DEPARTMENT OF OCEANOGRAPHY UNIVERSITY OF WASHINGTON

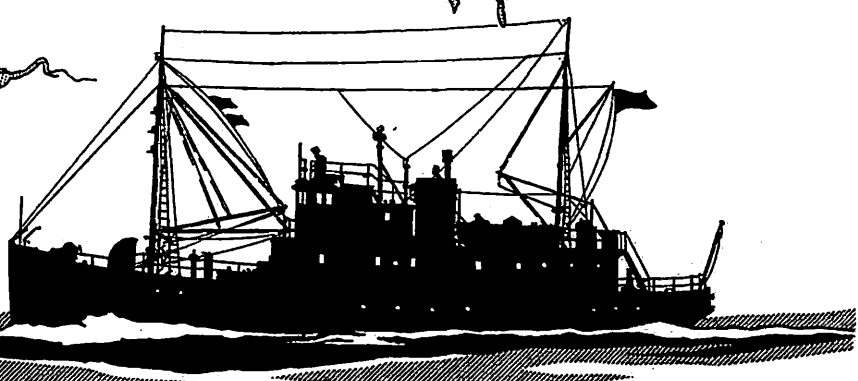
TECHNICAL REPORTS

Nos. 276, 277, 278 and 279

A COMPILATION OF ARTICLES REPORTING RESEARCH

Office of Naval Research
Contract Nonr-477(37)
Project Nr. 083-012

Reference M72-41
JUNE 1972



SEATTLE 5, WASHINGTON

UNIVERSITY OF WASHINGTON
DEPARTMENT OF OCEANOGRAPHY
Seattle, Washington 98105

Technical Reports

Nos. 276, 277, 278 and 279

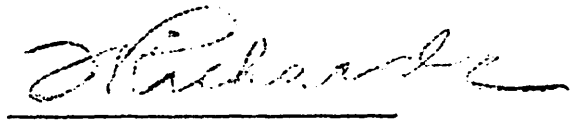
A COMPILATION OF ARTICLES REPORTING RESEARCH

SPONSORED BY

THE OFFICE OF NAVAL RESEARCH

Office of Naval Research
Contract Nonr-477(37)

Reference M72-41



FRANCIS A. RICHARDS
Principal Investigator

ARTICLES REPORTING RESEARCH SPONSORED BY THE OFFICE OF NAVAL RESEARCH

Technical Report No. 276

LATE QUATERNARY TECTONICS, NORTHERN END OF JUAN DE FUCA RIDGE (NORTHEAST PACIFIC), by Dean A. McManus, Mark L. Holmes, Bobb Carson and Sandra M. Barr. Marine Geology, 12: 141-164. 1972

Technical Report No. 277

A GYROCOMPASS FOR MEASUREMENT OF CORE ORIENTATION AND CORE BEHAVIOR, by Douglas R. Morrison and Bobb Carson. Deep-Sea Research, 18: 935-939. 1971.

Technical Report No. 278

VOLTAMMETRIC MEASUREMENT OF ZINC IN THE NORTHEASTERN TROPICAL PACIFIC OCEAN, by Alberto Zirino and Michael L. Healy. Limnology and Oceanography, 16(5): 773-778. 1971.

Technical Report No. 279

PH-CONTROLLED DIFFERENTIAL VOLTAMMETRY OF CERTAIN TRACE TRANSITION ELEMENTS IN NATURAL WATERS, by Alberto Zirino and Michael L. Healy. Environmental Science & Technology, 6(3): 243-249. 1972.

VOLTAMMETRIC MEASUREMENT OF ZINC IN THE NORTHEASTERN TROPICAL PACIFIC OCEAN

By Alberto Zirino and Michael L. Healy

Reprinted from Limnology and Oceanography
Vol. 16, No. 5, September 1971
pp. 773–778
Made in the United States of America

VOLTAMMETRIC MEASUREMENT OF ZINC IN THE NORTHEASTERN TROPICAL PACIFIC OCEAN[1]

Alberto Zirino[2] *and Michael L. Healy*
Department of Oceanography, University of Washington, Seattle 98195

ABSTRACT

Relative zinc concentrations in the upper 1,000 m of the northeastern tropical Pacific Ocean were measured by *p*H-controlled differential anodic stripping voltammetry (DASV) aboard ship. The waters above 125 m are significantly lower in zinc content than those between 125 and 1,000 m. A substantial fraction of the measured zinc appears to be adsorbed on particulate matter >0.45 μ. The adsorption can be reversed by lowering the *p*H to 5.6 with CO_2 gas.

