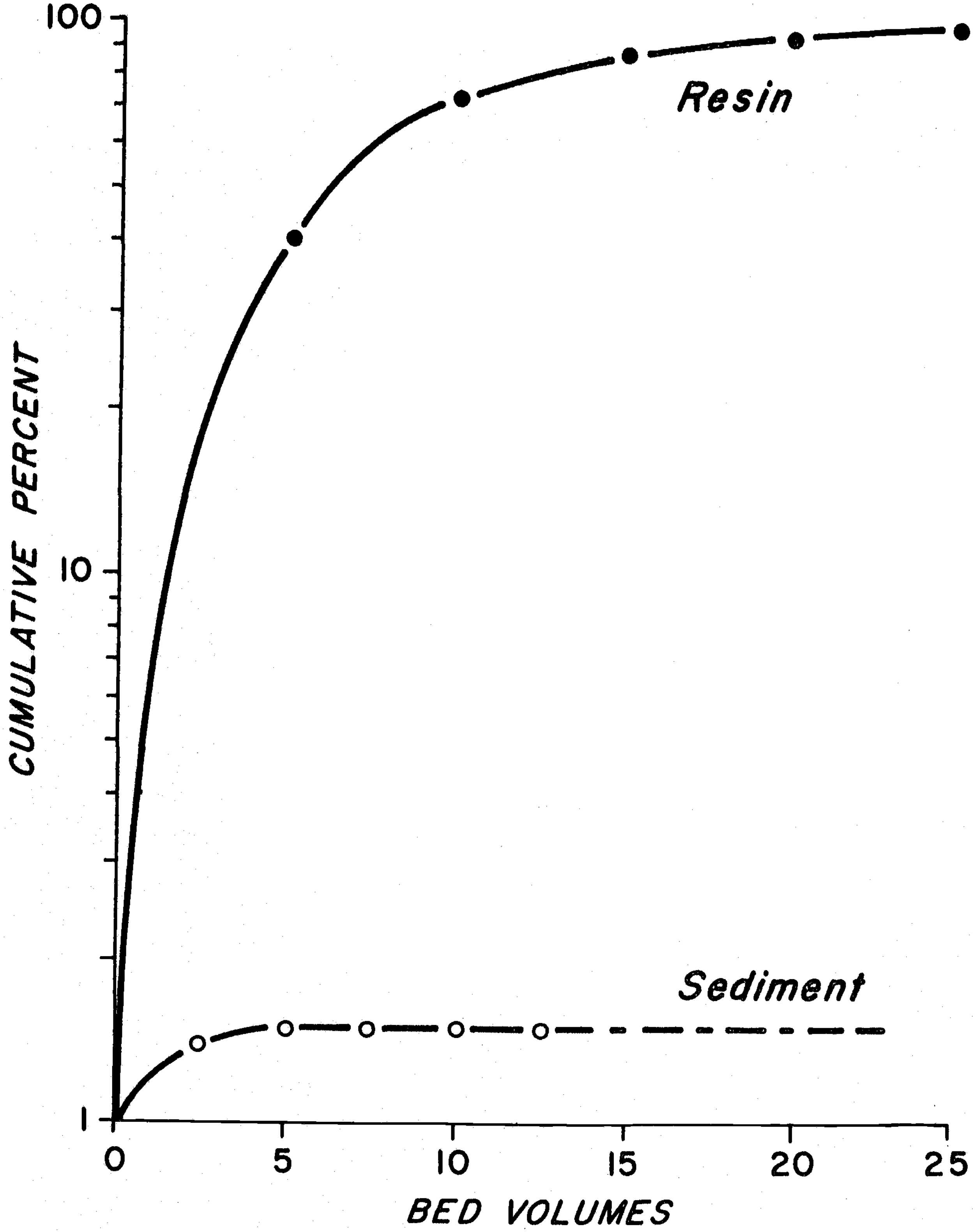

Fig. 2 Cumulative percent $^{65}Zn$ displaced from Dowex 50 resin and natural Columbia River sediment by successive volumes of synthetic seawater. Flow rate was ~5 ml/min. for the resin, and 3 ml/min. for the sediment. Bed volume in both cases was 10 $cm^3$.

of polyvinyl pyrrolidine (PVP), which has an affinity for phenol groups, was mixed with the residual dark brown concentrate. When the PVP was removed and analyzed for radionuclides, $^{65}$Zn and $^{51}$Cr were prominent in its spectrum, along with a few lesser peaks. While this work cannot be regarded as definitive since petroleum ether extracts some of the $^{65}$Zn from aqueous solution in the absence of dissolved organics, it seems probable that dissolved organic compounds bind to some of these radioisotopes.

Measurement of artificial radionuclides in seawater collected at some distance from the Columbia River is difficult. Decay, dilution, losses to biota, and the settling out of particulate matter reduce levels of radioactivity. Therefore, either more sensitive techniques, or larger samples, are required. We chose the latter approach, and constructed large tanks from which certain radionuclides can be coprecipitated with $Fe(OH)_3$. Neither the chemical techniques nor their use in large volume tanks at sea is new. We have simply modified the apparatus and procedures according to our needs.

Our two tanks are approximately 56 cm diameter by 275 cm high (Fig. 3). Stirring is accomplished with a jet of air introduced at the apex of the conical bottom, and precipitates are also drained at this point.

Use of the apparatus is as follows. The tanks are filled with seawater (~ 600 liters), stable carriers of the several artificial radioelements suspected of being present in the water are added, along with the bulk carrier ($FeCl_3$), and the mixture stirred for 30 minutes. The pH is adjusted to 9.5 with $NH_4OH$ and stirred for five minutes. A coagulating agent (Dow Chemical's Separan) is added to speed the settling rate, and the air is shut off. The precipitate collects in the cone at the bottom of the tank within two to three hours. The supernate is siphoned off, and the precipitate is drained into a 50-liter jug. The sample is reduced to about 8 liters by successive decantings. After returning to the laboratory, the sample is further reduced to 800 mls and analyzed by gamma ray spectrometry.

This apparatus performed so well that samples could be processed more or less independently of sea conditions. Successful performance of the tanks was largely due to their shape (tall, but narrow), since sloshing due to rolling of the ship was minimized, and the stirring by rising air bubbles was more effective.

In early experiments carried out near the mouth of the river with the large tanks $^{51}$Cr, $^{65}$Zn, $^{54}$Mn and possibly $^{124}$Sb were detected in the precipitates. To develop maximum recovery techniques of these gamma emitters, several tests were conducted using different combinations of

Fig. 3 Large volume tanks for removing trace metals from 600 liters of seawater by coprecipitation with $Fe(OH)_3$. The mixture is stirred by air, introduced into the bottom of each tank. After the air supply has been stopped and the mixture allowed to settle 2-3 hours, the residual water is siphoned off. The precipitate, concentrated in the conical bottom of the tanks, is drained out through the valve in the bottom. It can be retained in jugs for analysis, or can be made to flow into a counting chamber below deck (see Fig. 6).

stable carrier elements, and varying the pH with parts of the process. The work aboard the U. S. Coast Guard Lightship COLUMBIA gave peculiar results; carriers of Zn, Cr, Mn, and Sb (as chloride salts) caused a far greater recovery of $^{51}Cr$ than when no carriers were used. This was contrary to expectations, since we did not believe $CrCl_3$ would be necessary to optimize the yield of $^{51}Cr$.

Later experiments both at sea and in the laboratory by Cutshall et al. [19] demonstrated that the addition of Cr III (i. e. $CrCl_3$) carrier, indeed, had no effect on the yield of $^{51}Cr$, while Cr VI acted as a "hold back" carrier,[1/] reducing the yield. It was the antimony III, added to enhance the yield of $^{124}Sb$, which caused the marked increase in the amount of $^{51}Cr$ recovered (Fig. 4).

The role of Sb III was explained by Cutshall et al., who showed that it would reduce any $^{51}Cr$ VI in the water to $^{51}Cr$ III. Once reduced to Cr III, $^{51}Cr$ is efficiently removed, while $^{51}Cr$ VI is not. Another reducing agent, Sn II, was equally effective. They concluded that most of the $^{51}Cr$ from Hanford which remains in the plume is Cr VI, and that any reduced to Cr III by natural mechanisms would tend to adsorb to particles and settle out of surface waters.

In June-July 1965 the large chemical apparatus was placed on the U. S. Coast Guard Cutter MODOC. Using Sb III as a reducing agent, and all carriers previously mentioned, the plume of the Columbia River was followed 350 km to sea (Fig. 5). The technique is so sensitive that $^{51}Cr$ was easily measurable at this distance, and only lack of time prevented us from following it farther [21]. In August, when the plume became diffuse, we traced it 525 km from the river's mouth without reaching the limit of detectability. Since no other source of $^{51}Cr$ exists in the northeast Pacific Ocean, this isotope is a positive and sensitive tracer for Columbia River water at sea. Furthermore, the short 28-day half-life and the relatively small losses to sediment and biota make $^{51}Cr$ appear useful as a timing mechanism for measuring rates of movements of the water.

A recent improvement made by Frederick eliminates the need to return the precipitate to the laboratory for analysis. The 50 liters of "concentrate" (from coprecipitation of 600 liters of seawater) are drained into a second container on shipboard where further settling occurs while the sample is heated to room temperature (16 - 22° C). Excess water is removed. About 20 liters of concentrate drains into a counting chamber, which surrounds a 5.1 x 11.5-cm NaI(Tl) crystal-detector. By heating the

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[1/] The terminology used here is that of Friedlander and Kennedy [20].

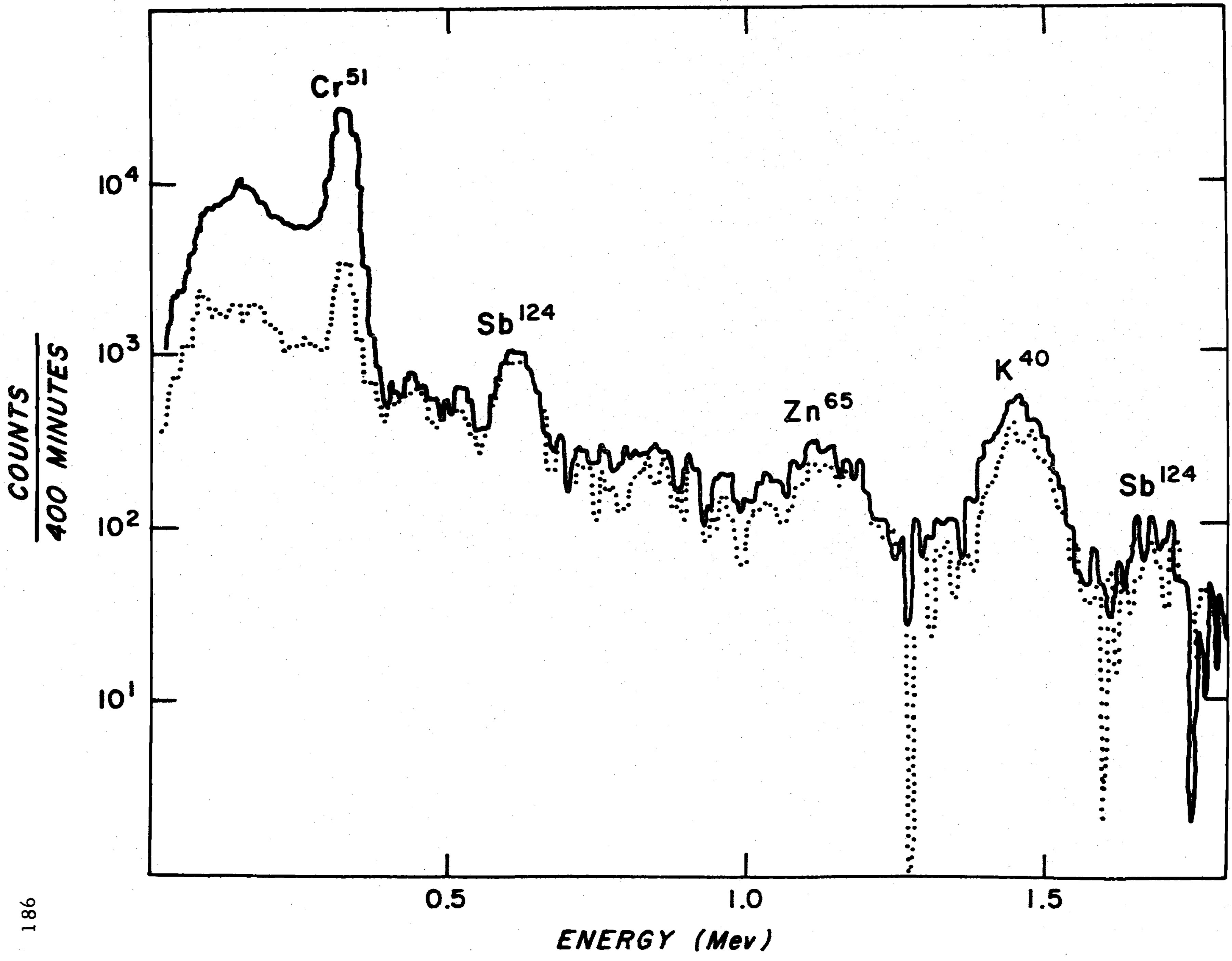

Fig. 4 Comparison of spectra of precipitates from duplicate samples of seawater from off Oregon. The increase in $^{51}$Cr (solid line) results from the use of antimony as a reducing agent, prior to coprecipitation, (from Science, 1966).

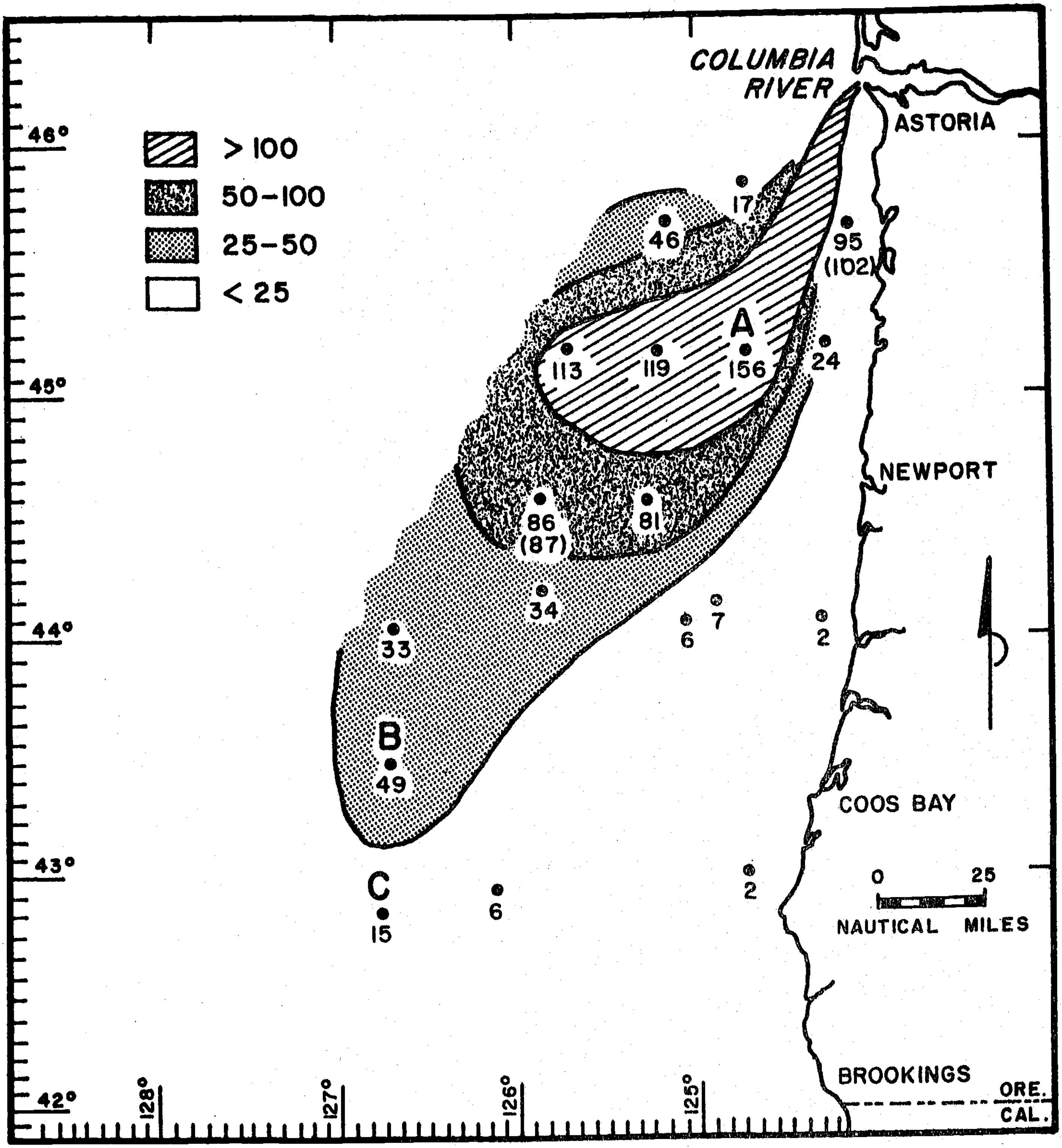

Fig. 5 Plume of the Columbia River in late June 1965, as determined from the $^{51}$Cr content of the water. Units are counts per 100 liters of surface water. To convert to picocuries per liter, multiply by 0.861. Parenthesis indicate duplicate samples. The greatest velocity of water movement was between points A and B, (from Science, 1965).

sample to room temperature, before counting, possible damage to the crystal and instrumental drift are both minimized. The entire counting chamber is shielded with 10.1 cm of lead (Fig. 6). The detector is attached to a 512 channel gamma ray spectrometer. Data are recorded on paper punch-tape. The limit of detection of this system is less (~3 pCi/l versus ~1.2 pCi/l)[2] than is obtained when the sample is reduced to 800 ml and counted in the laboratory. However, the sample can be recounted in the laboratory if a more sensitive measurement is required. The greatest sensitivity results when the precipitate is dried and compressed before counting. Since the shipboard counting chamber provides information on the radioactivity within four hours from the time of sample collection, and new data are generated at two-three hour intervals (there are two primary and two secondary tanks), the cruise plan can be altered to investigate interesting features which may occur. This equipment was tested at sea in February 1966, when $^{51}$Cr from the Columbia River was followed northward to Cape Flattery (about 225 km).

One of the fringe benefits we receive from the nuclear age is the labelling of the environment with trace radionuclides, making biogeochemical cycles easier to follow. Because of the low levels of radioactivity introduced from the Hanford reactors on the Columbia River, the northeast Pacific Ocean is ideally suited for such studies.

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[2] Limit of detection is defined as [$3\sigma$]. The limits given are based on a 30-liter sample counted for 100 minutes in the seaboard detector; for the laboratory analysis, the sample is condensed to 800 ml and counted for 400 minutes. We have since modified the seaboard detector to use 20 liter samples. This added concentration factor should make the limits of detection more nearly comparable.

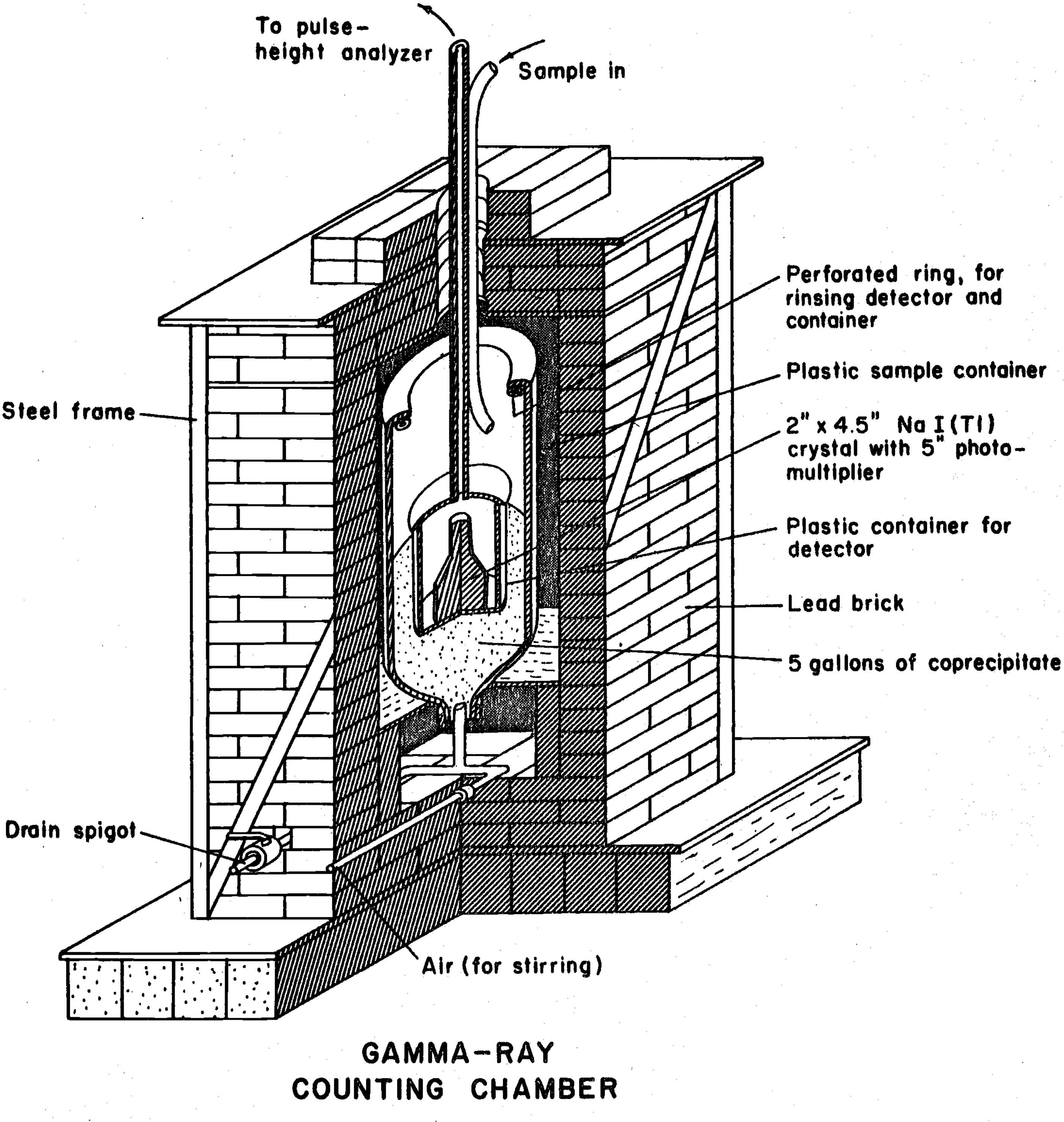

Fig. 6 Shipboard counting chamber, for analyzing coprecipitate (~ 20 l) concentrated from about 600 liters of seawater. This unit weighs about 4 tons, and is installed on the R/V YAQUINA.

## REFERENCES

[1] WATSON, D., DAVIS, J.J., HANSON, W., Zinc-65 in marine organisms along the Oregon and Washington coasts, Science 133 (1961) 1826.

[2] OSTERBERG, C., PATTULLO, J., PEARCY, W., Zinc-65 in euphausiids as related to Columbia River water off the Oregon coast, Limnol. Oceanog. 9 (1964) 249.

[3] NELSON, J.L., PERKINS, R.W., NIELSEN, J. M., HAUSHILD, W., Reactions of radionuclides from the Hanford reactors with Columbia River sediments (abst.). Symposium on the Disposal of Radioactive Wastes into Seas, Oceans, and Surface Waters, SM-72, Vienna, 16-20 May 1966.

[4] GROSS, M.G., BARNES, C., RIEL, G. Radioactivity of the Columbia River effluent, Science 3 (1965) 1008.

[5] GROSS, M.G., MCMANUS, D., CREAGER, J., Preliminary report on the sediments and radioactivity in the vicinity of the Columbia River effluent, Univ. of Wash., Seattle, Ref. M63-2 (1963) 32.

[6] OSTERBERG, C., KULM, L. D., BYRNE, J., Gamma emitters in marine sediments near the Columbia River, Science 139 (1963) 916.

[7] JENNINGS, David, CUTSHALL, N., OSTERBERG, C., Radioactivity: Detection of gamma rays in sediments in situ, Science 148 (1965) 948.

[8] HAERTEL, L., OSTERBERG, C., Ecology of the Columbia River estuary. (In preparation).

[9] NELSON, J. L., PERKINS, R. W., NIELSEN, J. M. Progress in studies of radionuclides in Columbia River sediments. A.E.C. Rept. HW-83614, Richland, Wash. (1964) 20.

[10] BACHMANN, R. W., "Zinc-65 in studies of the fresh water zinc cycle," Radioecology (Schultz, V., Klement, A., Jr., Eds.) Reinhold, New York (1963).

[11] BEAR, F.E., Chemistry of the soil. Amer. Chem. Soc. Monograph No. 160. Reinhold, New York (1964) 502.

[12] JOHNSON, Vernon, Retention of zinc-65 by Columbia River sediment, M. S. Thesis, Oregon State Univ., Corvallis (1966) 56.

[13] MURATA, K. J., Manganese in river and ocean muds, Amer. J. Sci. 237 (1939) 725.

[14] TILLER, K. G., HODGSON, J. F. The specific sorption of cobalt and zinc by layer silicates. Proceedings of the National Conference on Clays and Clay Minerals 9 (1962) 393.

[15] HODGSON, J. F., Cobalt reactions with montmorillonite. Proceedings of the Soil Society of America 24 (1960) 165.

[16] GOLDBERG, E. D., Biogeochemistry of trace metals, Ch. 12, Vol. I, Treatise on Marine Ecology and Paleoecology (Hedgpeth, J. W., Ed.) Geological Soc. of Amer. Memoir 67 (1957).

[17] NELSON, J. L., CUTSHALL, N. H., Studies of the mechanisms of retention of radionuclides in Columbia River sediments. A. E. C. Rept. BNWL-36 III, Richland, Wash. (1965) 375.

[18] CRONIN, John, OSTERBERG, C., Dissolved organics, Oregon State Univ., Corvallis, Ref. 65-14 51 (1965) 255.

[19] CUTSHALL, N., JOHNSON, V., OSTERBERG, C., Chemistry of chromium-51 in seawater, Science (in press).

[20] FRIEDLANDER, G., KENNEDY, J. W., Nuclear and Radiochemistry, Wiley, New York (1955).

[21] OSTERBERG, C., CUTSHALL, N., CRONIN, J., Chromium-51 as a radioactive tracer of Columbia River water at sea, Science 150 1585 (1965).

# ARTIFICIAL RADIONUCLIDES IN MARINE ORGANISMS IN THE NORTHEAST PACIFIC OCEAN OFF OREGON, U. S. A.*

Andrew G. Carey, Jr., William G. Pearcy, Charles L. Osterberg

## INTRODUCTION

Marine organisms modify the distribution of radioisotopes in the oceanic ecosystem. Various vital processes of plants and animals concentrate elements. The distributions of the biota are often independent of their watery environment; they may actively migrate vertically or horizontally or may remain in place while the water moves past them. In the case of plankton, the concentrating organisms passively move with the currents.

The Pacific Ocean off Oregon is ideally suited for research on the biological fate of artificial radionuclides. A constant supply (steady-state) of low level radionuclides is transported into the ocean environment from the Columbia River, a point source. These radionuclides are derived primarily from the atomic works at Hanford, Washington, where the waters of the Columbia River are used to cool the reactors. Radioactive elements are induced from the trace elements in the river water as it passes through the high neutron flux within the reactors [1] . The cooling water is returned to the river , and many of the radioisotopes ultimately reach the sea. Approximately 900 curies per day were discharged into the Pacific Ocean during the period 1961-1963 [2] [3] [4].

The Columbia River enters the northeast Pacific Ocean at the boundary between Oregon and Washington. Its discharge of fresh water into the ocean, the Columbia River plume, varies in position from season to season [5] [6] . Because the direction of wind stress changes from northerly in the winter to southerly in the summer, the plume is found

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near shore to the north in the winter and off Oregon to the southwest in summer. In addition, when coastal surface waters are blown offshore by the summer winds, deeper water upwells in its place forming a band of upwelled water between the plume and the coast of Oregon.

Radionuclides from atomic testing and the resulting worldwide fallout of fission products have also been present at low levels off the northwest coast of the United States during the period of study.

Induced radionuclides from the Hanford reactors and fission products from fallout have been detected in a variety of animals in the northeast Pacific Ocean as far as 490 km off the coast of central Oregon and to depths of 2860 m. Zinc-65 is biologically the most important gamma emitter entering the ocean from the Columbia River. It occurs in phytoplankton, zooplankton, and nekton in the upper layers of the water column [7] [8] [9] [10] [11]. Zinc-65 and other man-made radioelements have also been detected in the sediments [12] and in bottom invertebrates [13] [14].

Marine animals must be efficient feeders to survive. Filter-feeding organisms must process large volumes of water to obtain enough energy from living and non-living organic particulate material for maintenance, growth, and reproduction. Benthonic deposit-feeding invertebrates must pass large quantities of sediment through their guts to provide enough organic material to support life processes. Carnivores feed on both the above animal groups and ingest protoplasm that has already incorporated elements collected from large volumes of seawater or sediment. Organisms, then, are mechanical concentrators and integrators of elements, or their radioisotopes, used in life processes. The radioactively-tagged elements present in the sea off Oregon and Washington make this area ideal for a study of the transfer of elements through the food web.

## MATERIALS AND METHODS

Numerous stations off Oregon and Washington were sampled during a four-year period to provide planktonic, nektonic, and benthonic organisms from a range of depths and environments for radioanalysis. The large zooplankton and nekton were collected by an Isaacs-Kidd Midwater Trawl, the benthonic organisms by a 7-m semi-balloon shrimp trawl, and sediment by a 0.1-$m^2$ Smith-McIntyre bottom grab. Phytoplankton and detritus were collected by passing seawater through a membrane filter.

Animal samples were preserved in 10% neutral seawater-formalin or deep-frozen on board ship. The samples were usually sorted to species in the laboratory. They were then counted and dissected into major tissue levels or organ systems, when possible. The samples were prepared for radioanalysis by drying to a constant weight at 65° C in a drying oven, ashing at approximately 550° C in a muffle furnace, grinding carefully with a mortar and pestle, packing into 15-cc plastic tubes, and sealing the tubes with a cork and paraffin wax. When the number and volume of a species were low, whole organisms were packed in the tubes. Total samples of mixed species were sometimes counted in a polyethylene bottle on top of the crystal. Gamma-ray emissions were counted with a 512 channel Nuclear Data ND-130 Gamma-ray Spectrometer for 100 or 400 minutes.

To measure artificial radioactivity in the sedimentary environment of the benthos, we have taken two approaches. One method used a bottom grab with hinged top flaps to obtain the top 1 cm of sediment for radioanalysis in the laboratory. The sediment was dried, and a standard volume in a 15-cm plastic petri dish was counted on top of the crystal. The other method was to use an in situ gamma-ray probe in shallow water [15] .

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## RESULTS

The amount of radionuclides from fallout and Columbia River sources varied in both time and space off the coast of Oregon. Amounts varied among species and among animal feeding types. Variations were noted in both the pelagic and benthonic organisms.

### Geographic Variations

Induced radionuclides flowing into the sea from the Columbia River have been found to vary geographically both in pelagic and bottom animals. Highest levels of zinc-65 in fauna were generally found near the mouth of the Columbia [7][14][16].

The picture of $^{65}$Zn concentrations in plankton and nekton in relation to geographic variations is a complex one, probably affected by advection with currents and by lateral and vertical motion of the organisms. Osterberg, *et al.* [7] found the highest levels of radiozinc in the euphausiid *Euphausia pacifica*, near the mouth of the Columbia River in the spring, but further south off Newport in the summer after the plume had extended to the south. The latter animals probably had been in the plume waters for longer periods of time and had accumulated higher amounts of radionuclides than euphausiids found near the river's mouth. Throughout the year off Oregon, radiozinc concentrations in *E. pacifica* remained higher than in the same species beyond the influence of the Columbia River. Samples of this euphausiid from Alaska and California waters were much lower in zinc activity [7].

The amount of zinc-65 in bottom invertebrate organisms at the same depth generally decreases with increasing distance from the mouth of the Columbia River (Table 1). The decrease in radioisotope concentrations with distance from the river is not surprising. The animals involved generally remain in one spot with the river plume flowing overhead in the surface waters. Those closer to the river would receive larger amounts of radioisotopes for longer periods of time. This differs from the plankton and nekton which are at least partially transported in the plume itself.

Table I

Zinc-65 in *Allocentrotus fragilis* (sea urchin)

| Distance from Columbia River (km) | Depth (m) | Date | Zinc-65 pCi/g ash-free dry wt) (with standard deviation) | | |
|---|---|---|---|---|---|
| | | | body | gonad | test |
| 59 | 200 | 8/28/65 | 89.8 ± 7.5 | 75.0 ± 3.3 | 0.0 |
| 90 | 200 | 8/28/65 | 119.2 ± 6.8 | 64.3 ± 2.1 | 0.0 |
| 122 | 200 | 8/28/65 | 48.3 ± 3.4 | 38.0 ± 1.6* | 0.0 |

*counting error

Increasing distances offshore to the west produce a rapid reduction in radiozinc concentrations in bottom animals. Bathymetric effects greatly reinforce the general decrease with distance.

In contrast to the localized geographic distribution of Columbia River radioisotopes, fission products from worldwide fallout from atomic testing were fairly broadly distributed. Geographic differences usually were not apparent in ecologically similar animals off Oregon [13] [17].

## Bathymetric Variations

The distribution and concentration of the induced radionuclides in the plume vary markedly with depth. Generally, deep-living mesopelagic fishes have lower concentrations of zinc-65 than shallow-living species (Figure 1). However, Pearcy [18] and Pearcy and Osterberg [9] have shown that the pattern of zinc-65 concentrations in animals collected with the midwater trawl is a complex one, varying both daily and seasonally. This changing pattern is related to the diurnal vertical migrations of animals and to the shifting position of the Columbia River plume.

Radiozinc in pelagic animals is affected by seasonal variation in the upper 150 m. Highest values of 2 pCi ( wet preserved weight) were found during the summer, and lowest values of 0.2 pCi were found in mid-winter in the upper water layers. In depths of 150-500 m, the same seasonal pattern was evident, but damped; below 500 m, the activity was generally less than 0.2 pCi/g with little or no seasonal change. Hence, in the winter, $^{65}$Zn concentration in the animals was fairly uniform within the entire 1000 m water column, while in the summer, significantly higher amounts of $^{65}$Zn were found in organisms in the upper 150 m (Figure 2).

Vertical migrations affect the average concentration of $^{65}$Zn in organisms, particularly in surface waters. The average $^{65}$Zn activity was usually higher for animals collected during the night than for those collected during the day (Figure 2). This increase correlates with a diurnal change in species composition also evident at the surface. Consistent day-night differences in the amount of zinc-65 were not apparent at mid-depth or in deep water, however.

Concentrations of $^{65}$Zn in the bottom fauna are related to bathymetry. Below about 600 m depth, the $^{65}$Zn concentrations in all fauna drops off precipitously. Asteroids with the same feeding habits show this characteristic decrease of radiozinc concentrations in the animals with depth (Figure 3). The amount of $^{65}$Zn decreases from $32.1 \pm 1.3$ pCi/g (ash-free dry weight) at 100 meters depth to about $3.6 \pm 0.5$ pCi/g at 800 m. Below 800 m $^{65}$Zn generally remains at a low or undetectable level; however, it is sometimes found in fauna at the deepest (2860 m) and most distant (266 km) station from the river's mouth.

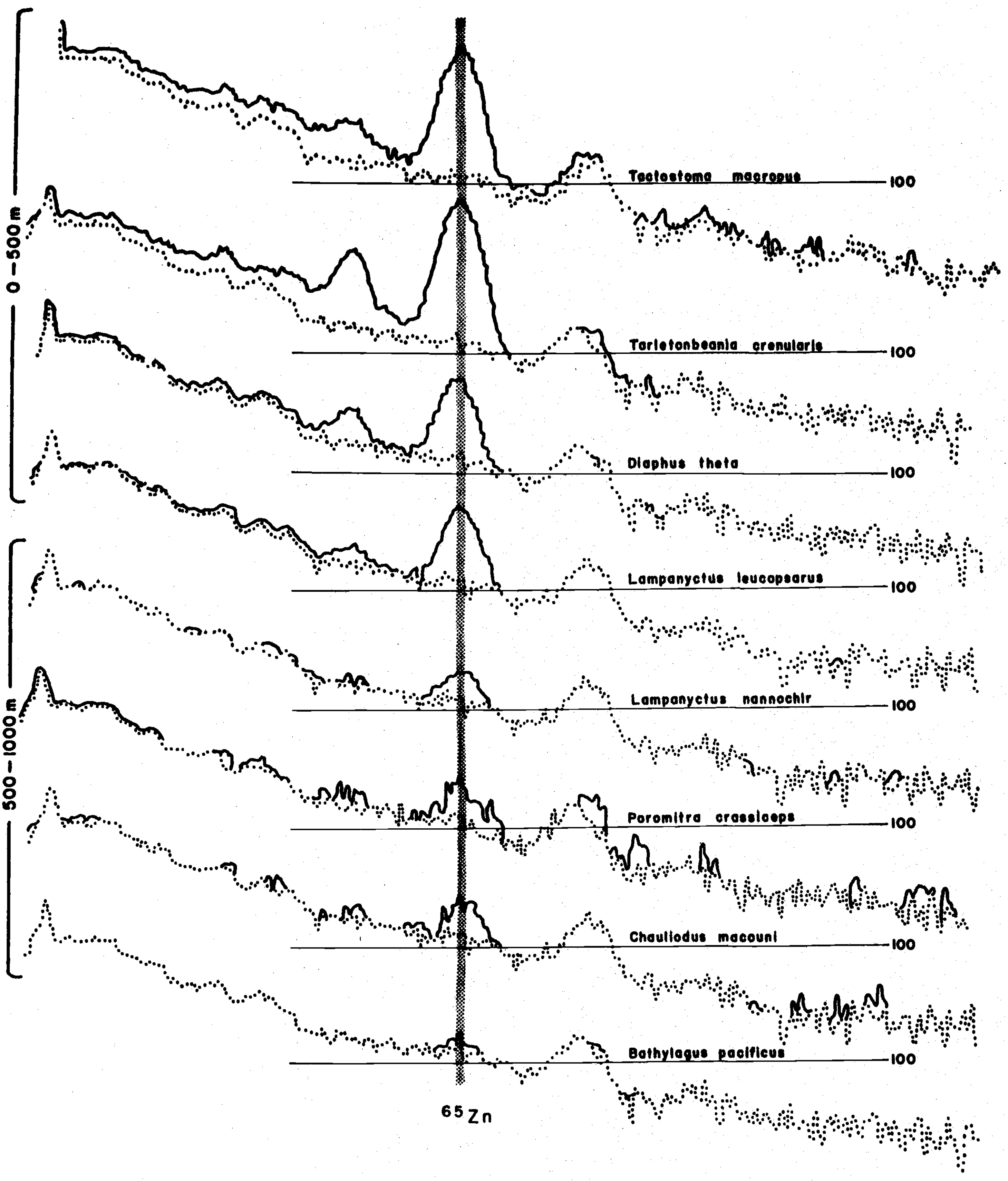

Fig. 1 Gamma spectra of mesopelagic fishes. The upper four species are shallow species compared to the lower four species. The ordinate indicates the total number of counts on a log scale.

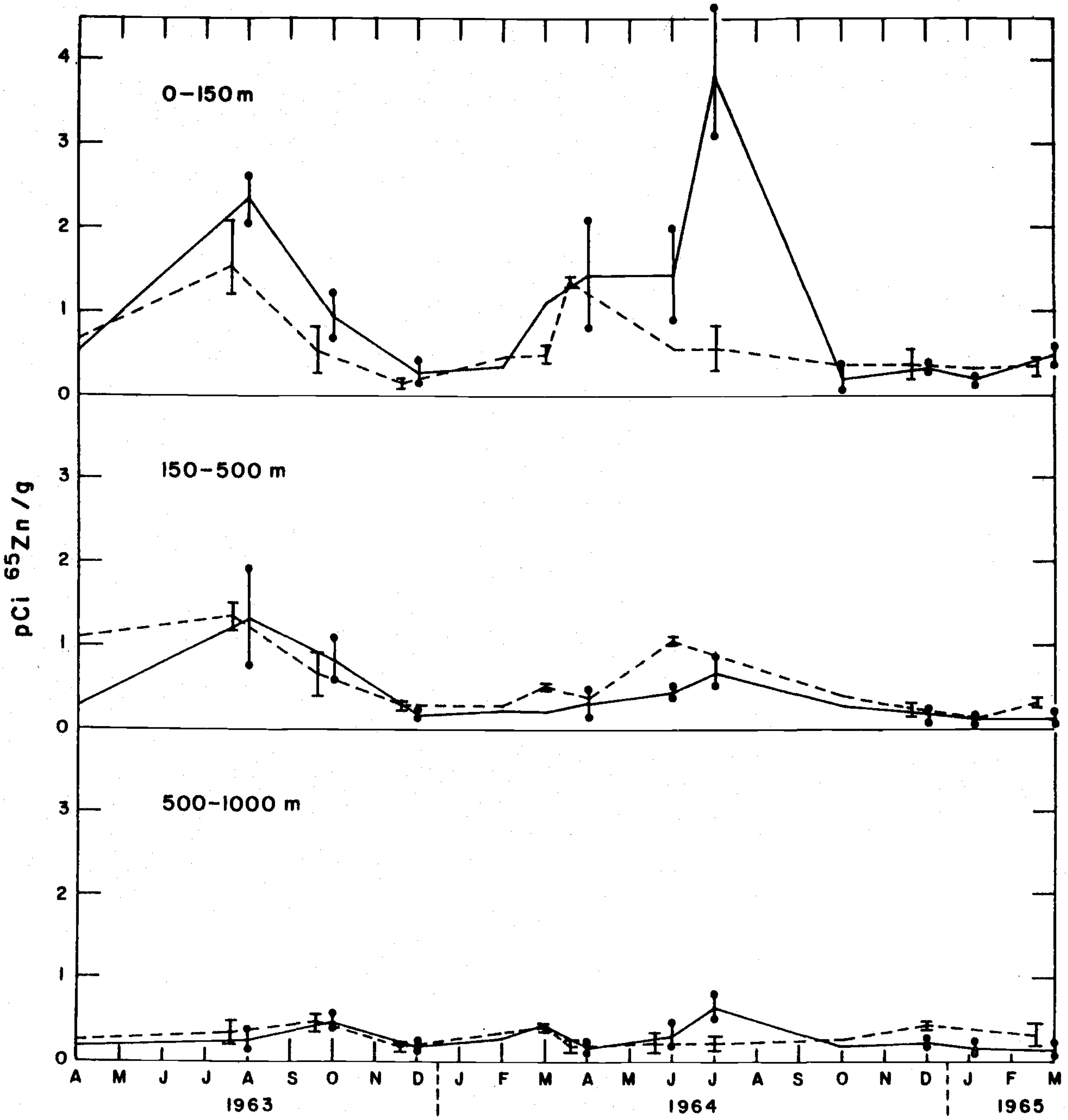

Fig. 2 Variations of zinc-65 (in picocuries/g, wet weight) in midwater trawl collections from the depths. The solid line connects averages for night collections, and the dotted line connects averages of daytime collections. Range of values is also indicated.

