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Geochemical cycling of cadmium in Los Angeles and Long Beach harbors

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GEOCHEMICAL CYCLING OF CADMIUM IN LOS ANGELES
AND LONG BEACH HARBORS

A Thesis

Presented to

The Faculty of Moss Landing Marine Laboratories
San Jose State University

In Partial Fulfillment
of the Requirements of the Degree
Master of Science
in
Marine Sciences

By

Debbie L. Colbert

May, 1999

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ABSTRACT

GEOCHEMICAL CYCLING OF CADMIUM IN LOS ANGELES AND LONG BEACH HARBORS

By Debbie L. Colbert

An on-line preconcentration method for determination of cadmium in seawater was developed for graphite furnace atomic absorption spectrometry. Average column recovery was 73% with a sample loading flow rate of 2.2 mL/min and a 55 s preconcentration time. The detection limit (3σ) for replicate blanks was 42 pM Cd ($n=5$) for a 2 mL sample. Method effectiveness was demonstrated using NASS-3 and NASS-4 certified reference materials as well as analysis of equatorial Pacific seawater.

Dissolved cadmium fluxes were measured directly using benthic chambers at stations in Los Angeles/Long Beach harbors and on the California continental margin. Cadmium fluxes ranged from -0.212 to $0.118 \mu\text{mol m}^{-2} \text{d}^{-1}$. Anaerobic microbial degradation was the major process controlling cadmium fluxes at harbor sites. A simple box model of the inner harbor suggested that sediments are the dominant source of cadmium. Cadmium distributions in the harbor system appeared to be dominated by natural processes.

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PREFACE

This thesis presents an adaptation of a method to measure cadmium in seawater together with its application in a study of cadmium geochemistry in Los Angeles/Long Beach harbors. The format of Chapters 1 and 2 reflects the style required by the scientific journals to which each chapter is published or will be submitted for publication. Chapter 1, which was published in *Analytica Chimica Acta* 377: 255-262, describes an adaptation of a method for the analysis of cadmium in seawater. Chapter 2 will be submitted to *Environmental Science & Technology* and presents a study of cadmium in benthic flux chambers deployed at sites throughout Los Angeles/Long Beach harbors and at sites along the California Continental Margin. The results are used to characterize the geochemical cycling of cadmium in this coastal environment.

CHAPTER 1

Determination of cadmium in seawater using
automated on-line preconcentration and direct
injection graphite furnace atomic absorption
spectrometry.

Determination of cadmium in seawater using automated on-line preconcentration and direct injection graphite furnace atomic absorption spectrometry.

Abstract

An on-line preconcentration method for the determination of cadmium in seawater was developed for graphite furnace atomic absorption spectrometry (GFAAS) using deuterium lamp background correction. The technique was adapted from a previously reported technique and was fully automated. Automated preconcentration of cadmium reduced the concentrations of matrix elements in samples to levels that did not interfere with the determination of cadmium at ultra trace levels. The soluble ligand, 1-Pyrrolidinecarbodithioic acid (APDC), was mixed with the sample in a continuous flow system to form a non-polar metal complex which was absorbed onto a C₁₈ column. The metal complex was then eluted from the column directly into the graphite furnace. The addition of an in-line nitric acid rinse step between sample load cycles allowed for the determination of cadmium with one elute cycle. Other modifications included laboratory purification of the ammonium acetate rinse solution, a nonbuffered APDC ligand solution, and a computer activated load cycle to reduce sample consumption. The average column recovery was 73% with a sample loading flow rate of 2.2 mL/min and a 55 s

preconcentration time. Sample throughput was approximately 15 samples per hour with 2 mL of sample preconcentrated and analyzed every 4 minutes. The small sample volume required made this method useful where sample volumes are limited. The 3σ limit of detection for replicate blanks was 42 pM Cd ($n=5$) for a 2 mL sample. The effectiveness of the method was demonstrated for the determination of Cd in certified open ocean reference materials NASS-3 and NASS-4. Analysis of Cd in equatorial Pacific seawater demonstrated that the system produces oceanographically consistent results.

Keywords: cadmium; on-line preconcentration; seawater; flow injection, atomic absorption spectrometry

1. Introduction.

Several techniques for the shipboard determination of trace metals in seawater have been developed. These include methods for cobalt [1], copper [2], manganese [3], iron [4,5,6], zinc [7], mercury [8], aluminum [9,10], and lead and cadmium [11]. However, there remains a large number of elements that cannot be analyzed in the field because of their low concentration or lack of suitable reagents. Also, shore based analytical systems often serve as referee systems for the development of methods that can be used on site. The continued development of automated analytical systems using shore based instruments is necessary to reduce potential problems due to contamination during sample processing and to facilitate analysis of large numbers of samples. Because few specific chemiluminescent reagents for cadmium exist and colorimetric indicators have low and non-specific molar extraction coefficients, analysis of cadmium in seawater samples has typically been performed in shore-based, ultraclean laboratories using graphite furnace atomic absorption spectrometry (GFAAS) [12,13,14].

Determination of trace elements in seawater by graphite furnace atomic absorption spectrometry (GFAAS) has been the primary tool for shore based analysis of metals dissolved in seawater. Direct analysis of seawater by GFAAS is limited not only because of the low concentration of many trace

metals, but also the high salt matrix of seawater may cause interferences [15]. To overcome these problems, many investigators have employed a preconcentration step such as organic extraction or ion exchange prior to analysis [16]. Those methods require clean room techniques, often use large sample and reagent volumes, and they can be time consuming. On-line continuous flow preconcentration systems can overcome these drawbacks as well as offer a number of advantages for ultratrace determinations: reduced risk of contamination; lower sample and reagent consumption; improved precision; and increased sampling frequency [17,18].

Several preconcentration methods have been introduced which couple flow injection and preconcentration with GFAAS. These systems typically involve manual steps for the preconcentration of analytes in seawater or are limited by the solvent volume accommodated by the graphite furnace. Few systems have successfully overcome both of these limitations.

Azeredo *et al.* [17] used a column of 8-hydroxyquinoline for the preconcentration of Cd and other trace metals from seawater using a discontinuous flow injection GFAAS system. They were able to directly inject the entire volume of eluent in the furnace. However, their system did not interface the on-line column with the autosampler of the spectrophotometer. The procedure required that the effluent from the column be directed into the graphite tube by manually turning the

autosampler arm into the inject position and holding it there for the 22 s duration of the elution phase prior to manually initiating the furnace program.

Liu and Huang [19] reported that by using a very small amount of C₁₈ material in their microcolumn (ca. 5 mg) and using an APDC complex, trace metals in seawater could be recovered with only 40 μ L of methanol, and that all of the eluate could be injected directly from the graphite furnace. The drawback of their work was the need for manual manipulation in the preconcentration procedure. Liu and Huang [15] improved this manual system and converted it into an automated preconcentration system. However, their system still involved manually pipetting sample, ligand, and buffer into autosampler cups before samples could be directly injected.

Porta et al. [20] developed a fully automated system which combined the chelating agent APDC and sample on-line with preconcentration onto a column inserted at the tip of the autosampler arm. The soluble ligand, APDC, was used to form a non-polar metal complex which was absorbed onto a column and eluted with an organic solvent. They tested various substrates, including C₁₈, XAD2, and XAD7. The metal complex was then injected directly into the graphite furnace. However, the eluate volume of the column was larger than the capacity of the graphite furnace. To achieve full sample

injection, the column was eluted twice and the solvent was evaporated in between injections.

