DOE/ER/60819--2

DE91 005576

VERTICAL AND HORIZONTAL FLUXES OF SELECTED RADIONUCLIDES AND
TRACE METALS OFF THE COAST OF SOUTHERN CALIFORNIA

ANNUAL REPORT
FOR THE PERIOD
15 NOVEMBER 1989-14 November 1990

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PREPARED FOR THE
U.S. DEPARTMENT OF ENERGY
ECOLOGICAL RESEARCH DIVISION
OFFICE OF ENERGY RESEARCH
UNDER GRANT DE-FG06-89ER60819

Received by JSTI
MASTER

JAN 02 1991

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I. INTRODUCTION

This is to report the progress of our trace metal and radionuclide studies for the California Basin Study (CaBS) program sponsored by the Ecological Research Division of the U.S. Department of Energy. The CaBS program started on 15 May 1985 and is currently in its second phase. The CaBS Phase II program, started on 15 May 1989, is scheduled for 2.5 years with three budget periods as follows:

Period 1: 15 May 1989 - 14 November 1989

Period 2: 15 November 1989 - 14 November 1990

Period 3: 15 November 1990 - 14 November 1991

This annual report is made in conjunction with our continuation application for the third (and final) project period. Included in this report are: (1) a reprise of our objectives, (2) a report of our progress to date, with special reference to work performed during the past budget period, (3) an updated list of our publications resulting from this work, (3) a detailed description of the proposed work for the ensuing year, and (4) one paper published during this reporting period (Appendix I).

II. OBJECTIVES - A REPRISE

The overall objective of our research, within the structure of the CaBS program, is to understand the transport pathways and mass balances of some metabolically-active and inactive chemical species in the Santa Monica/San Pedro (SM/SP) Basin. Our focus is to examine selected trace metals and radionuclides in seawater, sediment trap material, and bottom sediments. Knowledge of the inventories, fluxes, and routes of these nuclides and metals in or among these reservoirs should lead to a cogent model for these elements in SM/SP Basin, which in turn should shed light on the fate and effects of energy-related by-products in a coastal region impacted by intense human activities.

Specific scientific objectives (and the approaches) are:

- (1) To unravel the history of deposition and quantify the burial fluxes of selected trace metals, radionuclides and biogenic components in the SM/SP Basin (by sediment core studies);
- (2) To quantify, on seasonal and annual timescales, the fluxes of these components

throughout the water column (by sediment trap deployments and studies);

(3) To determine the sources and transport pathways of these chemical materials, and determine factors that control spatial and temporal variations in fluxes (by a collective analysis of sediment core, sediment trap, transmissometer, and current meter data);

(4) To construct a one-dimensional model to interpret the overall results (by using thorium isotopes as proxy tracers).

III. REPORT OF PROGRESS

Since the beginning of the CaBS Phase I program in May, 1985, we have participated in nine cruises and collected a large number of sediment core, sediment pore water, sediment trap, and water column samples for our studies of the system. Our first five progress reports were made semiannually, and they were included in the CaBS group report synthesized by the program coordinator, Dr. Ian Kaplan. In Progress Report VI, submitted along with our Phase-II proposal, our work completed prior to November 1988 were reported comprehensively. In conjunction with our last continuation request (for the second period of Phase II), we made our 7th progress report presenting results obtained during the first half of 1989. This is our eighth progress report. We will once again update the results of our work, and make plans for the next project period. As in the past, we shall only briefly summarize the results in the following sections. Where appropriate, interested readers and reviewers are referred to our CaBS publications (listed later) for more details.

1. Radiochemical Studies of Sediment Cores

Thus far we have collected 19 sediment cores from the SM/SP Basin and two cores from the Santa Cruz Basin (Table 1). Locations of the cores are shown in Fig. 1. In the SM/SP Basin, the cores fall primarily along two transects: an offshore transect from the basin slope toward the deep SM/SP Basin, and a longshore transect along the axis of the Santa Monica-San Pedro Basin and the sill passages in a NW-SE direction. Results on the cores from the offshore transect was published as our first CaBS contribution (Huh *et al.*, 1987). We have since then completed the analysis of other SM/SP Basin cores and the integrated results have just published (Huh *et al.*, 1990; Appendix I). In addition, we have also studied two cores collected from the Santa Cruz Basin to evaluate horizontal