INTRODUCTION

The importance of zinc in the biosphere has been well documented (Rice 1963; Polikarpov 1966). It is required as a constituent of several enzymes (Dixon and Webb 1964; Bonner and Varner 1965). Many, if not all, marine plants and animals concentrate it from seawater. Chipman et al. (1958) demonstrated the uptake of radioactive zinc by marine plankton, fish, and shellfish. Gutknecht (1961, 1963, 1965) demonstrated the uptake of ^{65}Zn by marine algae, and Osterberg et al. (1964) found that ^{65}Zn was concentrated at four trophic levels of the marine food chain. Although zinc uptake is evident, the removal of zinc from oceanic waters has not been shown, probably because zinc measurements are relatively difficult to make in the field and are subject to contamination.

The purpose of this work was to investigate the use of *p*H-controlled differential anodic stripping voltammetry (DASV) (Zirino and Healy 1972) as a technique for routine zinc analysis at sea and to examine the zinc distribution at certain stations in the northeastern tropical Pacific Ocean for the purpose of correlating its concentration with other oceanographic parameters. Differential anodic stripping voltammetry lends itself to such a study because: 1) samples can be analyzed for zinc without preconcentration, 2) no reagents are required, 3) the analysis is relatively rapid, and 4) the apparatus functions well at sea. An added advantage is that distilled water can be analyzed without addition of an electrolyte, allowing blanks to be easily determined.

There are, however, some disadvantages. The technique suffers from poor precision at sea and from lack of a direct comparison between values rendered by this method with those rendered by other methods such as atomic adsorption.

We are grateful to Drs. F. A. Richards and R. C. Dugdale for encouraging this research and for providing many stimulating discussions. The late Terry J. Chapo developed the instrument that made these measurements possible.

METHODS

Sample collection and preparation

Zinc measurements were carried out on three oceanic cruises to the eastern tropical Pacific Ocean by the University of Washington RV *Thomas G. Thompson*: the first, TT-026, from January to March 1968 and the second and third, TT-034 and TT-035, during February and March 1969. The purpose of these voyages was to initiate a chemical survey of North and Central American coastal waters and to study the low oxygen zones of the eastern tropical Pacific Ocean. The location of those sta-

[1] Contribution No. 559 from the Department of Oceanography, University of Washington. The research reported in this paper was supported in part by NSF Grant GA-10084 and ONR Grant N-0014-67-A-0103-0014.

[2] Present address: Marine Environment Division, Naval Undersea Research Development Center, San Diego, California.

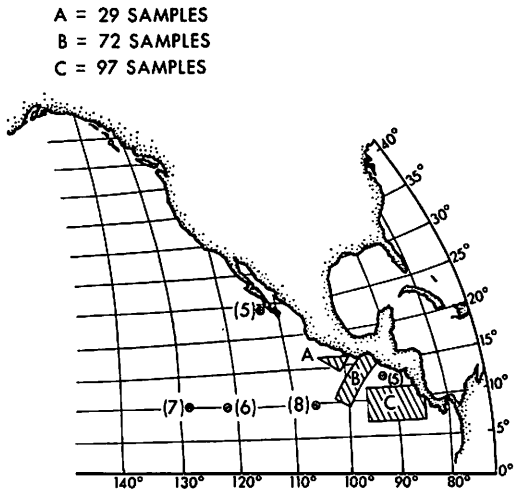


FIG. 1. Location of zinc sampling areas or stations in the eastern tropical Pacific Ocean. The numbers in parentheses represent the number of samples.

tions where samples of zinc were taken is shown in Fig. 1.

Temperature, salinity, dissolved oxygen, reactive phosphate, nitrate, nitrite, and *p*H were measured routinely at nearly all the stations occupied. Zinc samples were taken from regular hydrocasts, transferred from the Niskin plastic sampling bottles to precleaned 500-ml polyethylene bottles and analyzed within 24 hr in the ship's laboratory. To avoid systematic errors, an effort was made to pick samples for analysis randomly from the collected polyethylene bottles.