This paper describes an adaptation of the fully automated preconcentration system described by Porta *et al.* [20] for the determination of cadmium in seawater using one elute cycle. An in-line nitric acid rinse step was added between sample elutions. With this additional rinse step, the sample run time was reduced to one elute cycle with direct injection onto the graphite furnace. Other modifications included laboratory purification of the ammonium acetate rinse solution and a nonbuffered APDC ligand solution. Sample consumption was also reduced by activating the peristaltic pump only during the sample load cycle.

2. Methods.2.1.

Standards and reagents.

All reagent bottles were made of polypropylene or polyethylene and were stored and handled according to trace metal clean techniques [14]. Containers were soaked in Micro® detergent for one week, transferred to 10% HCl for another week, and thoroughly rinsed with 18 M Ω cm⁻¹ water (MQ water) from a Milli-Q® deionization system (Millipore Corp.). High grade reagents were used as received from the manufacturer. Sample manipulations and reagent preparations were conducted in a class 100 laminar flow hood

(Environmental Air Control, Inc.). Reagent and sample preparations were as follows:

Silica C₁₈ column. The preconcentration column consisted of 14 μ L of C₁₈ resin (Sep-Pak[®], Waters, Division of Millipore) packed between two porous polyethylene frits (Bolab Co.) inside 2.79 mm i.d. PVC tubing (Cole-Palmer Instrument Co.) and fitted onto the tip of the AS-40 autosampler arm (Perkin-Elmer) (Figure 1 inset). An identical column was also fitted on the ligand line for in-line purification of the ligand solution. Identical columns were used to remove trace metal contamination from the ammonium acetate rinse (described below). A slurry of Sep-Pak[®] C₁₈ resin and methanol was drawn into 2.79 mm i.d. PVC tubing using a syringe and each end of the column was then fitted with a porous polyethylene frit.

Ligand. The ligand solution was prepared weekly by dissolving 0.06 g of APDC (1-Pyrrolidinecarbodithioic acid, Aldrich) in 250 mL of 0.2 M ammonium acetate (CH₃COONH₄, Fisher Scientific). This solution (pH 6.7) was purified in-line using the preconcentration system shown in Figure 1.

Ammonium Acetate Rinse. One liter of a 0.01 M CH₃COONH₄ (Fisher Scientific) rinse solution was acidified with 1.2 mL of 6 N double-distilled HCl (GFS Chemicals) to obtain a pH of 4.5. The rinse solution was purified by dissolving 0.18 g APDC (Aldrich) into the solution and pumping the solution

through two laboratory prepared C₁₈ columns (14 µL each, Sep-Pak®, Waters, Division of Millipore).

Nitric acid rinse. A 1.5 M nitric acid rinse solution was prepared by adding 10 mL of 14.7 N HNO₃ (GFS Chemicals) to 90 mL of MQ water.

Cadmium standards. A 10 µM stock standard was prepared by adding 56 µL of 8.9 mM (1000 ppm) cadmium AA standard stock (Fisher Scientific) to 50 mL of MQ water acidified with 80 µL of 14.7 N HNO₃ (GFS Chemicals). A 250 nM Cd standard was prepared monthly by adding 1.25 mL of the 10 µL stock standard to 50 mL of MQ water acidified with 80 µL of 14.7 N HNO₃ (GFS Chemicals). Working standards were made daily using low cadmium concentration seawater (3°S, 114.5° W) filtered to 0.45 µm and acidified to pH 1.7 with 14.7 N HNO₃ (GFS Chemicals).

Standard reference materials. NASS-3 and NASS-4 seawater reference standards were used as received from the Marine Analytical Chemistry Standards Program of National Research Council of Canada.

2.2. Automatic on-line preconcentration system.

A schematic diagram of the pre-concentration system used for the determination of Cd is shown in Figure 1. Sample and ligand were propelled by a Rainin Rabbit-Plus® eight channel peristaltic pump using Cole-Parmer PVC pump tubing. At a pump setting of 12.5 rpm, sample (1.52 mm i.d. tubing, coded

yellow/blue) and ligand (0.64 mm i.d. tubing, coded orange/white) flow rates were 2.2 and 0.5 mL min⁻¹, respectively. The peristaltic pump was activated only during the sample load cycle in order to reduce sample consumption. All other manifold lines were 0.8 mm i.d. Teflon® tubing. A silica C₁₈ column was used to concentrate and separate non-polar Cd-APDC complexes from the salt water matrix and was fitted onto the AS-40 autosampler arm (Perkin-Elmer) (Figure 1 inset). An identical column was also fitted on the ligand line for on-line purification of the ligand solution.

A Teflon® four way selection valve (Rheodyne, Inc.) was used to switch between the sample load position and the normal autosampler rinse/elute position. Before each sample load cycle, the sample column was rinsed with 0.8 mL of 1.5 M HNO₃ (GFS Chemicals) using a micro solenoid pump (Lee Co. Model LPLA 0520350L). Following the acid rinse step, the ligand-sample complex was loaded onto the column for 55 seconds. During this cycle, column effluent was sent to waste. Following the sample load period, the injection valve was switched, and the normal process of the autosampler was initiated. The column was flushed with 1.4 mL of 0.01 M CH₃COONH₄ rinse solution from the autosampler rinse solution reservoir. The sample was then eluted from the column with 80 µL of methanol (distilled in glass, GFS Chemicals) that was drawn through the autosampler inlet from an acid cleaned

autosampler cup. The autosampler injected this methanol aliquot with the eluted metals into the graphite furnace. The sample was dried, charred, and atomized. The temperature program for the graphic furnace analysis for cadmium is shown in Table 1. The subsequent sample load cycle was performed during the atomization cycle of the previous sample allowing for a larger number of analyses per hour.

Injection valve position, peristaltic pump activation, solenoid pump activation, and data acquisition were controlled by an IBM-PC compatible computer equipped with a Metrabyte Dascon-1 A/D converter and a digital interface. The atomic absorption spectrometer was a Perkin-Elmer 603 with deuterium arc background correction. The 603 spectrometer was equipped with a Perkin-Elmer HGA 500 graphite furnace and AS-40 autosampler.

2.3. Sample Collection and Treatment.

Seawater samples were collected aboard the R/V Wecoma on the FeLINE 1992 cruise to the equatorial Pacific (15°N, 149° W). Samples were retrieved from depths ranging from 25-2000 meters using Teflon® coated 30 L Go-Flo® bottles (General Oceanics, Inc.) suspended on a Kevlar wire and tripped with a teflon messenger. Samples were filtered (acid washed 0.2 µm Sartopure polypropylene filters, Sartorius, Inc.) inside a positive pressure class 100 portable laboratory and

immediately acidified with double-distilled 14.7 N HNO₃ (GFS Chemicals) to pH 2 until analysis.

3. Results and Discussion.

3.1. Optimization.

Our initial measurements using the system developed by Porta *et al.* [20] generally substantiated their findings. However, there were several difficulties that required modification of the system. Using the original conditions, only 73% of the cadmium was removed in one elute cycle (Table 2). Without the nitric acid rinse step, incomplete removal of Cd from the column in each analysis cycle caused sample carryover and a significant reduction in precision. A minimum volume of 0.5 mL of 1.5 M HNO₃ was determined necessary to return the absorbance signal to background after a single elution (Figure 2). However, a volume of 0.8 mL of 1.5 M HNO₃ was used to ensure complete clean-up of the C₁₈ column between sample loads. With the HNO₃ rinse step, the cadmium absorbance signal returned to background before the next sample load cycle preventing carryover between sample readings. Sperling *et al.* [21] used a similar nitric acid column wash between elute cycles in the determination of lead in high purity reagents.