Table 1. Sediment cores collected and studied

Cruise name	Box core number	Location		Depth (m)	Date of collection (mo/day/yr)
CaBS-I	BC-12	33°50.1'N,	118°41.3'W	750	10/08/85
	BC-40	33°51.1'N,	118°38.13'W	398	10/09/85
	BC- 89	33°41.5'N,	118°56.3'W	908	10/12/85
	BC-102	33°44.8'N,	118°50.3'W	910	10/14/85
	BC-113	33°50.64'N,	118°38.9'W	572	10/16/85
CaBS-III	BC-31	33°45.47'N,	118°49.57'W	910	5/18/86
	BC-1	33°44.58'N,	118°50.79'W	910	5/19/86
CaBS-V	BC-3	33°44.15'N,	118°53.75'W	906	4/08/87
	BC-6	33°46.18'N,	118°42.00'W	910	4/11/87
	BC-7	33°45.22'N,	118°47.45'W	910	4/12/87
	BC-8	33°49.96'N,	119°05.10'W	880	4/13/87
	BC-9	33°30.07'N,	118°20.39'W	896	4/14/87
CaBS-X	BC-2	33°50'N,	119°00'W	870	9/28/88
	BC-3	33°50'N,	118°45'W	890	9/28/88
	BC-4	33°45'N	119°28'W	1910	9/30/88
	BC-5	33°35'N	119°30'W	1985	9/30/88
CaBS-XI	BC-1	33°45.54'N	118°50.88'W	904	1/26/90
	BC-10	33°56.96'N	118°44.87'W	535	1/26/90
	BC-13	33°48.47'N	118°55.08'W	904	1/26/90
	BC-4	33°41.78'N	118°30.78'W	780	1/27/90
	BC-3	33°46.4'N	118°41.5'W	905	2/2/90

Figure 1. Locations of box cores (solid squares).

transport of anthropogenic materials out of the SM/SP Basin into the California Current system.

Major observations based on ^{210}Pb and ^{234}Th data are summarized below:

- (1) In the Santa Monica Basin, sedimentation rates decrease offshore over the basin slope (from $\sim 80 \text{ mg/cm}^2/\text{yr}$ at the upper slope to $\sim 30 \text{ mg/cm}^2/\text{yr}$ at the base of the slope) and are uniformly low ($13.4\text{--}18.8 \text{ mg/cm}^2/\text{yr}$) in the vast basin floor. In the Santa Cruz Basin, the southern core accumulated at a rate of $\sim 10 \text{ mg/cm}^2/\text{yr}$, and the northern core accumulated at a much higher rate of $\sim 100 \text{ mg/cm}^2/\text{yr}$, probably caused by enhanced supply from the nearby northern canyons or the sill passage between Santa Monica and Santa Cruz Basins.
- (2) Detailed examination of ^{210}Pb profiles downcore reveals that sedimentation rates have been decreasing during the past one to two centuries, probably resulting from (i) the expansion and intensification of the anoxia, and (ii) increasing urbanization and flood control of the natural drainage.
- (3) Based on ^{210}Pb chronology, turbidites found in some of the cores can be dated at hundreds of years B.P. (before present) to within a decade B.P. Younger turbidites (<20 years) can be related to major storms recorded in modern history.
- (4) Cores from the oxic basin slope indicated substantial sediment mixing in the upper 2-4 cm. Those in the anoxic deep basin showed annual varves, with very minor mixing (mixing coefficient = $0.2\text{--}4 \text{ cm}^2/\text{yr}$) restricted to the top ~ 1 cm.

2. Chemical Studies of Sediment Cores

On selected key cores, we have performed elemental analyses (major and trace metals, organic carbon and carbonate carbon). Based on data of three SM/SP Basin cores we have published two timely papers to update the history of heavy metal pollution in the Southern California Bight (Finney and Huh, 1989a, b). We have since then studied nine more cores and are currently analyzing the data. The expanded data base will allow us to calculate the budgets and discuss depositional processes of selected elements more thoroughly. Figure 2 shows some typical profiles of Cr, Zn, Sb and Pb in SM/SP Basin cores. All these profiles are characterized by pronounced subsurface maxima reflecting peak contamination during the time interval 1960-70 (Finney and Huh, 1989a,b). Metal concentrations began to increase above their natural, background levels from the onset of this century. The excess, anthropogenic components of the metals can be calculated using

Figure 2. Depositional history of heavy metals in the Santa Monica/San Pedro Basin.

Figure 2. Continued

Table 2. Inventories of excess metals in some SM/SP Basin cores

Core No.	<u>Inventory of excess metals ($\mu\text{g}/\text{cm}^2$)</u>			
	Cr	Zn	Sb	Pb
CaBS-3 BC-1	35.6	22.7		16.1
BC-31	44.2	31.7	1.17	
CaBS-5 PC-6	58.0	45.2		
BC-8	38.4	24.2		18.6
BC-9	39.4	14.8		18.7
CaBS-10BC-2	63.3	47.5	1.98	
BC-3	40.1	29.2		
Average	45.6	30.8	1.58	17.8

Table 3. Comparison of inventories (tons) of anthropogenic metals in the SM/SP Basin with combined mass emissions (tons) from the six largest municipal outfalls (see Fig. 3) during 1971-1988*.