On TT-026 no attempt was made to separate out the particulate material before analysis; during TT-034 and TT-035, however, many samples were run before and after filtration through a precleaned triacetate filter.

Analytical procedure

The technique of *p*H-controlled anodic stripping voltammetry has been described in detail by Zirino and Healy (1972). But for purposes of clarity, it will be summarized briefly. A 25-ml seawater subsample is placed in the electrolytic cell and purged of oxygen with a mixture of 20% CO_2 in N_2. This lowers the *p*H to about 5.6. Zinc and other metals in the sample are then electroplated into a mercury drop (hanging mercury drop electrode) for a predetermined period of time. During TT-026, plating times of 15 min were used, but on later cruises the electrolysis time was reduced to 5 min. After deposition, the reduced metals in the amalgam are oxidized and the resulting diffusion currents are measured. The current peak at approximately −1 V vs. a saturated calomel electrode is proportional to the amount of zinc plated into the drop and to the zinc concentration in solution. Then 100 μl of 10^{-6} M zinc standard are added to the sample and allowed to equilibrate with the seawater components for periods of 5 to 15 min. The electrolysis and stripping processes are then repeated, and the zinc concentration of the sample is obtained from the ratio of the zinc peak current of the sample to that of the sample plus standard.

Shipboard replicate analysis of samples whose zinc concentrations ranged between 5 and 9 μg/liter showed that the standard deviation at these levels was 1 μg/liter. The analytical error at lower levels was estimated from measurements made of samples taken at a station where the zinc concentration between 200 and 1,700 m was nearly homogenous at about 1 μg/liter. The coefficient of variation of the results of these measurements was about 50%. In a laboratory experiment, once a sample containing 2.6 μg/liter was enclosed in the cell, repeated electrolysis and stripping produced variation of only 3%. It is therefore believed that the large error occurs during the handling and transferring of the sample and standard.

Filtering

Both Millipore and Gelman filters leached considerable quantities of zinc when zinc-free deionized water was passed through them (Fig. 2). This contamination was removed by forcing through the filter pores about 1 liter of 3% (v/v) HNO_3 solution followed by deionized water and several hundred milliliters of open ocean water. This treatment did not appear to alter appreciably the filter clogging time.

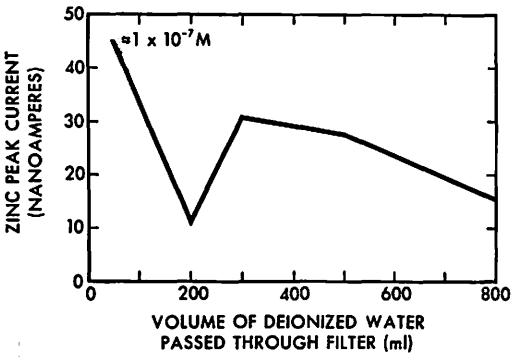


FIG. 2. Leaching of zinc by water from untreated cellulose triacetate filters (0.45 μ). Unfiltered deionized water produced no measurable zinc peak current.

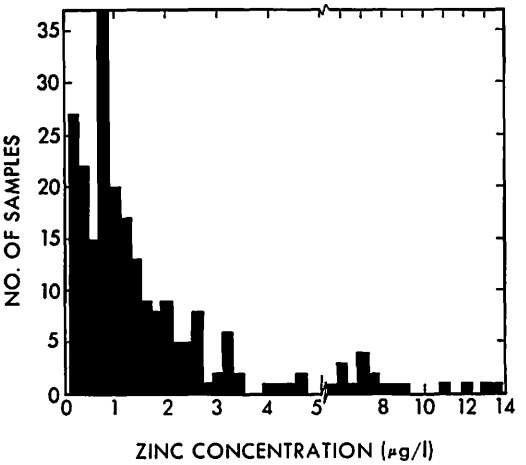


FIG. 3. Frequency distribution of observed zinc concentrations of eastern Pacific samples.

RESULTS AND DISCUSSION

Variations with depth

We made 238 zinc measurements in the upper 1,000 m of the eastern tropical Pacific Ocean. To determine if there was any significant difference as a function of depth, we treated the samples as if they originated from a single water column. The upper 1,000 m were divided into four regions: the surface, the mixed layer (1–40 m), the pycnocline (41–125 m), and the intermediate water (126–1,000 m).