Operating under the optimized conditions, Cd recovery from the column was less than 100%; however, the absorbance

signal for each sample analysis was reproducible and accurate. Other methods have used a similar approach for the determination of trace metals in water samples. Sperling *et al.* [22] successfully interfaced an on-line column to the electrothermal atomic absorption spectrometer using a reversed-phase C₁₈ column. Using their system, not all of the analyte placed on the column could be quantitatively eluted in the solvent volume accommodated by the furnace. To overcome this problem, they introduced a volume slug of eluent into the furnace that contained about 50% of the absorbed analyte. Fang *et al.* [23] introduced 75% of the eluate into the graphite furnace which contained only the highest analyte concentration.

Further optimization of the preconcentration system included laboratory purification of the ammonium acetate rinse solution to reduce the blank signal. Sample consumption was also reduced by activating the peristaltic pump only during the sample load cycle. This modification reduced sample consumption to approximately one-third the original volume required by the preconcentration system.

An additional modification was the use of a nonbuffered APDC ligand solution to achieve the desired column loading pH. In the method described by Porta *et al.* [20], the ligand solution required buffering to achieve their reported ligand pH of 9.2. However, their ligand solution produced an eluent

pH of 9 rather than the recommended eluent pH of 4.5 and resulted in poor column recovery ($< 50\%$). In the modified system, a nonbuffered ligand solution was used and achieved the desired column eluent pH (4.5).

The blank was determined by analyzing seawater which had been filtered to $0.45\ \mu\text{m}$ and passed through a cation exchange column of 8-hydroxyquinoline (8-HQ) immobilized on Fractogel [24]. This effectively stripped all Cd from the seawater prior to the preconcentration and determination procedures. Determined in this manner, the average value of the blank for cadmium was to $82 \pm 14\ \text{pM}$ ($n=5$). This blank represented a combination of cadmium in the reagents, a system blank, and also signal from nonatomic absorption. Prior to optimization, the blank determined with MQ water was $104 \pm 15\ \text{pM}$ ($n=5$). The blank values measured with 8-HQ cleaned seawater and MQ water are consistent with the results of Porta et al. [20] which suggested that the blank signal was mainly due to the washing and elution steps of the preconcentration procedure. The blank could be lowered by further purifying the solutions used to process the sample, especially the nitric acid used for the on-line rinse step. Azeredo et al. [17] determined that the eluent acid used in their procedure was a major source of their blank. In addition, the blank could be lowered further by using Zeeman background correction which has been shown to more effective

in correcting background absorption than deuterium arc background correction [25]. In spite of the relatively high blanks obtained, the values were constant and reproducible and did not compromise the integrity of the analyses.

3.2. Analytical Figures of Merit.

The accuracy and precision of the preconcentration system were examined by the determination of cadmium concentrations in open ocean standards, NASS-3 and NASS-4. The results in Table 3 show that this system provided analytical data within the ranges of the certified values.

The time required to preconcentrate and analyze 2 mL of sample using the automatic system was 4 minutes with a sample throughput of approximately 15 per hour. The 3σ limit of detection for Cd was 42 pM ($n=5$) for a 2 mL sample. This value was comparable to those reported by Porta *et al.* [20] as well as by other methods [15,22,26]. The precision based on the replicate analysis of samples containing 200 pM Cd was $\pm 3.2 \%$ ($n = 6$).

3.3. Comparison with oceanographically consistent profiles.

The reliability of a new technique can be evaluated by comparing results with previously published reliable data. Figure 3 shows the profile of dissolved Cd vs. depth from the FeLINE station and includes northeast Pacific data from Bruland [27] and unpublished Moss Landing Marine Laboratories

(MLML) data as an environmental intercomparison. The cadmium depth profile showed a typical oceanic distribution for this trace metal and compared well with the data reported at similar locations. Cadmium has a nutrient-like distribution with depletion in surface water and enrichment at depth [14,27,28,29]. Cadmium has been linearly correlated with phosphate in all oceans [11,30,31,27]. Cadmium concentrations measured by the preconcentration system were compared to PO_4 concentrations reported for this station [7,32]. The Cd: PO_4 relationship was found to be linear (slope = 0.39 nmol Cd: $\mu\text{mol PO}_4$ with a r^2 value of 0.97) and resembled that of Bruland [27], whose data yields a slope of 0.33 ($r^2 = 0.98$) as well as unpublished data from MLML (27°N, 153° W) which gives a slope of 0.32 ($r^2 = 0.99$).

The similarity of these cadmium profiles with those published previously, the results of the standard seawater analysis, and the oceanographic consistency of the data demonstrate the accuracy and reliability of this method.

The system described here achieves a fully automated preconcentration system for direct injection with GFAAS for determining cadmium in seawater. The nitric acid rinse between elute cycles could be added to similar systems to circumvent problems with elute volume accommodated by the graphite furnace.

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Figure Captions

Figure 1. Preconcentration system for direct injection of seawater with GFAAS. Inset depicts dimensions of C₁₈ column mounted on autosampler arm and on ligand line: 1. 0.8 mm i.d. Teflon[®] tubing; 2. 1.3 mm i.d. PVC tubing; 3. 2.06 mm i.d. PVC tubing; 4. 2.79 mm i.d. PVC tubing; 5. Sep-Pak[®] C₁₈ resin; 6. polyethylene frits; GF. graphite furnace.

Figure 2. Absorbance of Cd in subsequent elute cycle following nitric acid rinse. Absorbances are drift corrected with blank.

Figure 3. Results of FeLINE 1992 (15°N, 149°W) cadmium analysis using preconcentration system with GFAAS. (a) Depth profile of dissolved Cd. (b) Relationship of dissolved Cd to PO₄. Bruland (1980) data (32°N, 144° W) and MLML unpublished data (27°N, 153° W) from the northeast Pacific included for intercomparison: ● FeLine 1992 data; Δ MLML unpublished data; □ Bruland 1980 data.

Table 1. Temperature program for graphite furnace analysis of cadmium.

Step	Temperature (°C)	Ramp Time (s)	Hold Time (s)	Internal Gas Flow Argon (mL/min)
Dry	160	20	40	300
Char	300	30	20	300
Atomize	2200	1	4	0

Table 2. Elution efficiency for removal of cadmium ions in spiked sea water from a C₁₈ column with three successive methanol elute cycles (n=5). Elution efficiency indicates the percent of the total cadmium that is removed with a particular number of elutions.

Number of elutions	Elution Efficiency (%)
1	73
2	93
3	97

Table 3. Results of examination of the accuracy of the method.

Standard sea water	Cd	Cd
	This method (pM)	Certified value (pM)
NASS-3	259 $\pm$ 9	258 $\pm$ 36
NASS-4	152 $\pm$ 18	142 $\pm$ 27

Figure 1.

Figure 2.

Figure 3.

Chapter 2

Flux of cadmium across the sediment-water interface in
Los Angeles and Long Beach Harbors and at sites along
the California Continental Margin.

Cadmium flux in Los Angeles/Long Beach Harbors and at sites
along the California Continental Margin.