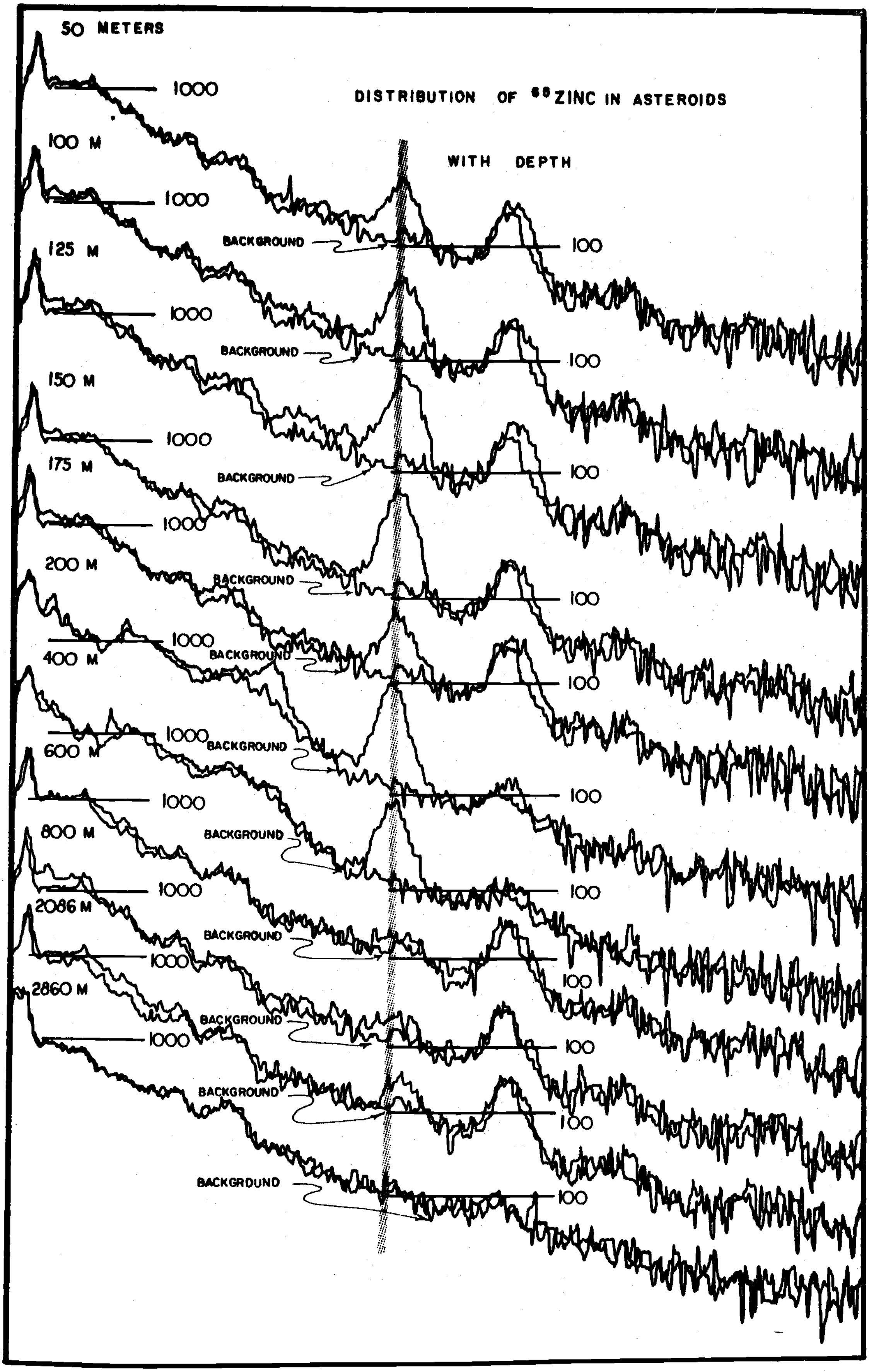

Fig. 3 Eight normalized gamma-ray spectra for starfish from various depths. Note the zinc-65 peak and its decrease with depth. All data from 50 to 800 meters from June 1963 - 1965. The sample from 2086 meters is from August 1963 and that from 2860 is from May 1963. The ordinate indicates the total number of counts in a log scale.

In contrast to the bathymetric distribution of $^{65}$Zn and other induced radionuclides originating from the reactors at Richland, Washington, fission products in fallout during the winter of 1961 were more concentrated in the surface than in mesopelagic organisms [9] . Surface animals (0-150 m) contained nine times as much zirconium-95 - niobium-95 as the deeper forms.

However, $^{95}$Zr-$^{95}$Nb were found in bottom animals in about the same amounts per unit weight in both shallow and deep water [13] . Yet, the bottom animals radioanalyzed are deposit-feeding, and the presence of the relatively short half-lived radioisotopes in the deep fauna suggested rapid sinking. The rate of sinking for very small fallout particles in the sea would be expected to be very slow from purely physical processes (Stoke's Law). It was suggested that filter-feeding zooplankton in the surface waters were compacting ingested phytoplankton along with adsorbed fission products into faecal pellets which, being much larger, fell to the bottom at a much faster rate than the minute,individual fallout particles. A comparison of the decline of fallout fission products in the air [19] and of fission products in the deep bottom fauna at 2860 m depth shows very little lag. The rapid decrease of the fission products in the air during the latter part of the summer of 1963, after the cessation of atmospheric testing, was repeated a short time later in the bottom fauna at 2860 m depth, 106 km off the central Oregon coast (Figure 4).

## Seasonal Variations

The amount of artificial radionuclides in the marine biota off Oregon is intimately linked to seasonal growth and reproductive changes of the organisms and to the geographic position of the Columbia River plume. Cycles in $^{65}$Zn in the fauna are suspected to respond to both types of cyclical phenomena. To date, only the effect of the seasonal shift of the plume position has been demonstrated to be of major importance.

During the summer, surface animals from a single station off Oregon showed greater amounts of radiozinc than deep water fauna (Figure 2). The Columbia River plume usually includes this station during summer months. During the winter, on the other hand, when the plume is oriented to the north off the Washington coast, the station does not show the effects of the plume, and the amount of $^{65}$Zn is about the same in both surface and deep animals.

Seasonal changes in the distribution patterns of induced radionuclides in bottom animals are similar to those in the pelagic fauna (Table II). Further work will be necessary to draw conclusions, however. The summer maximum of $^{65}$Zn concentrations appears to come at a later time of year

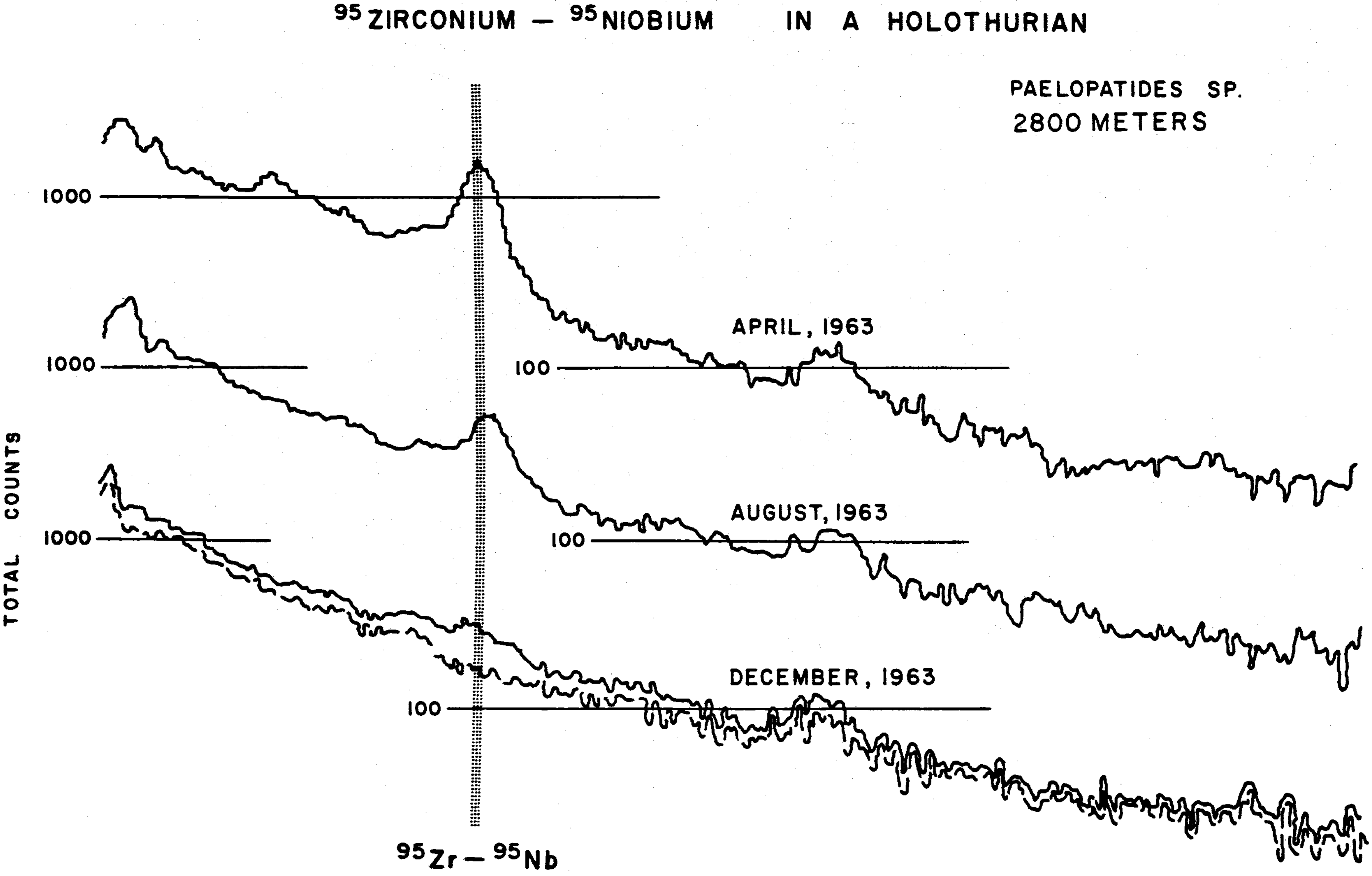

Fig. 4 Weight normalized gamma-ray spectra for deep sea cucumber, (<u>Paelopatides</u> sp.). Total number of counts are indicated on a log scale.

Table II

**Seasonal changes in Zinc-65 in shrimp, Pandalus jordani**

| Date | Depth (m) | (Zinc-65 pCi/g ash-free dry wt. with standard deviation) |
|---|---|---|
| 2/7/65 | 245 | 8.6 ± 0.5 |
| 6/4/65 | 175 | 44.3 ± 0.9 |
| 10/24/65 | 200 | 17.7 ± 0.7 |

in animals from greater depths [14]. A seasonal increase in the total radiozinc in the gonad of sea urchins has been noted, though it has not been shown yet whether this increase is relative with respect to other organs or whether it reflects an increase in the total amount of $^{65}$Zn in the organism.

Variations within the Food Web

Position of animals in the food chain affects both the induced radionuclide and fission radionuclide concentrations in the pelagic and bottom fauna [8] [14].

Osterberg, Pearcy, and Curl [8] demonstrated that $^{65}$Zn increases up the food chain in the pelagic environment relative to the fission products, $^{95}$Zr-$^{95}$Nb, but an absolute increase is not always apparent. Zinc-65 was found in every organism analyzed, but zirconium and niobium were concentrated mainly by primary producers and herbivores, and not by carnivores. Fission products from fallout were less evident in predaceous pelagic animals than in herbivores.

The same relationships between feeding habits and trophic level and the abundance of radionulides are evident in the bottom invertebrates, though the food webs are usually shorter. During the period when they were detectable, $^{95}$Zr-$^{95}$Nb were found only in sediment-feeding organisms while the amount of $^{65}$Zn generally increased in predatory organisms. The fission products were probably in the gut of the organisms. The simple food chain illustrated in figure 5 shows little or no radiozinc in the sedimentary environment of the ophiuroids (Ophiura sp.), but the efficient, sediment-feeding brittle stars have concentrated a significant amount of $^{65}$Zn. This genus of ophiuroids is known for its deposit-feeding habit [20] [21]. Gut content analyses have shown that the top carnivore,

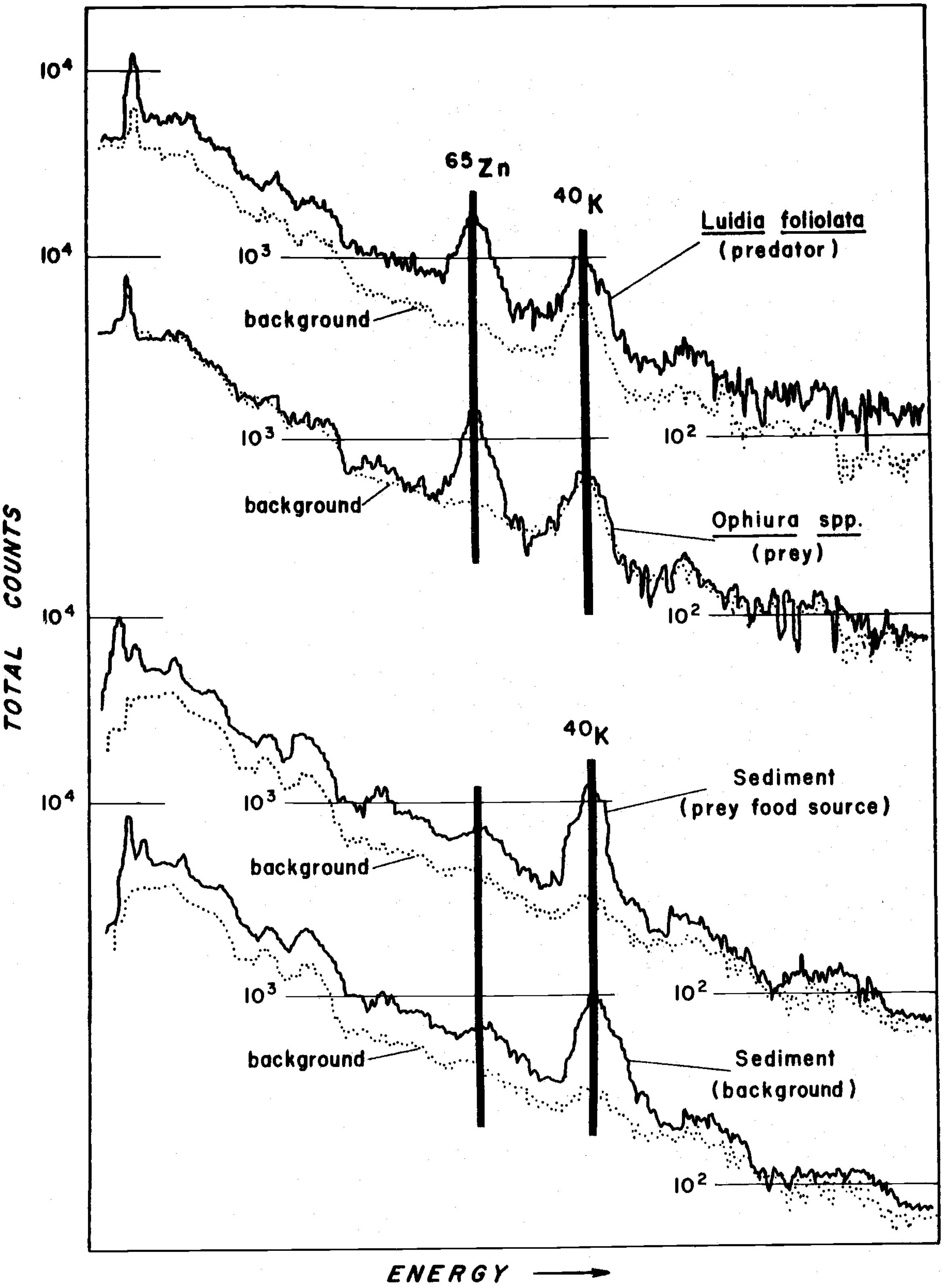

Fig. 5 A comparison of the gamma-ray spectra of components of a benthonic food chain. From top to bottom the spectra represent: (1) a predaceous asteroid, Luidia foliolata; (2) the major prey, an ophiuran, Ophiura spp.; (3) sediment from the environment of the two echinoderms; and (4) sediment from a similar environment beyond the influence of the Columbia River Plume. The top two spectra have been weight normalized. The bottom two spectra are not significantly different. The peak in the zinc region in the sediment spectra is probably due to Compton scatter.

Luidia foliolata, feeds predominately on this genus of brittle stars in this area (Carey, unpublished data). In this case the predaceous animal has less radiozinc per unit weight than the deposit-feeding forms, but our previous work has shown that among closely related animals, the predator has a higher concentration of $^{65}Zn$ than the deposit-feeder living on the organic material in the sediment [12].

Variations between the Organisms and their Environment

Off central Oregon we have found the amount of man-made radionuclides to be very low in water and sediment, the abiotic environment of the animals. The radionuclides may be too low to measure, but readily detected in organisms from the same place collected at the same time. Osterberg [22] has noted there is little similarity between the gamma-ray spectra of the benthic invertebrates and those of the sediments in, or on, which they are living.

## DISCUSSION

The distribution in the fauna of fission products, e.g. $^{95}Zr$-$^{95}Nb$ and neutron induced radionuclides, e.g. $^{65}Zn$, are basically different through time and space. Radiozinc varies both geographically and bathymetrically with time and is found in significant concentrations thoughout the trophic structure of the pelagic and bottom faunal assemblages. Fallout radionuclides, on the other hand, were found in greatly reduced amounts in carnivores, and were widely distributed geographically in all fauna and with depth in the benthos.

The contrasting distributions of $^{65}Zn$ and $^{95}Zr$-$^{95}Nb$ in space, time, and organisms can be explained by biological and physical means. Zinc, being a biologically important element [23], is concentrated by the biota in surface waters, and radiozinc off Oregon and Washington is primarily associated with a point source, the surface-located Columbia River plume. The extensive seasonal position shift of the $^{65}Zn$-rich plume waters explains many of the seasonal phenomena described. Furthermore, $^{65}Zn$ has a long biological half-life and is, therefore, retained for relatively long periods of time by the fauna. Zirconium, on the other hand, is not important to biological functions [24] and is not retained by the organisms for any significant period of time. Also, fallout is more or less uniform over the area that we have studied. Though $^{95}Zr$-$^{95}Nb$ concentrations in pelagic animals may be higher in the surface waters, they do seem to pass through the pelagic food chain fairly quickly and thus can be found in about the same concentrations in both shallow and deep benthonic invertebrates.

Radioecological studies in another marine environment with a continuously controlled radioactive discharge from a point source have been reported by Mauchline, Taylor, and Ritson [25] and Mauchline and Taylor [26]. The liquid effluent from the Windscale Works of the United Kingdom Atomic Energy Agency is discharged from a pipeline 2.5 km offshore. In contrast to the radionuclides from the Hanford reactors, those produced at Windscale are primarily fission products. The distribution and concentration of these radioactive elements have been studied in a population of the carnivorous thornback ray (Raia clavata) and beach organisms in the vicinity of the effluent. The guts and gut contents of the rays were generally much more radioactive than the internal organs and tissues. Fission radionuclides were not accumulated in the rays to any great extent. There appeared to be a correlation of radioisotope concentration in the intertidal environment with position in the food chain; animals in higher trophic levels had smaller concentrations of radionuclides. Although the physiology of different taxonomic groups may have more effect than feeding relationships [25] [27], these results are similar to those found for pelagic organisms off the Oregon coast.

Lowman [28] has pointed out that there are many biological factors affecting the uptake of radioisotopes in marine organisms. Feeding habits are just one. The degree to which an isotope is taken up by an animal also depends on the amount of stable isotope present, and on other biological factors.

Further research is necessary to understand fully the cycling of elements in the marine ecosystem in the northeast Pacific Ocean off Oregon. Measurement of stable elements in the organisms will hopefully give us a truer picture of the rates and routes of the cycling of these elements through the food web.

## SUMMARY AND CONCLUSIONS

1- $^{65}$Zn is found in all groups of animals in the pelagic and benthic environments, in higher concentrations in some animal groups than others. The highest levels measured, however, are still very much below hazard levels.

2- Highest concentrations of $^{65}$Zn in the fauna usually were found near the Columbia River, a point source. However, pelagic organisms further to the south showed high concentrations during the summer.

3- Bathymetric, seasonal and diurnal effects on the distributions of radionuclides in the biota are interconnected, particularly in the macroplankton and nekton. $^{65}$Zn stratified in the pelagic organisms in the summer, was uniformily distributed with depth in the winter. $^{65}$Zn concentrations were higher in the macroplankton and nekton in surface waters at night. $^{65}$Zn decreases with depth in the benthos.

4- $^{95}$Zr-$^{95}$Nb, ubiquitous in geographic distribution, were found at all depths, though in the pelagic fauna they were in higher concentration in surface waters.

5- $^{65}$Zn was found throughout the food chain, while $^{95}$Zr-$^{95}$Nb decreased rapidly after the first two trophic levels.

6- Man-made radionuclides, in very low concentrations in water and sediments of the marine environment off central Oregon, are readily detected in the fauna. Organisms are important determiners for the distribution and concentration of radionuclides in the marine ecosystem.

## REFERENCES

[1] U.S. ATOMIC ENERGY COMMISSION. Evaluation of radiological conditions in the vicinity of Hanford 1960. Rep HW-68435 (1961).

[2] U.S. ATOMIC ENERGY COMMISSION. Evaluation of radiological conditions in the vicinity of Hanford for 1961. Rep HW-71999 (1962).

[3] U.S. ATOMIC ENERGY COMMISSION. Evaluation of radiological conditions in the vicinity of Hanford for 1962. Rep HW-76526 (1963).

[4] U.S. ATOMIC ENERGY COMMISSION. Evaluation of radiological conditions in the vicinity of Hanford for 1963. Rep HW-80991 (1964).

[5] ANDERSON, G. C., BANSE, K., BARNES, C. A., COACHMAN, L. K., CREAGER, J. S., GROSS, M. G., McMANUS, D. A. Columbia River effects in the northeast Pacific. Department of Oceanography, Univer. Washington. Ref M62-5 (1962).

[6] DUXBURY, A. C. The union of the Columbia River and the Pacific Ocean - general features. Ocean Science and Ocean Engineering (MTS-ASLO). 2 (1965) 914.

[7] OSTERBERG, C. L., PATTULLO, J., PEARCY, W. G. Zinc-65 in euphausiids as related to the Columbia River water off the Oregon coast. Limnol. Oceanog. 9 2 (1964) 249.

[8] OSTERBERG, C. L., PEARCY, W. G., CURL, H. C., Jr. Radioactivity and its relationship to oceanic food chains. J. Mar. Res. 22 1 (1964) 2.

[9] PEARCY, W. G., OSTERBERG, C. L. Vertical distribution of radionuclides as measured in oceanic animals. Nature 204 4957 (1964) 440.

[10] LEWIS, G. B., SEYMOUR, A. H. Distribution of zinc-65 in plankton from offshore waters of Washington and Oregon, 1961-1963. Ocean Science and Ocean Engineering (MTS-ASLO). 2 (1965) 956.

[11] GROSS, M. G., BARNES, C. A., RIEL, G. K. Radioactivity of the Columbia River effluent. Science 149 3688 (1965) 1088.

[12] OSTERBERG, C., KULM, L. D., BYRNE, J. V. Gamma emitters in marine sediments near the Columbia River. Science 139 3558 (1963) 916.

[13] OSTERBERG, C., CAREY, A. G., Jr., CURL, H., Jr. Acceleration of sinking rates of radionuclides in the ocean. Nature 200 4913 (1963) 1276.

[14] CAREY, A. G., Jr., OSTERBERG, C. L., Occurence and activity of radioisotopes in marine benthos off Oregon. (in preparation).

[15] JENNINGS, D., OSTERBERG, C. L. Radioactivity: detection of gamma-ray emission in sediments in situ. Science 148 3672 (1965) 948.

[16] OSTERBERG, C. $Zn^{65}$ content of salps and euphausiids. Limnol. Oceanog. 7 4 (1962) 478.

[17] OSTERBERG, C. Fallout radionuclides in euphausiids. Science 138 3539 (1962) 529.

[18] PEARCY, W. G. Depth, daily, and seasonal variations in the biomass and zinc-65 in midwater animals off Oregon. (in preparation).

[19] PERKINS, R., NIELSEN, J., THOMAS, C. Air concentrations of twelve radionuclides from 1962 through mid-1964. Science 146 3645 (1964) 762.

[20] HYMAN, L. H. The Invertebrates: Echinodermata. McGraw-Hill, New York (1955).

[21] FELL, H. B. The fauna of the Ross Sea, Part 1. Ophiuroidea. N. Z. Dept. Sci and Industr Res Bull 142., N. Z. Ocean. Inst. Mem. No. 18 (1961).

[22] OSTERBERG, C. Radioactivity from the Columbia River. Ocean Science and Ocean Engineering (ASLO-MTS). Vol 2 (1965) 968.

[23] RICE, T. R. "Review of zinc in ecology," Radioecology , (Schultz, V., Klement, A. W., Jr., Eds.) Reinhold, New York (1963).

[24] HELD, E. E. " Some aspects of the biology of Zirconium-95. " Radioecology. (Schultz, B., Klement, A. W., Jr., Eds.) Reinhold, New York (1963).

[25] MAUCHLINE, J., TAYLOR, A. M. RITSON, E. B. The radioecology of a beach. Limnol. Oceanog. 9 2 (1964) 187.

[26] MAUCHLINE, J., TAYLOR, A. M. The accumulation of radionuclides by the thornbark ray, Raia clavata L., in the Irish Sea. Limnol. Oceanog. 9 3 (1964) 303.

[27] MAUCHLINE, J., TEMPLETON, W. L. "Artificial and natural radioisotopes in the marine environment." Oceanog. Mar. Biol. Ann. Rev., (BARNES, H., Ed.) George Allen and Unwin, London (1964).

[28] LOWMAN, F. Marine biological investigations at the Eniwetok test site. Proc. Conf. on Disposal of Radioactive Wastes, Vienna 2 (1959) 106.

# ARTIFICIAL RADIONUCLIDES IN MARINE ORGANISMS IN THE NORTHEAST PACIFIC OCEAN OFF OREGON, U.S.A. *

Charles L. Osterberg, Andrew G. Carey, Jr., and William G. Pearcy

## ABSTRACT

Marine organisms modify the distribution of radioisotopes in the oceanic ecosystem by concentration of elements and by their movements and migrations. Induced radionuclides, e. g. zinc-65, from the cooling waters of the Hanford (Washington) reactors and fission products from atmospheric testing have been detected in animals in the northeast Pacific Ocean as far as 490 km off the coast of central Oregon and to depths of 2860 m. Zinc-65, detected in every species analyzed, is associated with the surface-lying Columbia River plume and is an active element in biological systems. Geographic, seasonal, and bathymetric variations in the concentrations of radionuclides have been found in both the nektonic and benthonic animals off Oregon.

Radiozinc levels in the benthos decreased with distance from the mouth of the Columbia River. At times similar trends were found in pelagic animals.

Seasonal maxima of $Zn^{65}$ concentration were apparent in the fauna due to the seasonal shifts in the position of the Columbia River plume. During the winter, $Zn^{65}$ concentration was fairly uniform in midwater trawl samples from the surface to 1000 m, but during the summer it was much higher in near-surface than in deep-water animals. Zinc-65 in the benthos also varied seasonally on the continental shelf due to both the shifting plume and reproductive cycles within the animals. Beyond the shelf $Zn^{65}$ levels were low, and seasonal variations were not apparent.

Before cessation of atmospheric testing, we detected zirconium-95-niobium-95 in the fauna from all depths. Amounts of these relatively short-lived radionuclides were much higher than expected in the benthic fauna from the deeper stations (2800 m).

The position of the fauna in the food chain affects the concentration of radionuclides. Particulate fission isotopes were prominent only in the spectra of the herbivores or detritus and sediment feeders. The carnivorous benthos contained higher amounts of zinc-65 than the sediment-eating forms.

Artificial radioisotopes are difficult to measure in the water and sediment off central Oregon, although they are readily measurable in the fauna. The organisms, then, are important in determining the distribution and concentration of artificial radionuclides in the marine environment.

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* This paper was presented by Dr. Charles L. Osterberg at the Second International Oceanographic Congress in Moscow, U.S.S.R., on June 1966, and appears as paper 320 on pages 275-276 in the Abstract of Papers.

# STUDIES ON THE ECOLOGY OF BENTHIC INVERTEBRATE FAUNA IN THE NORTHEAST PACIFIC OCEAN OFF OREGON, U.S.A. *

by Andrew G. Carey, Jr.

## ABSTRACT

The distribution, abundance, and ecology of the large and small marine benthic macrofauna off Oregon have been studied. A line of stations across the continental shelf, continental slope, and Cascadia Abyssal Plain has been sampled repeatedly during the past 3-1/2 years with trawl, dredge, and grab to a depth of 3000 meters and a distance of 322 kilometers offshore. The fauna shows a layered distribution, many species being limited to a narrow depth range. Six depth zones exhibit transitions from one animal assemblage to another. These transitional areas are generally associated with changes in sediment type, one of the complex of environmental factors affecting distributions. The benthic invertebrates are most abundant beyond the edge of the shelf at 225 meters; a slightly smaller peak in abundance occurs inshore at 25 meters. The abundance on the slope, though quite variable because of irreuular topography and non-uniform sediment distribution, generally decreases with increasing depth. On the abyssal plain at 2800 meters depth, the faunal density decreases with increasing distance from shore. Decreased primary production in surface waters and decreased transport from land probably account for this decrease. Animal abundance on the plain at the base of the slope (2860 m) is relatively high for the abyssal zone in the northeast Pacific. In general, the relative abundance of deposit feeders increases in the finer sediments containing organic material. Food habits and reproductive activity of echinoderms from the sublitoral, bathyal, and abyssal environments have been studied.

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* This paper has been accepted for presentation at the 11th Pacific Science Congress in Tokyo, Japan, August 22 - September 10, 1966. It will be presented in the Chemical and Biological Oceanography Division of the Oceanography Section (2).

# THE DISTRIBUTION AND BIOLOGY OF THE PELAGIC SHRIMP SERGESTES SIMILIS OFF THE OREGON COAST*

by Carl L. Forss and William G. Pearcy

## ABSTRACT

The offshore distribution of Sergestes similis was related to the depth of the water. Where the bottom depth was less than 200 m or greater than 2000 m, fewer shrimp were taken. The highest catches of S. similis were observed from July through February, lowest catches from February to July. In general, one-fourth of the total catch of S. similis consisted of adults and three-fourths consisted of juveniles. The proportion of adults to juveniles varied with both season and distance from shore. Growth rates, estimated from monthly length-frequency histograms, indicate accelerated growth during the spring and summer months and retarded growth during the fall and winter. Spawning appears to occur during the spring and lasts for three to four months.

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* Presented by Carl L. Forss of Walla Walla College at AAAS - ASLO meeting in Seattle on 14 June 1966.

# Chromium-51 as a Radioactive Tracer of Columbia River Water at Sea

Abstract. *The plume of the Columbia River was followed 350 kilometers to sea by measurement of its chromium-51 content. This radioactive tag, introduced into the river by nuclear reactors at Hanford, Washington, promises to provide a useful oceanographic tool for determining rates of transport and mixing, and for identifying plume waters in the presence of other sources of fresh water.*

The Columbia River is a major source of radioactivity, carrying some 25,000 curies per month from the Hanford, Washington, reactors to the sea (*1*). During the summer when vertical mixing is at a minimum, Columbia River water can be detected far from shore as a low salinity plume, floating on top of denser, saltier, sea water. Because of the large amount of water, levels of radioactivity in the river present no health hazard. In the plume, radioactivity is so low that it has become a challenge to those interested in its measurement.

Oceanographers have risen to the challenge because the radioactivity uniquely labels Columbia River water at sea, making it different from fresh water from nearby rivers or rainfall, a difference not detectable with the usual salinity measurements. Furthermore, radionuclides which move with the plume can provide information on the rates of water flow and vertical diffusion because of their known half-lives.

We succeeded in following the plume of the Columbia River from the mouth of the river, near Astoria, Oregon, to a point in the ocean southwest of Coos Bay, Oregon, some 350 km away, by measurements of its Cr$^{51}$ content. This study, carried out on the U.S.C.G. *Modoc* (26 June to 1 July 1965), did not thoroughly test the sensitivity of our technique, since Cr$^{51}$ was easily measurable in the spectrum of the sample from the collecting site most distant from the river's mouth (Fig. 1). Significantly, our data imply that mixing of radionuclides with ambient sea water can be a slow process. In the absence of losses by mixing, Cr$^{51}$ remaining in plume waters is sufficient for use as a radioactive tag and timing device.

In previous efforts, Osterberg *et al.* (*2*) attempted to relate the Zn$^{65}$ content of euphausiids (small shrimp-like animals) to the Columbia River plume. The euphausiids were taken with trawls from surface waters at a number of stations off Oregon over a period of 15 months. Plume location was defined by salinity measurements made simultaneously at each station. Although some correlations were apparent, it was realized that animals are essentially integrators and may not reflect the radioactivity of their immediate environment. These authors suggested that Cr$^{51}$ might be a better indicator of Columbia River waters, since, unlike Zn$^{65}$, it remains in solution and is not appreciably concentrated by the biota. Gross *et al.* (*3*) were able to measure Cr$^{51}$ directly in the water with an *in situ* $\gamma$-ray probe, but lack of sensitivity of the technique prevented detection beyond about 115 km from the mouth of the river. Chakravarti *et al.* (*4*) found Cr$^{51}$ and other radionuclides in samples taken near the mouth of the Columbia River. The exact locations of their sampling sites were not given. Curl *et al.* (*5*) found Cr$^{51}$ as far as 72 km from the mouth of the river on filters, through which surface sea water had been pumped. Since most of the chromium passes through the filters, their method had serious limitations. Our efforts to concentrate the Cr$^{51}$ in the filtrate on ion-exchange or chelating resins were largely unsuccessful. These experiments led, however, to the development, by Cronin and Osterberg, of a large volume chemical apparatus with which coprecipitation of trace metals from sea water could be carried out aboard ship.

Surface water samples (600 liters each) were pumped through 10.5-inch (26.7 cm) membrane filters (0.45 $\mu$ pore size) with glass-fiber prefilters (Gelman Instrument Co.) into tanks coated with an inert liner (Sherwin-Williams Kem Cati-Coat enamel). Stable isotopes (as chlorides) of the several radioelements known to be in the Columbia River were added as carriers, along with FeCl$_3$. After 30 minutes of stirring, the *p*H was raised to 9.5 by adding NH$_4$OH, forming a ferric hydroxide precipitate (*6*). A flocculating agent (Separan ND 10, Dow Chemical) was added, and, after 5 minutes of stirring, the mixture was allowed to settle. In 2 to 3 hours the precipitate was concentrated in the conical bottom of the tank. After the bulk of the water was siphoned off, precipitate and residual water were drained into 50-liter plastic bottles. By successive decantings, after appropriate settling periods, sample volumes were reduced to less than 8 liters each.

In the laboratory, precipitates were dissolved in hydrochloric acid and reduced to 800 ml by heating in a water bath. The 800-ml samples were placed in plastic bottles and analyzed on top of a 5 by 3 inch (12.5 by 7.5 cm) NaI(Tl) detector, coupled to a Nuclear Data 130 AT multichannel analyzer. Considerable speed of collection and processing is mandatory because of the short half-life (27.8 days) of Cr$^{51}$.

Results (Fig. 2) show that the plume of the Columbia River, as reflected by the Cr$^{51}$ in surface waters, moves to the southwest off the Oregon coast in late June. This general summertime position is well known to oceanographers and can be (and was) verified by salinity measurements. There is no question of the relation

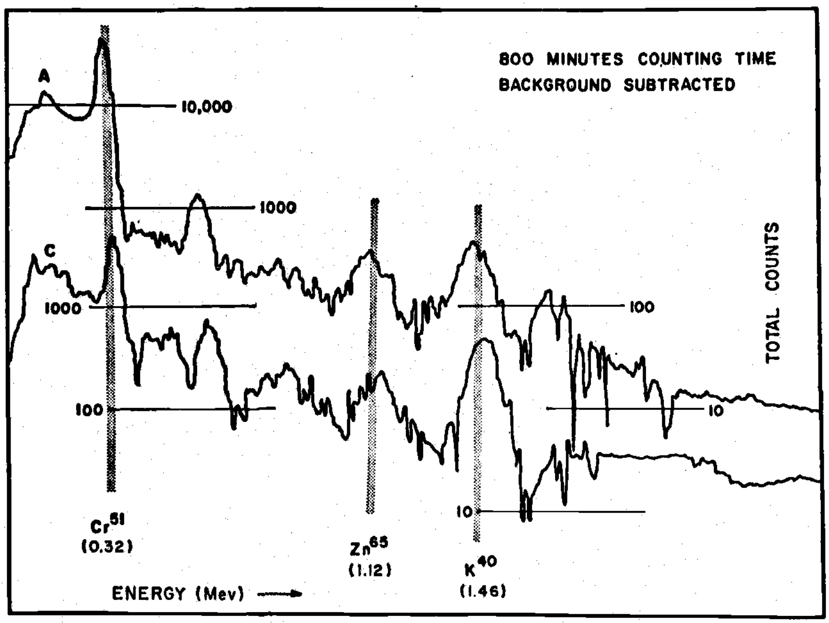

Fig. 1. Spectra of coprecipitates from sea water from the station with most Cr$^{51}$ activity (*A*), and from the station at greatest distance from the mouth of the Columbia River (*C*). Collection sites of the two surface-water samples are points *A* and *C*, respectively, on the map in Fig. 2.

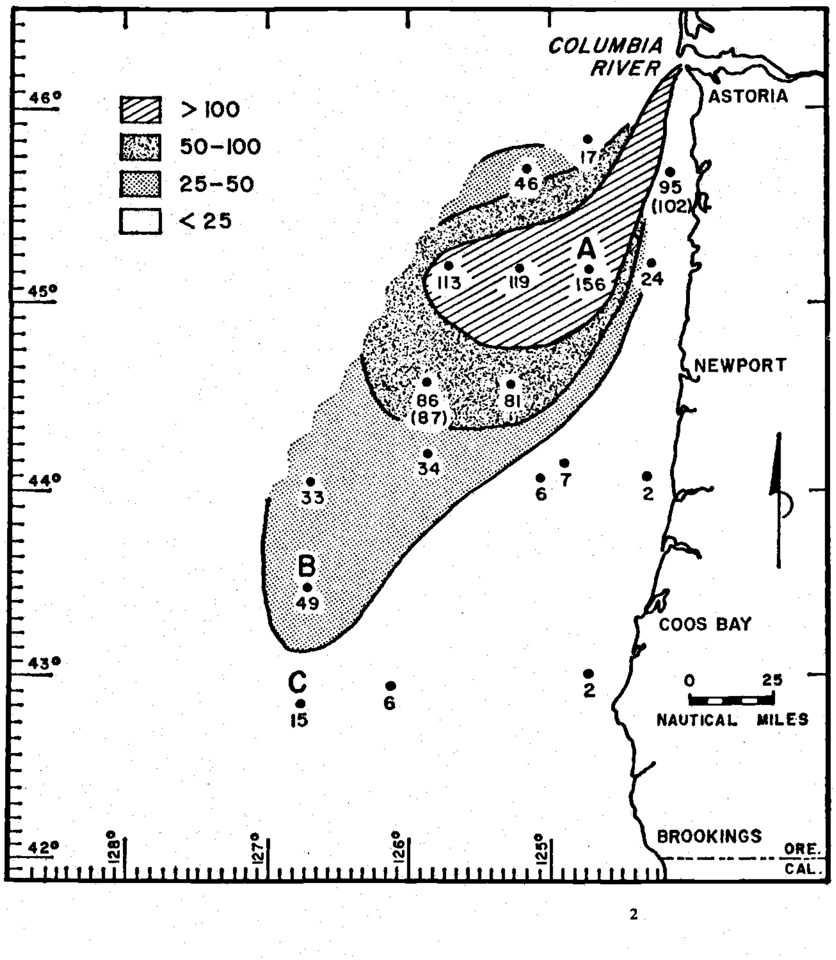

Fig. 2 (left). Chromium-51 (counts per minute per 100 liters of surface sea water), corrected to date of collection, 26 June to 1 July 1965. Parentheses indicate duplicate samples. The number of counts per minute per 100 liters can be converted to picocuries per liter by multiplying by 0.861. The greatest velocity of water movement was between points *A* and *B*.

of Cr$^{51}$ activity to the plume, since the Hanford reactors are the sole source of this radionuclide in the northeastern Pacific Ocean.

In order to use Cr$^{51}$ data to determine absolute transport rates, chromium must be conserved (that is, not lost to animals or sediments) in the plume waters. While some losses do occur, Cr$^{51}$ is probably the most conservative of the more abundant radionuclides in the Columbia River, since in the form present it is not appreciably concentrated by most oceanic animals. An allowance must also be made for "dilution" of the plume as the distance from the river's mouth increases, although, in this case, fresh water is being diluted with sea water. This is done by correcting the Cr$^{51}$ activity of each 600-liter sample for the amount of sea water present in it, based on salinity measurements. When the correction is made, we find that the maximum rate of plume movement, based on loss of Cr$^{51}$ by radioactive decay, is 11.4 km per day (*7*). This is a minimum speed, since Cr$^{51}$ losses other than to radioactive decay would decrease the apparent rate of flow. Likewise, addition of fresh water from any other source, though not likely in summer, would decrease the apparent rate.

The value thus determined agrees well with those based on physical measurements but is faster than the apparent southward movement derived from measurements of Zn$^{65}$ in euphausiids (*2*). This difference was expected since Zn$^{65}$ is biologically active and subject to losses other than radioactive decay; that is, Zn$^{65}$ does not remain in solution in the plume to the same extent that Cr$^{51}$ does.

Techniques for following the Columbia River plume at sea based on measurements of Cr$^{51}$ have their greatest potential during the winter months. Then, Columbia River flow is at a minimum, and the salinity pattern is confused. A seasonal change in prevailing winds drives the reduced plume northward and shoreward off Washington where it quickly loses its identity in the flood of fresh water from swollen coastal streams and winter rains. How far north the plume extends or how deep it mixes under these conditions have been problems beyond solution by the classical tools of oceanography (*8*). Radiochemical techniques should help resolve these uncertainties (*9*).