	Cr	Zn	Sb	Pb
Standing stock in sediments	1370	924	47.4	534
Mass emissions from outfalls	6047	14279		2790

* From SCCWRP Annual Report, 1988-89.

Figure 3. Locations of six municipal wastewater treatment facilities.^a

the equation:

$$\text{Excess metal} = [(\text{Metal/Al}) - (\text{Metal/Al})_{\text{bkgd}}] \times \text{Al}$$

Where $(\text{Metal/Al})_{\text{bkgd}}$ is the metal to Al concentration ratio in uncontaminated sediments, which can be determined from sediments deposited prior to 1900. Integrating excess metals down core gives their standing stock per unit area. Some preliminary data are listed in Table 2. Cr and Zn data show somewhat higher inventories in the eastern part of the basin, which is clearly due to proximity to the source region. On a basin-wide scale, the spatial variations are not dramatic, however.

The area of the SM/SP Basin floor deeper than 737 m (the sill depth) is about 3000 km². Multiplying the average inventories of excess metals listed in Table 2 by the area gives the total anthropogenic inputs of these metals to the basin. The results, given in Table 3, are compared with the emissions of these metals from major outfalls since 1971. There are no mass emission data prior to 1971. Therefore, for a more meaningful comparison between these two sets of data, we still need to figure out how much of the sewage metals were deposited after 1971. It is also necessary to sort out mass emissions from the three largest and nearest outfalls (i.e., JWPCP, Hyperion and CSDOC) that are most responsible for inputs to the study area (see Fig. 3). Both of the above two calculations can be and will be done. For now, to get a rough idea about how much sewage metals are trapped in the basin floor (below the sill depth), let's assume that 90% of the combined emissions have come from the three most responsible outfalls and that the total emissions prior to 1971 match that after 1971. From this, it is estimated that the percentages trapped in the basin are 13%, 4%, and 11% for Cr, Zn and Pb, respectively.

It should be noted that these partial and preliminary data are yet to be confirmed. In addition, our chemical analyses on many other cores are still underway. Upon completion of the laboratory work, we intend to write up these data and contribute a paper in the coming fall to the special CaBS monograph (to be published by *Progress in Oceanography*, Guest Editor, Lawrence F. Small).

3. Water Column Studies

(1) Radiochemical and chemical analyses of sediment trap material

Radiochemical and chemical analyses of sediment trap samples collected by the PMEL sequentially-collecting traps and Scripps long-term traps have been finished. The radiochemical results are discussed in Appendix I. The chemical data will be written up in the next several months, to be included in our 10th CaBS contribution (see later).

(2) Th isotopes in the water column and along an offshore surface transect

In the first year of the CaBS program, we measured the distribution of Th isotopes (^{234}Th , ^{232}Th and ^{230}Th) between dissolved and particulate forms in a water column at the central SM Basin, and a surface transect of ^{234}Th across the SM Basin. The water column results have been published (Huh and Beasley, 1987). The surface transect data are not yet synthesized for publication. Briefly, there is a general trend that dissolved ^{234}Th increases, whereas particulate ^{234}Th decreases, with distance offshore. The scavenging residence time of Th varies from 21 days (inshore) to 72 days (offshore).

IV. PUBLICATIONS

Listed below is an updated list of papers and meeting abstracts written under the full or partial support of the CaBS program. Most of them have just been cited in section III. Items 8, published in this reporting period, is appended to this report. Items 9 and 10 are being prepared.

- (1) Huh, C.-A., D. L. Zahnle, L. F. Small and V. E. Noshki (1987) Budgets and behaviors of uranium and thorium series isotopes in Santa Monica Basin sediments. *Geochim. Cosmochim. Acta*, 51, 1743-1754.
- (2) Huh, C.-A. and T. M. Beasley (1987) Profiles of dissolved and particulate thorium isotopes in the water column of coastal Southern California. *Earth Planet. Sci. Lett.*, 85, 1-10.
- (3) Huh, C.-A. (1987) Profiles of ^{230}Th and ^{232}Th measured on small-volume seawater samples by mass spectrometry. *EOS, Trans. Am. Geophys. Union*, 68, 331.
- (4) Finney, B. P. and C.-A. Huh (1987) Profiles of heavy metals, organic carbon and other elements in sediment cores from the Santa Monica Basin, California, *EOS, Trans. Am. Geophys. Union*, 68, 1325.
- (5) Huh, C.-A. (1988) Determination of thorium in seawater by neutron activation analysis and mass spectrometry. In: *Radionuclides: A Tool for Oceanography* (eds.