Abstract

Fluxes of dissolved cadmium were measured *in situ* using benthic flux chambers at stations in Los Angeles/Long Beach harbor and at sites on the California continental margin. Cadmium fluxes ranged from -0.212 to $0.118 \mu\text{mol m}^{-2} \text{d}^{-1}$ indicating that Cd may either be released or taken up at the sediment-water interface. Correlations between Cd flux and carbon oxidation rate and between carbon oxidation rate and the portion of carbon consumption via sulfate reduction indicate that anaerobic microbial degradation was the major process controlling cadmium fluxes at stations in Los Angeles and Long Beach harbors. A simple box model based on sediment fluxes and water column concentrations indicates cadmium has a residence time of 50 days within the Los Angeles/Long Beach harbor system, similar to the hydraulic residence time. This value is, therefore, sufficient to account for water column cadmium concentration in inner harbor areas, suggesting that the sediments are the dominant source of cadmium in these areas of the harbor. The similarity between the cadmium:phosphate ratio for Los Angeles/Long Beach harbor and those reported for the northeast Pacific suggests that distributions of Cd in the study area were slightly elevated

over expected values but appear to be dominated by natural physical and biogeochemical processes. Unlike other metals, the direction of flux of cadmium over most of the harbor system is from the water column into the sediments.

Introduction

Natural processes such as upwelling (1), riverine input (2), and sedimentary fluxes (3, 4) can elevate trace metal concentrations in coastal waters over those observed in the open ocean. Anthropogenic inputs from adjacent land masses can act as point sources for trace metals, further elevating trace metal concentrations in coastal waters (5, 6, 7). Urbanized areas like the Los Angeles and Long Beach harbors serve as receiving waters for trace metals from point and non-point sources.

Although enrichment of trace elements in pristine coastal waters has been demonstrated, there have been few studies of cadmium geochemistry in anthropogenically impacted coastal zones (8, 4, 9, 10). Cadmium geochemistry has been investigated in a variety of other marine environments such as the open ocean (11), anoxic basins (12, 13), and continental margins (14). Several mechanisms for cadmium cycling between the sediment and water column have been proposed. These mechanisms include remobilization of cadmium during organic carbon remineralization (15), release of cadmium during reduction of Fe and Mn oxides (16, 17), and by precipitation of CdS (4, 18, 19). Cadmium geochemistry may be further complicated by the action of sediment mixing due to both physical and biological processes (20, 21). Because of the complexities involved, the processes leading to

exchange of Cd between sediments and the overlying water column are poorly understood. However, this knowledge is critical to fully understand biogeochemical cycling of this trace element in the marine environment, particularly in anthropogenically impacted coastal zones.

Metal fluxes have been calculated in most studies by modeling the pore water gradients of dissolved metals to estimate flux at the sediment-water interface (22, 23, 24). A disadvantage using this method is the difficulty in quantifying solute transport by processes other than molecular diffusion and the difficulty in measuring steep gradients that sometimes occur in the upper millimeters of surface sediments (25). The limitations in pore water modeling are even more pronounced in areas where high sedimentation and organic carbon consumption rates compress the diagenetic reaction sequence into the upper 1.5 cm of the sediments (26). Westerlund and coworkers (21) found large discrepancies between cadmium fluxes calculated from pore water profiles and those measured by benthic flux chambers. These discrepancies were attributed to limitations in pore water sampling due to a shallow oxygen penetration depth (1 mm).

Due to problems associated with a compressed oxic boundary and bioirrigation, dissolved metal fluxes across the sediment-water interface can best be studied using benthic

flux chambers. Flux chambers have been deployed extensively to study nutrient and carbon fluxes in shallow and deep waters (27, 28, 29). However, there have been relatively few measurements of metal fluxes using benthic chambers (3, 21, 30). Benthic chambers, which incubate sediment *in situ*, integrate the net transport of solutes between pore waters and the overlying water. Fluxes can be calculated directly from concentration changes within the chamber, which is important in settings where near-surface chemical gradients are very steep and where advective solute transport is significant (29).

The purpose of this study was to assess the role of the benthic flux of dissolved Cd in controlling the distribution of this dissolved metal in Los Angeles/Long Beach harbor systems using benthic chambers. Several sites on the adjacent pristine California continental margin were also studied to provide a contrast to measurements within the anthropogenically altered harbor system. Possible geochemical mechanisms which control cadmium fluxes were also investigated.

Methods

Los Angeles/Long Beach Harbor System.

The Los Angeles/Long Beach Harbor system was constructed in San Pedro Bay (Figure 1). This bay was naturally formed in the lee of the Palos Verdes Peninsula and was enlarged through dredging the alluvial fans of the Los Angeles and San Gabriel Rivers, both of which have since been diverted and controlled. Breakwaters lie at bottom depths of about 14 to 20 meters and protect an area of $58 \times 10^6 \text{ m}^2$ of water. This area includes the Ports of Los Angeles and Long Beach, the former Long Beach Naval Facility, and the City of Long Beach Harbor. Fresh water inputs are mostly seasonal and include the Los Angeles River, the Dominguez Slough, Harbor Lake, and the Terminal Island Treatment Plant. It has been estimated that approximately 90 tidal cycles (47 days) are required to replace all the water in the harbor (31). The composition of harbor waters generally reflects the waters of the Southern California Bight after modification by reduced circulation and the various uses of the harbor. Studies of the outer harbor indicate flushing times as short as two weeks (31).

Los Angeles/Long Beach Harbor sample collection.

During June and November 1994, benthic chamber deployments were made at stations in Los Angeles/Long Beach harbor from the R/V Seawatch (Figure 1). Location, water

depths, experimental manipulations, and lander types are presented in Table 1. Stations were numbered sequentially, and reoccupations of the same locations, as in the case of the Navy Mole (stations 10, 12, and 13), have different station numbers.

Trace element clean techniques were employed during field collection and sample preparation. All sample bottles were made of polypropylene, polyethylene, or Teflon[®] and were stored and handled according to trace metal clean techniques (32).

Benthic flux chambers (25) were deployed at each site to directly measure the flux of trace metals and nutrients from the sediment. The benthic chambers and methods of flux calculation used in this study have been previously described (25, 28, 33). Two different chambers styles were used during this study, a large lander with three incubation chambers designed for deep water deployment and a single chamber "mini" lander with identical dimensions and stirring characteristics as the replicates on the larger lander. Each lander chamber incubated approximately 7 liters of water overlying the sediments. Sediments were incubated *in situ* generally for 12-18 hours under stirred conditions. Overlying water samples were collected at preprogrammed intervals from each of three chambers on large benthic landers and from the single chamber on mini landers. At time

of deployment, each lander was visually inspected by divers for trapped air bubbles and chamber positioning. Chamber lids remained open for one hour after deployment to allow sediment for the equilibration of the inside and outside chamber oxygen electrodes. Chamber volume varied among deployments and individual chambers depending on depth of chamber penetration. A known amount of cesium chloride was injected into each chamber after lid closure to allow calculation of chamber volume by dilution of the cesium.

Time series samples were analyzed for trace metals, pH, total CO₂, ²²²Rn, total alkalinity, and nutrients. ²²²Rn was used as a tracer to assess the impact of bioirrigation on the distribution and flux of pore water constituents (34, 35). Oxygen concentrations both inside and outside of the chambers were continuously monitored with a pulsed oxygen electrode (36). After chamber recovery, trace metal samples were kept cool until filtered.

Water column samples for trace metals, total CO₂, O₂, and nutrients were collected using 8 L Teflon[®] coated Go-Flo[®] bottles (General Oceanics, Inc.). Trace metal samples were collected into 125 mL polyethylene bottles which were flushed with ambient seawater prior to collection. Water temperature at each depth was measured using a standard thermometer.