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**References and Notes**

1. This is the number usually reported by Hanford Laboratories, but some reduction should have occurred during the first 6 months of 1965, when phasing out of three of the eight reactors began.
2. C. Osterberg, J. Pattullo, W. Pearcy, *Limnol. Oceanog.* **2**, 249 (1964).
3. M. G. Gross, C. A. Barnes, G. K. Riel, *Science* **149**, 1088 (1965).
4. D. Chakravarti, G. B. Lewis, R. F. Palumbo, A. H. Seymour, *Nature* **203**, 571 (1964).
5. H. Curl, N. Cutshall, C. Osterberg, *Nature* **205**, 275 (1965).
6. The coprecipitation techniques used are well known to chemists. We checked our methods both in the laboratory and at sea to give maximum recovery of $Cr^{51}$, but yields for the other radioelements were not determined.
7. The estimate of speed depends on a constant rate of delivery of $Cr^{51}$ to the ocean. Probably changes in reactor output occur, but hopefully they are minimized by mixing in the river and in the three lakes through which the $Cr^{51}$ must pass on its 530-km trip to the sea.
8. K. Park, in our laboratory, has a paper in press, *Limnol.* and *Oceanog.*, in which specific alkalinity is used to identify Columbia River water at sea.
9. Supported by AEC contract AT(45-1)1750 and PHS training grant 1T1-WP-59-01. We thank the U.S. Coast Guard for making the *Modoc* available to us and L. Frederick and W. Vermeere for assistance with the sampling program.

23 September 1965

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# Chromium-51 in Sea Water: Chemistry

Abstract. *Chromium-51 introduced into the Pacific Ocean from the Columbia River remains in the hexavalent state. Analysis of this radionuclide in sea water by hydroxide coprecipitation with iron is best accomplished if the chromium-51 is first reduced to the trivalent state.*

Chromium-51 is one of the most abundant radionuclides in effluent coolant waters from nuclear reactors at Hanford, Washington. Because the chemistry of chromium in terrestrial waters is not well known, it is not a simple matter to predict the distribution of $Cr^{51}$ among solution, sediment, and biota. We now present data concerning the chemical form of $Cr^{51}$ in sea water and on the analysis of $Cr^{51}$ in sea water by coprecipitation with ferric hydroxide.

To precipitate certain radioactive trace elements, stable isotopes of the elements in question are usually added as carriers (*1*). Early efforts to recover radionuclides, produced at Hanford, from sea water samples taken off Oregon made use of carrier techniques (*2*). That is, $ZnCl_2$, $CrCl_3$, $CoCl_2$, and $MnCl_2$ were added to samples to assure recovery of $Zn^{65}$, $Cr^{51}$, $Co^{60}$, and $Mn^{54}$ neutron-induced radionuclides known to be present in the Hanford effluent. The metals were removed from sea water by coprecipitation as hydroxides.

We used a similar process in our first tests of Oregon coastal waters, except that we used ferric hydroxide as a bulk precipitate and added lesser amounts of carrier Cr(III), Zn(II), and Mn(II). Gamma-ray analyses of precipitates thus obtained from 560 liters of sea water collected off Newport, Oregon, indicate the possible presence of $Sb^{124}$ for which no carrier was added (Fig. 1, dotted line). In an effort to obtain maximum recovery of this radionuclide, we processed a duplicate sample using the same carriers with the addition of $SbCl_3$. Although no great increase in $Sb^{124}$ recovery occurred, there was a striking gain in yield of $Cr^{51}$ (Fig. 1, solid line). This phenomenon prompted a close examination of the chemistry of $Cr^{51}$ in sea water and the precipitation process itself.

Only the valence states Cr(III) and Cr(VI) need be considered for chromium in surface waters since Cr(II) is unstable in aerated aqueous solution. Chromium from the reactor is introduced to the Columbia River as a hexavalent anion, $Cr_2O_7^{2-}$. At the *p*H of river water and in the concentration at which chromium appears, this ion should dissociate to yield $CrO_4^{2-}$. Nelson (*3*) found that most of the $Cr^{51}$ in the river remains in solution as an anion, presumably $CrO_4^{2-}$. Krauskopf (*4*) calculated that $CrO_4^{2-}$ is thermodynamically stable in open ocean water and showed that it is not appreciably removed from sea water by most common mineral surfaces or by plankton.

Trivalent chromium would probably be $Cr(OH)_2^+$ if in solution, or the hydrous oxide if in the solid phase. Nelson and Cutshall (*5*) concluded that any Cr(III) formed in the river is rapidly sorbed to sediment particles. Curl *et al.* (*6*) reported rapid sorption of Cr(III) to glass beads or plankton from sea water solutions. Johnson (*7*) found that particle-bound $Cr^{51}$ is not displaced by sea water. Thus, Cr(VI) that becomes reduced to Cr(III) is susceptible to sedimentation and is not likely to be found in filtered water samples. However, it seems likely that most of the $Cr^{51}$ entering the ocean in solution will remain in solution as $CrO_4^{2-}$ and, indeed, our ability to measure $Cr^{51}$ many kilometers from the river's mouth (*8*) reinforces this hypothesis.

At intermediate values of *p*H Cr(III) will coprecipitate with $Fe(OH)_3$, whereas Cr(VI) will not. Instead, Cr(VI) may be adsorbed and occluded, especially at *p*H values at which ferric hydroxide has a positive zeta-potential (*p*H < 8.3).

Chromium(III) carrier should not affect the recovery of Cr(VI). On the other hand, Cr(VI) should act as a "hold-back" carrier, and its addition should diminish the yield. If, however, the Cr(VI) is reduced to Cr(III), coprecipitation should be efficient. It seemed probable that the addition of Sb(III) carrier had unexpectedly caused this reduction, the yield thus being enhanced.

The following experiments were designed to resolve this point. In the laboratory $Cr^{51}$ spikes, as Cr(III), were added to filtered sea water, and the yields checked with and without carriers. This was repeated for $Cr^{51}$ as Cr(VI), plus additional tests with Sb(III) and Sn(II) as reducing agents. Results (Table 1) show that recovery of Cr(III) by coprecipitation with $Fe(OH)_3$ was essentially complete, whether carrier was added or not. In the case of Cr(VI), recovery was incomplete and results were erratic when no carrier or Cr(III) carrier was used. Carrier Cr(VI) consistently reduced the yield. However, either reducing agent was effective in giving complete recovery.

Table 1. Recovery of $Cr^{51}$ spikes by $Fe(OH)_3$ precipitates in the laboratory (percent).

| Carrier added | | | Reducing agent added |
|---|---|---|---|
| None | Cr(III) | Cr(VI) | |
| | *Chromium(III)* | | |
| 98.3 | 99.1 | 98.1 | |
| 98.3 | 95.2 | 99.1 | |
| | *Chromium(VI)* | | |
| 72.4 | 38.4 | 1.9 | 99.5 [Sb(III)] |
| 27.3 | 15.9 | 2.2 | 99.6 [Sn(II) ] |

Table 2. Chromium-51 recovered from sea water samples by $Fe(OH)_3$ precipitates (pc/liter). All locations were 44°39′N.

| Carrier added | | | Reducing agent added |
|---|---|---|---|
| None | Cr(III) | Cr(VI) | |
| | *June 1965; 125°12′W* | | |
| 13.4 | 24.7 | 4.7 | 53.3 [Sb(III)] |
| | 8.2 | | 59.1 [Sb(III)] |
| | *August 1965; 125°38′W* | | |
| 5.8 | 2.0 | | 9.2 [Sb(III)] |
| | | | 10.2 [Sn(II) ] |
| | *August 1965; 125°02′W* | | |
| | | 0.9 | 23.5 [Sb(III)] |

Similar results were obtained at sea with proportionately larger samples and precipitates (Table 2). Laboratory and shipboard precipitates were made with 45 mg of Fe(III) and 0.64 ml of 28 percent $NH_4OH$ per liter of solution. Similarly, carriers and reducing agents were added in the same proportion (5.3 mg of chloride salts or $K_2Cr_2O_7$ per liter) to the 250-ml laboratory tests and to the 560-liter shipboard samples. Aboard the U.S. Coast Guard cutter *Modoc*, in June, sampling was extended over an 18-hour period, during which time the ship drifted through waters of varying salinity. It was therefore necessary to rectify the counts to allow for the changing fraction of Columbia River water in our samples. All counts were corrected to a salinity of 29.2 per mil.

To obtain truly duplicate samples, the tests were repeated in August aboard the research vessel *Yaquina*. Levels of $Cr^{51}$ were much lower be-

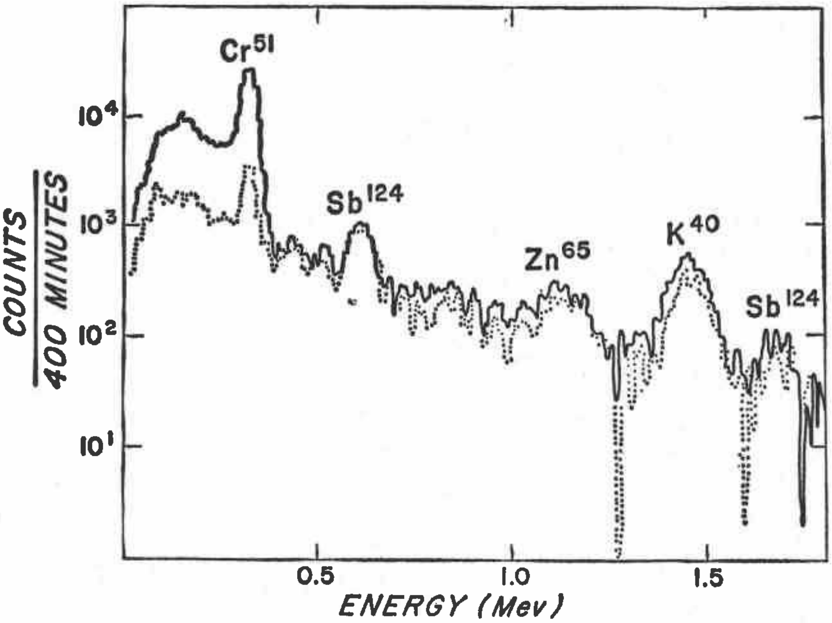

Fig. 1. Gamma-ray spectra of precipitates from 560-liter samples of sea water collected off Newport, Oregon, June 1965. Dotted line, Cr(III), Mn(II), and Zn(II) carrier were added; solid line, Sb(III), Cr(III), Mn(II), and Zn(II) were added. Enhancement of $Cr^{51}$ is attributed to reduction of Cr(VI) to Cr(III) by Sb(III). The 1.69-Mev photopeak for $Sb^{124}$ is not smooth because the counting rate is so low that random variations are seen.

cause the tongue of low-salinity water observed in June (*8*) had spread greatly and become saltier. Rectification of these data was not required, since salinity values did not vary during the tests.

In every case maximum yield of $Cr^{51}$ from sea water occurred when a reducing agent was added prior to precipitation. We conclude that Hanford-induced $Cr^{51}$ remains principally in hexavalent form in the ocean. This conclusion is supported by the "hold-back" effect of Cr(VI) carrier. Since the $Cr^{51}$ that we measure off Newport has been in contact with sea water for weeks or even months, we conclude that reduction of Cr(VI) to Cr(III) must occur only very slowly if at all. Any Cr(III) in the ocean or in the river would associate with particles and be lost to the sediments, while Cr(VI) would remain in solution. We have measured $Cr^{51}$ in filtered sea water up to 525 km from the mouth of the Columbia River, and the results indicate that losses due to reduction to Cr(III) are small.

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### References and Notes

1. G. Friedlander and J. Kennedy, *Nuclear and Radiochemistry* (Wiley, New York, 1955), pp. 115–19.
2. D. Chakravarti, G. Lewis, R. Palumbo, A. Seymour, *Nature* **203**, 571 (1964).
3. J. Nelson, *AEC Res. Develop. Rep.*, BNWL-36III, 122 pp. (1965), mimeograph.
4. K. Krauskopf, *Econ. Geol.* 50th Anniversary Volume 411 (1955); *Geochim. Cosmochim. Acta* **9**, 1 (1956).
5. J. Nelson and N. Cutshall, *AEC Res. Develop. Rep.* BNWL-36III, 122 pp. (1965), mimeograph.
6. H. Curl, N. Cutshall, C. Osterberg, *Nature* **205**, 275 (1965).
7. V. Johnson, in *Ecological Studies of Radioactivity in the Columbia River Estuary and Adjacent Pacific Ocean*, C. Osterberg, Ed. (Oregon State Univ. Prog. Rep. 65–14, Corvallis, 1965), 255 pp., mimeographed.
8. C. Osterberg, N. Cutshall, J. Cronin, *Science* **150**, 1585 (1965).
9. Supported by contract AT(45-1)1750 with the AEC and by training grant 5T1-WP-59-02 from USPHS.

10 January 1966.

# 総 説

# Electrolytic Conductance of Sea Water and the Salinometer*

## (Part 1)

Kilho PARK** and Wayne V. BURT**

## 1. Introduction

The specific conductance of sea water is about a million times greater than that of pure water. Furthermore, at a given temperature, the conductance increases almost linearly with increasing salinity. Therefore, the conductance should be a simple and yet far more precise measure of salinity than the usual silver nitrate titration method.

Since 1956 there has been a rapid development of electrolytic conductivity techniques, so that today more determinations of salinity are done by conductometry than titration. For instance, at Oregon State University, all the salinity samples taken after December 31, 1961 have been analyzed conductometrically.

This review paper presents a short history of the development of the conductivity techniques, discusses the nature of the electrolytic conductance of sea water and gives a brief description and precision of the various conductometric salinometers presently used. Problems in the use of international standard sea water as conductometric standard, and biogeochemical factors affecting the conductance of sea water in the ocean are also discussed.

### Historical sketch

According to THOMAS *et al.* (1934), KARSTEN (1897) first suggested the measurement of electrical conductivity as a means for ascertaining the concentration of the salts in sea water. TORNÖE (1895) and KNUDSEN (1900) continued the work. However, since, presumably, the chemical technique was then superior to the conductometric technique, Knudsen's main effort was directed towards an elaborate modification of Mohr's titration. The Knudsen titration and his chlorinity-salinity-density table have been one of the basic tools of the oceanographer ever since.

RUPPIN (1907) determined the specific conductance of seven sea water samples at 0°, 15°, and 25°C. THURAS (1918) and van del POL (1918) repeated the measurements at 25°C. WEIBEL and THURAS (1918) worked on a conductivity recorder. RIVERS-MOORE (1918), showed that the conductance did not vary with frequency changes as high as 100,000 cycles.

The first shipboard conductivity salinometer was developed by WENNER *et al.* (1930). This meter featured a good thermostat, a number of similar glass cells in the constant temperature bath to hold samples and a standard sea water, and a medium frequency (a.c., 1,000 cycles per second) for the bridge circuit. The instrument had a precision of 0.02‰ S, which was comparable to the precision of Knudsen's titration method.

The best available conductance values for sea water are that of THOMAS *et al.* (1934) although POLLAK (1954) pointed out two probable sources of errors in their data. They measured the specific conductance of eight sea water samples in the chlorinity range 5.147 to 19.227‰ at 5°C intervals from 0° to 25°C inclusive. Thirteen additional determinations were made at 25°C in the chlorinity range 1.476 to 21.398‰. Their sea water samples came from the Pacific Ocean, the Gulf of Alaska, Puget Sound, the Indian

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Ocean and the Mediterranean Sea from depths of 0 to 2,000 meters.

BEIN *et al.* (1935) measured conductance as a function of temperature and salinity. Their objective was to compare direct density measurements with values computed from various parameters including conductance. Their data are tabulated by DIETRICH (1963, p 83).

GHEORGHIU and CALINICENCO (1940) studied the temperature dependency of the sea water conductance at varying chlorinities. However, from Weyl's (1964) critical reexamination of the temperature dependency, it is clear that their data do not compare in precision with those of THOMAS *et al.* (1934).

A continuous salinity-temperature-depth recorder was developed by JACOBSON (1948). The instrument measures temperature over the range from 28° to 90°F and specific electrical conductance from 0.00 to 0.07 $ohm^{-1}\ cm^{-1}$, from which salinity is computed. Electrical conductance is measured with a tubular cell through which the sea water passes. The cell forms one branch of a Wheatstone bridge, and the circuit is retained in balance by an amplifier and a servomotor. The instrument has been used to a depth of about 400m (1,200 ft.) for inshore surveys in shoal water and in ocean areas where its precision of 0.2°F and 0.3‰ S are adequate.

FORD (1949) tested applications and operating characteristics of the Jacobson's instrument in estuaries and in the Gulf Stream. Between chemical analyses and the instrumental measurements of salinities, he found systematic errors of +0.13 to −0.48‰ and an inherent error spread of +0.21 to −0.27‰. Ideally, the systematic error may be reduced to zero but the inherent error is the real uncertainty in the instrument's ability.

HAMON (1955) has published preliminary notes on a temperature-salinity-depth recorder. His instrument gives a precision of 0.1°C for temperature and 0.05‰ for salinity. It can be lowered to a depth of 1,000 meters.

COX (1955) reviewed the works on the measurement of salinity by electrical means. He covered the works of JACOBSON (1948), FORD (1949) and MILLER (1954) on Jacobson's continuous temperature-salinity-depth recorder, of DORRESTEIN (1954) on the improvement of the continuous-recording instrument, and the radio-frequency instruments, about 10 Mc/s, of MCCOURT (1953) and HARWELL (1954ab).

SIEDLER (1963) briefly reviewed three methods of measuring conductance: (1) the electrode, (2) the capacitive, and (3) the inductive methods. The three methods differ in the manner in which the solution is coupled to the measuring circuit.

The electrode method was the most common procedure in early ***in situ*** applications (JACOBSON, 1948; DORRESTEIN, 1954; HAMON, 1955; ESTERSON and PRITCHARD, 1955, SCHIEMER and PRITCHARD, 1957 and others). The advantage of this method is that conductance is directly transformed into measurable resistance. A disadvantage is that electrodes are contaminated by sea water. The second method, capacity coupling with high frequency, eliminates the contamination of electrodes by sea water (HARWELL, 1954ab; HUEBNER, 1959) and gives an accuracy of about 0.05‰ S, but it has been primarily a laboratory model.

The inductive method does not have metallic electrodes to be contaminated by sea water. This method has been used in the open sea for a longer period by many investigators (ESTERSON and PRITCHARD, 1955; ESTERSON, 1957; HINKELMANN, 1958; PRITCHARD, 1959; GERMAN, 1960; WILLIAMS, 1961; BROWN, 1963, and others). SIEDLER (1963) used an improved model of the Hinkelmann type instrument, and obtained excellent field data. Siedler's instrument records temperature and conductance continuously down to a depth of 2,000 meters within a short period with precisions of 0.02°C for temperature and $2\times10^{-5} ohm^{-1}cm^{-1}$ (about 0.04‰ salinity equivalent) in specific conductance. His pressure measurements have a precision equal to about one percent of the total depth range.

Serious work on the design of precision conductivity meters (salinometers) begun around 1955 at Woods Hole Oceanographic Institution (U.S.A.), University of Washington (U.S.A.), and the National Institute of Oceanography (Britain), South Africa and Australia.

Brief descriptions of these modern salinometers are given in a later section.

The highest precision of salinity measurement is needed in the computation of the density of water columns, and the calculation of geostrophic currents. Therefore, with the improvement of salinometers, the elucidation of the conductivity-density relationship has become very important. In addition, various methods of density determination should give agreeable results, so that correlation of data among different methods becomes feasible.

In order to understand the relationships among conductivity-chlorinity-salinity-density of sea water, the International Council for the Exploration of the Sea started a program to measure concurrently the conductivity, chlorinity, and density of representative samples collected from all the oceans at surface, intermediate and deep layers. The National Institute of Oceanography, under the direction of COX, analyzed these parameters (COX *et al.*, 1962). In addition, chemical analyses and measurements of refractive index are underway for the same samples. The NIO work was assisted financially by Office of Oceanography, UNESCO.

To further consider the problems involved in the conductivity-chlorinity-salinity-density relationships of sea water, a joint panel on the equation of state of sea water was appointed by ICES (International Council for the Exploration of the Sea), SCOR (Special Committee for Oceanographic Research), IAPO (International Association of Physical Oceanography) and UNESCO. The panel members are: G. DIETRICH (Germany), E. E. CARRITT (U.S.A.), R. A. COX (U.K.), N.P. FOFONOFF (Canada), F. HERMANN (Denmark), G. N. IVANOFF-FRANTZKEVICH (U.S.S.R.), and Y. MIYAKE (Japan).

The first panel meeting was held in Paris in May 1962. The recommendations drafted by the panel were summarized by COX (1963a):

(1) Salinity should be redefined in terms of density at 0°C ($\sigma_0$); the relationship being chosen to presserve, on the average, the present relationship between salinity and chlorinity.

(2) New tables should be computed relating salinity so defined to conductivity and refractive index.

(3) As soon as practicable, Copenhagen Standard Sea-Water should be certified in conductivity as well as chlorinity.

Cox's data comparing conductivity, chlorinity, and density for sea waters obtained from all the oceans at various depths (Figure 1) are illustrated in the First Report of Joint Panel on the Equation of State of Sea Water (UNESCO, 1962) (Figures 2, 3, 4). Figure 2 shows the conductivity-chlorinity relationship. Considerable scatter exists. Therefore, the estimation of one parameter from the other suffers substantially in its precision. For instance, for two waters of same conductivity

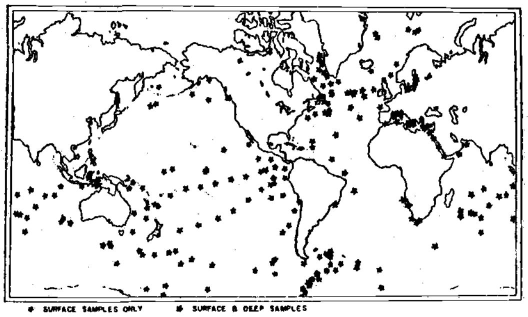

Fig. 1. Location of water sampling for the study of Conductivity-chlorinity-density relationship. (From UNESCO, 1962).

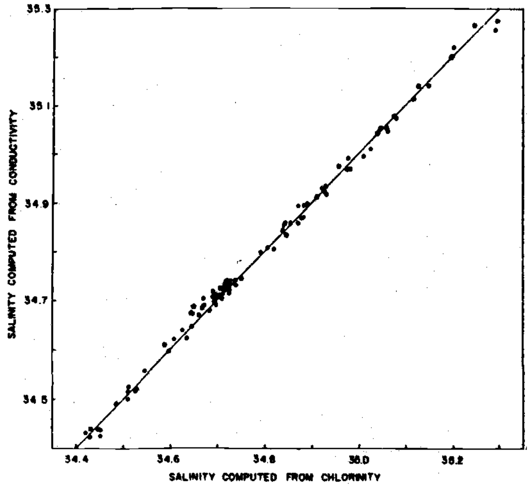

Fig. 2. Conductivity *vs.* chlorinity. (From UNESCO, 1962).

the chlorinity may vary by as much as 0.05‰. In addition, for waters of the same chlorinity, deep samples (below 1,000 m) tend to have a higher relative conductivity than shallow samples.

Figure 3 shows the chlorinity-density relationship. Scatter is as great as that shown in Figure 2. Two waters having the same density may differ as much as 0.025‰ Cl.

The conductivity-density relationship (Figure 4) shows much less scatter than the two previous relationships. The mean deviation from a fitted curve is about 0.005‰ in equivalent salinity. Samples showing large departure from the curve are a few deep samples and a few surface samples from high latitudes. For deep waters, the contribution of heavy water on the density cannot be ignored.

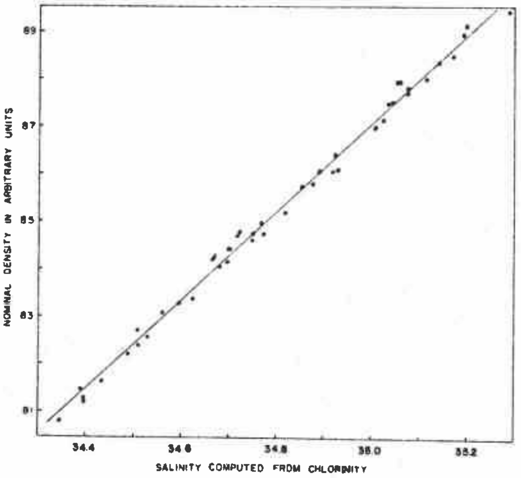

Fig. 3. Chlorinity *vs.* density. (From UNESCO, 1962).

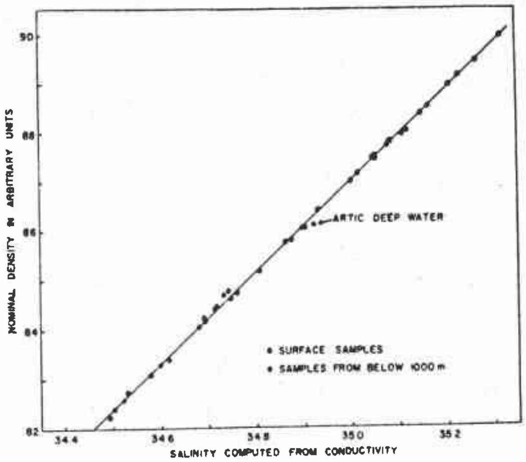

Fig. 4. Conductivity *vs.* density. (From UNESCO, 1962).

Cox's work (Figures 2, 3, 4) clearly shows that the use of the functional relationship between chlorinity and density ($\sigma_0$) as derived by KNUDSEN and tabulated in Knudsen's tables for the determination of density is much less sstisfactory than the use of the conductivity-density relationship. Measurement of electrolytic conductance of sea water provides a means of predicting the density of sea water more precisely than the chlorinity method.

The second meeting of joint panel on the equation of state of sea water was held at Berkeley, California (U.S.A.) in August, 1963. The panel reviewed the present knowledge of the equation of state of sea water, and in particular, of the properties of chlorinity, salinity, density, conductivity and refractive index, and the relationships among them (UNESCO, 1963). The panel considered the significance of work completed by Cox's laboratory (NIO) since the first report (UNESCO, 1962).

On the basis of variations in chemical compositon of sea water, the panel was able to explain the variation found in the conductivity/chlorinity ratio (Figure 2). For a variation of 0.04‰ salinity equivalent, the variations in sulfate/chlorinity among samples account for about 0.01‰, the dissolution of calcium carbonate in the deep-sea account for another 0.01‰, and the regional variations found in magnesium could account for the rest of the observed conductivity/chlorinity variations.

The panel further considered the redefinition of salinity making a conservative property, relating it to conductivity and density, and making it numerically as close as possible to the old salinity definition. Their restated recommendations pertinent to the conductivity problem included in UNESCO (1963):

(1) International standard sea water should be certified for its conductivity and chlorinity,

(2) The relationship between the conductivity at 15°C and the newly defined salinity from

the data of COX *et al.* (1962, and also given in UNESCO, 1962) should be established,

(3) The experimental determination of temperature and pressure effects on the conductance should be made, and

(4) Salinometers should be calibrated in terms of absolute conductance.

The third panel meeting was held in Paris in October, 1964. The panel was renamed as the "Joint ICES/IAPO/SCOR/UNESCO Panel of Experts on Oceanographic Tables and Standards." They considered the work needed for publication of new oceanographic tables and the certification of standard sea water. One of the most important new tables we expect the panel to prepare is undoubtedly that of conductivity-density.

## 2. Electrolytic conductance of sea water

### (1) General remarks

The specific conductance of sea water increases with increasing salinity, temperature and pressure. It is also a function of the nature and concentrations of the dissolved electrolytes in sea water.

Sea water is a complicated solution containing many ions, both simple and complex. Of these ions, $Na^+$, $Mg^{+2}$, $Ca^{+2}$, $K^+$, $Cl^-$, $SO_4^{-2}$, and $HCO_3^-$ together make up over 99% of the electrolytes. Each of these ions contributes to the overall conductance of sea water.

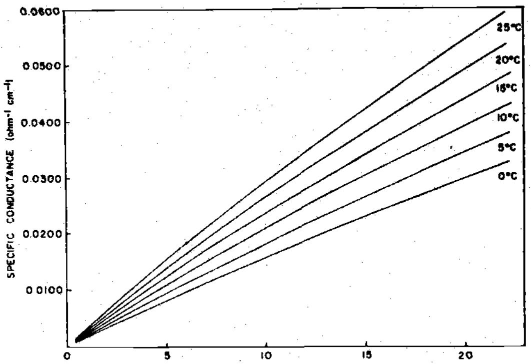

Fig. 5. Specific conductance of sea water at various temperatures and concentrations (From the data of THOMAS *et al.*, 1934).

Table 1. Errors involved in the conductance data of THOMAS *et al.* (1934) at high salinities, at temperatures other than 25°C (from COX, personal communication).

| Salinity ‰ | Error ‰ |
|---|---|
| 35.0 | 0.000 |
| 35.5 | 0.005 |
| 36.0 | 0.013 |
| 36.5 | 0.019 |
| 37.0 | 0.027 |
| 37.5 | 0.036 |
| 38.0 | 0.048 |
| 38.5 | 0.064 |
| 39.0 | 0.093 |

The fundamental date relating the specific conductance, temperatures and the chlorinity under one atmosphere were empirically determined by THOMAS *et al.* (1934) (Figure 5). However, POLLAK (1954) thought that the data of THOMAS *et al.* were inaccurate because (1) the value for the conductance of their reference KCl solution was slightly in error, and (2) the conductance cell they used was subject to slight systematic errors. Nevertheless, reexamination of the data by COX (1963 b and personal communication) shows that, in the range of 33 to 35‰ S, the data of THOMAS *et al.* are correct within the precision of Cox's measurements, and serious errors appear only at higher salinities. The results of THOMAS *et al.* at higher salinities were lower than the true values. The extent of the error is approximately 0.013‰ at salinity 36‰ to 0.093‰ at salinity 39‰ (Table 1).

Due to the errors at high salinites, the following interpolated equations derived by THOMAS *et al.* are applicable at chlorinities lower than 19.3% (the equation for 25°C is still applicable for higher salinities):

$$0^\circ\mathrm{C},\ L=1.7875\times10^{-3}(\mathrm{Cl}\ ‰)-2.9596\times10^{-5}(\mathrm{Cl}\ ‰)^2+1.127\times10^{-6}(\mathrm{Cl}\ ‰)^3-1.902\times10^{-8}(\mathrm{Cl}\ ‰)^4$$

$$5^\circ\mathrm{C},\ L=2.0818\times10^{-3}(\mathrm{Cl}\ ‰)-3.6859\times10^{-5}(\mathrm{Cl}\ ‰)^2+1.449\times10^{-6}(\mathrm{Cl}\ ‰)^3-2.520\times10^{-8}(\mathrm{Cl}\ ‰)^4$$

$$10^\circ\mathrm{C},\ L=2.3749\times10^{-3}(\mathrm{Cl}\ ‰)-4.1334\times10^{-5}(\mathrm{Cl}\ ‰)^2+1.554\times10^{-6}(\mathrm{Cl}\ ‰)^3-3.829\times10^{-8}(\mathrm{Cl}\ ‰)^4$$

$$15^\circ\mathrm{C},\ L=2.7009\times10^{-3}(\mathrm{Cl}\ ‰)-5.1390\times10^{-5}(\mathrm{Cl}\ ‰)^2+2.097\times10^{-6}(\mathrm{Cl}\ ‰)^3-3.829\times10^{-8}(\mathrm{Cl}\ ‰)^4$$

$$20^\circ\mathrm{C},\ L=3.0191\times10^{-3}(\mathrm{Cl}\ ‰)-5.6253\times10^{-5}(\mathrm{Cl}\ ‰)^2+2.181\times10^{-6}(\mathrm{Cl}\ ‰)^3-3.804\times10^{-8}(\mathrm{Cl}\ ‰)^4$$

$$25^\circ\mathrm{C},\ L=3.3524\times10^{-3}(\mathrm{Cl}\ ‰)-6.2481\times10^{-5}(\mathrm{Cl}\ ‰)^2+2.371\times10^{-6}(\mathrm{Cl}\ ‰)^3-4.049\times10^{-8}(\mathrm{Cl}\ ‰)^4$$

where $L$ denotes specific conductance of sea water in ohm$^{-1}$cm$^{-1}$.

For higher salinities at 15°C, COX (1963b) gives the following equation:

$$(\mathrm{S}\ ‰)=4356.6855-26{,}886.634\,(RL)+68{,}955.055\,(RL)^2-93{,}754.977\,(RL)^3+71{,}385.256\,(RL)^4-28{,}861.920\,(RL)^5+4841.533\,(RL)^6$$

where $(RL)$ denotes the ratio of the conductivity of sea water of salinity S to that of sea water of salinity 35 ‰ at 15°C. WEYL (1964) finds that at 25°C and in the chlorinity range from 17 to 20 ‰, the following expression fits the data of THOMAS *et al.* with high precision:

$$\log(L)=0.892\cdot\log(\mathrm{Cl}\ ‰)+0.057625\pm0.00005$$

Table 2 gives the specific conductance of sea water of THOMAS *et al.* at various temperatures and chlorinities.

### (2) Temperature dependency

The temperature coefficient of the electrical conductance of sea water varies considerably with temperature and slightly with chlorinity (Figure 6). At 0°C, the conductance of sea water increases by about 3 % per °C, while at 25°C, the increase is about 2 % per °C. At 15°C, the temperature coefficient is about 2.4 % for 1 ‰ Cl and 2.3 ‰ for 19 ‰ Cl. The chlorinity dependency of the temperature coefficient is great enough to affect the accuracy of salinometers if no compensation, or correction is made for the chlorinity dependency (COX, 1962).

WEYL (1964) critically reexamined the effect of temperature on the conductance of sea water. His comparison of the measurements of the conductance of sea water by THOMAS *et al.* (1934) and of NaCl solutions by BREMNER *et al.* (1939) shows that the temperature dependence of the two are essentially the same. He pointed out that the data of THOMAS *et al.* are consistent with those of GHEORGHIU and CALINICENCO (1940), but the conclusion of

Table 2. Specific conductance of sea water at various temperatures and chlorinities (from THOMAS *et al.* 1934). Specific conductances are in ohm$^{-1}$ cm$^{-1}$.

| Cl ‰ | 0°C | 5°C | 10°C | 15°C | 20°C | 25°C |
|---|---|---|---|---|---|---|
| 1 | .001839 | .002134 | .002439 | .002763 | .003091 | .003431 |
| 2 | .003556 | .004125 | .004714 | .005338 | .005971 | .006628 |
| 3 | .005187 | .006016 | .006872 | .007778 | .008702 | .009658 |
| 4 | .006758 | .007845 | .008985 | .010133 | .011337 | .012583 |
| 5 | .008327 | .009653 | .011019 | .012459 | .013939 | .015471 |
| 6 | .009878 | .011444 | .013063 | .014758 | .016512 | .018324 |
| 7 | .011404 | .013203 | .015069 | .017015 | .019035 | .021121 |
| 8 | .012905 | .014934 | .017042 | .019235 | .021514 | .023868 |
| 9 | .014388 | .016641 | .018986 | .021423 | .023957 | .026573 |
| 10 | .015852 | .018329 | .020906 | .023584 | .026367 | .029242 |
| 11 | .017304 | .020000 | .022804 | .025722 | .028749 | .031879 |
| 12 | .018741 | .021655 | .024684 | .027841 | .031109 | .034489 |
| 13 | .020167 | .023297 | .026548 | .029940 | .033447 | .037075 |
| 14 | .021585 | .024929 | .028397 | .032024 | .035765 | .039638 |
| 15 | .022993 | .026548 | .030231 | .034090 | .038065 | .042180 |
| 16 | .024393 | .028156 | .032050 | .036138 | .040345 | .044701 |
| 17 | .025783 | .029753 | .033855 | .038168 | .042606 | .047201 |
| 18 | .027162 | .031336 | .035644 | .040176 | .044844 | .049677 |
| 19 | .028530 | .032903 | .037415 | .042158 | .047058 | .052127 |
| 20 | — | — | — | — | — | .054551 |
| 21 | — | — | — | — | — | .056949 |
| 22 | — | — | — | — | — | .059321 |

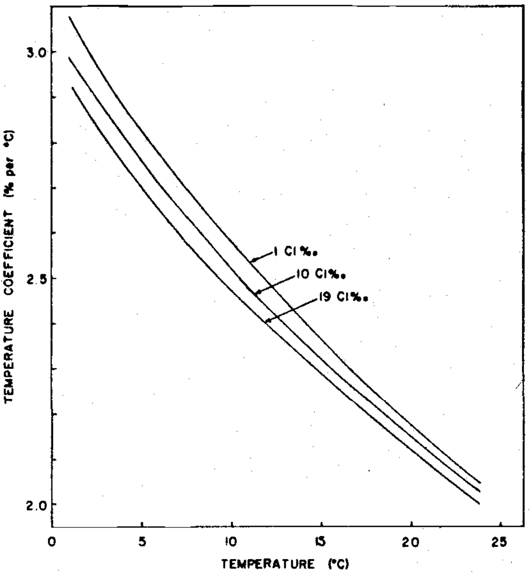

Fig. 6. Temperature coefficient of the electrical conductance of sea water as a function of temperature and chlorinity. (Plotted from the data of THOMAS *et al.*, 1934).

GHEORGHIU and CALINICENCO that the temperature coefficient of the conductance of sea water is measurably greater than that of NaCl solutions is in error.

WEYL (1964) derived a single empirical equation to express specific conductance in the chlorinity range 17‰ to 20‰ and the temperature range from 0° to 25°C. When $T=25\text{-}t$ (°C), then

$$\begin{aligned}\log(L)=&0.57627+0.892\log(\mathrm{Cl}\ ‰)\\&-10^{-4}T\ [88.3+0.55\,T+0.0107\,T^2\\&-(\mathrm{Cl}\ ‰)(0.145-0.002\,T+0.0002\,T^2)].\end{aligned}$$

Conductances calculated by the above equation differ from the measured data of THOMAS *et al.* (1934) by less than 0.1%.

### (3) **Pressure dependency**

There exists no sufficient data, as far as the authors are aware, on the effect of pressure on the electrical conductance of sea water. Earlier work was done by HAMON (1958) HORNE and FRYSINGER (1963). Albin BRADSHAW and K.E. SCHLEICHER (personal communication) of Woods Hole Oceanographic Institution are preparing a manuscript on this subject. Unpublished tentative results of BRADSHAW and SCHLEICHER were used by SIEDLER (1963) to evalute *in situ* salinometer measurements, and by BROWN (1963) to design an *in situ* salinity sensing system.

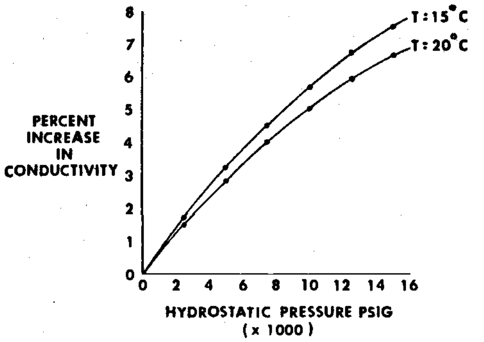

Fig. 7. Change of conductivity of sea water with pressure. (From unpublished of BRADSHAW and SCHLEICHER).

The effect of hydrostatic pressure on the conductance of sea water is considerable as shown in Figure 7 (unpublished data of BRADSHAW and SCHLEICHER, cited by BROWN, 1963). Also, the pressure effect is quite dependent on temperature as shown in Figure 8 (HAMON, 1958). The effect of pressure at 0°C is twice as great as at 30°C. Consequently, any pressure compensation must take the temperature into account.

HAMON (1958) measured the pressure coefficient of the conductance of sea water (19.7‰ Cl) at various temperatures. The coefficients vary from $1.50\times10^{-5}$ decibar$^{-1}$ at 0.5°C to 0.82

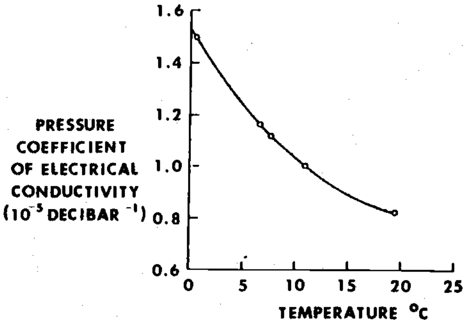

Fig. 8. Effect of temperature on pressure coefficient of electrical conductivity at 1,500 P.S.I.G. (From HAMON, 1958).

$\times 10^{-5}$ decibar$^{-1}$ at 19.5°C (Figure 8).

HORNE and FRYSINGER (1963) measured the conductance of three sea water samples, 9.68, 17.61 and 19.376‰ Cl, at 0°, 5°, 15°, and 25°C over the pressure range 1 to 1,380 bars. They proposed the following empirical equation to express the conductance in the temperature range of 0° to 25°C and chlorinity range of 9.68‰ to 19.38‰ over the pressure range of 1 to 689 bars:

$$L_p = L_1 + (0.35 \pm 0.25) + (0.18 \pm 0.028)\ (\mathrm{Cl}\ ‰) \times 10^{-6} p$$

where $L_p$ and $L_1$ are the specific conductance of sea water at pressures $p$ and 1 bars respectively, and $p$ the hydrostatic pressure in bars. Due to the uncertainty expressed within, the above equation is useful only for a first approximation of the conductance under high pressure.

As pressure is applied, sea water is compressed. Therefore, the concentration of charge-carrying species per unit volume will increase. In addition the ionization of weak electrolytes increases with increasing pressure (cited from HORNE and FRYSINGER, 1963). These facts may account for the increase in conductance with increasing pressure. Further experimental verification is needed, however, to explain the pressure effect on conductance.

### (4) **Electrolytes in sea water**

Practically no data exist on the relationship between conductance and the kinds and concentrations of the electrolytes present in sea water. As a first approximation PARK (1964b) measured the effect of 16 electrolytes on the conductance of sea water. The effect was measured by comparing the specific conductance before and after the addition of one of the electrolytes to sea water, 35‰ S, at 23°C.

Apparent inceases in salinity due to the addition of one gram of various reagents to one kilogram of 35.00‰ S sea water at 23°C as determined by an inductive salinometer, Hytech Model 621, are given in Table 3. The results from 35.22‰ for $KH_2PO_4$ to 36.06 for KCl, except for HCl and NaOH. The additions of KCl, NaCl, $MgCl_2$ and $CaCl_2$ gave results near the correct value of 35.96‰.

Table 3. Apparent increase in salinity due to the addition of one gram of various reagents to one kilogram of 35.00‰ S sea water at 23°C as determined by the inductive salinometer. Hytech Model 621 (from PARK and BURT, 1963).

| Reagent | Salinity (‰) | Difference of Salinity from 35.96 ‰ |
|---|---|---|
| KCl | 36.06 | 0.10 |
| NaCl | 36.04 | 0.08 |
| $MgCl_2$ | 36.02 | 0.06 |
| $CaCl_2$ | 35.96 | 0.00 |
| KBr | 35.69 | −0.27 |
| $SrCl_2$ | 35.68 | −0.28 |
| $K_2SO_4$ | 35.61 | −0.35 |
| $Na_2SO_4$ | 35.50 | −0.46 |
| $KHCO_3$ | 35.49 | −0.47 |
| $K_2CO_3$ | 35.48 | −0.48 |
| $NaHCO_3$ | 35.38 | −0.58 |
| $MgSO_4$ | 35.37 | −0.59 |
| $Na_2CO_3$ | 35.32 | −0.64 |
| $KH_2PO_4$ | 35.28 | −0.68 |
| NaOH | 35.22 | −0.74 |
| HCl | 40.8 | 4.8 |

PARK (1964b) assumed that the conductance of sea water could be expressed as the sum of the conductances of the ions, or electrolytes, in sea water. For each liter of sea water,

$$1000L = \sum_i C_i^+ \bar{\Lambda}_i^+ + \sum_i C_i^- \bar{\Lambda}_i^- = \sum_i C_i \bar{\Lambda}_i$$

where $C$ are concentrations in equivalant/liter and $\bar{\Lambda}^+$, $\bar{\Lambda}^-$ and $\bar{\Lambda}$ are the partial equivalent conductances of cation, anion, and electrolyte respectively. The partial equivalent conductance at a given volume, temperature, and pressure was defined by PARK as:

$$\bar{\Lambda}_i = 1000 \left. \frac{\partial L}{\partial C_i} \right|_{V,T,P.}$$

where $V$ denotes volume, $T$, temperature and $P$, pressure.