To calculate the concentration means and medians for each region, we assigned a value of 0.1 μg/liter, the mean between no zinc and the detection limit, to those samples in which zinc was below the limit of detection. A histogram of the observed zinc concentrations is presented in Fig. 3, and the calculated means, medians, and standard deviations are in Table 1. Because the distribution of zinc values was asymmetric, testing for the significance of the differences between the means by a z-test necessitated transformation of the data by the function $y = \ln x$. Samples more than 3σ away from the logarithmic population mean were suspected of contamination and were not included in the analysis. This procedure excluded only 9 of 238 samples.

The mixed layer and pycnocline regions were lower in zinc concentration than the intermediate water (126–1,000 m). These differences were significant at the 99% confidence level. The surface was lower than the intermediate water at the 95% confidence level.

In an alternate treatment of the data, a median test (Tate and Clelland 1957) was used to compare the zinc concentration between the surface and 125 m to the zinc content of the intermediate water. This test also indicated that the intermediate water

TABLE 1. *Means, standard deviations, and ranges of zinc concentrations and the average* pH *of samples*

Depth (m)	No. of samples	Median	Avg	σ	Range	Avg pH*
		(μg/liter)				
0	28	0.8	1.6	2.0	ND†– 7.2	8.4
1–40	52	0.8	1.2	2.0	ND –13.59	8.3
41–125	44	0.7	1.2	1.6	ND – 8.50	7.9
126–1,000	105	1.4	2.2	2.5	ND –12.80	7.5
0–1,000	229	1.6	1.7	2.2		

* Apparent pH as measured with a glass combination electrode calibrated against a dilute phosphate buffer.
† Not detectable at the 0.2–0.3 μg/liter level.

was higher in zinc at the 99% confidence level.

Individual stations

The decrease in zinc content of the waters in the upper 125 m of the northeastern tropical Pacific Ocean may be the result of uptake by organisms and particulate matter found in the upper layers. At most individual stations, the large analytical error, as well as the possibly large natural variance in the distribution, makes the removal of zinc difficult to detect. Moreover, there was, in general, little correlation between individual zinc measurements and other chemical variables at the same depth.

In regions of pronounced upwelling, however, where the upward movement of the water was accompanied by vigorous phytoplankton production, zinc depletion became apparent. This was observed in the Gulf of Tehuantepec in winter 1968 when strong northerly winds produced patches of upwelled water hundreds of square kilometers in area. Many patches were discernible by their green hue. Zinc, density, and NO_3-N distribution of two stations occupied in the Gulf of Tehuantepec are contrasted in Fig. 4. Station 16 was located at a region of upwelling, as indicated by depressed surface temperatures and by the high nutrient and low oxygen concentrations below 20 m. Nitrate in the mixed layer was essentially depleted. Zinc was barely detectable in the upper 10 m, higher in the pycnocline region, and very high (from 3.0–7.4 μg/liter) below the pycnocline to 260 m. Evidence of abundant planktonic growth was deduced from the green color of the water and from the 4-m Secchi disk reading. At station 18, 230 km northeast of station 16, the zinc concentration was high at the surface, nearly uniform at about 1.5 μg/liter to a depth of 250 m (except for one anomalously high value), and then appeared to increase slightly. The clearly detectable values in the upper 60 m implied that planktonic uptake was not extensive. This appeared to be confirmed by the 29-m Secchi disk reading and the blue color of the water.

A similar comparison was made for stations 20 and 21, also in the Gulf of Tehuantepec (Fig. 4). Although these stations were only 100 km apart, there was a significant difference in the zinc distributions. At station 20, zinc was clearly detectable in the