Benthic chamber and water column samples were filtered (acid washed 0.5 µm Millex LCR filters, Millipore Corp.)

directly into 60 mL teflon bottles. Filtration and sample aliquoting were conducted inside a class 100 laminar flow hood (Environmental Air Control, Inc). All filtered water samples were frozen until analysis.

Experimental stations in Los Angeles/Long Beach harbors.

Benthic chamber experiments involving manipulation of the chemical and biological environment within the waters underlying the flux chamber were performed at several stations (Table 1). Manipulative experiments were performed to identify the biological and chemical pathways that may affect cadmium flux into the water column. Experimental treatments included adding oxygen to a flux chamber, adding formalin to eliminate both bioirrigation and microbial remineralization in the chamber, and dredging the top 10 cm of sediment. Perturbations were performed by divers after the lander was deployed on the bottom. In the dredging experiment (Stations 7 and 13), divers scraped away a 10 cm deep layer of sediment and hand placed the mini lander in the center of the cleared zone. At Station 10, one chamber of a three chamber benthic lander was injected with 50 mL of 37% formalin (Malincrodt, unbuffered) after the chamber lid was manually closed by divers. At Station 12, 280 mL of oxygen (STP) was injected into the chamber of one of two single chamber landers deployed.

Continental Margin sample collection.

Benthic chamber deployments at continental margin sites occurred during May 1992 and were performed from the R/V Point Sur (Figure 2). A large lander was deployed as a free vehicle at each site, and the sediment underneath each of the device's three chambers was incubated under stirred conditions for 12-72 hours (29). Each 45 mL sample was split for analysis of trace metals (3), pH, total CO₂, ²²²Rn, total alkalinity, and nutrients (29). The trace metal split was filtered (acid washed 0.5 µm Millex LCR filters, Millipore Corp,) and an aliquot was frozen for later cadmium analysis.

Bottom water at continental margin sites was not collected for cadmium analysis. Concentrations of cadmium were ascertained from bottom water phosphate concentrations (29). An average phosphate to cadmium ratio of 325 Cd/P (pM/µM) reported for the Pacific was used to calculate cadmium concentrations in bottom water (37, 38, 39).

Cadmium analysis.

Prior to analysis, chamber water and bottom water samples were thawed and acidified to pH 1.7 with double distilled (DD) 14.7 N HNO₃ (GFS Chemicals). Most samples contained high cadmium concentrations and were diluted with acidified Milli-Q water (Millipore) to suitable levels prior to analysis. Standards were made in a seawater/MQ water

matrix matched to that of the diluted sample using low cadmium concentration filtered (acid washed 0.5 μ m Millex LCR filters, Millipore Corp.) seawater (3°S, 114.5° W) similarly acidified. Dissolved cadmium concentrations in benthic chamber and water column samples were measured using an on-line preconcentration system with graphite furnace atomic absorption spectrometry (40). The system was adapted from the method developed by Porta *et al.* (41). The soluble ligand, 1-Pyrrolidinecarbodithioic acid (APDC), was used to form a nonpolar metal complex which was absorbed onto a C₁₈ column. The metal complex was eluted from the column with methanol and then injected directly into the graphite furnace.

Cadmium flux calculations.

Fluxes were determined by least squares regression of cadmium concentration as a function of incubation time. Each concentration was corrected for dilution by bottom waters that entered the chamber as each sample was withdrawn. Uncertainties in the linear fit, analytical uncertainties, and uncertainties in chamber height were combined to estimate error limits for each flux value (29). When data was obtained from more than one chamber, all fluxes were averaged, with equal weighting, to describe the mean flux for a site. Benthic flux chambers which showed evidence of

leakage or anoxia were not included in analyses. In some cases, Cd concentrations dropped to near zero values during the incubation. In these cases, the initial slope of the Cd concentration versus time relationship for the non-zero portion of the incubation was used to calculate flux. This treatment was used for stations 8, 9, and 15.

Carbon oxidation rates.

At stations in Los Angeles/Long Beach harbor, total CO₂ (TCO₂) fluxes were measured directly using benthic chamber samples (method described in 29). The carbon oxidation rate (C_{ox}) was determined from a budget of total CO₂, O₂, NO₃⁻, and alkalinity fluxes. At continental margin stations, carbon oxidation rates were corrected for calcium carbonate dissolution as described in Berelson *et al.* (28, 42).

Results and Discussion

Dissolved cadmium.

Cadmium concentrations ranged from 0.187 to 0.642 nM in surface waters of Los Angeles/Long Beach harbors (Table 2). Bottom water Cd concentrations were not significantly different from surface concentrations and ranged from 0.201 to 0.419 nM (unpaired t-test; $P_{0.05}=0.22$). Cadmium concentrations in the harbor system were elevated compared to the range of Cd concentrations reported for northeast Pacific surface waters (0.04-0.16 nM) (38, 37). However, values were similar to cadmium concentrations reported for pristine coastal waters along Washington, Oregon, and California (0.1 - 0.8 nM: 1). Cadmium concentrations observed in Los Angeles/Long Beach harbors were less than those reported in other anthropogenically impacted embayments such as South San Francisco Bay (0.5-1.4 nM; 9) and San Diego Bay (0.5-1.7 nM; 7).

The impact of processes that may add Cd to coastal systems can be partially resolved from comparisons of cadmium and phosphate concentrations. Deviation of dissolved Cd from the linear relationship between Cd and PO_4 may be indicative of other Cd sources (37, 43, 8). Observed Cd concentrations were consistent with the predicted values at some outer harbor stations (Figure 3: Stations 8,9,10,12,13,15). Other stations, particularly those in the inner harbor, exhibited

elevated Cd concentrations when compared to the Cd value estimated from the observed PO_4 concentrations and the open ocean Cd/ PO_4 relationship (Stations 2,3,4,5,6,7). The elevated Cd levels at these harbor stations may reflect internal Cd sources, possibly Cd input from the sediments. Flegal and Sanudo-Wilhelmy (7) attributed elevated water column concentrations of cadmium to the diagenetic remobilization of cadmium from contaminated sediments in both San Francisco Bay and San Diego Bay. Other studies of estuarine sediment have also indicated sediments as a source of Cd to the overlying water column (44, 10). Although this study found elevated cadmium concentrations with respect to Cd: PO_4 ratios at some stations, there did not appear to be a strong anthropogenic influence. Cadmium concentrations were higher than predicted Cd concentrations, based on observed phosphate ratios, by 0.019 to 0.271 nM. Similarities between the Cd: PO_4 (Figure 3) relationship from outer harbor stations in Los Angeles/Long Beach harbors and values reported for northeast Pacific waters suggest that Cd in outer harbor waters were typical of open ocean waters that have experienced moderate inputs of Cd due to upwelling.

Cadmium flux.

Trends in cadmium concentration during chamber incubations were consistent among chambers at replicated

stations (Figure 3: Stations 3,6,8,9,15). Cadmium fluxes calculated at these stations were also similar among chambers (Table 3: Stations 3,6,8,9,15). The interchamber agreement at these stations indicated a high degree of precision associated with this method. The Fish Harbor station (Station 1) was excluded from all comparisons due to historically high organic carbon loading rates from an adjacent fish canning facilities. The change in these loading rates dramatically altered the geochemistry at that station and was visibly noticeable in sediment cores.