With this assumption and definition, PARK (1964b) estimated the partial equivalent conductances of electrolytes in sea water. He measured the change in the specific conductance of the sea water samples before and after the addition of a small amount of an electrolyte.

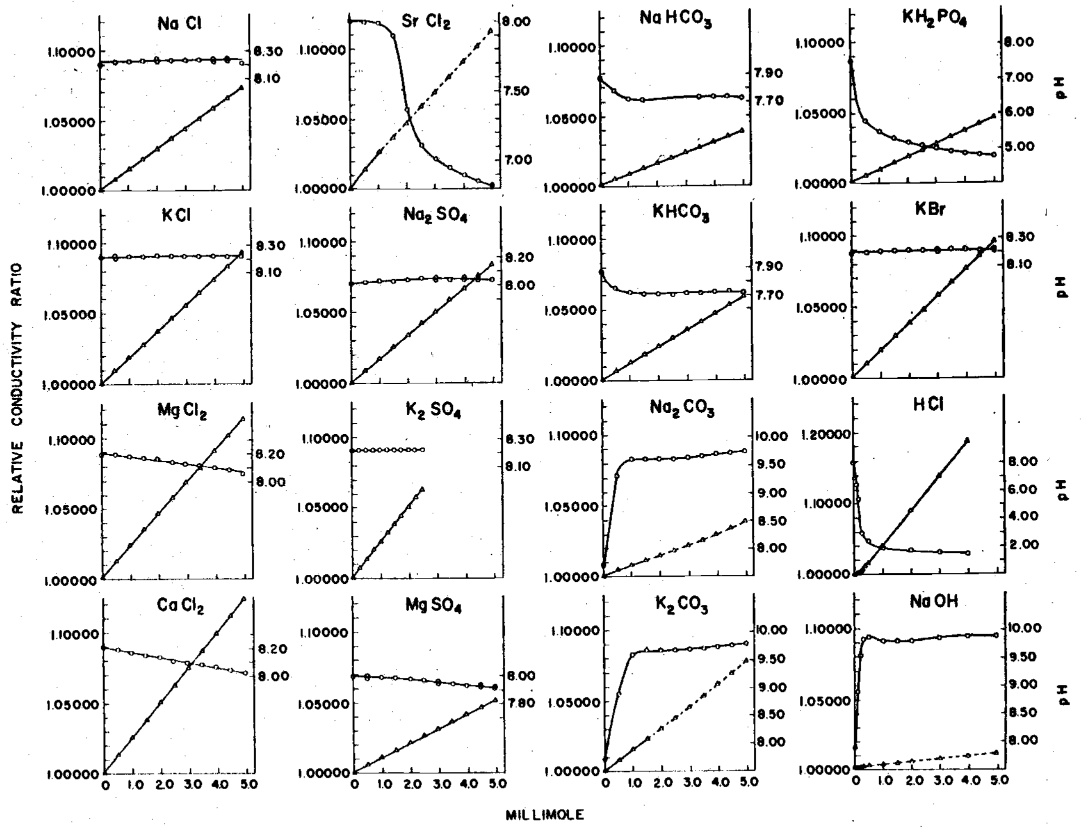

Fig. 9. Changes in relative conductivity ratio and pH *vs.* millimoles of reagents added to 100.00 m*l* sea water, 36.75 ‰, at 23°C. (Final vol. 105.00 m*l*). (From PARK, 1964b).

His calculation was based on the slope of the conductance increase (Figure 9) and on calibration of the inductive salinometer (relative conductivity ratio *vs.* salt content per liter of sea water, not *vs.* salinity). His results are listed in Table 4.

Recently, Peter K. WEYL of Oregon State University measured the partial equivalent conductances of electrolytes in sea water 25°C. His unpublished data indicate that Park's data are about 10% too high. He further showed that it is impossible to estimate the conductive contribution of dissolved ions to the overall conductance of sea water. He defined partial equivalent conductance of salt as follows:

$$\bar{\Lambda} \equiv \Lambda^{+} + \Lambda^{-} + \sum_i C_i\left(\frac{\partial \Lambda_i}{\partial C^{+}} + \frac{\partial \Lambda_i}{\partial C^{-}}\right)$$

where $\Lambda^{+}$ and $\Lambda^{-}$ are the ionic conductance of the cationic and anionic constituents of the salt, respectively, and $\frac{\partial \Lambda_i}{\partial C^{+}}$ and $\frac{\partial \Lambda_i}{\partial C^{-}}$ denote the effect of added cation or anion on the conductance of various components in sea water. Since it is not possible to measure $\sum_i C_i\left(\frac{\partial \Lambda_i}{\partial C^{+}} + \frac{\partial \Lambda_i}{\partial C^{-}}\right)$ at present, WEYL states that the measured conductance of salt cannot be resolved into ionic constituents.

However, Park's data satisfy his assumed additivity of the conductance of electrolytes in the estimation of the over conductance of sea water:

$$\begin{aligned} 1000L &= \sum_i C_i \bar{\Lambda}_i \\ &\doteq C_{(\mathrm{NaCl})}\bar{\Lambda}_{(\mathrm{NaCl})} + C_{(\mathrm{MgCl_2})}\bar{\Lambda}_{(\mathrm{MgCl_2})} \\ &\quad + C_{(\mathrm{Na_2SO_4})}\bar{\Lambda}_{(\mathrm{Na_2SO_4})} + C_{(\mathrm{CaCl_2})}\bar{\Lambda}_{(\mathrm{CaCl_2})} \\ &\quad + C_{(\mathrm{KCl})}\bar{\Lambda}_{(\mathrm{KCl})} + C_{(\mathrm{NaHCO_3})}\bar{\Lambda}_{(\mathrm{NaHCO_3})} \end{aligned}$$

Table 4. Partial equivalent conductance of electrolytes in sea water and limiting equivalent conductance of electrolytes in aqueous solutions ($ohm^{-1}\ cm^2$) (from PARK, 1964).

| Electrolyte | $\bar{\Lambda}$* | $\Lambda_0$** | $\bar{\Lambda}/\Lambda_0$*** |
|---|---|---|---|
| NaCl | 90 | 126.45 | 0.71 |
| KCl | 116 | 149.86 | 0.77 |
| KBr | 120 | 151.9 | 0.79 |
| $^1/_2$ $MgCl_2$ | 72 | 129.40 | 0.56 |
| $^1/_2$ $CaCl_2$ | 78 | 135.84 | 0.57 |
| $^1/_2$ $SrCl_2$ | 80 | 135.80 | 0.59 |
| $^1/_2$ $Na_2SO_4$ | 52 | 129.9 | 0.40 |
| $^1/_2$ $K_2SO_4$ | 78 | 153.5 | 0.51 |
| $^1/_2$ $MgSO_4$ | 34 | 133.1 | 0.26 |
| $NaHCO_3$ | 47 | 94.6 | 0.49 |
| $KHCO_3$ | 73 | 118.00 | 0.62 |
| $^1/_2$ $Na_2CO_3$ | 23 | | |
| $^1/_2$ $K_2CO_3$ | 49 | | |
| $KH_2PO_4$ | 57 | | |
| HCl | 310 | 426.16 | 0.73 |
| NaOH | | 247.8 | |

* Partial equivalent conductance in sea water at 35.00‰ and at 23°C.

** Limiting equivalent conductance of electrolytes in aqueous solution at 25°C. (From HARNED and OWEN, 1958. p 231 and p 697).

*** The 2°C increase in temperature, from 23°C to 25°C, corresponds to approx. 4% increase in the conductance. The ratios given here are not corrected from the temperature change.

$$+C_{(KBr)}\bar{\Lambda}_{(KBr)}+C_{(SrCl_2)}\bar{\Lambda}_{(SrCl_2)}$$
$$=51.4\ ohm^{-1}cm^2$$

The concentrations of the salts in equivalents per liter of sea water, 35.00‰ S, were based on the table for artificial sea water compiled by LYMAN and FLEMING (1940). The value of $51.4\ ohm^{-1}cm^2$ computed from the above relationship differs by about 1% from the original value of $50.96\ ohm^{-1}cm^2$ for $1000L$ (THOMAS *et al.* 1934). The apparent percentage contribution of various electrolytes and ions in sea water to its overall electrical conductance at 23°C are given in Tables 5 and 6 (PARK, 1964b). For the construction of Table 6, PARK (1964b) assumed that the cation transference number of KCl in sea water is 0.49.

It should be added here that changes in the conductance while sea water is titrated with HCl (Figure 9) was utilized by PARK *et al.* (1963) to develop a conductometric method of alkalinity determination.

Table 5. Percentage contribution of various electrolytes in sea water to its overall electrical conductance 23°C (from PARK, 1964b).

| Electrolyte | Equivalent/ liter* | Weight (%) | Conductivity (%) |
|---|---|---|---|
| NaCl | 0.4192 | 68.08 | 73 |
| $MgCl_2$ | 0.1092 | 14.45 | 15 |
| $Na_2SO_4$ | 0.0576 | 11.36 | 5.8 |
| $CaCl_2$ | 0.0207 | 3.20 | 3.1 |
| KCl | 0.0093 | 1.93 | 2.1 |
| $NaHCO_3$ | 0.0024 | 0.557 | 0.21 |
| KBr | 0.00084 | 0.278 | 0.19 |
| $H_3BO_3$ | 0.00044** | 0.075 | |
| $SrCl_2$ | 0.00032 | 0.070 | 0.05 |
| NaF | 0.00007 | 0.009 | |

* Calculated from the data of LYMAN and FLEMING (1940). Neglected on the calculation of the conductivity per cent.

** Considered $H_3BO_3 \rightleftarrows H^+ + H_2BO^-_3$ only.

Table 6. Percentage contribution of major ions in sea water to its overall electrical conductance at 35‰ and 23°C (from PARK, 1964b).

| Ion | Equivalent/liter* | Weight (%) | Conductance (%) |
|---|---|---|---|
| $Na^+$ | 0.483 | 30.7 | 29 |
| $Mg^{+2}$ | 0.109 | 3.7 | 2.7 |
| $Ca^{+2}$ | 0.021 | 1.2 | 0.77 |
| $K^+$ | 0.010 | 1.1 | 1.1 |
| $Sr^{+2}$ | 0.0001 | 0.0 | 0.004 |
| $Cl^-$ | 0.558 | 55.2 | 64 |
| $SO_4^{-2}$ | 0.057 | 7.7 | 2.3 |
| $HCO_3^-$ | 0.002 | 0.1 | 0.06 |
| $Br^-$ | 0.001 | 0.2 | 0.12 |

* From HARVEY (1960, p 4).

In summary, we emphasize that very little is understood about the fundamental electrochemical properties of ions dissolved in sea water. Each dissolved ion contributes to the conductance of sea water, but much more work is needed to ascertain each ionic role in the conductance of sea water.

## 3. Salinometers

Three types of salinometers have been

developed: the electrode, the inductive and the capacitive salinometers (See Introduction). At present, the electrode and the inductive salinometers are the most frequently used by oceanographers.

Since Roland A. COX of the National Institute of Oceanography (England) is summarizing the details and performances of various salinometers for publication elsewhere, we limit our discussion to the listing of the main features of the salinometers.

### (1) Electrode-type salinometer

COX (1963b) gives a brief and concise account of the development of the electrode-type salinometer. We excerpt mainly from his article.

The prototype of this instrument is that of WENNER, *et al.* (1930). By making fundamental changes in the use of an electronic oscillator and amplifier, SCHLEICHER and BRADSHAW (1956) of Woods Hole Oceanographic Institution developed a precise salinometer. The earlier model used a 25°C constant temperature bath with seven glass cells having a typical resistance of about 1,000 ohms. The bridge was a conventional slide-wire a.c. Wheatstone bridge, with Wagner earth circuit, driven by a 1,000c/s oscillator. The later model used a 15°C thermostat (in order to avoid the "bubble effect" on the surface of electrode) and a self-balancing bridge with recorder.

The Uuiversity of Washington salinometer (PAQUETTE, 1958 and 1959ab) used a 15°C constant temperature bath. The earlier instrument had 6 cells, with a resistance of about 100 ohms, but the later models had up to 11 cells with a resistance of about 1,000 ohms. COX (1963b) notes that the shortcoming of this salinometer is that each cell has a different cell constant.

The British National Institute of Oceanography salinometer (COX, 1958) has a constant temperature bath of 15°C, and 8 cells with a resistance of 3,500 ohms. The bridge power supply is a 1,700c/s oscillator. A transformer ratio-arm bridge achieves the balance by switching-in turns on a transformer. All the cells are adjusted to have equal cell constants.

The South African instrument (ANDERSON, *et al.*, 1957) uses only one cell with four electrodes. An alternating current is passed through the outer electrodes, and the voltage drop across the inner electrodes is measured.

The Woods Hole instruments are currently used Woods Hole Oceanographic Institution, while the University of Washington instruments are used by Texas A & M University, University of Miami, Pacific Oceanographic Group (Canada), and University of Washington. The British type (National Institute of Oceanography) is currently used by Bedford Institute of Oceanography (Canada) and the National Institute of Oceanography (Britain).

### (2) Inductive salinometer

The unique feature of this instrument is the absence of electrodes and the constant temperature bath (BROWN and HAMON, 1961). The reference resistor is a thermistor immersed in the sample, chosen and adjusted with metal resistors so that it has a similar temperature coefficient to sea water over a limited temperature range and limited oceanic salinity range (HAMON, 1956). The current is induced in the sea water by making the water form a conducting loop in a transformer bridge.

This instrument is commercially sold in Australia, U.S.A. (Hytech) and Japan (Tsurumi). It is widely used by various oceanographic laboratories in U.S.A. (Texas A & M, University of Miami, Oregon State University, Scripps Institute of Oceanography, U.S. Naval Oceanographic Office, U.S. Coast Guard, University of Alaska, Coast and Geodetic Survey, etc.); and in Australia and Japan.

### (3) Capacitive salinometer

Developmental work on the radio frequency salinometer was carried out at Texas A & M University by HARWELL (1954ab) and HUEBNER (1959). This instrument has not been perfected for field uses.

The instrument has no metallic contact with sea water. Its bridge is operated at 10 megacycles. Coupling to sea water is made through coated glass walls of the cell which act as capacitive coupling elements.

### (4) *In situ* salinometer

The most attractive feature of the *in situ* instrument is its capacity to monitor the desired parameter continuously from the surface to depth. It also eliminates water sampling.

However, in order to have reliable instruments, study of the temperature and pressure effects on the conductivity of sea water and on the sensing device is necessary. The results of such studies should then be used in the development of a sensing device which will compensate for their effects. At present these effects have not been studied thoroughly enough.

Nevertheless, various *in situ* salinity sensing devices have been proposed (AAGAARD and VANHAAGEN, 1965; BROWN, 1963; and SKINNER, 1963) and tested SIEDLER, 1963). In order to eliminate the problems of electrode polarization and contamination, inductively-coupled conductivity sensors with a network of temperature and pressure sensors have been preferred. BROWN (1963) gives a detailed account of his research on the temperature and pressure compensations for his proposed inductive sensing device.

## ERRATA

Page 25 footnote line 6 should read: ... NSF grants GP-2232 and GP-2876...

Page 69 line 14 should read: ...... and van der POL

Page 70 line 15 should read: ESTERSON and PRITCHARD, 1955; ....

Page 71 line 4 should read: .... is needed in the computation of the density and stability of ...

Page 71 paragraph 3 should read: SCOR (Special Committee for Oceanic Research) .... D. E. CARRITT (U. S. A.), ....

Page 71 line 3 from bottom should read: ... chosen to preserve, ...

Page 72 a caption in Figure 4 should read: ARCTIC DEEP WATER

Page 75 second sentence in paragraph on pressure dependence should read: by HAMON (1958) and HORNE.....

Page 75 Figure 7 should read: from unpublished data of ....

Page 76 line 8 from bottom should read: Apparent increases ...

Page 76 four lines from bottom should read: The results ranged from 35.22‰ for ...

Page 79 line 6 should read: used by Woods Hole Oceanographic.....

Page 80 line 3 should read: vanHAAGEN; 1963;...

## 総　説

# Electrolytic Conductance of Sea Water and the Salinometer*

## (Part 2)

Kilho PARK** and Wayne V. BURT**

### 4. Precision of salinometers

The reproducibility of results by the various salinometers is more precise than that of the chlorinity method. All of the electrode-type and inductive salinometers give precisions better than 0.01‰ S. Since it is very important that the salinity results obtainable by the chlorinity titration and conductivity methods be comparable, many intercalibration tests have been made (COX, 1963b; BERTHOLF, 1963; ROCHFORD, 1964; BERTHOLF and BELLER, 1964). Several examples are shown here.

### (1) Comparison between chlorinity titration and conductivity methods

Cox's (1963b) intercalibration among the precise chlorinity titrations and various salinometers were in excellent agreement (Table 7). The differences observed between the two methods are practically within the precision of the titration method.

Table 8 gives a comparison of the salinity determination by two different salinometers (University of Washington type, and inductive salinometer) and by the chlorinity titration method. The average difference between the inductive salinometer and the titration methods was 0.01‰ S, which is within the precision of the titration technique.

### (2) Comparison among various salinometers

Cox's (1963b) comparison among four different types of salinometers, all electrode type, gave a maximum difference of 0.015‰ S and average random error of the less than ±0.004‰ for the samples in salinity range 33.36～37.97‰ (Table 7).

Table 7. Results of analyses on various salinometers (from COX, 1963b).

| Salinity by titration | Salinometer A | B | C | D | E | F | Average |
|---|---|---|---|---|---|---|---|
| 33.362 | 33.356 | 33.354 | 33.369 | 33.364 | 33.369 | 33.361 | 33.362 |
| 33.861 | 33.858 | 33.857 | 33.868 | 33.865 | 33.867 | 33.860 | 33.863 |
| 35.149 | 35.148 | 35.147 | 35.147 | 35.147 | 35.144 | 35.149 | 35.147 |
| 36.438 | 36.438 | 36.436 | 36.436 | 36.443 | 36.437 | 36.439 | 36.438 |
| 37.972 | 37.963 | 37.964 | 37.960 | 37.975 | 37.965 | 37.999† | 37.965 |

Salinometer A—N.I.O. type No. 5 at Wormley.
B—N.I.O. type No. 2 at Lowestoft.
C—Woods Hole No. 1 (25°C thermostat).
D—Woods Hole No. 2 (15°C thermostat).
E—University of Washington.
F—I.M.C. (South Africa).

† This high value is due to the calibration of this instrument being based on the extraporeted formula of THOMAS *et al.*, (1934). This value is omitted from the calculation of average values and random errors.

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Presented in part at American Society of Limnology and Oceanography, Pacific Division Meeting, Stanford, June 1963, and at Japanese Oceanographical Society, Sapporo, September, 1964. Supported by NSF grants GP-2232 and GP-2867 and by ONR contract Nonr 1286 (10), Project NR 083-102.

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Table 8. Comparison of salinity analysis by different salinometers and $AgNO_3$ titration (from PARK and BURT, 1963). Unit: ‰ S.

| OSU Inductive salinometer | Univ. of Washington salinometer | Difference | $AgNO_3$ Method | Difference |
|---|---|---|---|---|
| 30.999 | 31.006 | 0.007 | 30.98 | 0.02 |
| 32.018 | 32.021 | 0.003 | 32.00 | 0.02 |
| 33.002 | 33.008 | 0.006 | 33.01 | 0.01 |
| 34.008 | 34.015 | 0.007 | 34.01 | 0.00 |
| 34.998 | 35.012 | 0.014 | 35.00 | 0.00 |
| 36.007 | 36.016 | 0.009 | 35.98 | 0.03 |
| | Constant error +0.008<br>Random error ±0.003 | | Average difference 0.01 | |

The data of PARK and BURT (1963) comparing the University of Washington salinometer with the inductive salinometer gave a constant error of 0.008‰ and a random error of ±0.003‰. Since the international standard sea waters used to standardize the two salinometers were not certified for conductivity but for chlorinity, the constant error of 0.008‰ may contain the descrepancies within the standard waters (See standard sea water section). The random error of 0.003‰ is about the precision specified by the manufacturer of the inductive salinometer.

The U.S. Navel Oceanographic Office conducted two controlled tests of various types of salinometers to compare the instruments and techniques used. The first test was held in May 1962 and the second in November 1963 (BERTHOLF, 1963; BERTHOLF and BELLER, 1964). The second test is described below.

Three separate batches of homogeneous samples (30, 35, and 39‰ S) were prepared and put into Jena glass ampoules. Thirty salinometers at 15 different laboratories obtained ten replicas of each salinity. The analyses were made on the same date (20 November 1963). As a further check on repeatability, each salinometer made 20 determinations of its own substandard sea water. Eighteen inductive salinometers, five University of Washington type, four National Institute of Oceanography (British) type, two Woods Hole type, and one Wenner-Smith-Soule type salinometer (manufactured by U.S. National Bureau of Standards), were used in the test.

The frequency distribution of salinity values for the three batches tested is shown in Figure 10. Comparison factors for the salinity intercalibration are given in Table 9. Although standard deviations obtained from the experiment are between ±0.004 and ±0.007 ‰ S (Table 9), some salinity values are considerably scattered (Figure 10).

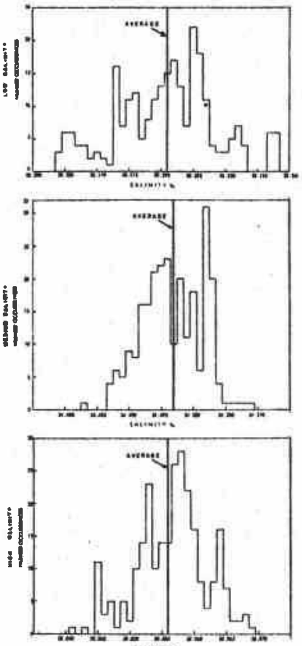

Fig. 10. Frequency distribution of salinity values from identical samples. (From BERTHOLF and BELLER, 1964).

Table 9. Comparison factors for salinity intercalibration experiment (from BERTHOLF and BELLER, 1964).

| Comparison factor | Salinity ‰-Control samples | | |
|---|---|---|---|
| | Low | Medium | High |
| International Association of Physical Oceanography (I.A.P.O.) | 30.220 | 34.497 | 38.861 |
| Overall average value of all bridges | 30.221 | 34.497 | 38.856 |
| Lowest average bridge value | 30.205 | 34.488 | 38.346 |
| Highest average bridge value | 30.238 | 34.504 | 38.867 |
| Difference | 00.033 | 0.016 | 0.021 |
| Average deviation of individual bridge from IAPO values | ±0.006 | ±0.004 | ±0.006 |
| Standard deviation | ±0.0072 | ±0.0043 | ±0.0069 |

### (3) Comparison between shipboard and shore analyses

The salinometer intercalibration tests described heretofore have been carried out under optimal shore laboratory conditions. The differences shown in Figure 10 are mainly the variations among the salinity bridges. It is therefore, very important that the variations resulting from different collecting and storing procedures and conditions, including shipboard analytical conditions, be examined. We report our test results with an Australian inductive salinometer (PARK and BURT, 1963).

For shipboard test, we used a small constant temperature bath on gimbals to warm sea water samples to 22°C. Sea water samples were collected in 350 m$l$ citrate bottles and immediately placed in the bath. After ten minutes, they were analyzed for salinity beginning with the surface samples. Within one hour after the Nansen bottle cast, conductometrically analyzed salinity values were obtained.

A set of identical samples was analyzed at the campus laboratory a week later. Table 10 gives a portion of the results. The average difference between the shipboard and shore analyses for 70 duplicate samples was 0.003 ‰ S. No apparent decrease in reproducibility of salinity analysis due to the ship's motion was encountered.

Table 10. Comparison of shipboard and shore salinity analysis. Cruise: ACONA 6209-D; station NH-53; September 1962. (From PARK and BURT, 1963).

| Depth (m) | Salinity (‰) | | |
|---|---|---|---|
| | At sea | Shore | Difference |
| 0 | 32.113 | 32.114 | 0.001 |
| 10 | 32.267 | 32.272 | 0.005 |
| 20 | 32.264 | 32.268 | 0.004 |
| 30 | 32.505 | 32.511 | 0.006 |
| 50 | 32.621 | 32.625 | 0.004 |
| 60 | 32.720 | 32.721 | 0.001 |
| 65 | 32.795 | 32.796 | 0.001 |
| 80 | 33.089 | 33.091 | 0.002 |
| 100 | 33.521 | 33.521 | 0.000 |
| 150 | 33.885 | 33.886 | 0.001 |
| 200 | 33.939 | 33.941 | 0.002 |

Although OSU's test results were excellent, only a single salinometer was used. Further shipboard tests comparing various salinometers aboard their respective ships are needed in order to understand the extent of the combined variations resulting from the sampling and salinity bridges.

## 5. Effects of biogeochemical processes on salinometer precision

Variances in the ionic ratios among the major constituents in sea water undoubtedly affect salinometer precision. These variances may be divided into two groups: (1) inherent and (2) biogeochemical.

The first group consists of random and patchy distribution of ions having no correlation with apparent biogeochemical processes. For instance, COX (personal communication and in UNESCO, 1963) finds that magnesium concentration shows no correlation with depth but does exhibit strong regional trends. His analyses illustrate that all deep Mediterranean samples possess a Mg/Cl ratio well below the average, while surface samples from the North Atlantic are all high. The variations found in magnesium could account for about half of the observed chlorinity/conductivity (Figure 2) variances.

Contrarily, dissolution of calcium carbonate in the deep oceans increases both the calcium and the alkalinity with depth. Photosynthesis and respiration affect the carbon dioxide system in sea water, which in turn affects the concentrations of ionic and nonionic species of the carbon dioxide system. These are some of the examples of the effect of biogeochemical processes.

In this section we briefly describe the effects of carbon dioxide, calcium carbonate dissolution, and photosynthesis and respiration on the electrolytic conductance of sea water.

### (1) Effects of the carbon dioxide system

Any addition of molecular carbon dioxide causes an adjustment among the dissolved carbon dioxide species, and hence a decrease in pH of the water. Such a change is produced in the sea by biological activity and by exchange with the atmosphere.

The effect on the conductance of the addition and removal of carbon dioxide gas from sea water was investigated by BRADSHAW of Woods Hole Oceanographic Institution, GRASSHOFF of Institut für Meereskunde der Universität Kiel, and PARK and WEYL of Oregon State University. The WHOI and OSU data are given in Figure 11 (PARK *et al.*, 1964). The data of GRASSHOFF (personal communication), shown in Table 11, agrees very well with that of BRADSHAW, PARK

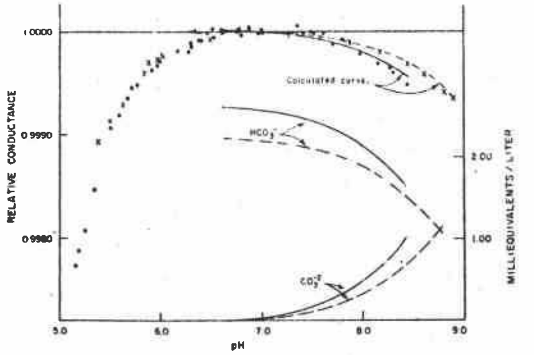

Fig. 11. Changes in the electrical conductance versus pH in sea water with carbon dioxide addition, with the calculated $HCO_3^-$ and $CO_3^{-2}$ concentrations in sea water as a function of pH. (From PARK *et al.*, 1964).

Table 11. Changes in pH and conductance of sea water by carbon dioxide (from GRASSHOFF, personal communication).

| pH | Relative conductance | Computed salinity (‰) | Difference of salinity (‰) | Remarks |
|---|---|---|---|---|
| 8.4 | 1.00046 | 35.018 | −0.012 | Constant chlorinity |
| 8.3 | 1.00051 | 35.021 | −0.009 | |
| 8.2 | 1.00058 | 35.023 | −0.007 | |
| 8.1 | 1.00064 | 35.025 | −0.005 | |
| 8.0 | 1.00068 | 35.027 | −0.003 | |
| 7.9 | 1.00071 | 35.029 | −0.001 | |
| 7.8 | 1.00074 | 35.029 | −0.001 | |
| 7.7 | 1.00075 | 35.030 | 0.000 | |
| 7.6 | 1.00076 | 35.030 | 0.000 | |

and WEYL.

From both Figure 11 and Table 11, it is apparent that systematic errors may be introduced in the conversion of conductivity to density or salinity if changes in the carbon dioxide system are not taken into consideration. The magnitude of changes in a typical oceanic pH range of 7.6 to 8.4 are a function of alkalinity (Figure 11), and they could be as 0.012 ‰ salinity equivalent (Table 11). The changes in the conductance are due to the transformation of bicarbonate to carbonate ions or *vice versa* (PARK *et al.*, 1964). The bicarbonate ion is more conductive than its equivalent carbonate ion (PARK, 1964b).

When the pH of sea water is lowered below 7 by the addition of carbon dioxide gas, the conductance decreases rapidly with decreasing pH (Figure 11). When conductance is plotted as a function of the concentration of molecular carbon dioxide, we find the conductance decreases linearly with increasing molecular carbon dioxide at a rate of 0.013 % per millimole per liter (Figure 12).

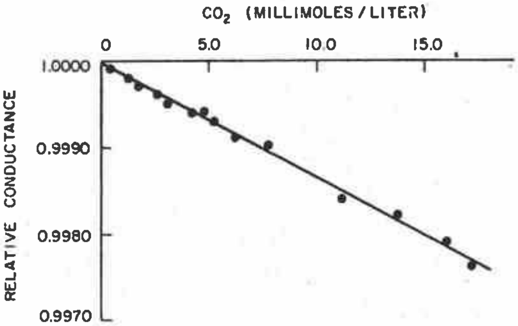

Fig. 12. Electrical conductance of sea water as a function of molecular carbon dioxide content. (From PARK *et al.*, 1964).

The exact mechanism of the decrease in the conductance by uncharged carbon dioxide molecules has not been verified by experiment. PARK *et al.* (1964) attempted to explain it by partial molal volume of carbon dioxide in sea water. BRADSHAW pointed out that the increase in viscosity due to the increase in carbon dioxide content (OSTWALD and GENTHE, 1903) would account for the conductance decrease found in the measurements of PARK *et al.* (1964). Obviously more work is needed to understand the exact mechanism of the conductance decrease with the addition of uncharged carbon dioxide.

MIYAKE *et al.* (1964) calculated the magnitude of variance on the conductance due to the changes in the carbon dioxide species in the deep sea. Their estimation was based on Bradshaw's $CO_2$-conductivity relationship (in PARK *et al.*, 1964), and Sugiura's total carbon dioxide determination obtained during the 1960 Japanese Deep-Sea Expedition. They found that a variance as much as 0.01 ‰ salinity equivalent was induced by changes in the carbon dioxide species.

### (2) Effect of dissolved oxygen

Recently BRADSHAW (personal communication) carried out an experiment to measure the effect of dissolved oxygen on the conductance of sea water. His measurements with zero-alkalinity sea water (pH 5.8) at 15°C show that the addition of 1 millimole of oxygen to the sea water decreases the conductance by about 0.01 ‰ salinity equivalent. For a typical oxygen concentration range found in the ocean, 0 to 7 m*l*/*l*, the corresponding conductance change could be as large as 0.003 ‰ salinity equivalent.

The mechanism of the effect of oxygen may be similar to that of uncharged carbon dioxide.

### (3) Effect of calcium carbonate dissolution

COX (personal communication, and in UNESCO, 1963) theoretically estimated the effect of carbonate dissolution. PARK (1964c) measured it experimentally. These two investigations show that the dissolution of calcium carbonate as calcium bicarbonate would increase the apparent salinity by about 0.01 ‰.

Cox's direct calcium measurements (UNESCO, 1963) for the sea water samples obtained in various oceans give a calcium/chlorinity range from 0.02132 to 0.2165, lower values for the surface and higher for deep-sea waters. The increase in ratio, if due to the dissolution of calcium carbonate in deep waters, would correspond to about 0.1 millimole $CaCO_3$ dissolution per liter of sea water. Independently, if we assume that the increase in specific alkalinity with the depth, from 0.12 to 0.13 meq/*l* (KOCZY, 1956), is due to carbonate dissolution, we obtain the same 0.1 millimole of carbonate dissolution per liter of sea water.

Park's experiment (1964c) consisted of dissolving oolite (aragonite) in sea water in the presence of excess carbon dioxide (Figure 13). The specific conductance of sea water was increased by about $6\times10^{-5}$ ohm$^{-1}$cm$^{-1}$ per millimole of carbonate dissolved. The net increase in conductance is the result of the dissolution of the crystals as calcium bicarbonate, the hindrance effect of uncharged carbon dioxide on the conductance, and the transformation of some of the initial carbonate ions into bicarbonate ions. The first of these is the most important to the calculation of the effect of carbonate dissolution.

It should be stressed here that reglardless of calcium carbonate dissolution in deep water, the chlorinity of the water will remain a conservative property. On the other hand, the increase in conductance due to the dissolution of carbonate minerals will compensate, in some degree, for the increase in density. Therefore, when a conservative property is needed, precise measurements of chlorinity should be used rather than the conductance. Furthermore, the conductivity/chlorinity ratio can be used to estimate the carbonate dissolution in deep waters.

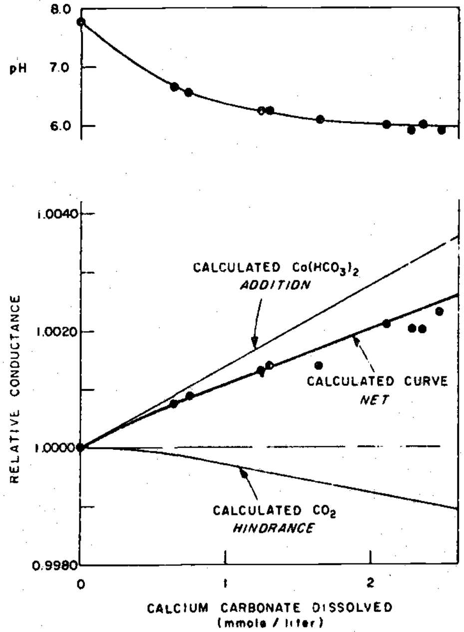

Fig. 13. Changes in pH and electrical conductance of sea water with calcium carbonate dissolution. (From PARK, 1964c).

### (4) Effect of photosynthesis and respiration

During photosynthesis, the oxygen content of sea water increases and carbon dioxide content decreases. In a typical oceanic pH range from 7.6 to 8.3, photosynthesis is accompanied by an increase in pH and by the transformation of bicarbonate to carbonate ions. Both oxygen increase and carbon dioxide decrease favor a decrease in conductance.

On the other hand, during respiration, both oxygen decrease and carbon dioxide increase favor an increase in conductance. Therefore, photosynthesis will accompany a decrease in conductance, while respiration will be reflected in an increase.

In addition, we must consider the effect of ionized organic excretion by biological activities.

When all of these parameters are wholly investigated, we may be able to utilize conductometry in the estimation of photosynthesis and respiration. The realization of such a goal appears to be in the remote future, but this possibility should not be ignored in our future studies.

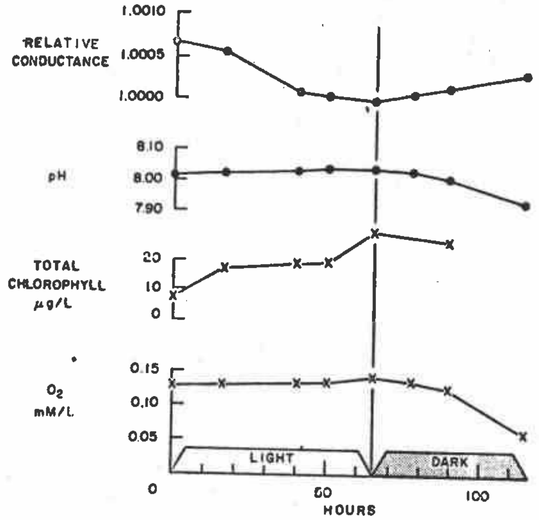

Fig. 14. Concurrent changes in electrical conductance, pH, chlorophyll and dissolved oxygen during the photosynthesis and respiration studies of marine diatom, *Skeletonema costatum*. (From PARK and CURL, 1965).

As an example, the effect of photosynthesis and respiration on the conductance of sea water is given by PARK and CURL (1965) (Figure 14).

## 6. International standard sea water

COX showed clearly that the conductance of sea water varies substantially even at a constant chlorinity (Figure 2). It is, therefore, quite possible that standards having identical chlorinity posses different electrical conductances.

PARK (1964a) examined the anomalies between chlorinity and conductivity by comparing 12 different batches of international standards. His data are summarized in Table 12. He observed no systematic correlations between changes in salinity (conductometry *vs.* chlorinity) and pH, nor between salinity and the age of the standards (Figure 15). In general, salinities determined by the conductometric means are in good agreement with values computed from the certified chlorinities.

Table 12. Difference of salinity values computed from certified chlorinities and determined by conductivity measurements for twelve different batches of the international standard sea waters taking batch $P_{37}$ as a reference standard (from PARK, 1964a).

| Batch number | Preparation date | Certified chlorinity ‰ | Computed salinity ‰ | Salinity from conductivity ‰ | Difference of salinity ‰ | pH |
|---|---|---|---|---|---|---|
| $P_{15}$ | 30/6 1937 | 19.393 | 35.034 | 35.032 | 0.002 | 7.90 |
| $P_{18}$* | 4/12 1949 | 19.376 | 35.004 | 35.016 | 0.012 | 7.92 |
| $P_{24}$ | 6/5 1956 | 19.378 | 35.007 | 35.011 | 0.004 | 7.92 |
| $P_{25}$ | 6/1 1957 | 19.378 | 35.007 | 35.007 | 0.000 | 8.09 |
| $P_{26}$ | 8/12 1957 | 19.367 | 34.987 | 34.990 | 0.003 | 7.98 |
| $P_{29}$ | 27/9 1959 | 19.370 | 34.993 | 35.010 | 0.017 | 8.06 |
| $P_{30}$ | 28/2 1960 | 19.370 | 34.993 | 34.995 | 0.002 | 7.78 |
| $P_{31}$ | 28/8 1960 | 19.375 | 35.002 | 35.002 | 0.000 | 7.90 |
| $P_{32}$ | 8/1 1961 | 19.376 | 35.004 | 35.006 | 0.002 | 7.81 |
| $P_{35}$ | 4/3 1962 | 19.373 | 34.998 | 35.004 | 0.006 | 7.72 |
| $P_{36}$ | 23~24/9 1962 | 19.375 | 35.002 | 35.004 | 0.002 | 7.70 |
| $P_{37}$ | 16/12 1962 | 19.369 | 34.991 | 34.991 | 0.000 | 7.90 |

* $P_{18}$ contained white suspended material in its ampoule.
Salinometer used: Australian C.S.I.R.O. Inductive Salinometer.
Analysis temperature: 23.5°C~23.7°C.
Date of analysis: 13 August 1963.

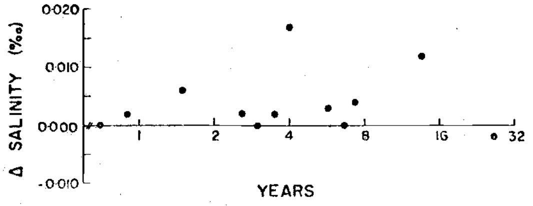

Fig. 15. Differences between salinity values computed from certified chlorinities and determined by conductivity measurements *vs.* the ages of the international standard sea waters, taking batch $P_{37}$ as a reference standard. (From PARK, 1964a).

Copenhagen standard sea water has a pH range of 7.7 to 8.1 (Table 12). This is somewhat lower than the surface pH, although the water is obtained from the surface layers of the Atlantic. The change implies that the pH of the water has changed during storage. If the changes in pH during storage are due to changes in carbon dioxide, then the conductance of the standards would increase during the storage (Figure 10). In order to overcome this problem, GRASSHOFF of Germany (personal communication) suggests that the pH of the standards be changed arbitrarily to about 7.7~7.8 before measuring the absolute conductivity and chlorinity and sealing.

Since use of the salinometer has become widespread, and since the conductivity-density ratio (Figure 4) of sea water is intrinsically more consistent than the chlorinity-density ratio (Figure 3), we need to know accurately the electrical conductivity of standard sea water. At present, both the Standard Sea Water Service and the National Institute of Oceanography (English) are actively working on the certification of the standards in conductivity as well as chlorinity.

## 7. Concluding remarks

As it has been and as it will be always, research in oceanography is international in scope. Together, but not a man alone, nor a country alone, we understand the description and the dynamics in the oceans. One good example of the cooperative effort is on the conductivity problem of sea water. The work began almost a century ago, and it still continues by many workers. Although this review paper reveals the extent of our knowledge and our ignorance about the electrolytic properties of sea water, we sincerely hope that this article may help to focus the critical eyes of many coworkers throughout the world on one of the urgent problems in oceanography.

## References

AAGAARD, E. E. and R. H. VAN HAAGEN (1963): A probe type induction conductivity cell. Marine Science Instrumentation, **2**, 11—17.

ANDERSON, F. P., R. W. GUELKE, M. C. B. HOTZ and A. H. SPONG (1957): An A. C. potentiometric method of measuring electrolytic conductance. Chem. and Ind., 8 June, 732—733.

BEIN, W., H. G. HIRSKEBORN and L. MÖLLER (1935): Konstantebestimmungen des Meerwassers und Ergebnisse über Wasserkörper. Veröffent. Inst. für Meereskunde, Berlin Univ., n. f. (A. Geogr.-Naturwiss. Reihe), **28**, 239.

BERTHOLF, L. B. (1963): Methods for determination of salinity of sea water. U.S. Naval Oceanogr. Newsletter, **2**(2), May, 1—3.

BERTHOLF, L. B. and J. W. BELLER (1964): Report of second salinity bridge comparison by controlled experiment. U.S. Naval Oceanogr. Office, Mar. Sci. Dept. Informal Manuscript Report No. 0—28—64, 16 pp. (Unpublished manuscript).

BRADSHAW, A. and K. E. SCHLEICHER (Personal communication): The effect of pressure on the specific conductance of sea water.

BRADSHAW, A. (Personal communication, 1964): Effect of dissolved oxygen on the specific conductance of sea water.

BREMNER, R. W., T. G. THOMPSON and C. L. UTTERBACK (1939): Electrical conductance of pure and mixed salt solutions in the temperature range 0 to 25°. Jour. Amer. Chem. Soc., **61**, 1219—1223.