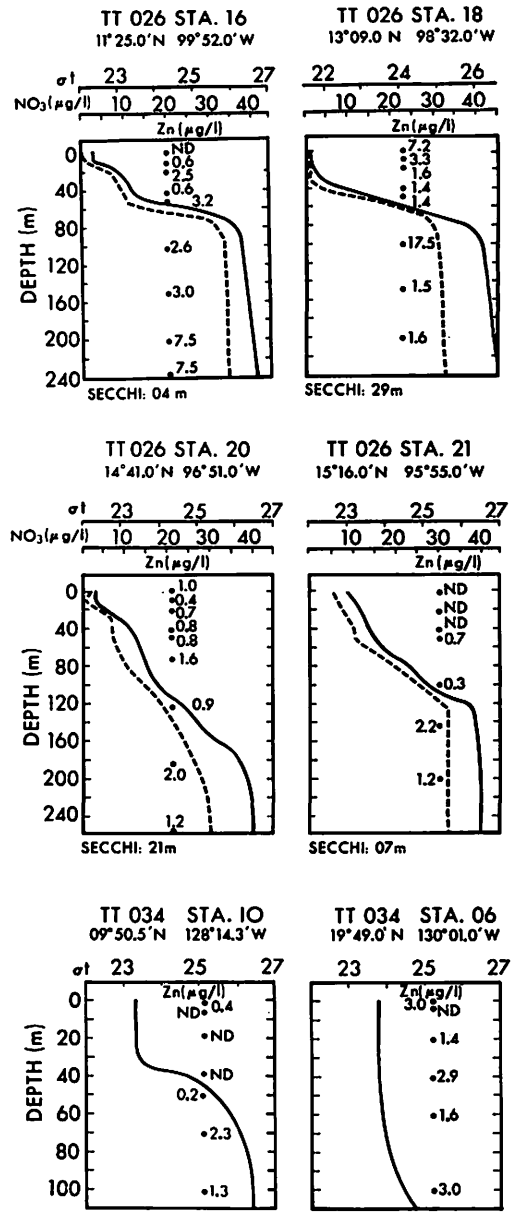


FIG. 4. Comparisons between stations 16–18, stations 20–21, and stations 06–10. Zinc concentrations are tabulated at the depth they were sampled, and ND values are for concentrations not detectable at 0.2 μg/liter. Solid lines are sigma-*t* and dashed lines are nitrate distributions.

mixed layer, and the 21-m Secchi disk reading implied that uptake had been minor. At station 21 zinc was undetectable above 40 m. The distribution of density, nutrients, and oxygen suggested upward motion of the water at station 21, and the 7-m Secchi disk reading suggested a substantial phytoplankton population. The correlation between low zinc, high surface nutrients, and low transparency again suggested uptake by a phytoplankton bloom as a result of local upwelling.

The effect of the local hydrography on the zinc distribution was similarly observed if a station from a semitropical, well-mixed, unproductive region was contrasted with a station taken a few days later along the equatorial divergence at 9°N (Fig. 4). With the exception of the first 5 m, zinc at station 06 appeared to be clearly detectable to 100 m. On the other hand, at the divergence, zinc was not detectable in the mixed layer but was measurable below the pycnocline. Although no other measurements were made at these stations, it appears likely that zinc removal is associated with the high production found at the divergence.

Filtered samples

Zinc measurements by *p*H-controlled DASV yield values that may include the zinc fraction adsorbed on particulate surfaces and released into solution when the *p*H of seawater is decreased to 5.6. To estimate the magnitude of this particulate zinc fraction, open ocean samples were analyzed before and after filtration through a 0.45-μ triacetate filter (Table 2) (four of the samples were passed through a 0.2-μ filter).

Zinc values obtained after filtration were on the average 45% lower. Inspection of the data revealed no particular correlation between percent zinc removed and depth at which sample was collected. Although the data are insufficient to differentiate between particulate and soluble zinc fractions, they do suggest that in the open ocean zinc may be adsorbed by particulate matter and that the adsorption can be reversed by a relatively small decrease in *p*H. This would extend to the open ocean the findings of Gutknecht (1963). He observed that the alga *Ulva lactuca* rapidly lost adsorbed ^{65}Zn when the *p*H of a 3% NaCl wash solution was lowered to 6.0. In the sea, adsorption by cells and subsequent sinking may provide a path by which zinc is removed from the euphotic zone. This adsorption would be aided by *p*H increases occurring during photosynthesis.