Cadmium fluxes measured at stations in Los Angeles and Long Beach harbors indicated that Cd may either be released (positive flux) or taken up (negative flux) at the sediment-water interface (Table 3, Figure 4). Inner areas of the Los Angeles/Long Beach harbor system (Stations 4, 5, and 6) exhibited a flux of cadmium out of the sediment ranging from 0.004 to 0.055 $\mu\text{mol}/\text{m}^2\text{d}$. Stations in the outer areas of the harbor exhibited fluxes of Cd into (Stations 7, 8, 9, and 15) and out of (Stations 2, 3, 10, and 12) the sediment. Outer harbor fluxes ranged from -0.027 to 0.118 $\mu\text{mol}/\text{m}^2\text{d}$. At the two deep continental margin sites (CC2-2 and CC2-3), there was no net flux of Cd into or out of the sediment (0.000 ± 0.005 $\mu\text{mol}/\text{m}^2\text{d}$) while the shallow margin site (CC2-1) had a positive flux of Cd from the sediment (0.065 ± 0.006 $\mu\text{mol}/\text{m}^2\text{d}$). Cadmium fluxes measured in this study were similar

to those reported for coastal marine sediments using benthic flux chambers (0.011 - $0.013 \mu\text{mol}/\text{m}^2\text{d}$, 21). However, Cd fluxes measured in South San Francisco Bay were somewhat larger, both positive and negative, than those found in this study (0.571 , -0.137 , $-0.331 \mu\text{mol}/\text{m}^2\text{d}$, 45).

Residence time.

If cadmium concentrations are at a steady state in the Los Angeles/Long Beach harbor system, then the input rate must equal the removal rate. In this study, Cd residence time in the harbor waters was calculated using a box model in which fluxes from the sediments represented a source of Cd and fluxes into the sediments plus tidal mixing represented sinks for dissolved Cd. In the inner harbor, sediments were a source for Cd. Cd concentrations in the inner harbor exceeded the values in the outer harbor, which appears to reflect this input. Tidal exchange was a sink for Cd.

The time required for input from the sediments to create the dissolved Cd concentration anomaly observed in the inner harbor was calculated using the average depth for the harbor (10 m), the difference in Cd concentration of the inner ($0.38 \pm 0.05 \text{ nM}$: Stns. 4, 5, 6) and outer harbor stations ($0.24 \pm 0.03 \text{ nM}$: Stns. 3,7,8,15) measured in this study (Table 2), and the mean flux of Cd from sediments at inner harbor stations ($0.03 \pm 0.03 \mu\text{mol}/\text{m}^2 \text{ d}$: Stns. 4,5,6; Table 3).

These calculations yield a time of 50 days for the flux of Cd from sediment within the Los Angeles/Long Beach harbor system to produce the elevated values in the inner harbor. The hydraulic residence time of harbor water is about 47 days (31). The elevated Cd concentration in the inner harbor can be supported entirely by the minimal flux from sediments. Any additional large Cd sources would have to be balanced by sinks of equivalent size.

Geochemical mechanisms for control of Cd flux.

Studies in pristine coastal areas such as Monterey Bay and the adjacent continental slope indicate that Mn is mobilized from sediments in concert with the microbial oxidation of organic carbon. In these systems, manganese fluxes are highly correlated with oxygen flux (3). Cadmium appears to follow a similar trend in the open ocean shelf area of central California. A positive flux of Cd out of the sediment was found at 97 m and declined to values that were not significantly different from zero within the oxygen minimum. Shine et al. (46) found a correlation between Cd flux and benthic oxygen demand in coastal marine sediments; however, their results included the effect of seasonal fluctuations in bottom water temperature. At stations in Los Angeles and Long Beach harbors, oxygen flux was not a good proxy for cadmium flux ($r^2 = 0.20$), suggesting that aerobic

respiration was not driving observed Cd fluxes. Variation in bottom water temperature at sites in Los Angeles and Long Beach harbors was minimal (15 to 18°C: Table 2) and was not correlated with changes in Cd fluxes ($r^2 = 8 \times 10^{-6}$).

In the Los Angeles/Long Beach harbor system, carbon oxidation is not dominated by the use of oxygen as a terminal electron acceptor. Rather, most organic carbon is oxidized by sulfate reduction (Figure 5). Cadmium flux had a strong negative correlation with carbon oxidation rates ($r^2 = 0.80$, Figure 6a). A strong negative correlation of Cd flux with carbon oxidation via sulfate reduction ($r^2 = 0.83$; Figure 6b) was also observed. This indicates that the oxic layer may be shallow and that the underlying anoxic sediment controlled the net flux of cadmium. The correlation between Cd and carbon consumption via sulfate reduction suggests that anaerobic microbial degradation was the major process controlling cadmium fluxes at stations in Los Angeles/Long Beach harbor.

The strong negative correlation between Cd flux and carbon consumption via anaerobic respiration observed in Los Angeles and Long Beach harbor suggests that CdS may control cadmium cycling in anoxic and suboxic sediments. It appears, therefore, that the direction of cadmium flux is critically dependent on the redox state of the sediments, the depth of

the redox boundary, and the rate at which sulfides are being produced.

Precipitation of CdS has been used to explain the depletion of Cd in anoxic basins (13) and its removal from porewater in anoxic sediments (47). Rosenthal *et al.* (18) proposed the precipitation of cadmium sulfide, CdS, as the mechanism of Cd removal in reducing sediments based on solubility calculations indicating precipitation of CdS in the presence of trace levels of hydrogen sulfide. Suboxic sediments contain small amounts of free sulfide that are below typical chemical detection limits, perhaps diffusing upward from underlying anoxic sediments. Rosenthal *et al.* (18) suggested that this low concentration of free sulfide is sufficient to support precipitation of Cd-sulfide. Significant Cd uptake also occurs in suboxic sediments where reducing conditions occur in close proximity to the sediment/water interface but H₂S is not detected (14, 15, 48). Likewise, precipitation of CdS is predicted in seawater containing low to moderate amounts of hydrogen sulfide (49). Kuwabara *et al.* (45) found that sulfide complexation with metals could also be important in the well oxygenated water column of San Francisco Bay and could exert transient controls on metal speciation even at submicromolar concentrations. These studies would suggest even low concentrations of free sulfides could produce the observed

correlation of Cd flux to carbon oxidation via sulfate reduction in Los Angeles/Long Beach harbor.

Patterns of Cd removal underlying reducing and anoxic conditions differ markedly from the geochemistry of Cd in oxic sediments where Cd porewater studies (11, 50) indicated the release of Cd during early diagenetic oxidation of organic matter. Sulfate reduction did not occur or was minimal at some stations in Los Angeles/Long Beach harbors. At those stations, carbon oxidation occurred via other electron acceptors (Figure 5: y intercept at approximately 25 $\mu\text{mol}/\text{m}^2 \text{ d}$). A positive flux of cadmium from the sediment could be predicted at sites with low values of organic carbon oxidation via sulfate reduction by assuming that organic carbon degradation was completely aerobic. Low organic carbon degradation via sulfate reduction was found at inner harbor stations, which may account for the net positive flux in this region.

McCorkle and Klinkhammer (14) found evidence that Cd was rapidly removed from solution in suboxic sediments. The bulk of the removal appeared to take place within the 2-3 cm thick zone of Fe and Mn precipitation just below the sediment-water interface. Their evidence suggested that Cd was being taken up onto the surfaces of newly formed Fe and Mn oxides. Laboratory studies have shown that Cd was readily adsorbed onto a variety of synthetic and natural metal oxide surfaces

(51, 52, 53, 54, 55). For stations in Los Angeles/Long Beach harbor, cadmium flux was not correlated with iron flux ($r^2=0.04$) but was slightly correlated with manganese flux ($r^2=0.50$). These results indicate that Fe and Mn oxides do not provide major adsorbing surfaces for Cd. Similarly, Rosenthal et al. (18) found a slight association of Cd with Mn oxides but no association with Fe oxyhydroxides in pelagic sediments.