BROWN, N. L. (1963): A proposed *in situ* salinity sensing system. Marine Science Instrumentation, **2**, 19—24.

BROWN, N. L. and B. V. HAMON (1961): An inductive salinometer. Deep-Sea Res., **8**(1), 65—75.

COX, R. A. (1955): Recent work on the measurement of salinity by electrical means. Jour. Conseil, Cons. Perm. Inst. Expl. Mer., **20**(3), 306~309.

COX, R. A. (1958): The thermostat salinity meter. Nat. Inst. Oceanogr. Internal. Rept., C2, March (Unpublished manuscript).

COX, R. A. (1962): Temperature compensation in salinometers. Deep-Sea Res., **9**, 504—506.

COX, R. A. (1963a): Definition of the salinity of sea water. Nature, **197**, 785—786.

COX, R. A. (1963b): The salinity problem. Progress in Oceanography, **1**, 243—261.

COX, R. A., F. CULKIN, R. GREENHALGH and J. P. RILEY (1962): The chlorinity, conductivity and density of sea water. Nature, **193**(4815), 518—520.

DIETRICH, G. (1963): General Oceanography. Interscience Publishers, New York, 588 pp.

DORRESTEIN, R. R. (1954): "Een registrerende electrische Zoutgehalte-en Temperatuurmeter voor Gebruik op Zee. Kon Nederlands Meteor. Inst. Medd. en Verhand., **59**, 387—402.

ESTERSON, G. L. (1957): The inductive conductivity indicator: a new method for conductivity measurement at sea. Chesapeake Bay Inst. Tech. Rept., **14**, Ref. 57—3.

ESTERON, G. L., and D. W. PRITCHARD (1955): C.B.I. salinity-temperature meters. Proc. First Conf. Coastal Eng. Instruments, Council on Wave Res., The Eng. Found., 260—271.

FORD, W. L. (1949): The field use of a S.T.D. recorder. Jour. Mar. Res., **8**, 84—96.

GERMAN, J. C. (1960): An inductive salinity meter for *in situ* measurements. Jour. Conseil, Cons. Perm. Int. Expl. Mer., **26**, 21—32.

GHEORGHIUS, V. G. and N. CALINICENCO (1940): Etude sur la variation de la conductibilité électrique de léau de la Mer Noire avec la température et son emplor a la mesure de la température de léau marine. Ann. Sci. Univ. Jassy, **26** (Sect. II), 3—18.

HAMON, B. V. (1955): A temperature-salinity-depth recorder. Jour. Conseil, Cons. Perm. Int. Expl. Mer., **21**, 72—73.

HAMON, B. V. (1956): A portable temperature-chlorinity bridge for estuarine investigations and sea water analysis. Jour. Sci. Instruments, **33**, 329—333.

HAMON, B. V. (1958): The effect of pressure on the electrical conductivity of sea water. Jour. Mar. Res., **16**, 83—89.

HARNED, H. S. and B. B. OWEN (1958): The Physical Chemistry of Electrolytic Solutions, Reinhold, New York.

HARVEY, H. W. (1960): The Chemistry and Fertility of Sea Waters, Cambridge Univ. Press, Cambridge.

HARWELL, K. E. (1954a): Radio frequency salinity instrument model E. Texas A & M Res. Found. Project 48, Tech. Rept. 4, 37 pp.

HARWELL, E. K. (1954b): Wien bridge and Twin-T salinity instruments. Texas A & M Res. Found. Project 48, Tech. Rept. 5, 41 pp.

HEUBNER, G. L. (1959): Notes on radio frequency salinity measuring equipment at Texas A & M College. Physical and Chemical Properties of Sea-Water, U.S. Nat. Acad. Sci.-Nat. Res. Council Publ. **600**, 155.

HINKELMANN, H. (1958): Ein Verfahren zur elektrodenlosen Messung der elektrischen Leitfähigkeit von Elektrolyten. Z. Angew. Physik, **10**, 500—503.

HORNE, R. A. and G. R. FRYSINGER (1963): The effect of pressure on the electrical conductivity of sea water. Jour. Geophys. Res., **68**, 1967—1973.

JACOBSON, A. W. (1948): An instrument for recording continuously the salinity, temperature, and depth of sea water. Trans. Am. Inst. Elec. Eng., **67**, 714—722.

KARSTEN, G. (1897): Wiss, Meeresunters, Kiel und Helgoland, N.F., **1**(2), 174. (Cited from THOMAS *et al.*, 1934).

KUNDSEN, Martin (1960): Maaling of havvandets temperatur og saltholdighed ved hjaelp of elektrisk telefonbro. Beretning fra Kommissioner for Videnskabelig Undersøgelser af de Danske Farvande, Copenhagen, **2**(3), 15.

KOCZY, F. F. (1956): The specific alkalinity. Deep-Sea Res., **3**, 279—288.

LYMAN, J. and R. H. FLEMING (1940): Composition of sea water. Jour. Mar. Res., **3**, 134—146.

McCOURT, C. F. (1953): An instrument for the measurement of the density of aqueous ionic solutions. Jour. Sci. Instruments, **30**, 241—243.

MILLER, A. R. (1954): A suggestion for the correlation of salinity data obtained with the S.T.D. recorder. Woods Hole Oceanogr. Inst. Tech. Rept. No. 54—17, March.

MIYAKE, Y., Y. SUGIURA and K. PARK (1964): Effect of $CO_2$-system components on the electrical conductivity of deep-sea water. The Fouth Deep-Sea Symposium, Tokyo, 2 Dec. 43—47 (In Japanese).

OSTWALD, W. and A. GENTHE (1903): Ueber den Einfluss der gelösten Salze und Gase auf die innere Reibung des Wassers. Zool. Jahrb. Abth. F. System, Geog., Biol. d. Theire, **18**, 3—15.

PAQUETTE, R. G. (1958): A modification of the Wenner-Smith-Soule salinity bridge for the determination of salinity in sea water, with details of construction, operation, and maintenance. Univ. Wash., Dept. of Oceanogr., Tech. Rept. No. 54—14, 58 pp. (Unpublished manuscript).

PAQUETTE, R. G. (1959a): Salinometers. Physical and Chemical Properties of Sea Water, U.S. Nat. Acad. Sci.-Nat. Res. Council Publ., **600**, 128—145.

PAQUETTE, R. G. (1959b): A modification of the Wenner-Smith-Soule salinity bridge for the determination of salinity in sea water. Univ. Wash., Dept. of Oceanogr. Tech. Rept. No. 59—2, 5 pp.

(Unpublished manuscript).

PARK, K. (1964a): Reliability of standard sea water as a conductivity standard. Deep-Sea Res., **11**, 85—87.

PARK, K. (1964b): Partial equivalent conductance of electrolytes in sea water. Deep-Sea Res., **11**, 729—736.

PARK, K. (1964c): Electrolytic conductance of sea water: effect of calcium carbonate dissolution. Science, **146**, 56—57.

PARK, K. and W. V. BURT (1963): Experimental determination of reliability of an inductive salinometer. Presented at Am. Soc. Limnol. Oceanogr., Pacific Div., Stanford, Calif., June.

PARK, K. and H. C. CURL, Jr. (1965): Effect of photosynthesis and respiration on the electrical conductance of sea water. Nature, **205**, 274—275.

PARK, K., M. OLIPHANT and H. FREUND (1963): Conductometric determination of alkalinity of sea water. Anal. Chem., **35**, 1549—1550.

PARK, K., P. K. WEYL and A. BRADSHAW (1964): Effect of carbon dioxide on the electrical conductance of sea water. Nature, **201**(4926), 1283—1284.

POLLAK, M. J. (1954): The use of electrical conductivity measurements for chlorinity determinations. Jour. Mar. Res., **13**(2), 228—231.

PRITCHARD, D. W. (1959): The *in situ* measurement of 'salinity' with the induction conductivity indicator. Physical and Chemical Properties of Sea Water, U.S. Nat. Acad. Sci.-Nat. Res. Council Publ. **600**, 146—154.

RIVERS-MOORE, H. G. (1918): Electrician, **82**, 174—176 (cited from THOMAS *et al.*, 1934).

ROCHFORD, D. J. (1964): SCOR-UNESCO Chemical Intercalibration Tests. Results of 3rd Series, R.R.S. Discovery May-June, Indian Ocean, 28 pp.

RUPPIN, E. (1907): Krümmel's Handbuch der Ozeanographie, **1**, 289. (Cited from THOMAS *et al.*, 1934).

SCHIEMER, E. W. and D. W. PRITCHARD (1957): The Chesapeake Bay Institute conductivity-temperature-Indicator, Chesapeake Bay Inst. Tech. Rept. **12**, (Unpublished manuscript).

SCHLEICHER, K. E. and A. BRADSHAW (1956): A conductivity bridge for the measurement of the salinity of sea water. Jour. Conseil, Cons. Perm. Int. Expl. Mer. **22**, 9—20.

SIEDLER, G. (1963): On the *in situ* measurement of temperature and electrical conductivity of sea water. Deep-Sea Res., **10**, 269—277.

SKINNER, D .C. (1963): An *in situ* conductivity meter. Marine Science Instrumentation, **2**, 25—28.

THOMAS, B. D., T. G. THOMPSON, and C. L. UTTERBACK (1934): The electrical conductivity of sea water. Jour. Conseil, Cons. Perm. Int. Expl. Mer., **9**, 28—35.

THURAS, A. L. (1918): An instrument for recording sea water salinity. Jour. Wash. Acad. Sci., **8**, 676—678.

TORNÖE, H. (1895): Nansen's Oceanography of the North Polar Basin, 197. See also Nyt Magazin for Naturoid., **34**, 232. (Cited from THOMAS *et al.*, 1934).

UNESCO (1962): Reports of joint panel on the equation of state of sea water, NS/9/114B, Paris, 17 pp., 4 Dec.

UNESCO (1963): Second report of joint panel on the equation of state of sea water. NS/9/114B, Berkeley, California, 8 pp., 19 August.

van der POL (1918): Balth, Phil. Mag., **36**, 88. (Cited from THOMAS *et al.*, 1934).

WENNER, F., E. H. SMITH, and F. M. SOLE (1930): Apparatus for the determination aboard ship of the salinity of sea water by the electrical conductivity method. U.S. Bur. Stand., Jour. Res. Washington, D.C., **5**, 711—732.

WEIBEL, E. E. and A. L. THURAS (1918): An electrical conductivity recorder for salinity measurements. Jour. Ind. Eng. Chem., **10**, 626—627.

WEYL, P. K, (1964): On the change in electrical conductance of sea water with temperature. Limnol. Oceanogr., **9**(1), 75—78.

WILLIAMS, J. (1961): A small portable salinomenter. Chesapeake Bay Inst. Tech. Rept., **23**, (Unpublished manuscript).

# ERRATA

| | |
|---|---|
| Page 30 | footnote column 2 line 1 should read: ...GP-2232 and GP-2876... |
| Page 124 | first sentence in paragraph on comparison among various salinometers should read: ...average random error of less than... |
| Page 125 | Table 9, lowest average bridge value should read: 32.205, 34.488, 38.846 |
| Page 128 | last line should read: ... that regardless of ... |
| Page 129 | Table 12 should read: Differences of salinity ... |
| Page 131 | Reference 6 should read: ESTERSON, G. L., ...<br>Reference 7 should read: FORD, W. L. (1949): The field use of an S. T. D. ...<br>Reference 9 should read: GHEORGHIUS ... de l'eau de la Mer Noire avec la température et son emploi a la measure de la température de l'eau marine<br>First reference on PAQUETTE should read: Tech. Report. No. 58-14, 58 pp. |

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# Total Carbon Dioxide in Sea Water*

Kilho PARK**

**Abstract:** Analytical techniques to determine total carbon dioxide in sea water are reviewed. Carbon dioxide system components are expressed as a function of total carbon dioxide. The relationship between alkalinity and total carbon dioxide, biological changes in the total carbon dioxide and dissolved oxygen content of the sea are discussed along with possible application of total carbon dioxide to the study of the direction of deep-sea water flow.

## Introduction

Total carbon dioxide in sea water is defined as the sum of the molar concentrations of molecular carbon dioxide, carbonic acid, bicabonate ion which are dissolved in sea water. Dissolved organic carbon is excluded by this definition.

In the surface layers above the thermocline the carbon dioxide exchange across the air-sea interface is an important regulator of total carbon dioxide concentration. In the euphotic zone, photosynthesis reduces carbon dioxide to organic carbon. Respiration by marine organisms and decomposition of organic matter augment the carbon dioxide concentration throughout the water column, from the surface to the sea floor. Carbonate mineral precipitation removes some carbon dioxide while the dissolution of carbonate minerals adds it to the water. Addition of carbon dioxide by river water is a localized surface phenomenon. Rain adds atmospheric carbon dioxide directly into the surface layer.

In the past, several workers expressed the importance of this quantity. But, due to the analytical difficulties involved, few measurements were made. With the advent of infrared absorption spectroscopy (KANWISHER, 1960) and gas chromatography (PARK *et al.*, 1964) we are now in the position to study the total carbon dioxide directly and routinely at sea. This paper describes some of the beneficial uses of the total carbon dioxide in sea water.

## Analytical techniques

Total carbon dioxide in sea water is generally determined by acidifying sea water and expelling the gases by boiling, by diffusion with or without vacuum, or by aerating with an inert gas. The quantity of carbon dioxide in the expelled gases has been found by several methods. WELLS (1918) trapped the evolved carbon dioxide in soda lime weighing bottles. THOMPSON *et al.* (1929) and SARUHASHI (1953) absorbed the expelled carbon dioxide into a standard barium hydroxide solution. GREENBERG *et al.* (1932) measured it by the Van Slyke manometric apparatus. PARK *et al.* (1964) used gas chromatography. Although not reported, it is quite feasible to determine total carbon dioxide by the infrared absorption apparatus described by KANWISHER (1960) and by WILSON (1961).

Total carbon dioxide is most frequently determined indirectly by the pH-alkalinity method (HARVEY, 1960, p 172). This method relies on the measurement of pH, alkalinity, salinity, inorganic boron concentration, and temperature of sea water. In addition the dissociation constants of carbonic acid and boric acid in sea water are needed to calculate the total carbon dioxide.

Most of the methods described above are time consuming and not well suited for routine oceanographic investigations which require numerous analyses, often under difficult working conditions. Infrared absorption spectroscopy has been used to determine very accurately the partial pressure of carbon dioxide at sea (KANWISHER, 1960 and others), but has not

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been applied to the study of total carbon dioxide. Recently, PARK *et al.* (1964) conducted a shipboard test of the gas chromatographic method for determining total carbon dioxide. The sea water sample size was 3 m*l*, analysis time was less than 5 minutes per sample, and the relative standard deviation obtained from five replicate runs was ±0.7 percent. This method should be useful in future for oceanographic work.

### Theoretical consideration of the carbon dioxide system in sea water

Carbon dioxide and carbonate minerals play an important role in numerous chemical reactions and equilibria in sea water. In the study of relationships between bicarbonate ion, and carbonic acid (including molecular carbon dioxide) we use the first and second dissociation equations of carbonic acid and carbonate alkalinity as shown below:

$$K_1'=\frac{[A_{H^+}][HCO_3^-]}{[H_2CO_3+CO_2]} \qquad (1)$$

$$K_2'=\frac{[A_{H^+}][CO_3^{-2}]}{[HCO_3^-]} \qquad (2)$$

$$\begin{aligned}[\text{Carbonate Alkalinity}]&=[HCO_3^-]+2[CO_3^{-2}]=[\text{Titration Alkalinity}]\\&-[H_2BO_3^-]-[OH^-]+[H^+]\\&-[\text{Surplus Alkalinity}] \qquad (3)\end{aligned}$$

where $K_1'$ and $K_2'$ are the first and second apparent dissociation constants of carbonic acid. $[A_{H^+}]$ is the activity of the hydrogen ion and surplus alkalinity is the alkalinity arising from all weak acids (other than carbonic acid and boric acid) contained in the sea water. The concentrations of bicarbonate ion, corbonate ion and carbonic acid (plus molecular carbon dioxide) are obtained from equations (1), (2), and (3) [HARVEY, 1960, p 173].

Total carbon dioxide in sea water is defined as follows (unit: mole/liter):

$$\Sigma[CO_2]=[H_2CO_3+CO_2]+[HCO_3^-]+[CO_3^{-2}] \qquad (4)$$

From equations (1), (2), and (4) the concentration of the carbon dioxide components are derived:

$$[H_2CO_3+CO_2]=\frac{[A_{H^+}]^2}{[A_{H^+}]^2+[A_{H^+}]K_1'+K_1'K_2'}\Sigma[CO_2] \qquad (5)$$

$$[HCO_3^-]=\frac{[A_{H^+}]K_1'}{[A_{H^+}]^2+[A_{H^+}]K_1'+K_1'K_2'}\Sigma[CO_2] \qquad (6)$$

$$[CO_3^{-2}]=\frac{K_1'K_2'}{[A_{H^+}]^2+[A_{H^+}]K_1'+K_1'K_2'}\Sigma[CO_2] \qquad (7)$$

Equations (5), (6) and (7) should be quite useful in the study of the carbon dioxide system in sea water. One advantage of this approach is that surplus alkalinity data are not necessary.

Using Buch's (1951) dissociation constants for carbonic acid and similar relationships shown in equations (5), (6), and (7) SARUHASHI (1955) tabulated the percentage molar fraction of carbonic acid (including molecular carbon dioxide), bicarbonate ion, and carbonate ion as a function of temperature (0 to 30°C), pH (7.4 to 8.4), and chlorinity (15 to 21‰).

### Relationship between total carbon dioxide and alkalinity

From equations (3), (4), (5), and (7), carbonate alkalinity and titration alkalinity can be expressed as a function of total carbon dioxide:

$$[\text{Carbonate Alkalinity}]=\left\{\frac{[[A_{H^+}]+2K_2']K_1'}{[A_{H^+}]^2+[A_{H^+}]K_1'+K_1'K_2'}\right\}\Sigma[CO_2] \qquad (8)$$

$$\begin{aligned}[\text{Titration Alkalinity}]&=\left\{\frac{[[A_{H^+}]+2K_2']K_1'}{[A_{H^+}]^2+[A_{H^+}]K_1'+K_1'K_2'}\right\}\Sigma[CO_2]\\&+[OH^-]-[H^+]+[\text{Surplus Alkalinity}] \qquad (9)\end{aligned}$$

From equation (8) it is evident that for a given hydrogen ion activity the relationship between the carbonate alkalinity and total carbon dioxide is linear. However, for the relationship between titration alkalinity and the total carbon dioxide, we need to know not only the concentration of borate ion, but also that of other weak acids and the presence of their salts (Surplus Alkalinity).

The importance of the surplus alkalinity concept has been emphasized by GRIPENBERG (1960). She attributed surplus alkalinity partly to anions of organic acids transported by rivers or formed as a result of the metabolism within the sea. In her work in the Gulf of Bothnia and the Baltic Sea, GRIPENBERG found a surplus alkalinity of approximately 0.1 milliequivalent per kilogram of sea water. She concluded that the surplus alkalinity which is not a function of salinity is possibly an organic constituent of sea water, such as the organic boron complexes discovered by GAST and THOMPSON (1958) and by NOAKES and HOOD (1961).

The apparent effect of some amino acids on the titration alkalinity of sea water was studied by PARK (1961, pp 232~238). He found that the increment of alkalinity due to the addition of organic acid is generally additive in nature. For each millimole of glycine added to a liter of sea water (20.1‰ Cl) the alkalinity increase was 0.06 milliequivalent.

Surplus alkalinity should be higher in estuaries than the open sea, because of high organic content and land drainage. Therefore, total carbon dioxide calculated from titration alkalinity data without consideration of surplus alkalinity would frequently be higher than the actual concentration. Our field work shows that Oregon estuarine waters (Alsea Bay, Siletz Bay, and Yaquina Bay) possess a surplus alkalinity of about 0.1 milliequivalent per liter. Summary of the Yaquina Bay study is as follows.

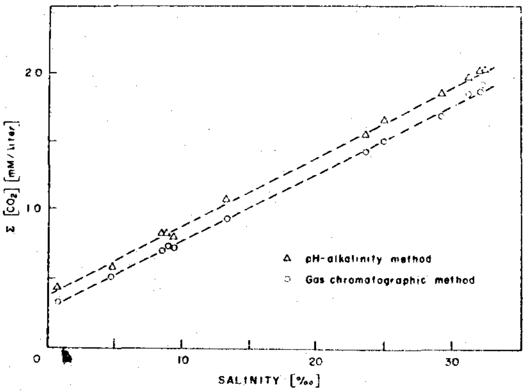

Fig. 1. Comparison of the two methods for the determination of total carbon dioxide in Yaquina Bay waters, Oregon, 21 February 1964.

For the indirect determination of total carbon dioxide, we measured alkalinity, pH, salinity and temperature of bay waters. The apparent dissociation constants of carbonic acid and boric acid of LYMAN (1956) were used to calculate the total carbon dioxide. For the direct determination of total cabon dioxide, the gas chromatographic method of PARK *et al.* (1964) was used. Figure 1 shows the comparison of the two methods for the total carbon dioxide determination for Yaquina Bay. The pH-alkalinity method gave consistently higher total carbon dioxide values than the direct gas chromatographic method, with an average difference of about six percent. This difference is greater than the experimental error expected. Laboratory controlled experiments gave less than two percent difference between the two methods (PARK, *et al.*, 1964). Since our data indicate the existence of surplus alkalinity in bay waters, it is important to study the chemical nature of the constituents of surplus alkalinity.

## Relationship between biological changes in total carbon dioxide and dissolved oxygen in the sea

At all depths of the sea, carbon dioxide is biologically produced by the respiration of marine life and by bacterial decomposition of organic matter in the presence of dissolved oxygen. Changes in the carbon dioxide content are accompanied by concurrent changes in the oxygen content of sea water.

Oxygen and carbon dioxide are involved in the photosynthetic formation and respiratory decomposition of organic matter. The ratio of changes in total carbon dioxide and oxygen $(|\Delta\Sigma[\mathrm{CO_2}]/\Delta \mathrm{O_2}|)$ have been investigated by many workers. The ratios reported are generally unity [SVERDRUP *et al.*, 1946, p 239]. RYTHER (1956) summarized available data on the ratio of oxygen produced to carbon dioxide assimilated (photosynthetic quotient; $|\Delta \mathrm{O_2}/\Delta\Sigma[\mathrm{CO_2}]|$) with an average value of about 1.20. This value is approximately in accordance with the statement of THOMPSON and GILSON (1937, p 31). They pointed out that since phytoplankton tissues contain nitrogen and carbon atoms in ratio of one to seven, one-fifth of the oxygen produced must originate from nitrate.

REDFIELD (1934, p 182) found that in the oxidation of organic matter in deep water, the ratio of the carbon dioxide produced to the oxygen consumed was 1.17. However, he considered the accuracy of the determination low. With the development of rapid and direct methods for the determination of total carbon dioxide by infrared spectroscopy and gas chromatography such a ratio study can be executed with ease.

During cruise 6311 of the R/V ACONA of Oregon State University (21 November 1963), salinity, oxygen (Winkler method) total carbon dioxide (gas chromatography), pH, and alkalinity of sea water off the Oregon coast were measured. Typical vertical profiles of these parameters at the station 44°39′ N, 125°07′ W are given in Figure 2. Beneath the euphotic zone, temperature and salinity did not change appreciably (Figure 2). If we assume the same history of water masses for the water column below the halo- and thermocline, between 75 and 513 meters, then the oxygen decrease within this column is concurrently reflected by the increase in the total carbon dioxide. At this station the effect of carbonate mineral dissolution and precipitation is much smaller than the biological effect, since thc specific alkalinity increase is very slight, from 0.122 at 76 meters to 0.124 at 513 meters.

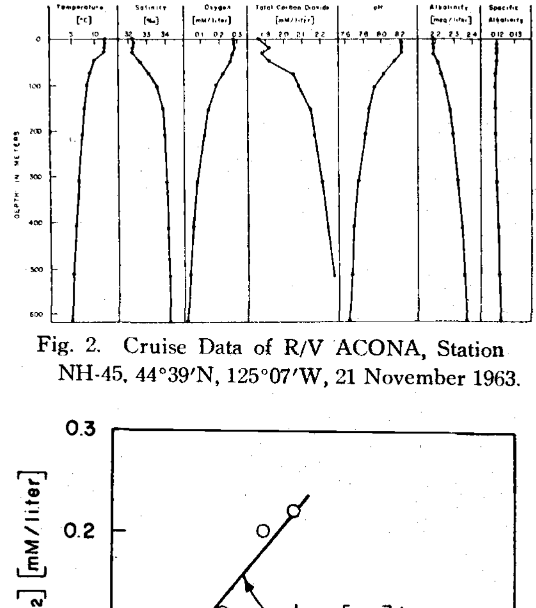

Fig. 2. Cruise Data of R/V ACONA, Station NH-45, 44°39′N, 125°07′W, 21 November 1963.

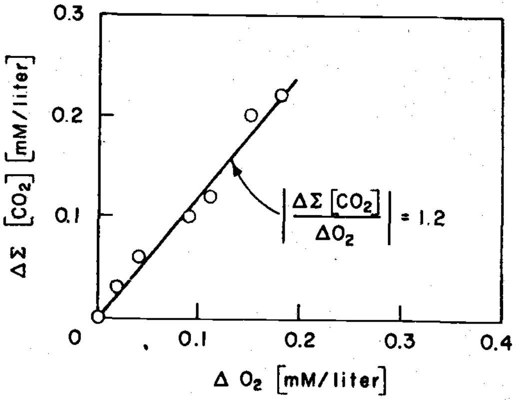

Fig. 3. Biological changes in the total carbon dioxide and dissolved oxygen concentrations.
Reference depth: 513m
Station: NH-45, 44°39′N, 125°07′W
Date: 21 November 1963

Figure 3 shows the biological changes in the concentrations of total carbon dioxide and dissolved oxygen with respect to the data at the 513-meter depth. The changes in the total carbon dioxide due to calcium carbonate dissolution below 76 meters were calculated from the changes in the specific alkalinity for deep waters by the use of the following equation:

$$\Delta[CO_2]_{(CaCO_3)} = \frac{\dfrac{[\text{Specific Alkalinity}_{(Zm)}] - [\text{Specific Alkalinity}_{(76m)}]}{2}}{[\text{Chlorinity}]} \qquad (10)$$

These quantities have been subtracted from the net changes in the total carbon dioxide. The effect of calcium carbonate dissolution was found to be about ten percent of biological alteration of the total carbon dioxide content.

Although the data are scattered (Figure 3), the ratio of biological changes in the total carbon dioxide to dissolved oxygen shows an average value of about 1.2. This is the same as Redfield's (1934) earlier value of 1.17. In order to understand the relationship between the observed $|\Delta\Sigma[CO_2]/\Delta O_2|$ ratio and the chemical nature and concentration of organic matter and organisms, much more work is needed.

## Total carbon dioxide in deep-sea water

The total carbon dioxide content of deep-sea water is affected by the decomposition of organisms as well as by the dissolution of calcium carbonate. Tolal carbon dioxide for deep water can be expressed as:

$$\Sigma[\mathrm{CO_2}]_{(\text{Deep Sea})}=\Sigma[\mathrm{CO_2}]_0+\Delta\mathrm{CO}_{2(\text{Biological})}+\Delta\mathrm{CO}_{2(\mathrm{CaCO_3})} \qquad (11)$$

Under given conditions the total carbon dioxide at the time of submergence, $\Sigma[\mathrm{CO_2}]_0$, can be determined by the partial pressure of atmospheric carbon dioxide, temperature, and salinity of the surface water from which the deep-sea water was formed. This quantity is a conservative property. Biological addition of carbon dioxide, $\Delta\mathrm{CO}_{2(\text{Biological})}$, may be obtained by subtracting the observed oxygen content from "biologically uninfluenced" oxygen content which originated from surface layers. The resulting "biologically consumed" oxygen content may be converted into corresponding "biologically added" carbon dioxide by multiplying the ratio of changes in total carbon dioxide to dissolved oxygen for the particular water mass under investigation. The ratio may be 1.2, instead of unity, if the water studied is similar to the water off the Oregon coast (See previous section). The "biologically uninfluenced" oxygen content can be calculated from the observed inert gas contents of deep-sea water (RICHARDS, 1957). Nitrogen/oxygen ratio has been used for this purpose (RAKESTRAW and EMMER, 1938). Since the extent of fixation in the marine environment is not well known, use of the argon/oxygen ratio should be more useful than the nitrogen/oxygen ratio for the estimation of the "biologically uninfluenced" oxygen content.

Recently, PYTKOWICZ and CONNORS (1964) studied the effect of pressure on the solubility of calcium carbonate in sea water. They concluded that deep water is essentially undersaturated with respect to calcium carbonate minerals. Therefore, carbonate minerals on the sea floor tend to dissolve into the surrounding water. This would be reflected in the concurrent increases in the titration alkalinity and total carbon dioxide. The increment of carbon dioxide content due to the dissolution of carbonate minerals can be calculated by employing the relationship between total carbon dioxide and alkalinity shown in equation (8). It may be as large as 0.1 mM/liter, for the changes in specific alkalinity is often in the order of 0.01 between the surface and deep-sea waters.

In the past, the pH-alkalinity method was used to determine total carbon dioxide in deep-sea water. Since the effect of pressure on the apparent dissociation constants of carbonic acid in sea water is not fully known (PYTKOWICZ, 1963) this method may not be the best way to estimate total carbon dioxide. Direct carbon dioxide determination is needed to eliminate this uncertainty.

From equation (11), it is apparent that if the total carbon dioxide content is known, any parameter on the right side of the equation can be estimated when the rest of the parameters are known. Carbon-14 dating indicates that some deep-sea water is several hundred years old or older. Thus, if we assume that the deep-sea water of today was once equilibriated with respect to the ancient atmosphere before it submerged into the deep-sea, we may be able to estimate the partial pressure of atmospheric carbon dioxide of several hundred years ago.

Direction of the deep-sea water flow may be obtained from the study of the distribution of the total carbon dioxide. When equal concentration lines of the total carbon dioxide are plotted along the sea floor, the direction of water flow over the floor would be normal to the concentration lines, from low to high concentrations.

In summary, this paper attempts to emphasize the importance of the parameter "total carbon dioxide in sea water" in the study of the carbon dioxide system, ecological system, and deep-sea circulation in the sea.

## Acknowledgments

This work was supported by the National Foundation grants GP-2232 and GP-2876, and by the Office of Naval Research contract Nonr 1286 (10), Project NR 083-102. I gratefully thank Hugh H. DOBSON, Magdalena CATALFOMO and Marilyn GEORGE for technical assistance.

## References

BUCH, K. (1951): Das kohlensaure Gleichgewichtssystem in Meerwasser. Havsforskn Inst. Skr., Helsingf., 151.

GAST, J. A., and T. G. THOMPSON (1958): Determination of the alkalinity and borate concentration of sea water. Anal. Chem., **30**, 1549-1551.

GREENBERG, D. M., E. G. MOBERG, and E. C. ALLEN (1932): Determination of carbon dioxide and titratable base in sea water. Ind. Eng. Chem. Anal. Ed., **4**, 309-313.

GRIPENBERG, S. (1960): On the alkalinity of Baltic waters, J. Cons. Int. Explor. Mer., **26**, 5-20.

HARVEY, H. W. (1960): The Chemistry and Fertility of Sea Waters. Cambridge Univ. Press, Cambridge.

KANWISHER, J. (1960): $pCO_2$ in sea water and its effect on the movement of $CO_2$ in nature. Tellus, **12**, 209-215.

LYMAN, J. (1956): Buffer mechanism of sea water. Ph. D. Thesis, Univ. Calif., Los Angeles.

NOAKES, J. E., and D. W. HOOD (1961): The distribution of boron and boric acide complexes in the sea. Deep-Sea Research, **8**, 121-128.

PARK, K. (1961): A study of calcium carbonate chemistry in the oceans with emphasis on the effect of dissolved organic matter. Ph. D. Thesis, Texas A & M Univ., College Station.

PARK, K., G. H. KENNEDY, and H. H. DOBSON (1964): Comparison of gas chromatographic method and pH-alkalinity method for the determination of total carbon dioxide in sea water. Anal. Chem., **36**.

PYTKOWICZ, R. M. (1963): Calcium carbonate and the *in situ* pH. Deep-Sea Res., **10**, 633-638.

PYTKOWICZ, R. M., and D. N. CONNORS (1964): The high pressure solubility of calcium carbonate in sea water. Science **144**, 840-841.

RAKESTRAW, N. W., and V. EMMEL (1938): The relation of dissolved oxygen to nitrogen in some Atlantic waters. Jour. Mar. Res., **1**, 206-216.

REDFIELD, A. C. (1934): On the proportions of organic derivatives in sea water and their relation to the composition of plankton. James Johnstone Memorial Volume, 179-192. Univ. Press, Liverpool.

RICHARDS, F. A. (1957): Oxygen in the ocean. Geol. Soc. Amer. Memoir, 67, **1**, 185-238.

RYTHER, J. H. (1956): The measurement of primary production. Limnol. Oceanogr., **1**, 72-84.

SARUHASHI, K. (1953): On the total carbonaceous matter and hydrogen ion concentration in sea water. Papers Meteorol. Geophys. Japan, **3**, 202-206.

SARUHASHI, K. (1955): On the equilibrium concentration ratio of carbonic acid substances dissolved in natural water. *ibid.*, **6**, 38-55.

THOMPSON, E. F., and H. C. GILSON (1937): Chemical and physical investigations. John Murray Exped., 1 Rep. **2**.

THOMPSON, T. G., R. C. MILLER, G. H. HITCHINGS, and S.P. TODD (1929): Studies of the sea water near the Puget Sound Biological Station during the summer of 1927. Publ. Puget Sd. (biol.) Sta., **7**, 65-99.

WELLS, R. C. (1918): New determinations of carbon dioxide in water of the Gulf of Mexico. U. S. Geol. Survey, Professional Paper **120**, 1-16.

WILSON, R. F. (1961): Measurement of organic carbon in sea water. Limnol. Oceanogr., **6**, 259-261.

## ERRATA

Page 54 fourth line in "Introduction" should read: ... bicarbonate and carbonate ions which are ...

Page 55 fourth line in "Theoretical consideration of the carbon dioxide system in sea water" should read: ... between bicarbonate ion, carbonate ion, and ...

Page 59 Reference by Park et al. (1964) should read: Anal. Chem., 36, 1686.

# Columbia River Plume Identification by Specific Alkalinity[1]

The plume of the Columbia River in the Pacific Ocean is the site of many interesting oceanographic processes (Stefánsson and Richards 1963). This water, measurably diluted by the Columbia River outfall, is easily identified by its salinity. For convenience, the plume has been defined as those waters contiguous to the mouth of the Columbia River having salinity less than 32.5‰. This definition, however, also includes seawater diluted by rain and by other river waters. For example, during the 17-month period, July 1963 through November 1964, surface waters 150–200 km west of Newport, Oregon, had salinities of less than 32.5‰. Other means for distinguishing plume waters from low-salinity surface waters needed to be found.

Specific alkalinity (alkalinity : chlorinity ratio) is potentially useful for making this distinction. The specific alkalinity of Columbia River water is about 1,000 times that of seawater. The river water has a chloride concentration of about 6 mg/liter and an alkalinity of about 1 meq/liter. Columbia River water, then, has a specific alkalinity greater than 100 meq/liter/(‰ Cl). On the other hand, the average chlorinity of surface waters 300 km off Oregon is 18.0‰, and the typical alkalinity is 2.23 meq/liter. Therefore, the specific alkalinity of the surface ocean water is about 0.124.

Rain falling on the ocean decreases the salinity of surface waters, but it does not change the specific alkalinity, because the alkalinity and the chlorinity are diluted equally by the rain. Thus, plume water should have a higher specific alkalinity than rain-diluted surface water of the same salinity.

Oregon coastal streams are short. Their discharge volumes are small compared with the Columbia River, and their runoffs are minimal in summer. Also, during summer, coastal runoff mixes near the coast with highly saline upwelled waters. Thus, runoff from coastal streams has an insignificant effect on the plume during summer. During winter, the plume flows north along the Washington coast. Because both alkalinity and discharge data are not available for Washington coastal streams, the effect of coastal streams on the plume during winter cannot yet be evaluated.

Recently, the seasonal and spatial distri-

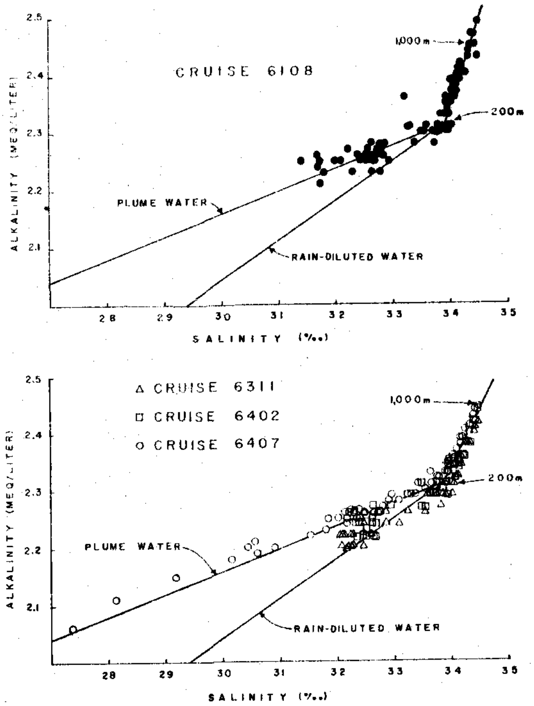

FIG. 1. Alkalinity vs. salinity. Samples are from RV *Acona* cruises 6108 (August 1961), 6311 (November 1963), 6402 (February 1964), and 6407 (July 1964) along the east–west line from the coast to 300 km off Newport, Oregon.

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[1] This work was supported by National Science Foundation Grants GP-2232 and GP-2876, and Office of Naval Research Contract Nonr-1286(10), Project NR 083-102. Field assistance of L. W. Latimer, W. A. DeBen, and H. H. Dobson is appreciated.

bution of alkalinity off Oregon was investigated (Park, in preparation). Below depths of 200 m, the salinity was consistently greater than 33.9‰ and the alkalinity was always greater than 2.31 meq/liter. The alkalinity–salinity correlation was linear below 200 m (Fig. 1). Conversely, above 200 m the alkalinity–salinity relationship was greatly affected by the plume, by rain-dilution, and by other local processes. These observations have proved to be useful in the estimation of alkalinity in plume water.

The alkalinity of Columbia River waters has been measured frequently at Clatskanie, Oregon, 85 km upstream from the mouth, by the Oregon State Sanitary Authority and the U.S. Public Health Service (U.S. Public Health Service 1961). Their data, converted to meq/liter from mg/liter, and daily river flow rates are shown in Fig. 2. It is apparent that the average alkalinity of the river is about 1 meq/liter.

To estimate the alkalinity of plume waters, it was assumed that the alkalinity was related to salinity by the straight line between points representing typical river water and typical ocean water. On the basis of the above data, it was assumed that river water was characterized by a salinity of zero and an alkalinity of 1 meq/liter. Typical ocean water was assumed to have a salinity of 33.9‰ and an alkalinity of 2.31 meq/liter. The alkalinity of the plume can then be expressed as a function of the salinity (S, in ‰):

$$\text{Alkalinity (meq/liter)} = \frac{(2.31 - 1.00)}{(33.9 - 0.0)} S + 1.00. \qquad (1)$$

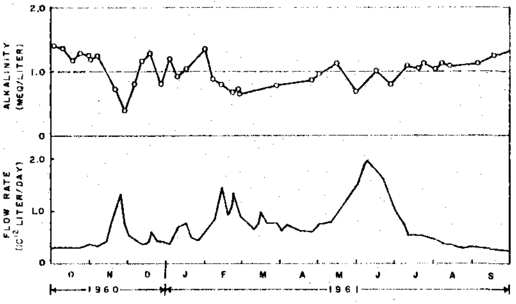

FIG. 2. Variation of alkalinity and flow rate of the Columbia River water at Clatskanie, Oregon, during the period October 1960 to September 1961. Data are from the U.S. Public Health Service (1961).

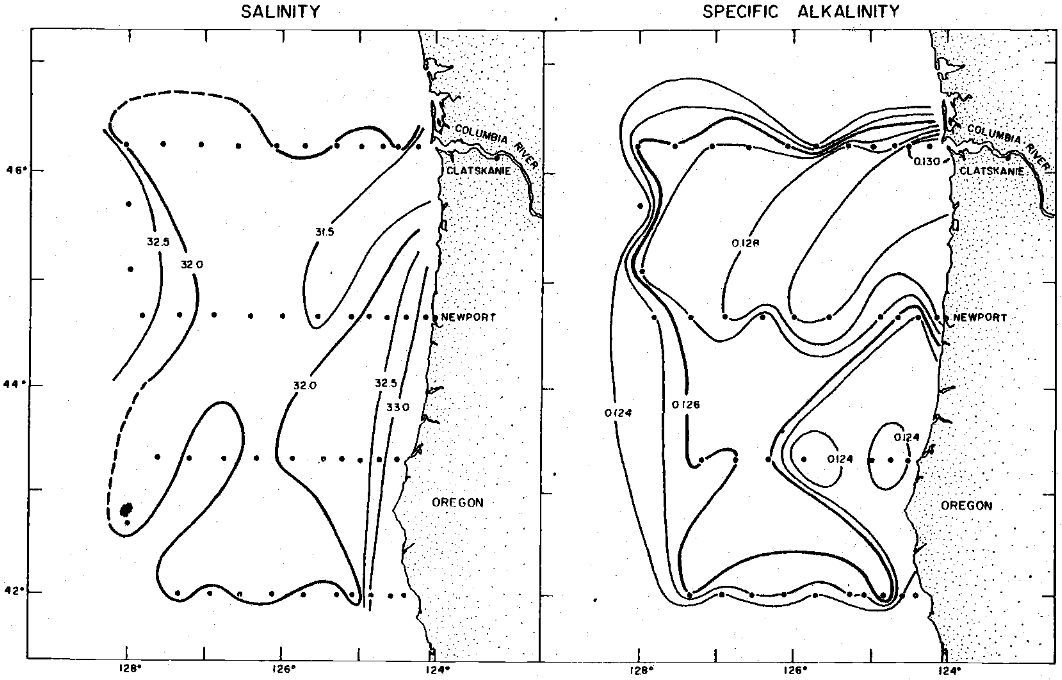

FIG. 3. Surface salinity and specific alkalinity distribution off Oregon, August 1961.

Alkalinities calculated from the above equation agree fairly well with *RV Acona* cruise data of August 1961 (Cruise 6108) and July 1964 (Cruise 6407) (Fig. 1). The data of November 1963 (Cruise 6311) and February 1964 (Cruise 6402) show evidence of the dilution of surface waters by rain (Fig. 1).

Plume water with a salinity of 32.5‰ would have, according to equation 1, an alkalinity of 2.25 meq/liter and a specific alkalinity of 0.127. Rain-diluted seawater of the same salinity would have an alkalinity of 2.21 meq/liter and a specific alkalinity of 0.124. The 2% difference in alkalinity at 32.5‰ salinity is barely distinguishable by the analytical method of Anderson and Robinson (1946) that was used. Data obtained by their method have a relative standard deviation of ± 0.9%.