TABLE 2. *Zinc concentrations of eastern Pacific Ocean samples before and after filtration*

Location	Depth (m)	Unfiltered	0.45-μ filtered
		μg/liter	
34° 28.2′ N 130° 02.2′ W	0	1.3	1.3
	20	2.7	2.6
	98	1.0	ND*
30° 51.0′ N 130° 00.0′ W	0	2.0	0.8
19° 49.0′ N 130° 01.0′ W	100	3.0	3.3
9° 50.5′ N 128° 14.3′ W	80	2.3	1.3
9° 58.4′ N 122° 41.8′ W	20	1.8	ND
	100	1.8	1.7
9° 23.0′ N 105° 54.0′ W	0	2.5	0.5
	40	1.2	0.4
	80	2.0	0.7
	100	0.7	
44° 02.0′ N 130° 49.2′ W	Surface	4.7	3.0
40° 32.0′ N 133° 00.0′ W	Surface	1.4	1.3
37° 03.1′ N 123° 25.0′ W	Surface	5.9	2.2
37° 57.6′ N 123° 11.2′ W	Surface	1.5	3.9†
38° 51.8′ N 122° 57.7′ W	Surface	1.3	1.0
8° 58.0′ N 85° 57.4′ W	Surface	1.1	1.0
	50	3.2	ND
	3,000	1.2	1.1
10° 18.0′ N 86° 48.0′ W	500	2.6	0.9
	1,000	0.7	ND
	3,000	1.4	0.7
	3,400	0.8	0.8
	4,000	1.3	0.3
	4,800	0.8	1.0

* ND = Not detectable at 0.2 μg/liter.
† Not used to calculate mean percent zinc removed by filtering.

REFERENCES

BONNER, J., AND J. E. VARNER. 1965. Plant biochemistry. Academic. 1054 p.

DIXON, M., AND E. C. WEBB. 1964. Enzymes, 2nd ed. Academic. 950 p.

CHIPMAN, W. A., T. R. RICE, AND T. J. PRICE. 1958. Uptake and accumulation of radioactive zinc by marine plankton, fish and shellfish. U.S. Fish Wildl. Serv. Fish. Bull. **58**: 279–292.

GUTKNECHT, J. 1961. Mechanism of radioactive zinc uptake by *Ulva lactuca*. Limnol. Oceanogr. **6**: 426–431.

———. 1963. Zn^{65} uptake by benthic marine algae. Limnol. Oceanogr. **8**: 31–38.

———. 1965. Uptake and retention of $cesium^{137}$ and $zinc^{65}$ by seaweeds. Limnol. Oceanogr. **10**: 58–66.

OSTERBERG, C., W. G. PEARCY, AND H. CURL. 1964. Radioactivity and its relationship to oceanic food chains. J. Mar. Res. **22**: 12.

POLIKARPOV, G. G. 1966. Radioecology of aquatic organisms. Reinhold. 314 p.

RICE, T. R. 1963. Review of zinc in ecology, p. 619–631. *In* Proc. 1st Nat. Symp. Radioecol., Colorado State Univ., 1961. Reinhold.

TATE, N. W., AND R. C. CLELLAND. 1957. Nonparametric and short cut statistics. Interstate. 171 p.

ZIRINO, A., AND M. L. HEALY. 1972. pH controlled differential voltammetry of certain trace transition elements in natural waters. Environ. Sci. Technol. IN PRESS.

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)*

University of Washington, Dept. of Oceanography

2a. REPORT SECURITY CLASSIFICATION

2b. GROUP

3. REPORT TITLE

Voltammetric measurement of zinc in the Northeastern tropical Pacific Ocean

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Reprint from journal

5. AUTHOR(S) *(First name, middle initial, last name)*

Albert Zirino and Michael L. Healy

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
Limnology & Oceanography 16(5), 1971	773-778 6 pp.	

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
N-0014-67-A-0103-0014	Cont. No. 559
b. PROJECT NO. NR 083 012	Tech. Report No. 278
c.	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
d.	

10. DISTRIBUTION STATEMENT

For public release; distribution unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	Office of Naval Research

13. ABSTRACT

Relative zinc concentrations in the upper 1,000 m of the northeastern tropical Pacific Ocean were measured by pH-controlled differential anodic stripping voltammetry (DASV) aboard ship. The waters above 125 m are significantly lower in zinc content than those between 125 and 1,000 m. A substantial fraction of the measured zinc appears to be adsorbed on particulate matter $> 0.45\ \mu$. The adsorption can be reversed by lowering the pH to 5.6 with CO_2 gas.

DD FORM 1 NOV 65 1473 (PAGE 1)

0102-014-6600

Security Classification