Experimental chambers.

Cycling of cadmium and other trace elements may be influenced by either biological (i.e. microbially mediated redox reactions) or chemical (e.g. free solution redox reactions) processes (56, 57). Microbially mediated processes dominate in some environments, while chemical reactions dominate in others (58, 59, 56, 60). Few studies have attempted to distinguish between biological and chemical pathways (60). In this study, several experiments were performed to manipulate the chemical and biological environment within flux chambers at the Navy Mole station within Los Angeles/Long Beach harbor.

In harbor areas, accumulated sediments are often dredged to maintain navigable waterways. Studies have investigated the potentially toxic effect of contaminated sediment which has been transported to other aquatic environments (61, 62).

Few studies, however, have evaluated the effect of dredging in terms of exposure of deeper layers of sediment in the existing environment. The removal of surficial sediment can disrupt the geochemical environment of the sediment and can result in the remobilization of trace metals (63). Cadmium flux increased by $0.046 \mu\text{mol}/\text{m}^2\text{d}$ at the outer Navy Mole station and $0.085 \mu\text{mol}/\text{m}^2\text{d}$ at the Navy Mole station in dredged chambers over the flux observed in unmanipulated chambers (Table 3). The net increase in cadmium flux in the dredged chambers may indicate the oxidation of sulfides by oxygenated bottom water and the subsequent release of dissolved cadmium.

In order to examine the mechanisms that might produce the increased Cd flux observed in the dredged sediments, oxygen was injected into a chamber of undisturbed sediment. The addition of oxygen (280 mL @ STP) to a benthic chamber resulted in a 6-fold increase in cadmium flux out of the sediment (Table 3, Figure 7). The increased cadmium flux in the well oxygenated chamber may reflect the oxidation of sulfides and subsequent release of dissolved cadmium. The addition of oxygen might also increase aerobic respiration. If cadmium was released in connection with aerobic microbial carbon degradation, an increase in cadmium flux from the sediment would be predicted. However, the total amount of organic carbon remineralized was not significantly different between the experimental and control chambers (Table 3).

This suggests that the flux increase in dredged sediments and in sediments exposed to higher oxygen is driven by the oxidation of solid phase sulfides and release of dissolved Cd.

The activities of burrowing benthic organisms may transport metals between oxygenated bottom water and the suboxic sediment layer. This would be analogous to the recycling of redox sensitive metals between the oxidizing surface layer and reducing subsurface layer of the sediment (21). As demonstrated for Mn, this recycling is greatly accelerated by bioturbation (64). Such cycling may have a large impact on Cd flux due to the tendency of Cd to precipitate in sulfidic environments. This possibility was tested by poisoning an experimental chamber. The addition of 50 mL of 37% formalin to the chamber was intended to kill any organisms in the chamber. This would allow diffusive flux to be measured without the influence of bioirrigation. Total carbon oxidation rates decreased in the experimental chamber with oxygen flux decreasing by a factor of four (Table 3). Differences in ^{222}Rn flux between the experimental and control chambers suggested that bioirrigation activities (^{222}Rn flux: *control chamber* = 270 ± 45 atoms/ m^2d ; *formalin injected chamber* = 133 ± 23 atoms/ m^2d , Berelson, pers. comm.) were inhibited by the injection of formalin. Cadmium flux increased to $0.159 \mu\text{mol}/\text{m}^2\text{d}$, at least an order of magnitude

over the flux observed in the control chamber (Table 3). The increase in Cd flux suggests that bioirrigation activities move dissolved cadmium in bottom water to suboxic sediments where it is precipitated as CdS. The results of this experiment would suggest that bioirrigation can have a dramatic effect on the net flux of Cd into the sediment.

^{222}Rn flux from sediment can be used as an indicator of diffusive flux as well as advective process if rates depart from expected values. Cadmium fluxes at harbor stations did not correlate with ^{222}Rn ($r^2 = 0.04$), assuming ^{222}Rn as an estimate of bioirrigation (^{222}Rn data, Berelson, unpublished data). Thus, while the formalin experiment may indicate a role for bioirrigation in Cd cycling, the Rn data would suggest that this role varies in magnitude and direction as a function of the geochemical environment and warrants further investigation.

Conclusions

Measurements of trace element concentrations, such as Cd, help to evaluate the processes of heavy metal contamination in restricted coastal systems. Inner harbor waters of Los Angeles/Long Beach harbors were slightly enriched with cadmium compared with outer harbor locations, but all values were within ranges reported for coastal waters. Other than solid phase sedimentary loading, cadmium cycling in the harbor system appeared to be dominated by natural physical and biogeochemical processes. The apparent predominance of natural processes suggested that anthropogenic perturbations of this harbor system for cadmium have been minimal, in spite of the metropolitan nature of the surrounding Los Angeles area. The results obtained here suggest that Cd concentration in inner areas of Los Angeles/Long Beach harbors are regulated by a balance between flux from sediments and removal due to tidal mixing.

At stations in Los Angeles/Long beach harbor, cadmium flux was negatively correlated with carbon oxidation via sulfate reduction, suggesting that the oxic layer was compressed and the net flux of Cd was controlled by the precipitation of CdS. The direction of flux is highly dependent on the production of sulfide via sulfate reduction and the depth in the sediment where sulfate reduction occurs. The remobilization of cadmium during organic carbon

remineralization as well as bioirrigating activities and scavenging of cadmium by Mn oxides may exert some influence on the net cadmium flux.

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Figure Captions

Figure 1. Study area for June and November 1994 stations in Los Angeles/Long Beach harbors.

Figure 2. Study area for stations off central California. Station ID's correspond with Table 1 designations.

Figure 3. Relationship of dissolved bottom water Cd to PO₄. Data from the northeast Pacific included for intercomparison: hollow circle, Los Angeles/Long Beach harbors bottom waters; filled circle, FeLINE 1992 (15°N, 149°W); triangle, MLML unpublished data, (27°N, 153° W); square, Bruland (38) (32°N, 144° W). Regression fit to Bruland (38) ($R^2=0.98777$).

Figure 4. Cadmium as a function of incubation time for all stations. Note that different symbols represent different chambers from the same lander deployment or different treatments among mini landers. Concentration at time = 0 indicates bottom water value.

Figure 5. Carbon oxidation rates (C_{ox}) versus portion of carbon oxidation due to sulfate reduction ($y = 1.13x + 1.39$, $R^2 = 0.98$) at stations in Los Angeles/Long Beach harbor and on the California continental margin. Station 1 excluded from analysis.

Figure 6. Cd fluxes and carbon oxidation rates at stations in Los Angeles/Long Beach harbor and on the California continental margin. Station 1 excluded from analysis. a. Cadmium flux versus carbon oxidation rate (C_{ox}) ($y = -0.001x + 0.056$, $R^2 = 0.80$). b. Cadmium flux versus carbon oxidation via sulfate reduction ($y = -0.001x + 0.043$, $R^2 = 0.83$).

Figure 7. Cadmium flux for experimental and control chambers at Navy Mole station in Los Angeles/Long Beach harbor. Experimental manipulations included 10 cm dredge, formalin addition, and oxygen addition.

Table 1. Station locations, depths, experimental manipulations, and lander types. Continental margin stations are denoted as CC.