It is concluded that Columbia River plume water has salinity less than 32.5‰ and specific alkalinity equal to or greater than 0.127. Because the specific alkalinity of surface waters outside the plume is generally 0.124 and seldom exceeds 0.125, a value of 0.126 may be taken as a reasonable lower limit for the specific alkalinity of the plume.

When the above specific alkalinity criterion is applied to the data obtained in August 1961, it is found that surface water satisfying both the salinity and specific alkalinity requirements for the Columbia River plume covers a large area off the Oregon coast (Fig. 3). For these data, specific alkalinity of 0.126 corresponds closely to the 32.0‰ salinity isopleth.

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### REFERENCES

ANDERSON, D. H., AND R. J. ROBINSON. 1946. Rapid electrometric determination of the alkalinity of sea water using a glass electrode. Ind. Eng. Chem. (Anal. Edition), **18**: 767–769.

STEFÁNSSON, U., AND F. A. RICHARDS. 1963. Processes contributing to the nutrient distribution off the Columbia River and Strait of Juan de Fuca. Limnol. Oceanog., **8**: 394–410.

U.S. PUBLIC HEALTH SERVICE. 1961. National Water Quality Network. Annual compilation of data, October 1, 1960–September 30, 1961, p. 109–110. Public Health Service Publ. No. 663, 1961 ed.

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# Strontium-90 and Caesium-137 in Columbia River Plume, July 1964

OCEANOGRAPHERS informally term the extension of Columbia River outflow into the Pacific Ocean as the 'Columbia River plume'. The plume can be identified by its low salinity even at a distance of several hundred kilometres from the mouth of the river (Fig. 1). The plume distributes dissolved and suspended substances in the river water over a wide surface area of the ocean and introduces annually to the euphotic zone over a billion moles of phosphorus and nitrogen fertilizers, as phosphate and nitrate. Equally significantly, the radionuclides contained in the river water are diffused over a wide region[1].

To understand the ocean mixing process of $^{90}$Sr and $^{137}$Cs originating in the river, we collected eight 100-l. surface-water samples from the river, the river plume, and its vicinity during July 12–24, 1964. The Millipore-filtered water samples were analysed for their $^{90}$Sr content

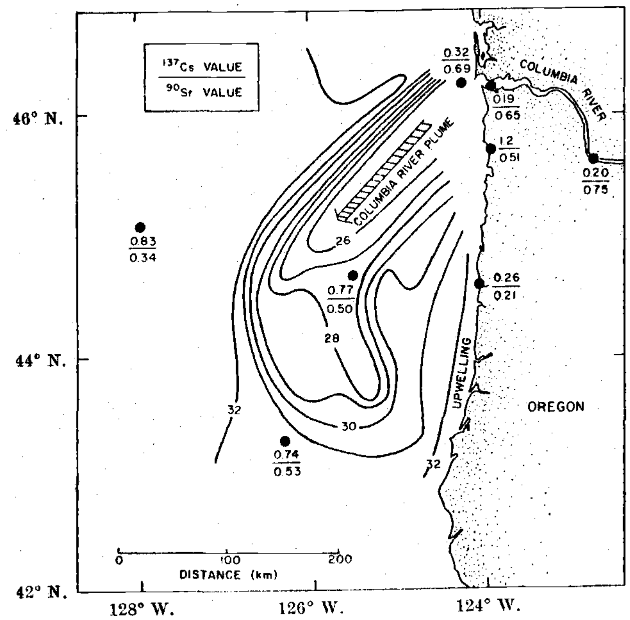

Fig. 1. **Surface salinity,** $^{90}$Sr and $^{137}$Cs distributions in the Columbia River plume, **July 1964.** Contours are surface salinity in parts per thousand. **$^{90}$Sr and $^{137}$Cs** concentrations are in $\mu\mu$c./l. with a relative **standard** deviation of ± 10 per cent

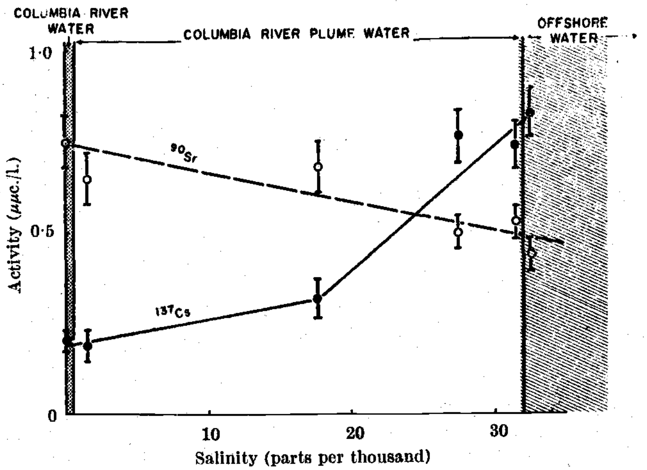

Fig. 2. $^{90}$Sr and $^{137}$Cs concentrations in and near the Columbia River plume, July 1964, as a function of salinity

by the fuming nitric acid method[2] and for $^{137}$Cs by the ammonium molybdophosphate method[3] at the Meteorological Research Institute, Tokyo. The results and the surface salinity pattern are shown in Fig. 1.

The river water near Portland, Oregon, gave $^{90}$Sr and $^{137}$Cs concentrations of 0·75 and 0·20 μμc./l. respectively. The river water contains the radionuclides from two sources: world-wide fall-out and by-product of the operation of the Hanford atomic reactor[4].

We have no measured concentrations in the river for the isotopes produced at Hanford, but they may be indirectly estimated by comparing the $^{90}$Sr and $^{137}$Cs content of Japanese river waters with that of Columbia River water. Japanese waters contain only fall-out. Average Japanese river waters contained 0·19 μμc./l. of $^{90}$Sr and 0·034 μμc./l. of $^{137}$Cs in 1961 (ref. 5). At Pasco, downstream from Hanford, the annual average concentration for $^{90}$Sr in 1962 was 0·7 μμc./l. (ref. 4). If we assume that the $^{90}$Sr concentrations in Japanese rivers were similar to the fall-out portion of the $^{90}$Sr content of Columbia River water, then about 0·5 μμc./l. of $^{90}$Sr would appear to be contributed by the Hanford operation in 1962. Similar $^{90}$Sr content could have originated from Hanford in 1964.

The sampling station most distant from the shore was more than 300 km off the Oregon coast (Fig. 1). Its water is the least affected by the river plume, and, therefore, should be representative of the oceanic water for this region. We found $^{90}$Sr and $^{137}$Cs concentrations of 0·34 and 0·83 μμc./l., respectively, and a salinity of 32·5 parts per thousand. Other waters collected off the coast are in the river plume and can be expected to show effects of a mixture of offshore water and river water. If physical mixing is the only mechanism regulating the concentration of the nuclides, then the plume waters should possess radioisotopic concentrations proportional to the contribution of the two parental water bodies. Fig. 2 confirms this simple mixing theory in first approximation. $^{90}$Sr appears to have a better linear correlation with salinity than $^{137}$Cs.

Comparison of the $^{90}$Sr content in the river water and the offshore water shows that the river water contains about 0·3 μμc./l. more than the offshore water (Fig. 2). Conversely, the $^{137}$Cs content in the river water is about 0·6 μμc./l. lower than that of the sea water.

A peculiarly high $^{137}$Cs concentration of 1·2 μμc./l. was observed in the estuarine water of the Nehalem River mouth, about 70 km south of the mouth of the Columbia River (Fig. 1). No satisfactory explanation is available at present.

The upwelled water at Newport, Oregon, had low $^{90}$Sr and $^{137}$Cs contents of 0·21 and 0·26 μμc./l., respectively. The salinity of this water, 33 parts per thousand, indicates that the water had been upwelled from 100 m depth. The data from the upwelled water appear to confirm the decrease of the nuclide concentration with increasing depth[6].

Folsom, Mohanrao and Winchell[7] determined the $^{137}$Cs content of sea water along and off the coast of California in 1959 and 1960. Their work is still continuing. According to Folsom (personal communication) $^{137}$Cs concentrations off California, between 30° and 35° N., and from the coast to 130° W., were about 0·7 μμc./l. in surface waters in 1964. His values are in agreement with ours.

In conclusion we find that both $^{90}$Sr and $^{137}$Cs concentrations of the Columbia River plume waters are, in first approximation, proportional to the contribution of the river waters as determined from salinity.

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[1] The river-originated $^{51}$Cr has been used to investigate the Columbia River plume in 1965 by Osterberg, C., Cutshall, N., and Cronin, J. (in preparation).

[2] Miyake, Y., Saruhashi, K., and Katsuragi, Y., *Papers Meteorol. Geophys., Tokyo*, **11**, 188 (1960).

[3] Miyake, Y., Saruhashi, K., Katsuragi, Y., and Kanazawa, T., *Papers Meteorol. Geophys., Tokyo*, **12**, 85 (1961).

[4] Wilson, R. H., *Evaluation of Radiological Conditions in the Vicinity of Hanford for 1962* (Hanford Laboratories, AEC Res. and Dev. Rep. *HI*-76526, 1963).

[5] Miyake, Y., Tsubota, H., *Radioisotopes in Hydrology*, 425 (Intern. Atomic Energy Agency, Vienna, 1963).

[6] Miyake, Y., and Saruhashi, K., *Disposal of Radioactive Waste*, 169 (Intern. Atomic Energy Agency, Vienna, 1960).

[7] Folsom, T. R., Mohanrao, J. G., and Winchell, P., *Nature*, **187**, 480 (1960).

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# PRELIMINARY STUDIES ON ANIMAL-SEDIMENT INTERRELATIONSHIPS OFF THE CENTRAL OREGON COAST

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## Abstract

Research on the distribution and abundance of benthic invertebrates off central Oregon is in progress. The effects of sediment composition on the fauna are being studied. An east-west line of 26 stations has been sampled from the coast to a depth of 2800 m and a distance of 165 miles offshore. Particle size generally decreases with depth and distance from shore, while organic content of the sediment increases with decreasing particle size. The macro- fauna are most abundant at the edge of the continental shelf and decrease to very low densities 165 miles from shore. Faunal abundance beyond the inner shelf is fairly well correlated with organic content of the sediment. On the outer shelf and beyond, the proportion of deposit-feeding, burrowing polychaetes increases with increasing organic content and decreasing particle size of the sediment. There are zones of faunal change which seem to be associated with marked changes in sediment composition. Though the distribution and abundance of the fauna is probably controlled by a complex of factors, the sediment appears to have significant effect along certain parts of the area under study.

## Introduction

The sedimentary portion of the marine benthic environment plays a major role in determining the distribution and abundance of benthic invertebrates. For macro- fauna the sediment comprises a major portion of their physical environment. In level bottom communities on the inner shelf, the major animal components are strongly influenced by the texture of the sediment, and specific communities are known to exist with certain sediment types (see the 1957 review by Thorson).

In the present study sediment composition along a line of stations off the central Oregon coast has been analyzed as part of a broad study of the ecology of bottom invertebrate organisms. Particle size and carbon content of the sediment have been investigated. These geologic studies provide data for determining the effects of sediment on the distribution and abundance of the fauna.

The author expresses his gratitude to Neil J. Maloney for undertaking a portion of the textural analyses; to Danil R. Hancock and Mary Ann Alspach for indispensable laboratory assistance with biological and geological samples; and to Dr. D. J. Reish and Dr. J. L. Barnard for identifications of polychaetes and gammarid amphipods, respectively.

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## Materials and Methods

The distribution and abundance of the benthos and their relation to various factors of their environment have been studied since June 1962, at 26 stations off Newport, Oregon. The stations extend across the continental shelf, down the continental slope, and onto Cascadia Abyssal Plain to a depth of about 2800 m and a distance of 165 miles offshore (Table 1). Routine stations on the shelf are at 25 m depth intervals to 200 m, and at 200 m intervals down the slope to 2600 m. On the plain, there are six stations spaced every 20 miles. Most stations have been sampled a number of times, and many of the data reported are averages.

TABLE 1

BENTHOS STATIONS

| Station No. | Distance From Shore (mi) | Position | | Depth (m) |
|---|---|---|---|---|
| | | Latitude | Longitude | |
| 1 | 1.7 | 44° 39.1'N | 124° 05.9'W | 30 |
| 2 | 4.8 | | 124° 09.8'W | 50 |
| 4 | 10.9 | 44° 44.0'N | 124° 18.2'W | 100 |
| 6 | 19.5 | | 124° 30.0'W | 150 |
| 7 | 22.2 | | 124° 34.2'W | 175 |
| 8 | 23.6 | 44° 39.1'N | 124° 36.0'W | 200 |
| 8A | 23.8 | | 124° 36.5'W | 225 |
| 9 | 33.8 | | 124° 50.7'W | 400 |
| 10 | 36.5 | | 124° 54.0'W | 600 |
| 11 | 39.2 | | 124° 57.6'W | 800 |
| 11A | 46.6 | | 125° 06.8'W | 800 |
| 12 | 47.4 | | 125° 09 1'W | 1000 |
| 13 | 48.0 | | 125° 10.0'W | 1200 |
| 14 | 48.8 | | 125° 11.0'W | 1400 |
| 15 | 49.2 | | 125° 11.7'W | 1600 |
| 16 | 49.5 | | 125° 12.1'W | 1800 |
| 17 | 51.5 | | 125° 14.9'W | 2000 |
| 17A | 53.8 | | 125° 19.5'W | 2000 |
| 20 | 55.1 | | 125° 20.5'W | 2600 |
| 21 | 65 | | 125° 20.5'W | 2600 |
| 22 | 86.0 | | 126° 03.0'W | 2800 |
| 23 | 95.1 | | 126° 16.3'W | 2800 |
| 25 | 147.0 | | 127° 28.2'W | 2800 |
| 26 | 165.5 | | 127° 54.3'W | 2800 |

The Oregon continental shelf is characteristically narrower, steeper, and deeper than the average shelf (Byrne, 1962); it is approximately 22 miles wide off Newport. The northern end of a rocky shoal, Stonewall Bank, lies 17 miles from shore, and Byrne (1962) has described a truncated seamount near the edge of the shelf. The continental slope west of Newport is about 32 miles wide and has an average inclination of about $3^{o}$. There are two troughs with seaward ridges with maximum depths of about 1100 and 2200 m (Byrne, 1962; and Maloney, Unpubl. Ph.D. Thesis). Cascadia Abyssal Plain begins approximately 54 miles offshore and maintains a depth of 2700-2800 m to 165 miles where a ridge and seamount province begins (Menard, 1964). Cascadia Abyssal Plain is actually a continental rise, but biologically and environmentally it is a plain in the abyssal zone as defined by Bruun (1957).

Sediment and faunal samples were collected with a Sanders Deep Sea Anchor Dredge (Sanders and Hessler, Unpubl. manuscript), which collects large quantities of sediment from a defined surface area. The dredge cuts into the sediment to a constant depth of 13 cm and can sample up to 2 $m^2$ of sediment surface. Faunal data come from 92 quantitative samples, mostly paired and averaging 0.6 $m^2$ in area. Sixty-six and eighty-five samples, respectively, were used for analysis of carbon content and sediment texture. On board ship moist subsamples were removed for particle size and carbon analyses. Those taken for carbon analyses were frozen to minimize biological activity. The remainder of the sediment was washed through a 0.42 mm aperture sieve (U.S. Standard No. 40) to collect the macrofaunal invertebrate organisms. These were picked out, sorted, and counted in the laboratory. Identifications and detailed studies of the fauna are in progress.

Particle size analyses were made by standard geological techniques with a graded series of sieves and settling tube for the sand and a soils hydrometer for the silt and clay (Krumbein and Pettijohn, 1938). Each sample analyzed contained 90 to 100 g (dry weight) of sediment.

Analyses of total carbon content were made on 0.4 g of sediment by complete combustion with a LECO electric induction furnace; the evolved $CO_2$ was measured with a LECO gas analyzer (Curl, 1963). Carbonate carbon was measured by adding 10 ml 6N HCl to 0.5 g of sediment and measuring the evolved gas in the gas analyzer. All analyses were run in duplicate. The induction furnace and gas analyzer were routinely standardized using reagent grade chitin and $CaCO_3$. Organic carbon was found as the difference between the total carbon and the carbonate carbon.

## Results

### SEDIMENT CHARACTERISTICS

Texture. Particle size of the sediment generally decreases with depth and distance from shore (Figure 1). However, the rugged topography causes interference of seaward transport of particulate material; variability and patchiness are characteristic of the slope. The median diameter abruptly decreases on the outer shelf and slope.

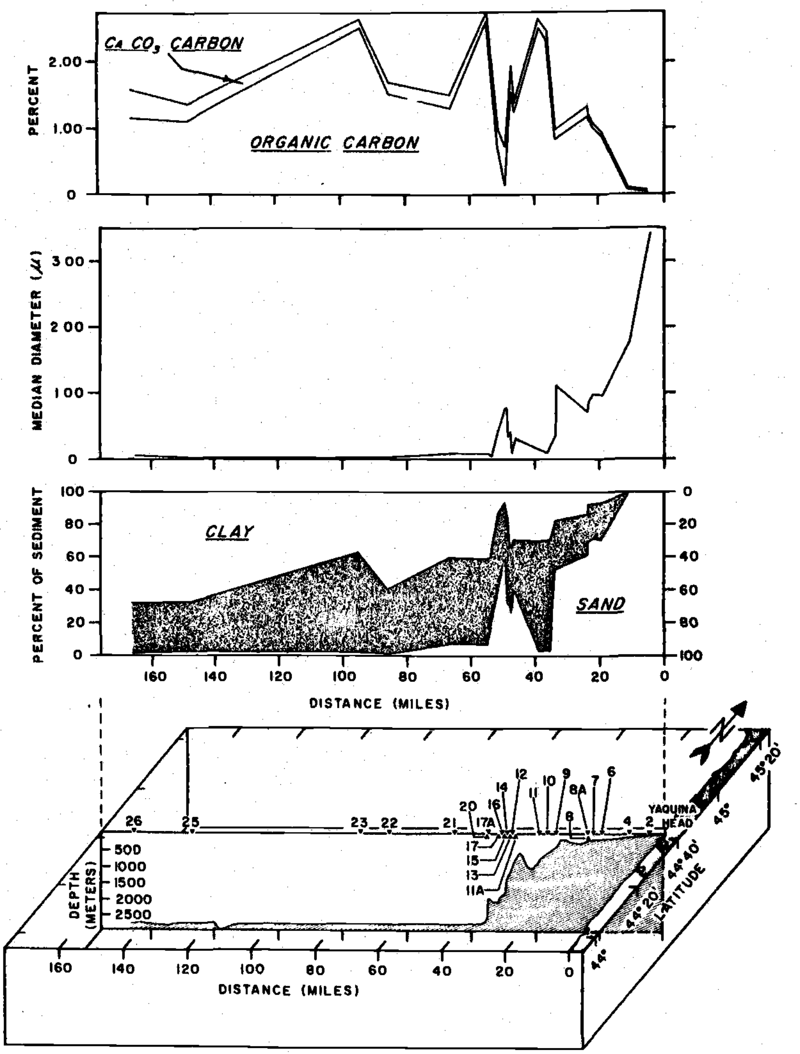

Figure 1. Sediment characteristics plotted against distance with topography and stations noted.

The proportion of terrigenous sands rapidly decreases with depth and distance, from 100% of the sediment at 100 m depth to 2.3% at the 800 m station (11) in the first slope valley. The sand component again increases on the seaward side of the valley ridge (station 11A) due to formation of the authigenic mineral, glauconite. The sands are well sorted at the 50 and 100 m stations, indicating the existence of reasonably constant current or wave conditions over the sediments. Further offshore the sediments are much more diverse.

The percentage of silt and clay gradually increases with distance. At stations 25 and 26, 145 and 165 miles from shore in depths of 2700 m, the clay makes up two-thirds of the total sediment. Silt reaches its maximum percentage 95 miles from shore at a depth of 2800 m.

There are marked changes in sediment composition between a number of stations, particularly on the outer shelf and slope where there are prominent topographic features (see Figure 1).

Carbon Content. The total carbon content remains very low in the sandy inner shelf sediments (Figure 1). It rises with a decrease in particle size, reaching several maxima at stations 6, 8A, 11, 20 and 23. The $CaCO_3$ carbon is a minor component at all stations studied; the carbon present is largely organic. As Trask (1939) has reported, the carbon content is most closely associated with the finer components of the sediment, the clays and fine silts. There is an inverse relationship between the organic carbon content and the median diameter.

## MACRO- FAUNA

The major taxa show changes in relative abundance with increasing depth and distance from shore (Figure 2). At the shallowest station the arthropods account for over 50% of the fauna; filter-feeding gammarid amphipods are the dominant members of this group. On the continental slope from 22 to 54 miles offshore the fauna, as well as the sediment, show great variation. The mollusks decrease seaward, and the polychaetes increase in relative abundance as the sediment becomes finer with depth. Near the base of the slope, the arthropods reach another maximum due to an abundance of isopods. Over most of the plain the polychaete worms are clearly the most important group. Wherever the sediment is soft and the organic content high, these deposit-feeding organisms are present in large numbers. Echinoderms, mainly ophiuroids, increase at the western end of the station line. The miscellaneous fauna, consisting mainly of the smaller worm groups, become proportionately greater in the middle of the plain.

There is a characteristic distribution pattern of fauna along the station series. Polychaetes and gammarid amphipods, for example, show similar zones where changes occur in species and species groups present (Figure 3). These are at 25, 175-200, 400, 800, 2000, 2600, 2800 m for species identified to date. This pattern is evident in all groups studied so far. Though a number of species have an extremely broad range in both sediment type and depth, the majority of the fauna are restricted to a portion of the total range, or even to one station.

The areas of transition are at stations where rather large and abrupt changes in sediment texture and composition have been noted (Figure 1). The 25 m station is an exception; the sandy sediment remains uniform out to 100 m.

Deposit feeders assimilate the organic material in the sediments; thus, they should be more abundant in areas with a higher organic carbon content in the sediments. Being efficient deposit feeders and burrowers, polychaete worms were used in this study as indicators of the relative

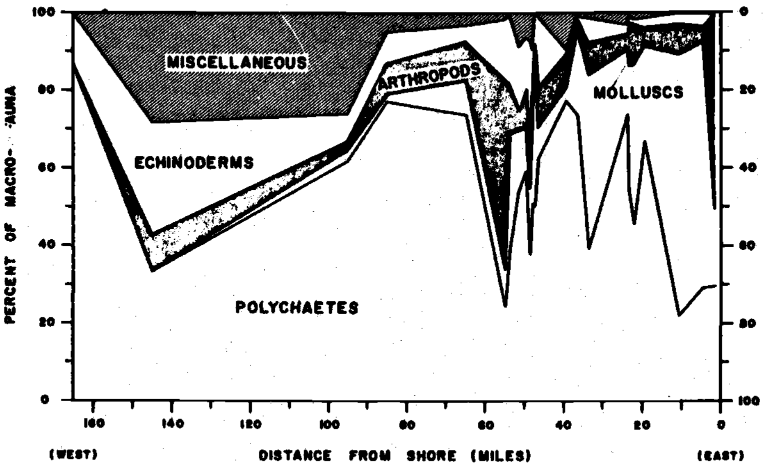

Figure 2. Relative abundance of major taxa of the macrofauna plotted against distance from shore.

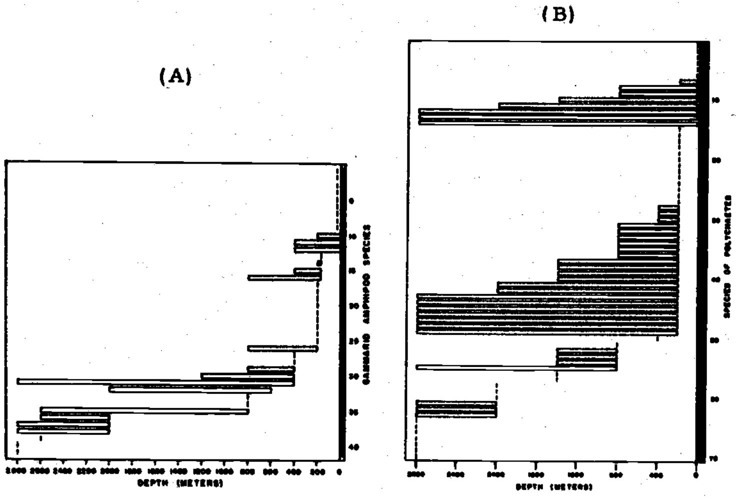

Figure 3. Distribution pattern with depth of gammarid amphipods (A) and polychaete worms (B).

importance of this ecologic group within the faunal assemblages. Soft sediment is important to the polychaetes for both easy burrowing and adequate food supply.

Of the sediment characteristics, organic carbon fits best with the polychaete distribution. The relative importance of polychaetes at the stations varies with the percent organic carbon in the sediment on the outer shelf, and over some of the slope and plain (Figure 4).

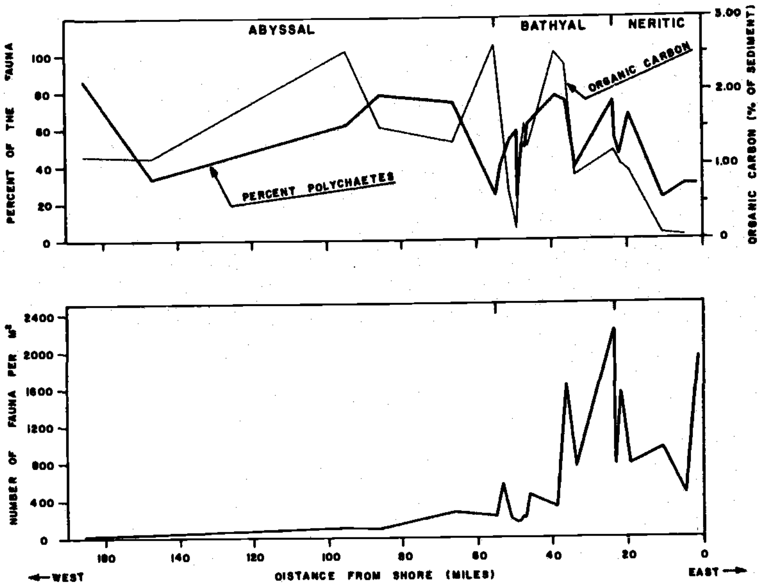

Figure 4. TOP - Frequency distribution of polychaetes with organic content of sediment plotted against distance from shore. Polychaete frequency is expressed as percentages of the total numbers of macro- fauna collected. BOTTOM - Abundance of macro- fauna (no/m$^2$) plotted against distance from shore.

The abundance of macro- fauna along the station line is illustrated in Figure 4. A total of 1943 individuals/m$^2$ was found at 30 m. The food supply in the water column is probably largely from primary production and terrestrial export, even though the organic content of the sediment is extremely low. The fauna increases in abundance near the edge of the shelf at a depth of 175 m, reaching an average of 1553 individuals/m$^2$. Here again plankton and detritus in the water column, turbulence, and a high rate of sedimentation would provide an adequate food supply, though only moderate amounts of organic material are present in the sediment. The greatest abundance of organisms, 2215/m$^2$, is found on the upper slope at 225 m. The density decreases down the slope and reaches a smaller maximum of 565 individuals/m$^2$ at 2000 m. The numbers then steadily decrease to the last station 165 miles offshore.

## Discussion

The sediment types found off central Oregon are typical for the topography and depths studied (Shepard, 1963); they are primarily of terrigenous origin. Though there are general trends of decreasing grain size with concomitant increasing organic content, the relationships with depth and distance from shore are non-linear. Trask(1939) and Revelle and Shepard (1939) have shown that sediment characteristics are related more to bottom configuration than distance from shore. This is particularly true of the shelf and slope in the present study. Patchiness is apparent on the slope; a variety of siltstones and some sandstone have been found as well as softer sediment (Maloney and Byrne, 1964).

The levels of organic carbon and carbonate carbon fall within the averages found by Trask (1939), Revelle and Shepard (1939), Emery (1960), and Bushnell (1963) for comparable environments. On the inner shelf off Oregon water motion is likely strong enough to prevent the light organic material from settling to the bottom. The sediments are well-sorted very fine and fine sands with very low organic content.

The carbon content reaches a maximum in the first slope valley where the smaller sediment components dominate. Organic material can reach the bottom by settling out similarly to the fine-grained sediments or by being adsorbed onto small sediment particles (Emery, 1960). On the plain organic carbon reaches a maximum 95 miles from shore where the silt fraction is at its maximum. The organic carbon values decrease seaward from this point, probably because of a decreased supply of material from productive waters inshore and from the surface waters. The length of time taken by particles to settle out at the abyssal stations would provide time for bacterial breakdown of much of the organic detritus being produced in surface waters. The smaller amount of organic material found toward the western end of the line probably reflects the decreasing supply from shallower areas.

The abundance of macro- fauna on the shelf off Newport, Oregon, does not appear to be very much greater than that of the slope. The densities of abyssal fauna decrease with distance, though those on the eastern half of Cascadia Abyssal Plain are the highest found for the northeast Pacific at comparable depths (Table 2).

Many difficulties are encountered comparing results from different benthic studies. Differences in sampling gear, screen sizes, and processing techniques can alter results drastically (e.g. Reish, 1959). Therefore, only trends can be suggested, unless similar techniques are used throughout.

Keeping these cautions in mind, a comparison of data from the present study and others indicate that the Oregon shelf fauna is probably less abundant than elsewhere (Table 2). Though larger screens were used by Hartman, Barnard, and Jones (1960) on the southern California shelf, larger numbers of organisms were found. As in the present study larger populations were found on the outer shelf than the inner shelf. Our techniques were similar to those used by Sanders and Hessler (Unpubl. manuscript; and Chave et al, 1962); thus, more direct comparisons can be made. Though the shelf fauna off the Northeast coast is three times as abundant as that off Oregon, the slope fauna appear in more comparable numbers. The Oregon abyssal macrofauna are less abundant than the fauna at similar depths in the northwestern Atlantic north of the Gulf stream. Under the Gulf Stream and in the Sargasso Sea, however, the densities are closer to those found in the present study.

TABLE 2

Numbers of Benthic Macro- fauna

| Zone | No/$m^2$ | Location |
|---|---|---|
| Shelf | 500-1900 | Oregon (present study) |
| | 2500-5000 | S. California (Barnard, Hartman, and Jones, 1960) |
| | 6000 | N.E. Coast (Sanders and Hessler, unpubl. manuscript) |
| | 700-5100 | Massachusetts (Wigley and McIntyre, 1964) |
| Slope | 200-2200 | Oregon (present study) |
| | 1500-3000 | East Coast (Sanders and Hessler) |
| | 100-1000 | Bermuda (Sanders and Hessler) |
| | 11- 123 | Deep California Basins (Hartman and Barnard, 1960) |
| Abyss | 14- 271 | Oregon (present study) |
| | 43 | Velero Basin, California (Hartman and Barnard, 1960) |
| | 5- 85 | N.E. Pacific (Filatova and Levenstein, 1961) |
| | 400-1000 | Atlantic, N. of Gulf Stream (Sanders and Hessler) |
| | 250 | Atlantic, Gulf Stream (Sanders and Hessler) |
| | 25- 100 | Atlantic, Sargasso Sea (Sanders and Hessler) |

Further research and comparisons of techniques and environmental parameters should be made before the differences between Oregon and other areas can be understood. Comparisons of biomass would be valuable. It may be that, except for the Bermuda region, the rate and amount of food supply off Oregon are smaller. In the present study animal abundance decreases westward to a minimum of 14 individuals/$m^2$ 165 miles from shore, presumably because of the decrease in organic content of the sediments.

As there are zones in the area under study off Oregon where the faunal assemblages undergo change, it is likely that a series of benthic animal associations are present. A complex of environmental factors, e.g. sediment, temperature, pressure, and food supply, would affect their distributions. Further research is necessary before the relative effects of the various environmental factors can be determined. In the northwest Atlantic Sanders (1963) has also found the benthic fauna to be layered in depth zones.

## Summary and Conclusions

Sediment size generally decreases with depth and distance from shore, though topography produces variability, particularly on the continental slope.

Organic carbon is found in low to moderate amounts, lowest in the inner shelf sediments and highest on the lower slope. It varies closely with the finer grain sizes of the sediment.

The relative abundance of deposit-feeding burrowing forms increases along with the finer components of the sediment and a concomitant increase in organic content.

There are zones where distributions of all groups studied undergo changes in species and species groups. These zones are associated with marked changes in the sediment composition.

The macro- fauna reach the greatest abundance at the shelf edge, Over much of the outer shelf and slope, the peaks of abundance are associated with the organic content of the sediments.

It is felt that sediment type is one of a complex of factors that affect the distribution and abundance of the benthic invertebrate fauna. It appears to be quite important in certain portions of the area under study.

## Bibliography

Bruun, A. F. 1957. Deep sea and abyssal depths. Chapt. 22 In Treatise on marine ecology and paleoecology. Vol. 1, Ecology. J. W. Hedgpeth, ed. Mem. 67, Geol. Soc. Amer. Waverly Press, Balto, p. 641-672.

Bushnell, D. 1963. Continental shelf sediments in the vicinity of Newport, Oregon. Unpubl. M. S. Thesis.

Byrne, J. V. 1962. Geomorphology of the continental terrace off the central coast of Oregon. Ore Bin. 24(5): 65-74.

Chave, K. E., H. L. Sanders, R. R. Hessler and A. C. Neumann. 1962. Animal-sediment interrelationships on the Bermuda slope and in the adjacent deep sea. Bermuda Biol. Sta. Final Report. ONR Contract Nonr 1135(02).

Curl, H. C., Jr. 1963. Analyses of carbon in marine plankton organisms. J. Mar. Res. 20: 181-188.

Emery, K. O. 1960. The sea off Southern California. John Wiley and Sons, Inc., New York 366 p.

Filatova, Z. A., and R. J. Levenstein. 1961. Quantitative distribution of deep sea bottom infauna in the northeastern Pacific. Trudy Inst. Okeonol. 45: 190-213. (In Russian).

Hartman, O. and J. L. Barnard. 1960. The benthic fauna of the deep basins off Southern California: continued studies in the seaward and deeper basins. Allan Hancock Pacific Exped. 22(2): 217-284.

Krumbein, W. C. and F. J. Pettijohn. 1938. Manual of sedimentary petrography. D. Appleton-Century Co., New York. 549 p.

Maloney, N. J. 1965. Physiography of the continental slope off the central coast of Oregon. Unpubl. Ph. D. Thesis.

Maloney, N. J., and J. V. Byrne. 1964. Sedimentary, rocks from the continental shelf and slope off the central coast of Oregon. Ore Bin. 26(5): 77-81.

Menard, H. W. 1964. Marine geology of the Pacific. McGraw-Hill, Inc. New York. 271 p.

Reish, D. J. 1959. A discussion of the importance of the screen size in washing quantitative marine bottom samples. Ecology. 40(2): 307-309

Revelle, R. and F. P. Shepard. 1939. Sediments off the California coast. In Recent marine sediments, P. D. Trask, ed., Amer. Assoc. Petrol. Geol. p. 245-282.

Sanders, H. L. 1963. The deep sea benthos. AIBS Bull. 13(5): 61-63.

Sanders, H. L. and R. R. Hessler. Unpublished manuscript.

Shepard, F. P. 1963. Submarine geology, Harper and Row, New York, 557 p.

Thorson, G. 1957. Bottom communities. Chapt. 17. In Treatise on Marine ecology and paleoecology. Vol. 1. Ecology. J. W. Hedgpeth ed., Mem. 67, Geol. Soc. Amer., Waverly Press, Balto. p461-534.

Trask, P. D. 1939. Organic content of recent marine sediments. In Recent Marine Sediments. P. D. Trask, ed. Amer. Assoc. Petrol. Geol. p. 428-453.

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# INSTRUMENTS and METHODS

## An Anchor-box Dredge for deep-sea sampling

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(*Received* 28 *July* 1965)

**Abstract**—The Anchor-Box Dredge, a modified Sanders Deep-Sea Anchor Dredge, has been developed for studying benthic fauna of the deep ocean floor. The dredge is capable of obtaining large samples of the top 10 cm of sediment from an area up to 1·3 m$^2$. A throat valve, frontal planing surface, and towing bale enable it to collect unwashed samples cut at a constant depth with a minimum of cable. The Anchor-Box Dredge has operated successfully in a variety of bottom environments in depths of 50 m–2800 m.

The collection of large samples with a definable area from the ocean bottom has been the aim of benthic ecologists for some time. Since the abundance of benthic fauna generally decreases with depth, a device which collects large samples is necessary for quantitative results in deep-sea sampling. The sampler must be of rugged construction to withstand abuses of a variety of topographies, particularly on steep continental slopes, and it should operate with a minimum of cable. An opening-closing device is necessary to guarantee unwashed samples from the deep sea. To meet these requirements, the Anchor-Box Dredge has been developed at Oregon State University by modifying the Sanders Deep-Sea Anchor Dredge (Sanders, Hessler and Hampson, 1965). It consists of a steel-plate box with cutting edges at the open end and a planing surface in the front (Figs. 1 and 2). It is simple to operate and easily emptied when on deck.

The Anchor-Box Dredge samples the upper 10 cm of sediment from the ocean floor. It has a sampling width of 57 cm and can collect 1·3 m$^2$ of sediment surface. It samples well on either side in hard sands and clays, on rocky outcrops, and in soft, fine silts. To date it has operated effectively to depths of 2800 m. The sampling efficiency of this type of dredge is, in our experience. superior to grab samplers in areas of diverse and rugged topography.

The front planing surface, cutting edges, and the basic dredge frame are derived from the Sanders Deep-Sea Anchor Dredge (Sanders, Hessler and Hampson, 1965). Ideas for the dredge box and the hinged back plate were taken from the McIntyre Box Dredge (McIntyre, 1964), We have combined all these features and added a throat valve and side cutting teeth.

The large plate on the front, together with the towing bale (we had found previously that a towing bale improved operation of the Anchor Dredge) enables the dredge to sample to a constant depth within the sediment with a minimum of cable (Fig. 1 and Table 1). The frontal planing surface of the Anchor-Box Dredge also prevents " nosing over," an advantage over previous box dredges. Cutting teeth have been added beyond the sampling blade to ensure proper operation in hard bottoms.

The dredge is equipped with a safety link to prevent loss should it get fouled on the bottom. The metal box with tightly fitting hinged back plate is better suited to the sampling of the rugged topography of the continental slope than the destructible canvas bag and nylon support net of the Anchor Dredge. A throat valve on the new dredge prevents sample washing and allows rapid recovery rates. The back plate is watertight when a gasket is added.

There has been no opportunity to observe this dredge in operation. However, the Deep-Sea Anchor Dredge has been shown to cut a rectangular channel through the sediment (Sanders, Hessler and Hampson, 1965).

*Construction Details*

The Anchor-Box Dredge was constructed of steel plate by Gallaher Welding Company of Corvallis, Oregon. It weighs 341 kg (750 lb) and has an overall length of 2·4 m.

The large planing surface which prevents the dredge from sampling below 10 cm is made of 13 mm ($\frac{1}{2}$ in.) steel plate and is equidistant from the two cutting blades. The box portion of the dredge is of 13 mm ($\frac{1}{2}$ in.) steel plate with the cutting blades and teeth ground from 13 mm ($\frac{1}{2}$ in.) hi-tempered steel. The outside dimensions of the box are 114 cm × 58·5 cm × 20·5 cm. Its total volume capacity is 133 litres.

The back plate and throat valve are of 5 mm ($\frac{3}{16}$ in.) plate machined to fit accurately. Two fabricated steel hinges and two 16 mm ($\frac{5}{8}$ in.) stainless steel bolts on swivel pins hold the back plate in place. The " v "-shaped throat valve swivels on a dead axle. When the dredge is in sampling position, the valve pivots and is pushed in line with the horizontal planing surface. It falls back in place when the dredge is pulled off the bottom.

The towing bale is a single piece of 29 mm ($1\frac{1}{8}$ in.) diameter cold-rolled steel forged to shape and gussetted at the peak and attached just forward of the balance point of the dredge. The arc of travel is regulated by a length of chain.

The safety release consists of a weak link of manila line between the two shackles of the towing bale and the safety cable. A safety cable is attached to the dredge box just behind the center of balance and allows the dredge to be pulled from the rear should fouling occur.

*Operation*

We are presently using the stern of the 180-ft Oregon State University R/V *Yaquina* for dredging and have used both $\frac{3}{8}$ in. (1 cm) and $\frac{1}{2}$ in. (13 mm) wire rope for towing. A Sanders Anchor Dredge (204 kg) was operated for two years from the well deck of the 80-ft R/V *Acona* with no trouble. Safe handling of these heavy dredges on deck demands hand lines and adequate deck gear.

Experience has shown that the best procedure for using this instrument is to stop the ship and lower the dredge vertically until it is just above the bottom. The ship then assumes towing speed (1 knot) while the scope is being payed out at a rate of 50–75 m/min. After the tow is made, the dredge is retrieved by reversing the above procedure, with the exception that the cable should be collected at 35–50 m/min. Good samples are then obtained without danger of cable kinking.

*Table* 1.

| *Depth* (m) | *Amount of Wire* (m) | *Scope Ratio* |
|---|---|---|
| 50 | 200 | 4 : 1 |
| 100 | 300 | 3 : 1 |
| 200 | 500 | 2·5 : 1 |
| 600 | 1400 | 2·3 : 1 |
| 800 | 1600 | 2 : 1 |
| 2000 | 2800 | 1·5 : 1 |
| 2800 | 3900 | 1·39 : 1 |

Table 1 shows wire ratios which have been adequate in sampling our stations. If too little wire is used, the dredge will not dig properly and will skip along the bottom.

*Acknowledgments*—This research was supported by the Atomic Energy Commission Contract AT(45–1) 1750 and by the National Science Foundation Grant GB-531.

## REFERENCES

McIntyre R. J. (1964) A Box Dredge for quantitative sampling of benthic organisms. *Limnol. and Oceanogr.*, **9** (3): 460–461.

Sanders H. L., Hessler R. R. and Hampson, G. E. (1965) An introduction to the study of deep-sea benthic fauna assemblages along the Gay Head—Bermuda transect. *Deep-Sea Res.* **12**, 845–867.