- J. C. Guarj, P. Guegueniat and R. J. Pentreath), p.84-91, Elsevier Applied Science.
- (6) Finney, B. P. and C.-A. Huh (1989) History of metal pollution in the Southern California Bight: An update. *Environmental Science and Technology*, 23(3), 294-303.
- (7) Finney, B. P. and C.-A. Huh (1989) High resolution sedimentary records of heavy metals from the Santa Monica and San Pedro Basins, California. *Marine Pollution Bulletin*, 20, 181-187.
- (8) Huh, C.-A., L. F. Small, S. Niemnil, B. P. Finney, B. M. Hickey, N. B. Kachel, D. S. Gorsline and P. M. Williams (1990) Sedimentation dynamics in the Santa Monica-San Pedro Basin off Los Angeles: radiochemical, sediment trap and transmissometer studies. *Continental Shelf Research*, 10, 137-164.
- (9) Huh, C.-A., J. Stull and B. P. Finney (in preparation) Budgets of anthropogenic metals in the Southern California Bight. To be submitted to *Progress in Oceanography* (special monograph, Guest Editor: L. F. Small).
- (10) Finney, B. P., C.-A. Huh and R. Jahnke (in preparation) Metal fluxes in the Santa Monica Basin, California: Sediment trap, sediment and benthic flux studies. To be submitted to *Marine Chemistry* (?).

V. PLANS FOR THE THIRD YEAR

1. Sediment core studies

We have performed chemical analysis on most of the 21 collected sediment cores. Currently I am analyzing the huge database for write-up, which will take up much of my time in the second half of this year, and possibly continue on into the early part of 1991. This major effort in data reduction and interpretation is expected to lead to the publication of two papers, one to be contributed to the CaBS monograph that is being planned (item 9 above), and one to be submitted to *Marine Chemistry* (item 10 above).

Our spatial coverage of the basin system, represented by the 19 cores, is fairly extensive (Fig. 1). Therefore, we do not contemplate taking further cores at other locations. To cover temporal changes that might occur during the 6-year span of the CaBS program, however, we plan to obtain a high quality Soutar box core in 1991 from one of our central SM Basin stations such as CaBS-3 BC-1. Results from that core will be compared with data obtained for the 1985 and 1986 cores. The 6 year follow-up will

allow us to further monitor how the sediments respond to changes in input, and test hypothesis we have developed regarding diagenetic processes.

2. Sediment trap studies

Our major analytical effort for the next year will be on time-series sediment trap samples. In collaboration with Dr. Mike Landry (University of Hawaii), we will study radionuclide and trace metals on sediment trap materials collected by VERTEX traps. There are two arrays in the Santa Monica Basin (see Landry proposal/report). We are most interested in and will focus our efforts on the deployment in central Santa Monica Basin. The traps are moored at eight depths (50m, 100m, 150m, 200m, 300m, 500m, 700m, and 850m) and they will be recovered/redeployed every 2-3 months during the 1990-91 biennium. The processed samples will be first delivered to Dr. Richard Ku's laboratory at USC for the measurements of ^7Be , ^{210}Pb , and ^{234}Th using a high-efficiency germanium detector. Following the non-destructive gamma-spectrometry, the samples will be returned to OSU and subjected to wet chemistry for the determination of radionuclides (U, Th, and Pu isotopes) by α -spectrometry, and a suite of trace metals (Al, Cr, Zn, Pb, etc.) by AAS. This is indeed a very precious opportunity to obtain a detailed time-series record of radionuclide and trace metal fluxes in the water column as related to other physical and biogeochemical processes.

Besides the short-term traps, we will continue to study samples collected by Scripps long-term traps, to be provided by Williams/Soutar. The results will be compared with those of short-term traps to evaluate and calibrate the performance of these two types of traps in collecting organic vs. inorganic materials.

3. Other contingent plans

Other plans described in our Phase II proposal but not specifically mentioned above are contingent upon the matching of our schedule with those of other CaBS colleagues in the final year. These include:

- (1) the role of bacteria in chemical scavenging (with Dr. F. Azam), and
- (2) the role of zooplankton in cycling metals/radionuclides (with Dr. L. F. Small).

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* Data from SCCWRP Annual Report, 1988-89.

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