Station Number	Station Location	Depth (m)	Date Collected	Type of Lander(s) Deployed
1	Fish Harbor	7	6/23/94	single chamber
2	West Basin	16	6/23/94	single chamber
3	Outer Harbor	8	6/24/94	3 chambers
4	Todd's Shipyard	14	6/25/94	single chamber
5	East Basin	9	6/25/94	single chamber
6	Inner Harbor	14	6/26/94	3 chambers
7	* Outer Navy Mole	17	6/27/94	2 single chambers
8	Queensway Bay	14	6/28/94	3 chambers
9	Dominguez Canal	11	11/8/94	3 chambers
10	** Navy Mole	15	11/9/94	2 single landers
12	*** Navy Mole	15	11/11/94	2 single chambers
13	* Navy Mole	15	11/13/94	single chamber
15	Queensway Bay	14	11/14/94	3 chambers
CC2-1	35.6° N, 121.3° W	97	5/10/92	3 chambers
CC2-2	35.2° N, 121.3° W	670	5/12/92	3 chambers
CC2-3	35.5° N, 121.6° W	1010	5/13/92	3 chambers

* Dredged.

** Formalin injection.

*** Oxygen injection.

Table 2. Summary of cadmium and phosphate concentrations in water column samples at stations in Los Angeles/Long Beach harbors.

Station Name	Sample depth (m)	Cd (nM)	s.d.	PO4 (uM)	s.d.	Temperature (°C)
1 Fish Harbor	6	0.363	± 0.005	0.42	± 0.17	na
2 West Basin	9	0.339	± 0.011	0.73	± 0.17	na
3 Outer Harbor	1	0.221	± 0.016			
	5.5	0.209	± 0.019	0.37	± 0.17	16
4 Todd's Shipyard	1	0.521	± 0.029			
	9	0.409	± 0.003	0.72	± 0.17	17
5 East Basin	1	0.642	± 0.034			
	5	0.419	± 0.077	1.05	± 0.17	17
6 Inner Harbor	1	0.316	± 0.010			
	9	0.325	± 0.014	0.82	± 0.17	16
7 Outer Navy Mole	1	0.187	± 0.017			
	13	0.201	± 0.029	0.48	± 0.17	15
8 Queensway Bay	1	0.253	± 0.017			
	11	0.212	± 0.029	1.05	± 0.17	18
9 Consolidated Slip	1	0.485	± 0.005			
	6.5	0.347	± 0.031	1.14	± 0.17	16
10, 12, 13 Navy Mole	1	0.219	± 0.019			
	13.5	0.223	± 0.024	0.84	± 0.30	16
15 Queensway Bay	1	0.529	± 0.022			
	12	0.275	± 0.045	1.38	± 0.30	16

Table 3. Chamber flux measurements. Letters (B, R, Y) indicate individual lander chambers. Average lander flux for each station listed. Negative fluxes indicate uptake by the sediments. The carbon oxidation rate (C_{ox}) was determined from a budget of total CO_2 , O_2 , NO_3^- , and alkalinity fluxes. Oxygen flux and carbon oxidation data for continental margin sites are from Berelson et al. (29).

Station Name	Lander type	Cd flux ($\mu\text{mol/s/m}^2 \text{ d}$)	O_2 Flux ($\text{mmol/m}^2 \text{ d}$)	C_{ox} ($\text{mmol/m}^2 \text{ d}$)
1 Fish Harbor	mini Y	-0.078 $\pm$ 0.023	-22.9 $\pm$ 8.2	21.8 $\pm$ 2.9
2 West Basin	mini B	0.118 $\pm$ 0.011	-26.4 $\pm$ 7.8	22.1 $\pm$ 4.7
3 Outer Harbor	B	0.075 $\pm$ 0.008		
	R	0.054 $\pm$ 0.011		
	Y	0.068 $\pm$ 0.024		
	mean	0.066 $\pm$ 0.011	-13.6 $\pm$ 2.5	18.5 $\pm$ 3.2
4 Todd's Shipyard	mini B	0.036 $\pm$ 0.011	-11.2 $\pm$ 3.6	24.3 $\pm$ 4.3
5 East Basin	mini Y	0.004 $\pm$ 0.012	-18.9 $\pm$ 5.9	55.5 $\pm$ 9.4
6 Inner Harbor	B	0.039 $\pm$ 0.010		
	R	0.044 $\pm$ 0.025		
	Y	0.081 $\pm$ 0.011		
	mean	0.055 $\pm$ 0.023	-18.9 $\pm$ 3.5	22.7 $\pm$ 2.0
7 Outer Navy Mole	mini B (dredged)	0.019 $\pm$ 0.029	-14.6 $\pm$ 4.5	9.7 $\pm$ 2.1
	mini Y (control)	-0.027 $\pm$ 0.015	-30.8 $\pm$ 10.4	39.2 $\pm$ 7.0
8 Queensway Bay	B	-0.076 $\pm$ 0.020		
	R	-0.042 $\pm$ 0.013		
	Y	-0.172 $\pm$ 0.122		
	mean	-0.097 $\pm$ 0.067	-14.0 $\pm$ 2.6	117 $\pm$ 28.1

Table 3. Continued.

Station Name	Lander type	Cd flux ($\mu\text{mol/s/m}^2$ d)	O ₂ Flux (mmol/m^2 d)	C _{ox} (mmol/m^2 d)
9 Consolidated SlipR		-0.198	na	
	Y	-0.226	na	
	mean	-0.212 $\pm$ 0.014	-36.3 $\pm$ 5.0	227 $\pm$ 79.2
10 Navy Mole	mini B (formalin)	0.159 $\pm$ 0.019	-4.8 $\pm$ 1.1	15.8 $\pm$ 2.4
	mini Y (control)	0.001 $\pm$ 0.023	-22.3 $\pm$ 3.5	*21.9 $\pm$ 3.9
12 Navy Mole	mini B (oxygen)	0.165 $\pm$ 0.070		17.0 $\pm$ 2.3
	mini Y (control)	0.026 $\pm$ 0.027	-19.5 $\pm$ 4.5	
13 Navy Mole	mini Y (dredged)	0.098 $\pm$ 0.023	-16.7 $\pm$ 6.6	12.7 $\pm$ 3.5
15 Queensway Bay	B	-0.143 $\pm$ 0.034		
	Y	-0.043 $\pm$ 0.013		
	mean	-0.093 $\pm$ 0.071	-34.9 $\pm$ 3.5	145 $\pm$ 44.4
CC2-1	R	0.060 $\pm$ 0.025		
	B	0.069 $\pm$ 0.005		
	mean	0.065 $\pm$ 0.006	-11.0 $\pm$ 1.4	7.3 $\pm$ 1.0
CC2-2	R	0.004 $\pm$ 0.006		
	B	-0.004 $\pm$ 0.003		
	mean	0.000 $\pm$ 0.006	-0.57 $\pm$ 0.08	1.1 $\pm$ 0.3
CC2-3	R	0.005 $\pm$ 0.009		
	B	-0.005 $\pm$ 0.006		
	mean	0.000 $\pm$ 0.007	-0.94 $\pm$ 0.13	0.9 $\pm$ 0.8

*Average rate for Navy Mole control (Stations 10 and 12).

Figure 2.

Figure 3.

Figure 4.

Figure 4. Continued.

Figure 4. Continued.

Figure 5.

Figure 6.

Figure 7.

IMAGE EVALUATION TEST TARGET (QA-3)

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