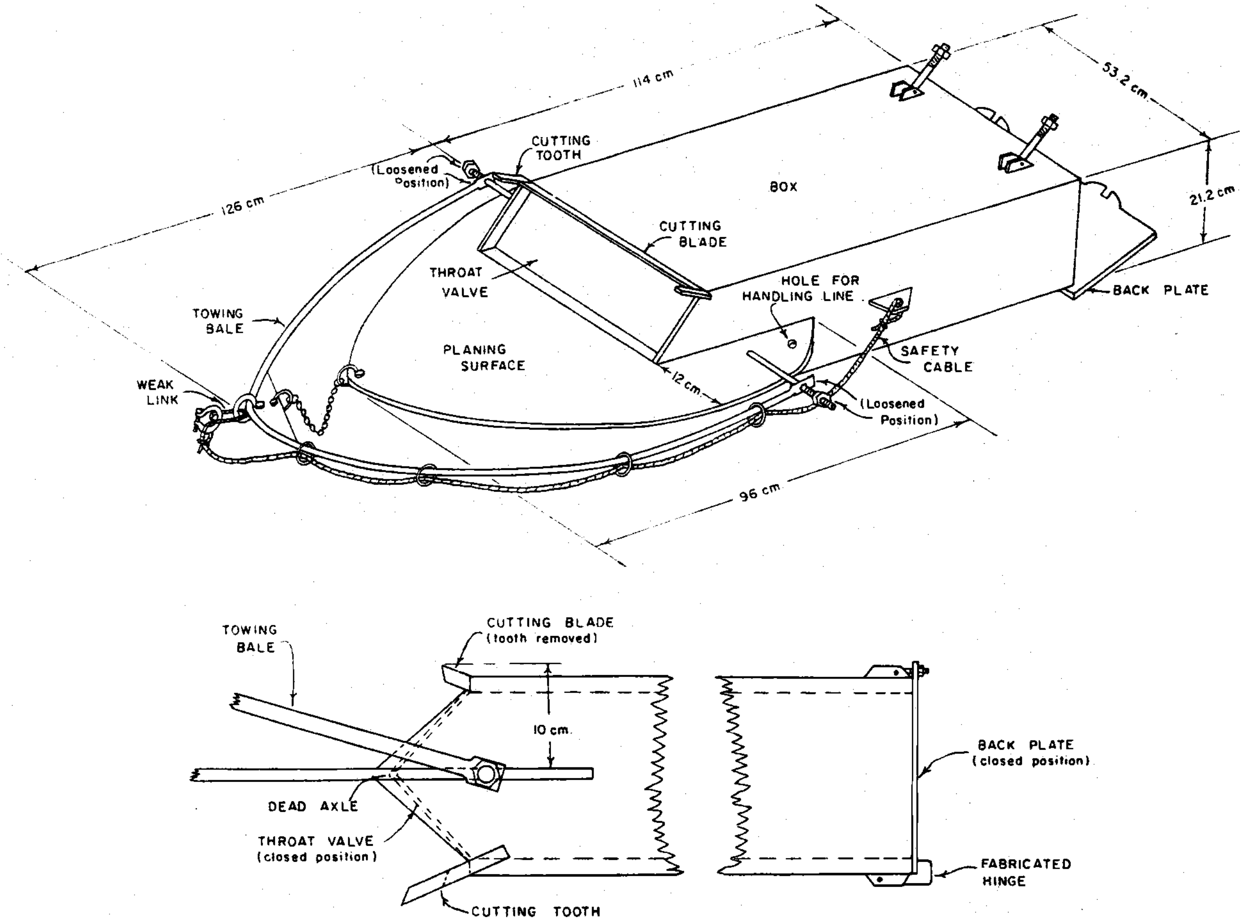

Fig. 1. Anchor-Box Dredge. The side view shows details of throat valve and hinge.

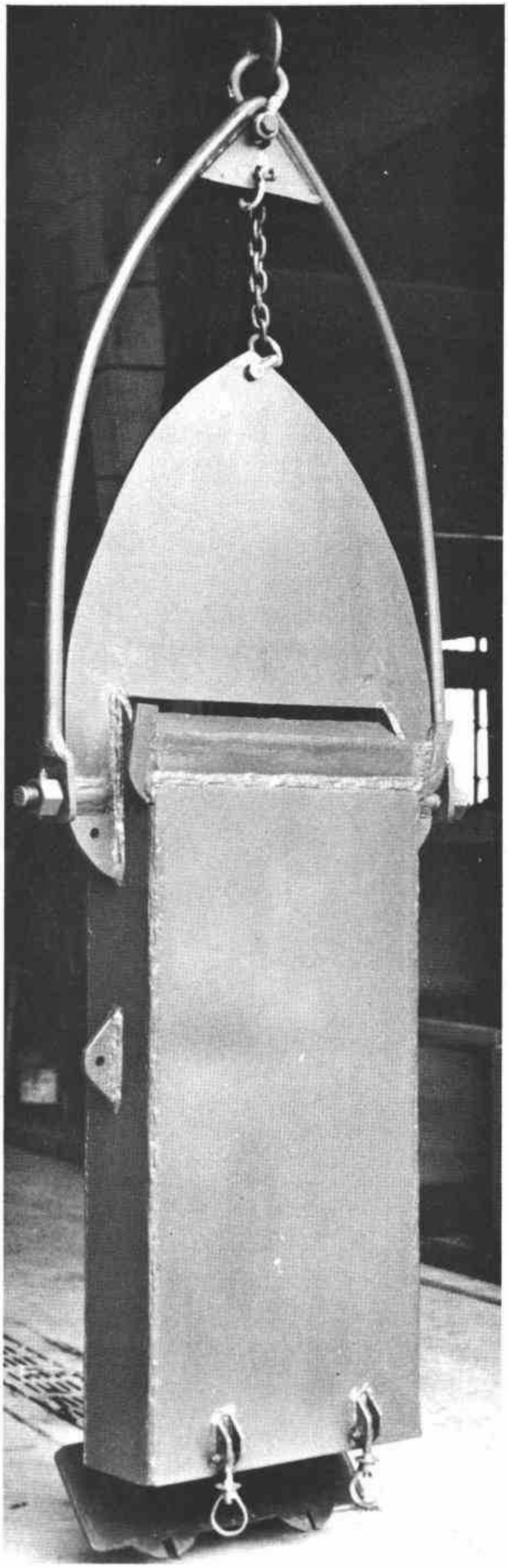

Figure 2. Anchor-Box Dredge

Deep-Sea Research, 1964, Vol. 11, pp. 933 to 934. Pergamon Press Ltd. Printed in Great Britain.

# INSTRUMENTS and METHODS

## A new swivel cable clamp for towing large plankton nets at different depths

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(*Received* 17 *June* 1964)

One of the major disadvantages of opening and closing release systems for large plankton nets is malfunction due to tangling of the complicated towing and bridle arrangements (Currie, 1962; Yentsch *et al.*, 1962). In our studies entanglement or fouling of net bridles around the towing cable was a common problem when towing at different depths. This appeared to be caused by the rotation of the cable, or laying and unlaying of its strands, especially when towing in deep water.

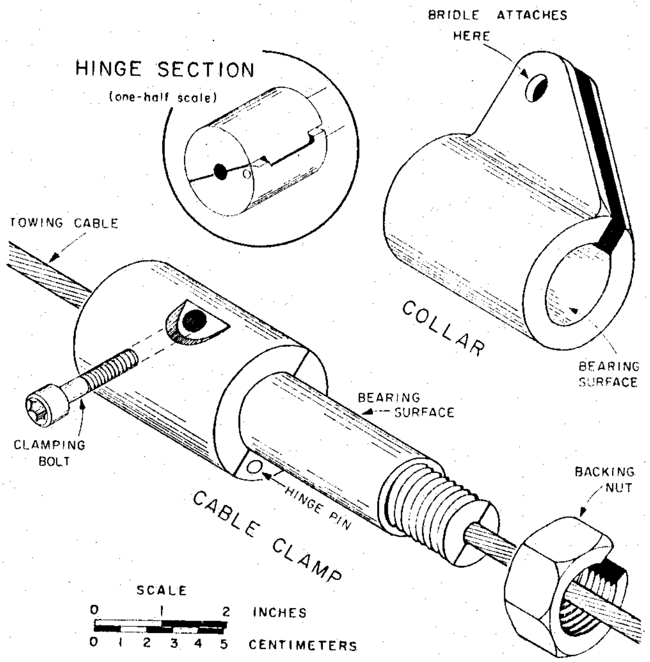

Fig. 1. Exploded view and scale drawing of the " BG " Clamp.

In an attempt to overcome this problem a new cable clamp, called the " BG " Clamp after its designer Captain Ben Gertulla, was made. This device is similar in design to the towed cable clamp used on the *Michael Sars* Expedition (Murray and Hjort, 1912).

The " BG " Cable Clamp (Fig. 1) is constructed of two main pieces, the hinged body of the clamp and the collar, which were cast of magnesium bronze, and four accessory pieces, which were purchased and adapted to the clamp.

The body of the clamp consists of a hinged cylinder with a hole bored 1 mm (1/32 in.) less than the diameter of the cable. The body of the clamp is held around the cable and secured by a 0·95 cm

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(3/8 in.) stainless steel socket cap bolt Allen head that fits through the wide base of the cylinder. This bolt can be screwed out of the base. The bolt is rounded (Allen head) and flush with the body to prevent tangling of lines.

The greased collar slides and rides freely under tension on the central portion of the body. A 2·5 cm (1 in.) nut with 3·5 threads to the cm (8 to the in.) screws on the threaded end of the body and holds the collar in place. A gap is cut in the nut so that it can be slipped onto the cable and unless the nut is tightened with a wrench it may back off.

Towing bridles are secured by a shackle and a 1·1 cm (7/16 in.) bolt to the collar of the clamp.

The cylindrical shape of the clamp is easily machined and construction of a mold relatively simple. The shape also provides a large surface area for gripping the towing cable and a large bearing surface for the rotation of the collar.

This clamp has been successful in allowing free rotation of the ship's cable while towing one-meter nets, thus preventing entanglement with net lines and bridles. Although this clamp has only been used with plankton nets, it may have other uses in oceanographic research.

*Acknowledgements*—This research was supported by the Atomic Energy Commission Contract AT (45–1) 1726.

## REFERENCES

Currie, R. I. (1962) Net Closing Gear. *Rapp. Proc. Verb. Cons. Perm. Int. Cons. Explor. Mer*, **153**, 48–54.

Murray, J. and Hjort, J. (1912) *Depths of the Ocean.* Macmillan, London, 821 pp.

Yentsch, C. S., Grice, G. D. and Hart, A. D. (1962) Some opening-closing devices for plankton nets operated by pressure electrical and mechanical action. *Rapp. Proc. Verb. Cons. Perm. Int. Cons. Explor. Mer.*, **153**, 59–65.

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# Vertical migration and distribution of mesopelagic fishes off Oregon

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(*Received* 30 *October* 1965)

**Abstract**—Using an Isaacs–Kidd midwater trawl with an opening and closing cod-end device, we collected samples of mesopelagic fishes from depths of 0–150 m, 150–500 m and 500–1000 m during periods of daylight and darkness. The observed day catches per unit volume of all mesopelagic fishes, as well as those of each of the four dominant species, were larger than the night catches at intermediate depths (150–500 m), whereas the opposite was true in the surface layer (0–150 m). These reversed trends in the upper 500 m indicated daily vertical migration, but in all cases the night-time increase in surface waters exceeded the daytime increase at mid-depths. Moreover, the number of fishes in a column of water 1000-m deep was always higher for night than day tows. There was no evidence for day–night differences in catches from the 500–1000 m stratum where catches were uniformly low.

The relative importance of avoidance and vertical migration was assessed by assuming (1) that the day–night difference per m$^2$ is a measure of the increased visual avoidance of the trawl in the upper 500 m during daylight periods, and (2) that the daytime increase at mid-depths is the best estimate of vertical migration. Calculations based on these assumptions showed that nearly all the night-time increase in surface water was attributable to vertical migration for one lanternfish. Avoidance alone, however, could explain most of the night-time increase in surface catches for three other common species.

The average number of mesopelagic fishes collected in a 0–1000 m column was 1·1/m$^2$ during the day and 1·5/m$^2$ during the night; wet-weight averaged 2·4 and 3·6 g/m$^2$ for day and night collections, respectively.

## INTRODUCTION

THE PROPORTION of the oceanic community migrating vertically, and the extent of these migrations, affect the vertical transport and cycling of elements as well as the degree to which these animals are predators or prey of other trophic levels. Evidence for vertical migrations of small nektonic animals, such as fishes, squids and shrimps, comes from three sources : (1) net collections, often containing high nighttime and low daytime catches of animals in near-surface waters (MURRAY and HJORT, 1912, and many others), (2) migration of sonic scattering layers (e.g. BODEN, 1962 ; HERSEY and BACKUS, 1962) and (3) from visual observations made from underwater vehicles (BARHAM, personal communication).

Since net collections can be quantitative, an estimate of the percentage of small nektonic animals that migrate vertically can be made from differences between night and day surface catches. The catches may be low during the day, however, for several reasons. These swimming animals may actually be absent from upper waters, or see the net and avoid it. Hence increased catches at night may merely be due to more effective sampling. Avoidance was suspected long ago as a cause for higher

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night catches by FOWLER (1905), FRANZ (1910), and TÅNING (1918) and was recently demonstrated by FLEMINGER and CLUTTER (1965) and BRIDGER (1958). The problem is, therefore, how to distinguish day–night, diel* or 24-hour changes in actual abundance caused by vertical migration from diel changes in catchability caused by differential avoidance.

This study attempts to quantitatively assess vertical migration of mesopelagic fishes, those common to depths of 200–1000 m during the day. Vertical migrations are determined from nightly increases in surface catches and from the nightly decreases in catches in mid-depths. Numbers and biomass of fishes are also estimated. It is not our intention to relate details of vertical distribution to hydrographic features, such as discontinuity layers, but rather to treat the general features of vertical distribution in broad, contiguous strata within the upper 1000 m.

## METHODS

Collections of mesopelagic fishes were made on twelve cruises of the R/V *Acona* between November 1962 and September 1964 at a station 50 nautical miles off the central Oregon coast (approximately 44° 39′N, 125° 15′W). This station is located just beyond the continental slope where the depth of water is about 2000 m. A Multiple Plankton Sampler (MPS) (BÉ, 1962) was adapted as an opening and closing cod-end collecting unit, as described by PEARCY and HUBBARD (1964), for a six-foot Isaacs-Kidd midwater trawl (IKMT). This provided samples from three consecutive depth intervals within the upper 1000 m. Successive tows within each depth stratum were made during 24–48-hour periods during both daylight and darkness. (Daylight was defined as extending from 30 min before sunrise to 30 min after sunset). In all, 152 collections were made.

The pressure-actuated release mechanism of the MPS, which operates on descent with increasing hydrostatic pressure, was calibrated in a pressure chamber and preset by the manufacturer† to operate at 150 m, 500 m and 1000 m, with a stated error of 2% of the maximum depth. It was recalibrated during this study by observing the depths of release in two ways : (1) by lowering the MPS vertically at sea to successively increasing depths, and (2) by use of a pressure chamber. The former method indicated releases between 150–160 m, 480–520 m, and 940–960 m during a cruise early in the study. On a later cruise the two deeper depth releases were re-adjusted to release between 490–500 m and 1000–1010 m.

Several series of tests were made in pressure chambers. Ten trials of the entire MPS unit in a large pressure chamber indicated release of the first two nets when the pressure was equivalent to 140–160 m and 487–533 m respectively. The most complete series of tests was performed at the end of the study when the pressure piston assembly was tested 46 times. During 17 of these tests tension was imparted to the release levers with rubber bands, but this caused no significant difference

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*According to Webster's Third New International Dictionary, "daily" and "diurnal" are synonyms meaning day to day or recurring every day. The word "diurnal" is ambiguous in that it may also mean daytime, as opposed to nocturnal or night-time. "Diel" means a 24-hour period including a day and the adjoining night.

Because we are referring to changes completed within a 24-hour period, "diel" is the most precise term. "Diurnal," which is more familiar through long usage, however, has often been used interchangeably with "diel," "24-hour," or "circadian" (about a day), especially in reference to biological rhythms (see CLOUDSLEY-THOMPSON, 1961).

†G. M. Manufacturing Company, 2417 Third Avenue, New York, N.Y.

in depth of release ($P > 0{\cdot}4$)*. The means and standard deviations for all release depths were 130 ± 4·5 m, 485 ± 8·6 m, and 951 ± 9·0 m. Weakening of the cylinder spring probably caused these mean values to be less than previously observed. Although the pressure-actuated release mechanism was readjusted several times during the study, indicating need for frequent recalibration, variation was not excessive. Depths of 150 m, 500 m and 1000 m were assumed for opening and closing of the MPS during all tows.

A depth-distance recorder, mounted on a post attached to the depth-depressor in the mouth of the trawl, provided estimates of the distance the trawl traveled within each depth interval. The recorder has horizontal fins and is self-adjusting for pitch. According to the manufacturer†, the error of the depth-distance recorders for depth, determined by pressure tests in the laboratory, is ± 3% of the maximum depth. Our vertical lowerings at sea indicated comparable depth variations. Depth-distance recorders were calibrated for distance by towing them while suspended in a 0·5-m ring (without a net) for a known distance determined from radar and loran fixes. The total chart distance of four calibration tows was 56·9 nautical miles compared to 57·7 miles from the depth-distance recorder; the average variation of the four separate tows was 10%. Recorders were also mounted on posts of different heights on the trawl depressor to see if this affected estimates of distance. Comparison of two heights on five tows showed no significant difference ($P > 0{\cdot}05$).

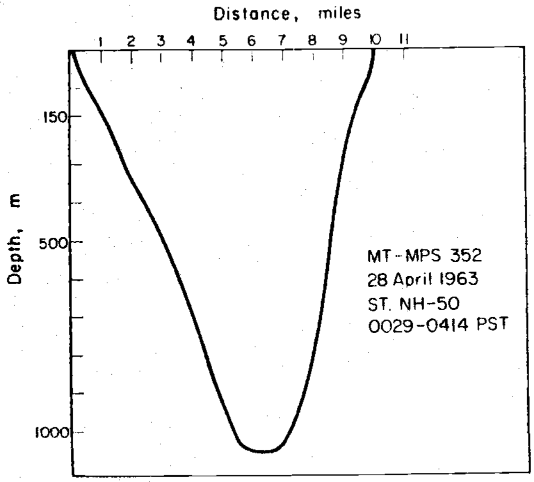

Fig. 1. Duplication of a trace made with the depth–distance recorder on a tow which sampled three depths within the upper 1000 m.

Figure 1 duplicates a depth-distance recorder trace from a typical tow. The rate of trawl descent was 30 m of wire per minute while the ship was underway at 4–5 knots. The first net, which was open at the surface, was closed at 150 m; simultaneously, the second net opened. The second net was closed and the third opened at 500 m; the last net was closed at 1000 m depth. The trace was approximately a straight line within each depth interval, 0–150, 150–500 and 500–1000 m indicating that

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*With two other piston assemblies, not used in this study, such tension caused large changes in release depths, by increasing friction during the piston stroke.

†Tsurumi Precision Instruments Company Ltd., 1506 Tsurumi-Machi, Yokohama, Japan.

nearly equal volumes of water were fished at all depths within each layer. If the trawl does not fish all depths equally and animals are not distributed uniformly within depths, estimates of abundance may be biased. By assuming that the flow of water through the depth-distance recorder is the same throughout the entire mouth of the trawl, we determined the volume of water filtered within each depth interval as a product of the cross-sectional area of the trawl, 2·89 $m^2$, and the distance traversed within each depth layer.

Geographic positions of the ship were determined by LORAN A at the start and finish of each tow, and at each closing depth. We assumed a 4 : 1 cable-to-depth ratio (PEARCY, 1964). The total distance towed, estimated from both depth-distance recorder and from geographic positions, was compared for each of 63 tows. The distance determined from the recorder averaged 85% (S.D. = 8·5%) of the chart distance. This is an estimate of filtration efficiency of the midwater trawl. Because a depth-distance recorder was not available during the first three cruises, distances were estimated from geographic positions after correcting for filtration efficiency and for the distance of the trawl behind the vessel. This latter correction presumed the towing cable was nearly straight as found by BACKUS and HERSEY (1956) and MEAD (1963).

To reduce the problems associated with different mesh sizes in the trawl net, the entire body of the net was lined with 5 mm or $\frac{3}{8}$ in. (squared measure) knotless nylon. Hence, with exception of the No. 0 (0·571-mm mesh opening) plankton net at the end of the MPS collecting nets, only one mesh size was used. This modification further improved the IKMT for quantitative sampling by reducing the problems associated with differential selectivity of various mesh sizes. A 5-mm mesh was also used aft of the MPS to enhance water flow and flushing of the trawl.

After each tow the net was thoroughly cleaned by towing it at the surface with the cod-end open and by washing it with fire hoses. Collections were preserved at sea with neutralized formalin in sea water. In the shore laboratory, fishes were removed from the collections, weighed (wet-preserved weight, usually about a week after preservation), identified, and counted. Larval fishes were not included in the analyses of mesopelagic fishes.

## RESULTS

Histograms showing the total number of mesopelagic fishes collected per 1000 $m^3$ (Fig. 2) reveal variations with both depth and day–night periods. Diel differences in the catches are obvious in the surface waters (0–150 m) where catches averaged about six times higher during darkness than daylight. At mid-depths (150–500 m) the opposite trend is apparent. Catches during the day are usually higher, averaging about twice those made during the night. No diel differences in the number of fishes in deep water between 500 and 1000 m are discernible; catches here are consistently low. Thus, during periods of daylight the largest catches are in mid-depths, while concentrations in surface and deep layers are comparatively low. After darkness, however, the highest catches are always in surface waters, and they are generally lower in successively deeper layers. These complementary changes within the upper two layers indicate vertical migration of fishes.

Considerable variability in the catches within a depth-diel period can be seen in Fig. 2. Highest variability is evident where catches are highest, i.e., in surface waters

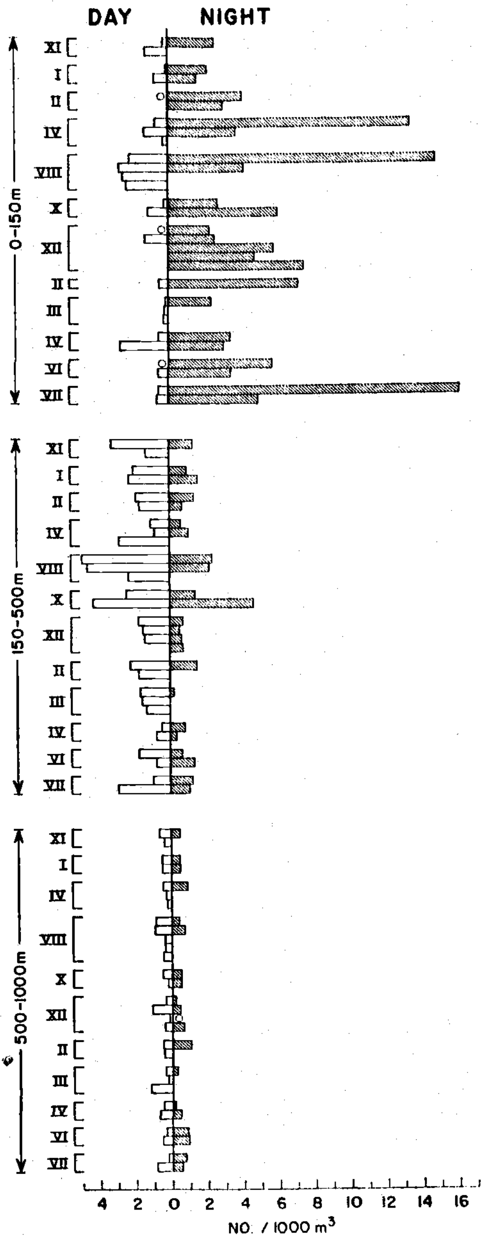

Fig. 2. Catches of mesopelagic fishes per 1000 m³ during day and night periods within the three depth strata. Cruises, extending from November 1962–July 1964, are denoted by months in Roman numerals. Horizontal bars indicate catches for each cruise. Open circles (O) show where no fishes were captured in a collection.

at night. In deep water, variability is clearly much lower. Some of this variation is associated with differences between cruises or seasons, some with differences within cruises. Within a cruise, collections that were made during the same depth-diel period, each represented by a horizontal bar, are grouped together. These are not true replicate samples because of the time elapsed between tows. For example, a day period separated some of the tows (e.g. 0–150 m night : months IV, VIII, 1963, and between second and third collections in XII). Even when tows that were made during the same period of daylight or darkness are compared, large differences may sometimes be found (e.g., 0–150 m night : X and VII). Many factors may contribute to this variability : patchy distribution of fishes (see Pearcy, 1964), sampling variability caused by differences in the time, location, or method of sampling, or changes in catchability caused by differences in light condition, moonlight, weather, etc. (see Cushing, 1951).

Analysis of variance of the data shown in Fig. 2, after a logarithmic transformation (Barnes 1952), substantiates several of the differences previously observed (Table 1) :

(1) The difference among the mean numbers of fishes captured per 1000 $m^3$ within the three depths is significant ($P < 0{\cdot}01$), indicating lower catches of mesopelagic fishes in deeper layers.

(2) Diel changes in the number of fishes captured within the strata are emphasized by the high depth × day–night interaction. This means that depth distribution depends upon whether collections are made during the day or night.

(3) A seasonal difference is also revealed in Table 1. Apparently, more fishes per unit volume were caught during cruises made in June–October than during cruises in October–June (see Fig. 2). Similarly, Pearcy (1964) reported higher catches of the dominant mesopelagic fishes during previous summers, the time of year when upwelling commonly occurs off Oregon. Season, however, appears to have little effect on either day–night variation, variation among depths, or a combination of these factors; this indicates a general increase in the numbers of fishes captured during the summer and not one related to depth or diel period.

(4) Regardless of depth, a significant difference occurred between the day and the night catches ($P < 0{\cdot}05$). Twice as many mesopelagic fishes on the average were captured per unit volume during the night as during the day. Because of the inequality of depth intervals, however, catches should be compared on a unit surface area rather than a unit volume basis. Calculation of the catches in a column of water 1000-m deep and one meter square gives values of 1·1 and 1·5 fish/$m^2$ for day and night periods.

We have shown day–night and the depth–diel effects, but at what depths do

*Table* 1. *Analysis of variance of the number of mesopelagic fishes* (log. No./$10^5$ $m^3$) *collected during the sampling period*

| *Source of variation* | *Degrees of freedom* | *Mean square* | *F* |
|---|---|---|---|
| Depth | 2 | 3·8389 | 6·42† |
| Depth × Season | 2 | 0·1504 | 0·25 |
| Depth × Day–Night | 2 | 6·1010 | 10·20† |
| Depth × Season × Day–Night | 2 | 0·1577 | 0·26 |
| Error (a) | 48 | 0·5983 | |
| Season | 1 | 2·0527 | 5·80* |
| Day–Night | 1 | 2·5902 | 7·32* |
| Season × Day–Night | 1 | 0·1895 | 0·53 |
| Cruises in Season | 10 | 0·2633 | 0·74 |
| Error (b) | 10 | 0·3538 | |
| Sampling error | 71 | 0·1567 | |

*Significant at 5% level. †Significant at 1% level.

*Table 2. The average number of mesopelagic fishes collected in the three strata during day and night periods, night/day catch ratios, and individual degree of freedom " F " tests on the* log No./10⁵ m³.

| *Depth* | *Average catch/1000 m³* | | *Night/Day ratio* | *F* |
|---|---|---|---|---|
| | (Day) | (Night) | | |
| 0–150 m | 0·88 | 5·36 | 6·1 | 23·12† |
| 150–500 m | 1·99 | 1·22 | 0·6 | 1·60 |
| 500–1000 m | 0·50 | 0·55 | 1·1 | 0·0004 |

†Significant at 1% level.

significant diel variations occur ? To answer this, average catches, night/day catch ratios, and individual degree of freedom " F " tests (LI, 1957) were determined (Table 2). A significant difference was found only for the surface waters where the night/day ratio is high. At mid-depths larger catches were made during the day

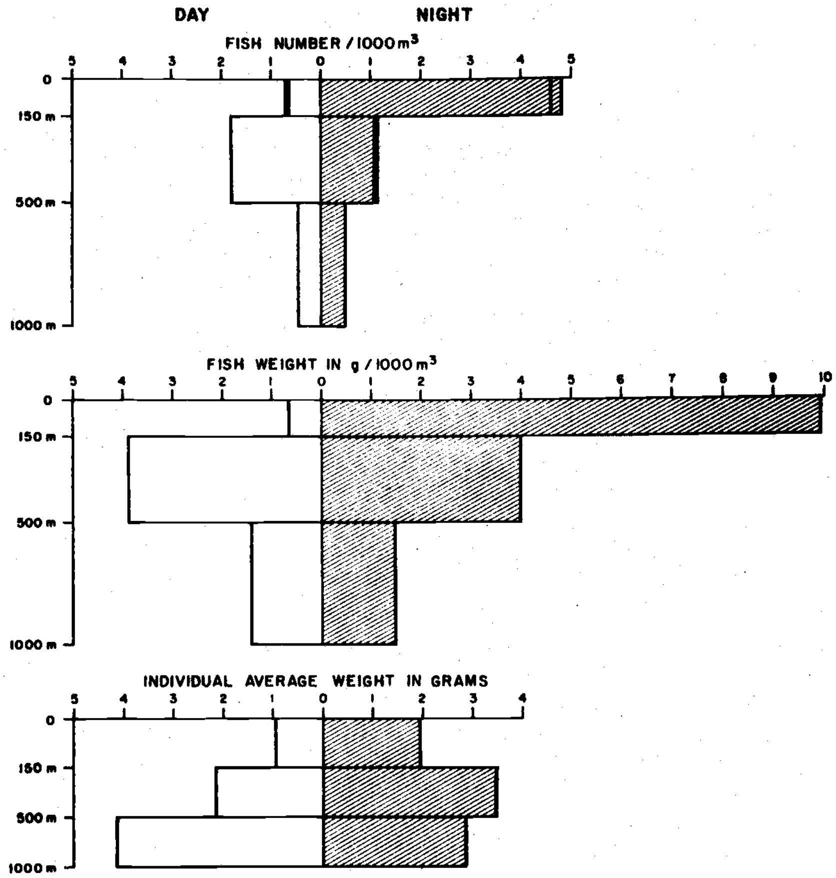

Fig. 3. Comparisons of the day and night catches of fishes for the three depth strata in (1) numbers per 1000 m³, (2) grams wet weight per 1000 m³, and (3) average individual weight. The spaces between the two outside lines in the upper histogram denote the number of larval fishes.

than at night, but the difference is not statistically significant ($P > 0{\cdot}05$). The day-night difference at 500–1000 m is so low that it indicates a surprising degree of diel uniformity in fish catches. The absence of a significant day-night difference at mid-depths is rather perplexing, for if vertical migration explains the high catches at night and the low catches in the day in the surface waters, then the reverse trend should be evident at mid-depths. This suggests the influence of factors other than vertical migration.

The average number and weight of fishes captured per 1000 $m^3$, as well as the average weight of individual fish from the three strata during day and night periods, are shown in Fig. 3. The number of fish per 1000 $m^3$, calculated by dividing total number of fishes collected by total volume of water filtered for all collections, shows the distinct nighttime increase in surface waters and the less marked daytime increase at mid-depths. The only observable day--night difference in biomass or weight is the nocturnal increase in the upper waters; no diel differences are apparent below 150 m. The biomass in wet weight per 1000-m column averaged 2·4 g/$m^2$ during the day and 3·6 g/$m^2$ during the night.

By dividing biomass by number, the average weight of the fishes captured was determined. Average size was generally smaller in surface catches than in deeper layers and smaller in day catches than in night catches within both the 0–150 m and 150–500 m depth intervals. Large fish such as *Tactostoma macropus* were captured only at night in the upper 0–150 m and partially explain the size differences between day and night. Although it cannot be discerned from Fig. 3, the weights of fishes per unit volume from 500–1000 m, unlike the number at this depth in Fig. 2, were much more variable than the weights of fishes found in overlying waters. This was due to the capture of occasional large fishes. For example, the average daytime weight of deep-water fishes shown in Fig. 3 would be lowered from 4·1 to 3·1, a value similar to that for the night catches, if only two large fishes (a *Chauliodus* and a *Macropinna*) were omitted from our calculations.

### *Vertical distribution of dominant species*

According to PEARCY (1964), who gives a preliminary list of mesopelagic fishes off Oregon, four species of mesopelagic fishes dominate the near-surface midwater collections at night : *Lampanyctus leucopsarus*, *Diaphus theta*, *Tarletonbeania crenularis*, and *Tactostoma macropus*. In this study these species composed about 74% of the total number of fishes in the upper 150 m and 56% of the number collected within all three depth intervals.

The vertical distributions of these species are shown as histograms in Fig.4. Night catches of all species in surface waters greatly exceeded day catches at this depth. Of even more interest are the complementary trends at mid-depths. Here the catches are clearly larger during the day than at night. Numbers are comparatively low for all species below 500 m, with no evidence of diel differences.

Though the general patterns are similar for all these species, there are interspecific variations in the degree of day–night differences. *T. crenularis* and *T. macropus* showed the largest differences between day and night catches in the upper 150 m. An order of magnitude less *T. crenularis* was captured during the day; and *T. macropus* was not captured at all from 0–150 m during the day.

The catches of all four species in a 1000-m column averaged higher in night

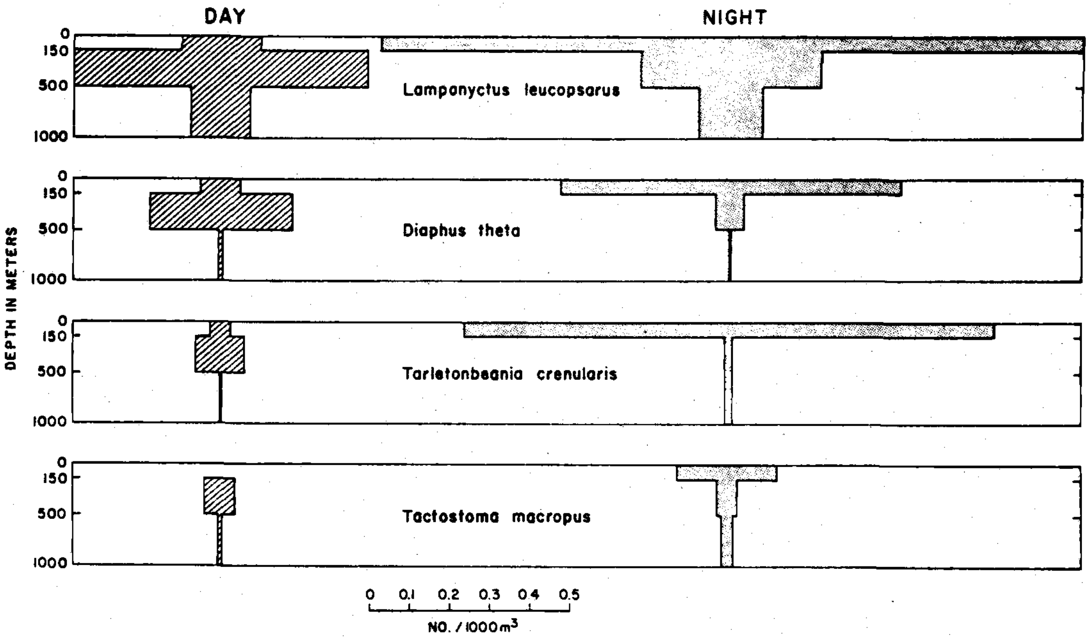

Fig. 4. The average vertical distributions of four dominant species of mesopelagic fishes shown as numbers collected per 1000 m$^3$.

*Table 3. Comparison of the number of mesopelagic fishes captured per unit surface area during day and night periods at various depth intervals*

| | *Catch*/$m^2$ 0–1000 m | 0–150 m (No./$10^5$ $m^2$) | | | 150–500 m (No./$10^5$ $m^2$) | | | D–N 150–500 / N–D 0–150 |
|---|---|---|---|---|---|---|---|---|
| | N/D | Night | Day | N–D | Day | Night | D–N | |
| *Lampanyctus leucopsarus* | 1·37 | 262·3 | 29·7 | 232·6 | 260·0 | 156·8 | 103·2 | 0·44 |
| *Diaphus theta* | 1·05 | 128·2 | 15·0 | 113·2 | 124·6 | 24·8 | 99·8 | 0·88 |
| *Tarletonbeania crenularis* | 4·21 | 197·4 | 7·0 | 190·4 | 43·0 | 7·3 | 35·7 | 0·19 |
| *Tactostoma macropus* | 1·70 | 36·9 | 0 | 36·9 | 26·2 | 17·5 | 8·7 | 0·24 |

collections than daytime collections giving night/day catch ratios that were always greater than 1·0 (Table 3). (This can also be seen in Fig. 3 since the shaded area of each histogram is proportional to the catch per $m^2$). The night/day ratios also vary among species. Nearly the same number of *D. theta* were captured per $m^2$ during the day and night periods, showing little daily change in the catchability, but over four times as many *T. crenularis* were caught during the night. The night/day ratios of *L. leucopsarus* and *T. macropus*, 1·37 and 1·70 respectively, are intermediate between those of *T. crenularis* and *D. theta.*

## DISCUSSION

After noting the catches of lanternfishes and *Astronesthes* in surface nets at night and their absence at the same depths during the day, MURRAY and HJORT (1912, p. 95) concluded that " a better proof of the vertical wanderings of these animals seems hard to find." Many other workers have also found larger catches of mesopelagic fishes in near-surface waters during the night than during the day (e.g. GÜNTHER, 1887; BRAUER 1906; TÅNING, 1918; BEEBE and VANDER PYL, 1944; TUCKER, 1951; ARON, 1962; KING and IVERSON, 1962; and PEARCY, 1964). Although some of these researchers recognized that changes in visual avoidance could influence their results, no attempt was made to distinguish between avoidance and vertical migration.

Since diel variations in catchability from both vertical migrations and avoidance are related to light intensity, either as an orientational cue or by affecting visual perception, separation of these two behavioral responses on a quantitative basis is difficult (WIBORG, 1955; MCALLISTER, 1961; KING and HIDA, 1957). Consideration of night/day ratios tells little. What is needed are (1) quantitative sampling of adjoining depths with opening and closing nets during day and night periods, and (2) sampling the entire vertical range of the animals, including the depths to which they migrate during daytime. If these criteria are fulfilled, then avoidance can be measured by the difference in catches between night and day on a $m^2$ basis, and vertical migration can be measured by the *daytime* increase at mid-depths. Since the fishes can see and avoid the trawl more effectively during daylight than darkness, larger day than night catches cannot be explained by enhanced visual avoidance. Larger night catches, on the other hand, could be explained by either reduced avoidance and vertical migration.

Using this rationale, we find both avoidance and vertical migration of mesopelagic fishes off Oregon. Night/day ratios for the total number of fishes and for the four common species in a 1000-m column were greater than one. Diel variations in catches are obvious above 500 m, but not between 500 and 1000 m (Figs. 2 and 4). That no significant number of fishes migrated downward into the 500–1000-m layer during the day is evident from a failure of daytime catches here to increase as they did at mid-depths (150–500 m). Another possibility is that fishes from 500–1000 m migrate downward to depths below 1000 m during the day with equal replacement by animals from above 500 m. If this is so, the same number of fishes must also migrate upward through the 1000-m and 500-m depths during the night.. In view of the lack of diel differences at 500–1000 m for the four dominant species as well as for mesopelagic fishes in general, this complex explanation seems unlikely. Because there is no evidence for vertical migrations of fishes below 500 m, and studies of sonic scattering layers off Oregon corroborate this conclusion, the simplest explanation for the night and day differences in a 1000-m column is avoidance of the net during daylight periods.

There is the possibility that some of our catches between 500–1000 m, and 150–500 m as well, may be due to contamination caused by the time required to flush the contents of the net into the cod-end unit. Though the opening-closing unit has been modified to increase the flushing rate (PEARCY and HUBBARD, 1964), some animals, for instance those captured at depths of 450 m, may actually be collected in the cod-end net which opens at 500 m. This may contribute to the occurrence of low numbers of some species, such as *D. theta* and *T. crenularis* in deep water. That this factor is relatively unimportant, however, is shown by that lack of correlation between any two consecutive strata, i.e. large catches in surface water at night do not result in highest catches at mid-depths at night, nor do the highest catches at mid-depths during the day result in high catches in deep water during the day (see Fig. 2).

We have said that the diel differences in catches in mid-depths are better evidence for vertical migration than the diel differences in catches in surface waters. The reason for this is that better visual avoidance is possible during daylight hours; therefore, the higher day catches cannot be caused by this differential avoidance ability. The daytime descent of mesopelagic fishes has rarely been documented by increased catches at mid-depths. ARON (1962) reported that midwater tows in the northeastern Pacific captured a larger number of fishes at night than during the day regardless of depth within the upper 400 m. Likewise HERSEY and BACKUS (1962) found that the night catch of myctophid fishes south of New England was higher than the day catch within the upper 300 m. To our knowledge, only TUCKER (1951) has clearly shown larger day than night catches of mesopelagic fishes at mid-depths (about 260–610 m) off San Diego, California. He noted, moreover, that the marked increase near the surface at night in the myctophid population, also dominated by *Lampanyctus leucopsarus*, was not accompanied by an equivalent decrease from deeper water. So he assumed that fish were moving up from depths below those fished. We submit that avoidance contributed to this discrepancy, as well as to the higher night catches reported by other workers.

Assuming that diel changes at mid-depths give the best estimate of vertical migration from our data and that vertical migration of fishes below 500 m can be neglected, we can partition avoidance and migration as follows :

$$\text{night at 0–150 m} - \overset{\text{the catches per m}^2\text{ during the}}{\text{day at 0–150 m}} = \text{avoidance and migration} = a + m, \qquad (1)$$

and the catches per $m^2$ during the

day at 150–500 m − night at 150–500 m = vertical migration = $m$; (2)

therefore,

$$(a + m) - m = \text{avoidance}, \qquad (3)$$

and

$$\frac{m}{a+m} \times 100 = \text{the percentage of the night minus day difference at 0–150 m that is accounted for by vertical migration, or the day minus night difference at 150–500 m.} \qquad (4)$$

This estimate of vertical migration ($m$) is minimal. Animals that avoid the net during the day may reside either at mid-depths or in surface waters. Since they are not captured, it is impossible to tell which is the case. These fishes are called avoiders, but obviously a fish can be both an avoider and a migrant. Moreover, animals may migrate within, rather than between, our broad depth intervals and hence not be detected as migrants. Nevertheless, the point is that all the animals that avoid the net during the day ($a$ of equation 3) could be avoiding without migrating.

Diel differences between the catches at 0–150 m and 150–500 m are compared in Table 3, thus enabling solution of the above equations from the data for the four common species. The results indicate wide interspecific differences. Eighty-eight percent of the 0–150 m night increase in the catch of *D. theta* is explained by the complemental 150–500 m increase during the day, thus vertical migration explains the major portion of the surface increase of this species at night. On the other hand, diel changes in catches at mid-depths explain only 19% of the surface changes of *T. crenularis*, 24% of *T. macropus* and 44% of *L. leucopsarus*. Thus, most of the night-time surface increase for these species can be attributed to reduced avoidance.

The more rapidly an animal can swim presumably the better it can avoid the net, and perhaps, the more likely it is to migrate. Consequently, we may expect that larger fishes, being stronger swimmers, are better able to dodge the net than smaller individuals of a species. Our results with larger fishes captured at night (Fig. 3), does, in fact, suggest higher avoidance by these animals during the day. King and Iverson (1962) likewise found that the average size of organisms collected in midwater trawl collections in the Central Pacific was always larger for night hauls than for day hauls. Ahlstrom (1954) has shown a good positive correlation between size of sardine larvae captured and night/day catch ratios, again suggesting the effect of size on avoidance ability.

The expected relationship between size and night/day ratios, however, was not clear from our data on the four most common species of fishes. For some reasons intermediate sizes of *L. leucopsaurus* and *D. theta* (about 40–60 mm in length) appeared to be sampled more effectively during the day than either smaller or larger size-groups. Perhaps differences in avoidance ability are related to differences in vertical distribution and ambient illumination. More data are needed before any definite conclusions can be reached.

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## REFERENCES

AHLSTROM E. H. (1954) Distribution and abundance of egg and larval populations of the Pacific sardine. *Fishery Bull. Fish Wildl. Serv. U.S.*, **56** (93), 83–140.

ARON W. (1962) The distribution of animals in the eastern North Pacific and its relationship to physical and chemical conditions. *J. Fish. Res. Bd. Can.*, **19**, 271–314.

BACKUS R. H. and HERSEY J. B. (1956) Echo-sounder observations of midwater nets and their towing cables. *Deep-Sea Res.*, **3**, 237–241.

BARNES H. (1952) The use of transformations in marine biological statistics. *J. Cons. perm. int. Explor. Mer*, **18**, 61–71.

BÉ A. W. H. (1962) Quantitative multiple opening-and-closing plankton samplers. *Deep-Sea Res.*, **9**, 144–151.

BEEBE W. and VANDER PYL M. (1944) Eastern Pacific expeditions of the New York Zoological Society, XXXIII. Pacific Myctophidae (Fishes). *Zoologica, N.Y.*, **29**, 59–95.

BODEN B. P. (1962) Plankton and sonic scattering. *Rapp. P.-V. Réun. Cons. perm. int. Explor. Mer*, **153**, 171–177.

BRAUER A. (1906) Die Tiefsee-Fische. I. *Wiss. Ergebn. dt. Tiefsee-Exped. ' Valdivia,'* Syst. Teil, **15** (1), 1–420.

BRIDGER J. P. (1958) On efficiency tests made with a modified Gulf III high-speed tow-net. *J. Cons. perm. int. Explor. Mer*, **23**, 357–365.

CLOUDSLEY THOMPSON J. L. (1961) *Rhythmic activity in animal physiology and behavior.* Academic Press, New York, 236 pp.

CUSHING D. H. (1951) The vertical migration of planktonic Crustacea. *Biol. Rev.*, **26**, 158–192.

FLEMINGER A. and CLUTTER R. I. (1965) Avoidance of towed nets by zooplankton. *Limnol. Oceanogr.*, **10**, 96–104.

FOWLER G. H. (1905) Appendix on the vertical distribution and movement of Schizopoda. *Trans. Linn. Soc. Lond.*, Ser. 2, **10**, 122–129.

FRANZ V. (1910) Phototaxis und Wanderung. Nach Versuchen auf Jungfischen und Fischlarven. *Int. Rev. Hydrobiol.*, **3**, 306–334.

GÜNTHER A. C. (1887) Report on the deep-sea fishes collected by H.M.S. *Challenger* during years 1873–1876. *Rep. Sci. Res. Challenger, Zool.*, **22**, 1–335.

HERSEY J. B. and BACKUS R. H. (1962) Sound scattering by marine organisms. In: *The Sea*, M. N. HILL, Ed., Interscience, New York, 498–539.

KING J. E. and IVERSON R. T. B. (1962) Midwater trawling for forage organisms in the Central Pacific 1951–1956. *Fishery Bull. Fish Wildl. Serv. U.S.*, **62**, (210), 271–321.

KING J. E. and HIDA T. S. (1957) Zooplankton abundance in the Central Pacific. *Fishery Bull. Fish Wildl. Serv. U.S.*, **57** (118), 365–395.

LI J. C. R. (1957) *Introduction to statistical inference.* Edwards, 568 pp.

MCALLISTER C. D. (1961) Zooplankton studies at Ocean Weather Station " P " in the Northeast Pacific Ocean. *J. Fish. Res. Bd. Can.*, **18**, 1–29.

MEAD G. W. (1963) Observations on fishes caught over the anoxic waters of the Cariaco Trench, Venezuela. *Deep-Sea Res.*, **10**, 251–257.

MURRAY J. and HJORT J. (1912) *The depths of the ocean.* Macmillan, London, 821 pp.

PEARCY W. G. (1964) Some distributional features of mesopelagic fishes off Oregon. *J. mar. Res.*, **22**, 83–102.

PEARCY W. G. and HUBBARD L. (1964) A modification of the Isaacs-Kidd midwater trawl for sampling at different depth intervals. *Deep-Sea Res.*, **11**, 263–264.

TÅNING A. V. (1918) Mediterranean Scopelidae (*Saurus, Aulopus, Chloropthalmus* and *Myctophum*). *Rep. Dan. oceanogr. Exped. Mediterr.* II, (Biol.) A. **7**, 1–154.

TUCKER G. H. (1951) Relation of fishes and other organisms to the scattering of underwater sound. *J. mar. Res.*, **10**, 215–238.

WIBORG K. C. (1955) Zooplankton in relation to hydrography in the Norwegian Sea. *Rep. Norw. Fishery mar. Invest.*, **11** (4), 1–64.

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# Species Composition and Distribution of Pelagic Cephalopods from the Pacific Ocean off Oregon

WILLIAM G. PEARCY[1]

MUCH OF OUR PRESENT KNOWLEDGE about the species composition and distribution of cephalopods of the Pacific Ocean is derived from collections made on cruises of the "Albatross," steamer of the U.S. Fish Commission, during the late nineteenth and early twentieth centuries. "Albatross" collections along the west coast of North America were taken mainly off California and Central America or Alaska, and comparatively few collections were made off Oregon (Townsend, 1901). Neither Berry (1912) nor Hoyle (1904) lists any cephalopods taken off Oregon. A description of a new species of squid (Pearcy and Voss, 1963) and an abstract (Pearcy, 1963) are the only reports of pelagic cephalopods off Oregon.[2] Clearly, more data are needed before comparisons of fauna and generalization on zoogeographic distribution can be made.

## METHODS

A total of 385 collections made between June 1961 and July 1963 with a six-foot Isaacs-Kidd midwater trawl from the "R. V. Acona" provided most of the data on pelagic cephalopods collected off the Oregon coast. Collections were made after dark within the upper 200 m (depth permitting) at a series of stations located 15, 25, 45, and 65 miles, and at another station located between 65 and 165 miles, offshore along parallels of latitude between the Columbia River and the California border (46° 14.4′N, 44° 39.1′N, 43° 20′N, and 43° 00′N). Generally the stations off the central Oregon coast, 44° 39.1′N (off Newport), were sampled every month and other stations bimonthly.

In addition to the 0–200m collections at various distances from shore, tows were made to provide data on the depth distribution of cephalopods. Over one hundred collections were made to successive depths of 200, 500, and 1000 m over the outer edge of the continental slope at a station 50 miles off Newport. For more details on sampling methods see Pearcy (1964).

Collections were preserved with 10% formalin in sea water. Cephalopods were removed from the collections, identified, and the dorsal mantle length (DML) was recorded.

Occasionally some cephalopods were collected with dip nets under lights at night and some with epibenthic otter trawls.

## RESULTS

The families and species of pelagic cephalopods collected are listed in Table 1. These include 17 species in 12 families. Six species are distributional records for the northeastern Pacific Ocean, reported previously only by Pearcy (1963). They are: *Abraliopsis* sp., *Octopoteuthis sicula, Gonatopsis borealis, Taonius pavo, Cranchia scabra,* and *Vampyroteuthis infernalis.* Only eight of the seventeen species are included in the study by Berry (1912) based mainly on benthic collections.

Although most of these species were collected in the midwater trawl, several were captured by other methods. Two *Moroteuthis robusta* (DML 650 and 1350 mm) were caught in otter trawls off the northern Oregon coast in water deeper than 150 m. This species, reported from California (Smith, 1963) and Alaska (by Dall, in Berry, 1912), was recently reported off Oregon.[2] *Loligo opalescens,* a common inshore myopsid of the west coast of

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[1] Department of Oceanography, Oregon State University, Corvallis, Oregon. Manuscript received February 14, 1964.

[2] Added in proof: J. M. Van Hyning and A. R. Magill. 1964. Occurrence of the Giant Squid (*Moroteuthis robusta*) off Oregon. Fish Comm. Oregon Research Briefs 10:67–68.

TABLE 1

List of Pelagic Cephalopods Collected from the Pacific Ocean off Oregon, June 1961–July 1963

| | |
|---|---|
| Loliginidae | *Loligo opalescens* Berry, 1911 |
| Sepiolidae | *Rossia pacifica* Berry, 1911 |
| Onychoteuthidae | *Onychoteuthis banksi* (Leach, 1817) |
| | *Moroteuthis robusta* (Dall) Verrill, 1876 |
| Enoploteuthidae | *Abraliopsis* sp. |
| Veranyidae | *Octopoteuthis sicula* Ruppell, 1844 |
| Histioteuthidae | *Meleagroteuthis hoylei* Pfeffer, 1900 |
| Gonatidae | *Gonatus fabricii* (Lichtenstein, 1818) |
| | *G. magister* Berry, 1913 |
| | *G. anonychus* Pearcy and Voss, 1963 |
| | *Gonatopsis borealis* Sasaki, 1923 |
| Chiroteuthidae | *Chiroteuthis veranyi* (Ferussac, 1835) |
| Cranchiidae | *Galiteuthis armata* Joubin, 1898 |
| | *Taonius pavo* Lesueur, 1821 |
| | *Cranchia scabra* Leach, 1817 |
| Vampyroteuthidae | *Vampyroteuthis infernalis* Chun, 1903 |
| Octopodidae | |
| Bolitaenidae | *Japetella heathi* (Berry, 1911) |

TABLE 2

Average Number of Pelagic Cephalopods Collected per Hour of Midwater Trawling in Tows to Various Depths at a Station 50 Miles off Newport, Oregon

| SPECIES | 0–200 M (72 TOWS) | | 0–500 M (23 TOWS) | | 0–1000 M (24 TOWS) |
|---|---|---|---|---|---|
| (A) *Gonatus fabricii* | 0.5 | | 0.5 | | 0.1 |
| *Gonatus* spp. | 1.2 | | 0.2 | | 0.1 |
| *Chiroteuthis veranyi* | 0.5 | | 0.1 | | 0.1 |
| *Abraliopsis* sp. | 0.7 | | 0.1 | | 0.1 |
| (B) *Japetella heathi* | 0.03 | | 0.21 | | 0.14 |
| *Octopoteuthis sicula* | 0.00 | | 0.04 | | 0.02 |
| *Galiteuthis armata* | 0.00 | | 0.04 | | 0.05 |
| *Taonius pavo* | 0.01 | | 0.14 | | 0.06 |
| | day (9 tows) | night (63 tows) | day (14 tows) | night (9 tows) | |
| (C) *Gonatus fabricii* | 0.2 | 0.6 | 0.7 | 0.2 | |
| *Abraliopsis* sp. | 0.0 | 0.7 | 0.2 | 0.1 | |

North America, was found in several otter trawl collections where the depth was 100 m or less, but was absent from midwater trawl collections. *Rossia pacifica,* another myopsid, was taken mainly in otter trawl collections, as was the large (DML 200 mm) *Gonatus magister. Gonatus anonychus* was collected only with a dip net under night lights (Pearcy and Voss, 1963).

The relative abundance of the cephalopods captured by midwater trawling from all stations and depths is shown in Figure 1. *Gonatus fabricii* comprised about 38 percent of the total catch. A group consisting of larval and juvenile individuals of the genus *Gonatus,* but without sufficient differentiation of hooks for specific identification, was next in numerical importance. At least three separate species of *Gonatus* may be represented (Table 1) but, judging from the relative abundance of larger gonatids, most are probably *G. fabricii.*

### *Geographic Distribution*

Little difference in the species composition of cephalopods was noted among the latitudes. *Gonatus fabricii, G.* spp., and *Abraliopsis* dominated the midwater trawl collections at nearly all series of stations. Pelagic cephalopods, as well as mesopelagic fishes (Pearcy, 1964), were rare at the inshore stations off Newport, where the depth of water was 300 m or less.

### *Depth Distribution*

The number of common squid captured per hour of towing appeared greater in tows to 200 m than in deeper tows; this was particularly true of *Gonatus* spp., *Chiroteuthis veranyi,* and *Abraliopsis* sp. (Table 2*A*). Since an opening and closing device was not used on the trawl, some of the animals found in tows to 500 and 1000 m were probably caught while the trawl sampled through the upper 200 m. Such differences in catches suggest that the four common squids are largely epipelagic in distribution during the night, when most of the 0–200 m collections were made. Comparisons of day and night catches of the two most abundant squids, *G. fabricii* and *Abraliopsis* sp., show that highest catches were made during the night in tows to 200 m depth but during the day in tows to 500 m (Table 2*C*). This

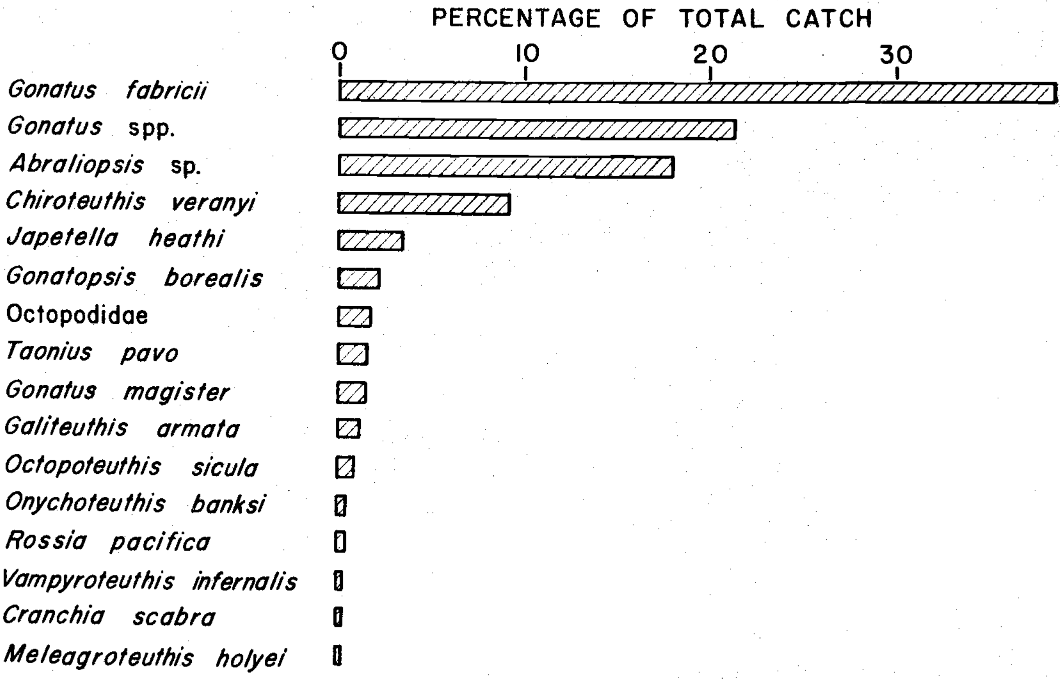

FIG. 1. The relative abundance of pelagic cephalopods found in midwater trawl collections off Oregon.

suggests diurnal vertical migration of these species.

Some of the cephalopods were uncommon in epipelagic waters and are considered to be of basically mesopelagic (200–1000 m) distribution. Four species were more abundant in deep tows than in shallow tows (Table 2*B*). With the exception of *G. armata*, individuals of these species were occasionally collected in 0–200 m tows after dark at other stations, but they were smaller than those from deeper collections. The bathymetric distribution of *G. armata*, summarized by Sasaki (1929), also suggests that it is a deep water species. *Vampyroteuthis infernalis*, another deep water species, was taken only in tows below 500 m.

*Seasonal Variations*

Seasonal differences in relative abundance were striking, though species composition apparently was not greatly influenced by season. The number of animals per tow during the summer was about an order of magnitude greater than it was during other months.

TABLE 3

SEASONAL OCCURRENCE OF COMMON CEPHALOPODS, 0–200 M COLLECTIONS, ALL STATIONS

| SPECIES | AVERAGE NUMBER PER TOW | |
|---|---|---|
| | JULY–SEPT. (79 TOWS) | OCT.–JUNE (205 TOWS) |
| *Gonatus fabricii* | 4.9 | 0.61 |
| *Gonatus* spp. | 1.9 | 0.32 |
| *Chiroteuthis veranyi* | 0.71 | 0.20 |
| *Abraliopsis* sp. | 1.9 | 0.33 |

Catches of *G. fabricii* were about eight times higher during the summer, of *Gonatus* spp. and *C. veranyi* about six times higher (Table 3).

Such seasonal differences indicate marked changes in the availability of cephalopods due to changes in susceptibility to capture or to changes in actual abundance. Since the differences could be related to the life history of the

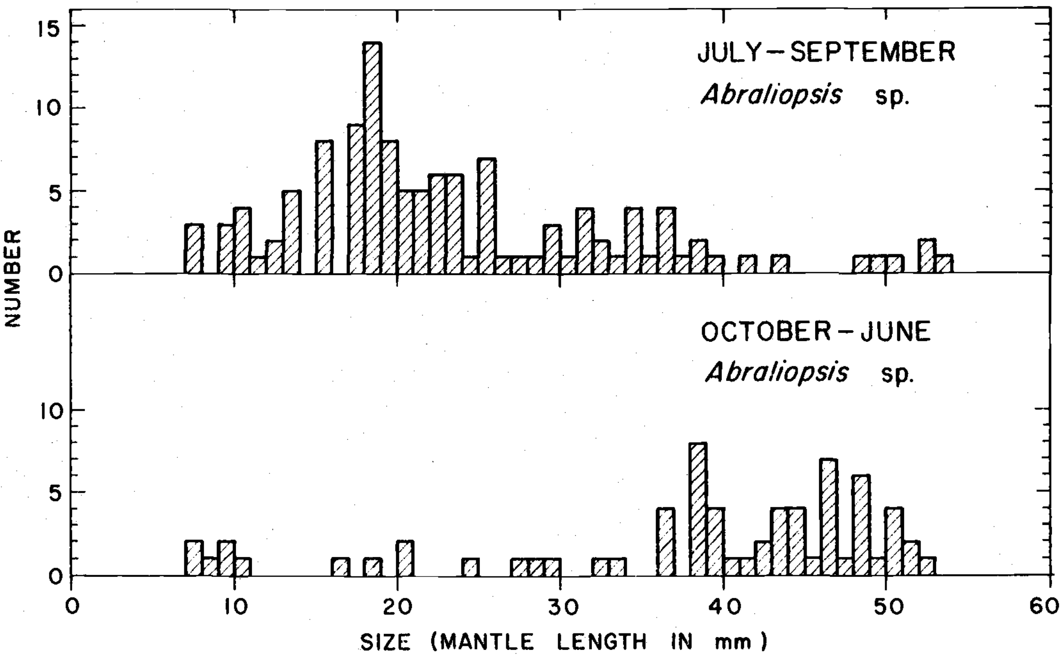

FIG. 2. Size-frequency distributions of *Abraliopsis* found in midwater trawl samples during the summer (July–September) and other seasons of the year (October–June).

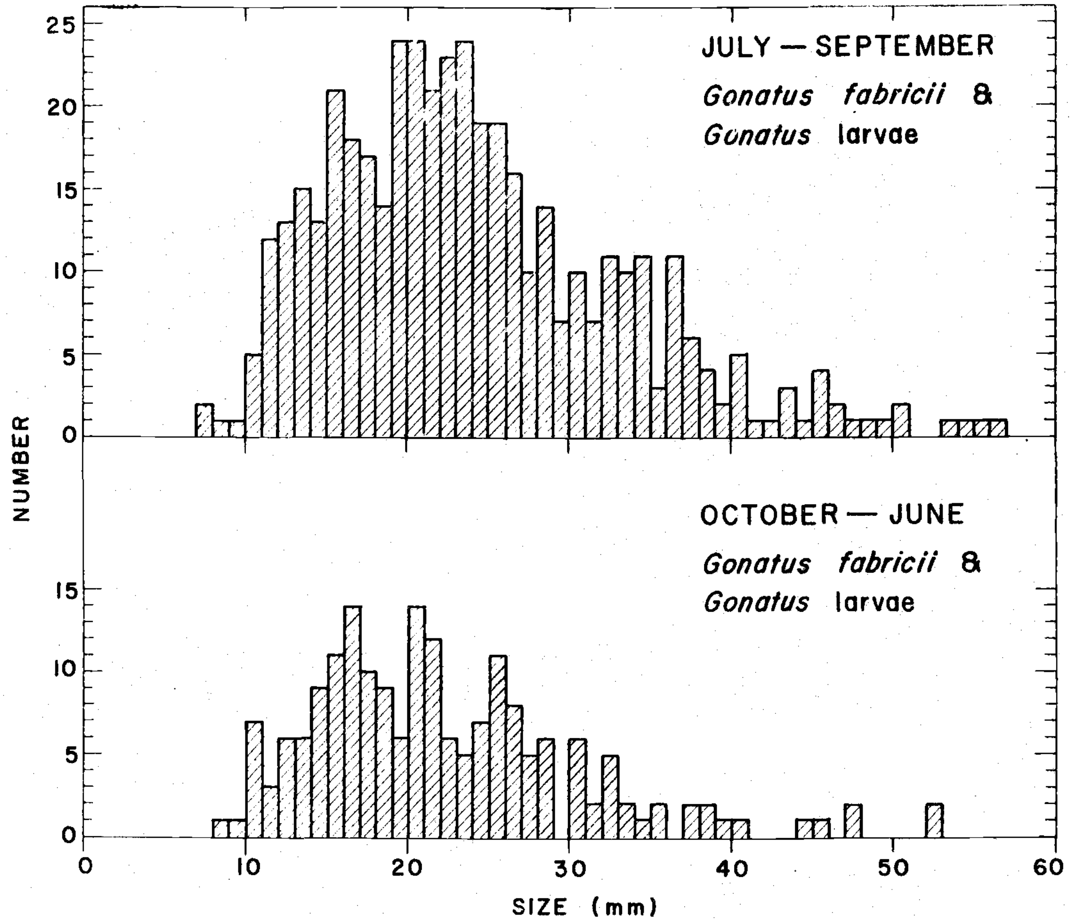

FIG. 3. Size-frequency distribution of *Gonatus fabricii* and *Gonatus* larvae found in midwater trawl samples during the summer (July–September) and other seasons of the year (October–June).

squid in either case, size–frequency distributions were examined.

During the summer the catch of *Abraliopsis* sp. consisted mainly of small individuals (less than 30 mm DML), whereas during other seasons larger squid predominated (Fig. 2). On the other hand, the size distribution of *Gonatus* larvae and *G. fabricii* (assuming they are in fact one species) are similar for both summer and non-summer periods (Fig. 3). This suggests that breeding of *Abraliopsis* is largely seasonal, while that of *Gonatus* is not.

Seasonal differences between the size structures of each species may result from growth, mortality, and movements of the populations. Growth, and attendant mortality, may explain differences between the size modes and relative abundance of *Abraliopsis* during the two periods. But other factors appear to be involved with *Gonatus*. *Gonatus* specimens over 30 mm in length constituted a larger proportion of the total catch during the summer than in other seasons (21% *versus* 7%). In addition, the catch of large *Gonatus* per tow during the summer was greater than that of small *Gonatus* (30 mm) during the other seasons. These differences suggest an influx or migration of these squid into slope waters during the summer. Perhaps this is caused by oriented swimming of squids or by a concentrating effect of ocean circulation.

## DISCUSSION

Some squid are notoriously fast swimmers; others are more planktonic than nektonic. Such differences in swimming ability obviously determine the catch composition by any sampling method. Most of the cephalopods collected in the midwater trawl were small. Although a large *Gonatopsis borealis* (DML, 250 mm) was captured, there was evidence that smaller squids than this readily avoid the midwater trawl. For example, *Onychoteuthis banksi* (DML of 100 mm and over) were often observed around night lights, but were rarely if ever captured in midwater trawl collections at the same station and time. The average size of squid was larger in otter trawl than in midwater trawl collections, and, in general, the largest squid were captured in the largest trawls.

Of the identifiable cephalopods found in the stomachs of 66 albacore tuna (*Thunnus alalunga*) collected off Oregon during the summer of 1962, small gonatids predominated. Inasmuch as predators often obtain effective samples of cephalopods (Clarke, 1963), this agreement between the catches of two independent sampling "devices," the midwater trawl and the albacore, was encouraging.

## ACKNOWLEDGMENTS

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## REFERENCES

BERRY, S. W. 1912. A review of the cephalopods of western North America. U.S. Bur. Fish. Bull. 30:267–336.

CLARKE, M. R. 1963. Information obtained by using squid predators as samplers. Proc. XVI Int. Congress of Zool. 1:67.

HOYLE, W. E. 1904. Reports on the Cephalopoda. "Albatross" Reports. Bull. Mus. Comp. Zool. 43(1):1–71.

PEARCY, W. G., and G. L. VOSS. 1963. A new species of gonatid squid from the northeastern Pacific. Proc. Biol. Soc. Washington 76:105–112.

——— 1936. Distribution of oceanic cephalopods off Oregon, U.S.A. Proc. XVI Int. Congress Zool. 1:69.

——— 1964. Some distributional features of mesopelagic fishes off Oregon. J. Mar. Res. 22:83–102.

SASAKI, M. 1929. A monograph of the dibranchiate cephalopods of the Japanese and adjacent waters. J. Fac. Agric. Hokkaido Univ. 20(Suppl.):1–357.

SMITH, A. G. 1963. More giant squids from California. Calif. Fish and Game 49:209–211.

TOWNSEND, C. H. 1901. Dredging and other records of the United States Fish Commission Steamer "Albatross," with bibliography relative to the work of the vessel. Rept. U.S. Commission of Fish and Fisheries, Pt. 26: 387–562.

# Distribution and Morphology of the Medusa, *Calycopsis nematophora*, from the North Pacific Ocean[1]

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## ABSTRACT

The medusa, *Calycopsis nematophora*, is reported from the North Pacific for the first time since its original description. It is restricted to arctic-subarctic surface waters. Radial canal variation and other morphological characters are discussed.

## INTRODUCTION

TEN SPECIES are generally recognized in the anthomedusan genus *Calycopsis* Fewkes. This world-wide genus shows geographic speciation, but most species are known from few localities. Also, due to the morphological variation of characters (such as radial canals) a few forms were described as new species or doubtfully identified as a previously described species. These were probably variants of known species.

Three species of *Calycopsis* have been reported from the Pacific Ocean from only a few captures in widely separated areas: *C. borchgrevinki* (Browne) from the Pacific subantarctic, *C. simulans* (Bigelow) from the tropical Pacific, and *C. nematophora* Bigelow from the arctic-subarctic. *Calycopsis nematophora* has not been reported since its original description by Bigelow in 1913. This paper is a report on *C. nematophora* collected in Pacific waters during 1961–63. Specimens collected over a large geographic area show morphological variations in relation to their distribution.

## MATERIAL AND METHODS

A total of 661 plankton samples from 67 stations was examined for *Calycopsis*: 215 from the subarctic North Pacific including the Bering Sea, 431 from 16 stations off the Oregon coast, and 15 from the northeastern central Pacific (Fig. 1). The samples from the Oregon coast were collected with a modified 6-ft Isaacs-Kidd midwater trawl towed at 6 knots. The other samples were collected with a 3-ft modified Isaacs-Kidd midwater trawl towed at 4 knots. All tows were oblique, but varied in depth. Most of the tows off the Oregon coast were 0–200 m; a few were 0–1000 m. Of the remaining tows, ten were 0–500 m and the rest 0–200 m or shallower. The tows in which specimens were captured are described in Table I.

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TABLE I. Tows in which *C. nematophora* were captured.

| Date | Latitude (*N*) | Longitude (*W*) | Range of depth of tows (*m*) | Number of specimens |
|---|---|---|---|---|
| **1961** | | | | |
| May 4 | 55°00′ | 155°00′ | 0–50 | 1 |
| 14 | 52°00′ | 166°20′ | 0–50 | 1 |
| June 1 | 50°00′ | 177°00′ | 0–50 | 1 |
| 1 | 49°00′ | 176°30′ | 0–50 | 1 |
| 10 | 53°02′ | 174°37′ | 0–50 | 3 |
| 12 | 53°28′ | 170°01′ | 0–50 | 2 |
| 13 | 54°20′ | 170°00′ | 0–50 | 1 |
| 13 | 55°09′ | 170°00′ | 0–50 | 1 |
| 23 | 58°02′ | 180°00′ | 0–150 | 2 |
| 24 | 58°04′ | 180°00′ | 0–100 | 1 |
| 24 | 58°07′ | 180°00′ | 0–25 | 9 |
| 24 | 58°12′ | 179°57′ | 0 | 1 |
| 24 | 53°26′ | 169°57′ | 0–50 | 2 |
| July 10 | 51°18′ | 176°50′ | 0 | 1 |
| 12 | 49°57′ | 178°09′ | 0–50 | 1 |
| Aug. 4 | 51°02′ | 175°27′ | 0–125 | 1 |
| 4 | 51°02′ | 175°27′ | 0–150 | 1 |
| 4 | 51°02′ | 175°27′ | 0–75 | 1 |
| Nov. 7 | 44°39′ | 125°32′ | 0–200 | 1 |
| 15 | 46°14′ | 125°15′ | 0–200 | 1 |
| **1962** | | | | |
| Jan. 9 | 44°39′ | 126°59′ | 0–290 | 1 |
| Sept. 3 | 49°50′ | 160°50′ | 0–100 | 1 |
| 4 | 49°50′ | 160°50′ | 0–250 | 3 |
| 4 | 49°46′ | 160°48′ | 0–500 | 1 |
| **1963** | | | | |
| Sept. 20 | 44°39′ | 127°00′ | 0–200 | 1 |

## DISTRIBUTION

Although Bigelow (1913) considered *C. nematophora* a surface form restricted to the Bering Sea region, the medusa appears to be epipelagic with a wider distribution. Its distribution (Fig. 1) agrees with the general surface water movements in the subarctic as outlined by Uda (1962). Of the 40 individuals of *C. nematophora* collected, 36 were obtained north of 49°N, and the other four were obtained off the Oregon coast. The occurrence of *C. namatophora* off the Oregon coast suggests expatriation from more northern latitudes, probably due to the West Wind Drift and the California Current system.

Only 11 of the 40 specimens were obtained from tows 100 m or deeper (Table I). This suggests that *C. namatophora* inhabits surface waters where its distribution is influenced by the surface water movements.

## MORPHOLOGY

Bigelow (1913) presented an excellent description of *C. nematophora* from 29 specimens collected at nine locations (Fig. 1). He stated that the medusae are higher than broad, except when contracted. The medusae examined in this study are contracted and are almost as broad as high (1 or 2 mm higher than broad). The margin of the bell cavity is withdrawn, turned inward and upward.

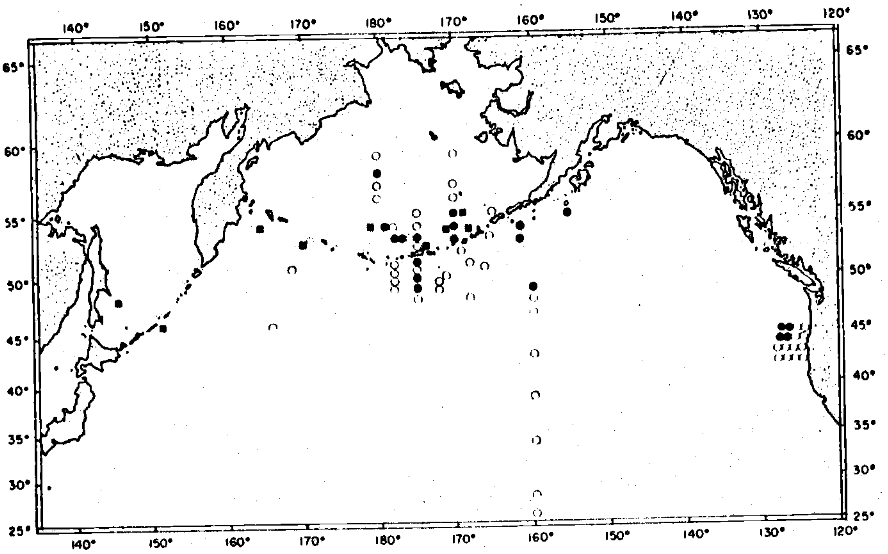

FIG. 1. Distribution of samples and of *Calycopsis nematophora*. Solid circles, *C. nematophora* present; open circles, *C. nematophora* absent; solid squares, *C. nematophora* reported by Bigelow in 1913.

The height ranges from 7 to 30 mm, with most of the specimens at least 20 mm high. As a rule, the larger the specimen, the thicker the gelatinous material of the bell. The jelly is thin and flexible in the three smallest specimens (7, 10, and 12 mm), while all of the larger specimens are rigid and have fairly thick jelly. The larger specimens also display the slight apical depression mentioned by Bigelow. This depression appears to be an adult characteristic of this species.

All but one of Bigelow's specimens were compressed either radially or interradially. Only seven of the recent collection are compressed, probably by preservation. Five live specimens observed on board the U. S. Coast and Geodetic Survey ship *Pioneer*, showed no compression.

The manubrium is only about one-fourth the length of the bell cavity in preserved specimens (Fig. 2), and one-third in live animals. In preserved specimens the lips of the manubrium are complexly folded, turned upward and out, while in the live animals they extend downward. Labial nematocyst knobs are contracted to such an extent in preserved medusae that they are difficult to observe.

## TENTACLES

The tentacles in both living and preserved material were in poor condition. Most specimens have four large tentacles (as shown in Fig. 2) each associated with one of the four primary canals. Each of the other canals has a smaller tentacle which terminates in a nematocyst knob. The small, intermediate tentacles are usually not associated with canals, but in one specimen, erratic canal branches (Fig. 3 h) are sometimes associated with an intermediate tentacle.

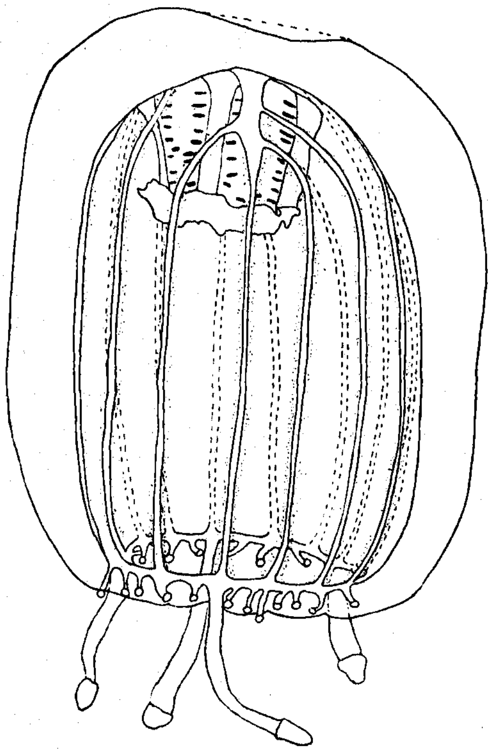

FIG. 2. A camera lucida drawing of *Calycopsis nematophora*, 28 mm high.

Bigelow (1913) believed that development of the tentacles precedes that of canals, and that each canal develops to associate with a tentacle. In the recent specimens some intermediate tentacles are not associated with canals.

The total number of tentacles ranges from 33 to 48. This agrees with the range given by Bigelow (1913).

### CANALS

The genus *Calycopsis* is characterized by four primary radial canals and a varying number of centripetal canals which usually join at the base of the manubrium. Kramp (1959) has arranged the species of this genus from the simplest (with four primary canals and four centripetal canals which do not fuse with the base of the manubrium) to the most complex (with four primary canals and up to 56 centripetal canals which may or may not join with the manubrium). *Calycopsis nematophora* has four primary canals and 11–15 centripetal canals that join with the base of the manubrium (Fig. 2). It is, therefore, intermediate in complexity.

The most common canal pattern is shown in Fig. 3a. It was found in the three smallest, the largest, and four other medusae as well as in one or more quadrants of all other medusae. Usually there are three centripetal canals in a

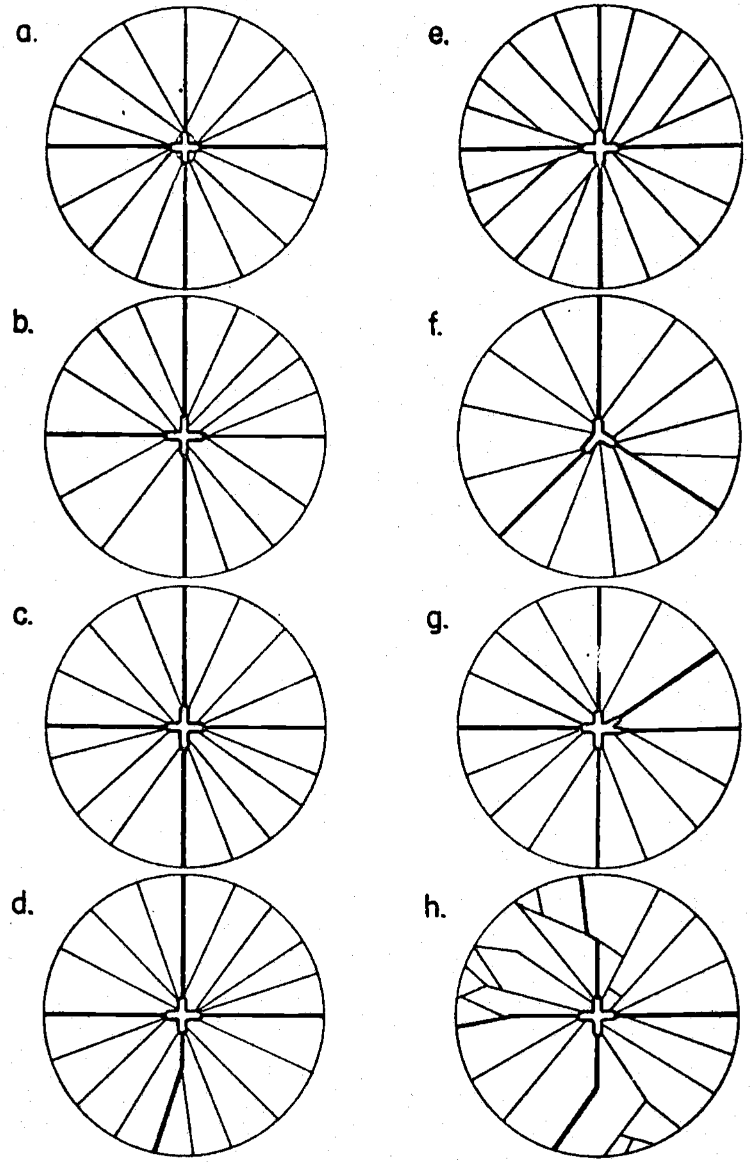

FIG. 3. Shematic drawing of the variation of raidal canals. a, common 16 canal pattern; b, variation of common pattern; c, 17 canals; d, 18 canals; e, 19 canals; f, three primary canals; g, five primary canals; h, branching centripetal canals.

quadrant which join with the cruciform base of the manubrium, although there is some variation. In four instances, a radial canal divided near the ring canal and rejoined near the manubrium. Two individuals had a transverse canal near the manubrium connecting two canals (Fig. 3h). The total number of canals varied from 14 to 19. The centripetal canals were complete except in one specimen where three blind centripetal canals were present. Two of the three canals were in the same quadrant; the third was in another quadrant. The remaining two quadrants had three complete centripetal canals. The blind centripetal canals extended up from the ring canal a distance of 3, 4, and 6 mm. The different lengths suggest that these canals are not just sporadic outgrowths of the ring canal as Bigelow indicated with his specimen, but may be developing canals which eventually would have joined with the base of the manubrium. Variations of the common canal pattern are shown in Fig. 3b–e. In addition to showing variations in centripetal canal pattern, three specimens had anomalous primary canal structure (Fig. 3f and g), although they were normal in other respects. Two of the four specimens obtained in the samples off the Oregon coast have numerous branched canals (Fig. 3h) that recall features mentioned by Bigelow (1938) in two specimens of *Calycopsis* sp. taken near Bermuda. The aberrant canal condition of the Oregon specimens appears to be caused by extreme environmental factors.

The edges of the canals are smooth to ragged, the degree of roughness varying along any one canal or between canals. Bigelow (1913) associated roughness with the ability with which the canal can send out other canals, but in the present material roughness does not appear to be associated with additional canals.

Every canal, including the three centripetal canals, possesses a subumbrellar muscle band, a characteristic unique to *C. nematophora.*

### COLOR

The color of the gonads, labial nematocyst knobs, and manubrium of the five live specimens was very dark red, almost purple, but after 30 days in preservative the manubrium and gonads were pale reddish brown, as Bigelow (1913) states, and the nematocyst knobs were white.

### NEMATOCYSTS

The labial knobs and the intermediate tentacles were examined by the method of Mackie (Totton and Mackie, 1960, p. 394) to determine the type of nematocysts present. Desmonemes were found in both areas. Russell (1940) reported both desmonemes and microbasic euryteles for other members of the family Calycopsidae.

In 13 specimens of *C. nematophora*, several amphipods (*Parathemisto pacifica*) were found attached to the manubrium. Since no nematocysts were present in the stomach contents of five amphipods examined, there is no evidence that amphipods were feeding upon the medusae. Interspecific relationships are suggested but their nature is not known.

## SUMMARY

Previously recorded only once from nine localities in the North Pacific, *C. nematophora* is reported from subarctic water in the Bering Sea, Gulf of

Alaska, and California Current, mainly from epipelagic waters. The three specimens from the California Current off Oregon differ from those collected further north in details of radial canals, possibly reflecting environmental differences.

A basic pattern of 16 canals, with three centripetal canals per quadrant, prevailed. Although considerable variation in this pattern was observed it was not related to umbrella height. The canals of the adult medusae are joined with the base of the manubrium, and every canal has a muscle band associated with it.

The only nematocysts found were desmonemes, and the amphipod *Parathemisto pacifica*, present on the manubrium, did not have any nematocysts in the gut.

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## REFERENCES

BIGELOW, H. F. 1913. Medusae and Siphonophorae collected by the U. S. Fisheries steamer "Albatross" in the North-western Pacific, 1906. *Proc. U. S. Nat. Mus.*, **44**: 1–119.

1938. Plankton of the Bermuda Oceanographic Expeditions. VIII. Medusae taken during the years 1929 and 1930. *Zoologica, N. Y.*, **23**: 99–189.

1940. Medusae of the Templeton Crocker and Eastern Pacific Zaca Expeditions, 1936–1938. *Ibid.*, **25**: 281–321.

KRAMP, P. L. 1959. The Hydromedusae of the Atlantic Ocean and adjacent waters. *Dana Rep.*, No. 46, pp. 1–283.

1961. Synopsis of the Medusae of the world. *J. Mar. Biol. Ass., U. K.*, **40**: 1–469.

RUSSELL, F. S. 1940. On the nematocysts of Hydromedusae. III. *J. Mar. Biol. Ass., U. K.*, **24**: 515–523.

TOTTON, A. K., AND G. O. MACKIE. 1960. *Physalia physalia*. *Discovery Rep.*, **30**: 301–408.

UDA, M. 1963. Oceanography of the Subarctic Pacific Ocean. *J. Fish. Res. Bd. Canada*, **20**: 119–179.