Cadmium in Plankton: Elevated Concentrations off Baja California

Abstract. *One hundred thirty-five plankton samples were collected in the northeast Pacific Ocean and analyzed for their cadmium content. Concentrations were generally low (2 to 5 micrograms of cadmium per gram, dry weight) in all samples, except for the plankton collected off Baja California, where high values (10 to 20 parts per million) were consistently found on two cruises.*

Plankton are well known for their ability to concentrate trace elements and, provided certain criteria are met, amounts in association with these organisms may reflect ambient levels in the environment. We have measured the concentration of cadmium in plankton from the northeast Pacific Ocean and, in almost all areas sampled, we have found relatively low concentrations of this element. However, on two cruises off Baja California we consistently observed elevated amounts of cadmium in the plankton collected south of San Diego.

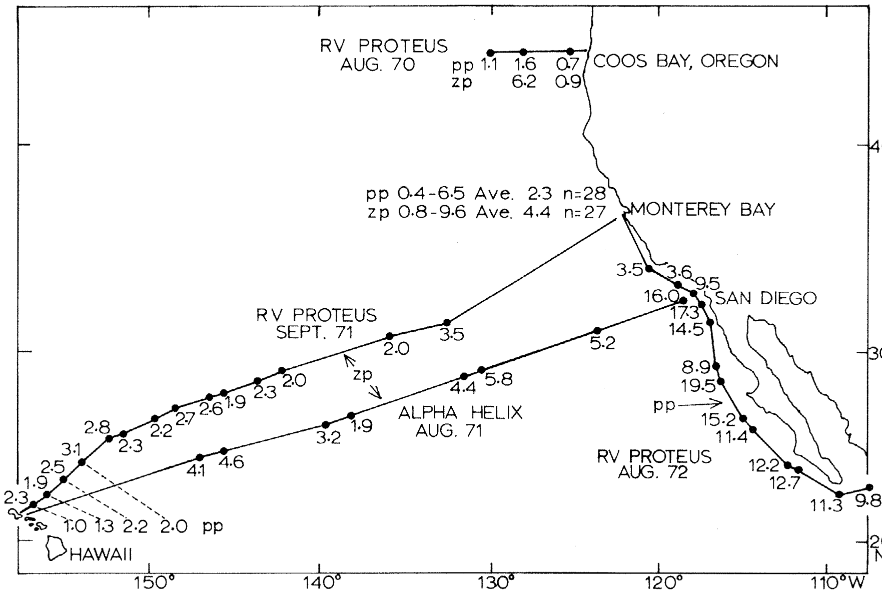
The data for the first Baja cruise and from previous studies (*1*) are shown in Fig. 1. South of San Diego, eight of ten samples contained more than 10 μg of Cd per gram, dry weight (range, 8.9 to 19.5; mean, 13.2); in contrast, only 1 of the 86 samples collected on two Hawaii-California transects, off Oregon, and in Monterey Bay, California, had a Cd concentration greater than 10 parts per million (ppm). The mean concentrations for these areas were always below 5 ppm. The single high value (16 ppm) was found at the last station of the R.V. *Alpha Helix* transect just west of San Diego (Fig. 1).

These data suggested that for some reason the plankton off Baja California concentrated more Cd than those in the other sampled regions of the northeast Pacific. Confirmation of these findings was of importance since Cd is known for its toxicity (*2*) and high concentrations in the primary producers and consumers (plankton) could represent a potential problem for organisms at higher trophic levels, where high concentrations of this element are sometimes found (*3*).

However, since trace element concentrations in plankton are highly variable, and since the collection methods usually employed can cause severe contamination problems, it was necessary that we have many more data before drawing any conclusion. Thus, we collected additional samples off Baja California in January and February 1974 (Fig. 2). Once again, high Cd concentrations were observed in almost all the collections south of San Diego. Values were especially high south of Punta Eugenia, where four samples contained 17.8 to 20.9 ppm. That this was not strictly a coastal phenomenon was also illustrated by concentrations of 16.2 and 17.2 ppm noted approximately 500 km southwest of Punta Eugenia. For all 32 samples collected south of San Diego, the range was 4.2 to 20.9 ppm and the average was 13.6 ppm. As with the first Baja cruise (Fig. 1), relatively low concentrations were observed in the plankton collected off Southern California. The lowest concentrations (1.8 to 3.4 ppm) on the entire cruise occurred at three closely spaced stations just off San Diego. Low values were also observed at the five remaining northerly stations (3.5 to 7.5 ppm) (*4*).

With the confirmation of our original findings, it now appears that Cd concentrations in the plankton off Baja California are approximately three times higher than in the plankton collected in other areas (*5*). However, scientists familiar with the problems of analyses of trace metals in plankton can view these results with justifiable skepticism. For example, paint and rust chips fall off almost all research vessels and are frequently caught in plankton nets towed in the vicinity of the ship, and high trace metal concentrations in plankton can result from this source of contamination. To avoid this problem, all of the samples on the second Baja cruise and half of those on the first cruise were collected from an inflatable dinghy rowed several hundred meters away from the main research vessel. The net employed (aperture, 64 μm) and other parts of the sampling gear were constructed of nylon or plastic materials, with the exception of the brass net rings and grommets, which were heavily coated with fiber glass. Precautions were also taken while digesting the samples in redistilled nitric acid and peroxide and while analyzing them by atomic absorption (*6*).

Another reason for the pattern we have observed could be natural variability due to differences in species composition. Many of the data presented in Fig. 1 are for relatively pure zooplankton, while others (those for Monterey Bay) are for pure phytoplankton. Almost all the samples collected off Baja California consisted of "microplankton," a mixture of phytoplankton, small zooplankton, and detritus. Although



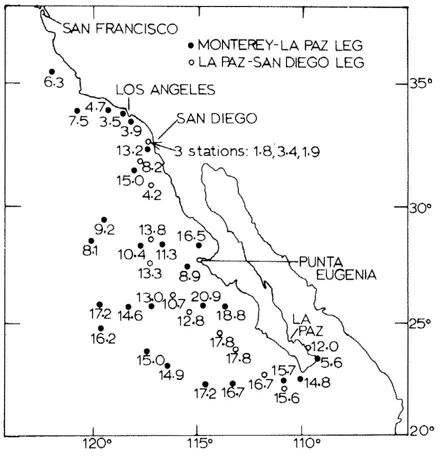


Fig. 1 (left). Cadmium concentrations (micrograms per gram, dry weight) in plankton collected on various transects in the northeast Pacific Ocean. Net mesh sizes are indicated by the letters *zp* for zooplankton nets (366 μm) and *pp* for phytoplankton nets (64 μm). Ranges and averages for phytoplankton collected in Monterey Bay throughout 1971 are also indicated. Fig. 2 (right). Cadmium concentrations (micrograms per gram, dry weight) in plankton (net mesh size, 64 μm) collected on R.V. *Cayuse*, January and February 1974.

we did not identify the organisms in our samples, we believe that it is unlikely that species differences are responsible for the pattern we observed. Practically pure diatom samples collected in upwelling areas off Baja California (water temperature, 14.3°C) had Cd concentrations of up to 16.5 ppm, while in 23 diatom samples from Monterey Bay (temperature, 9.8° to 15.7°C) the highest Cd concentration was 4.8 ppm. One pure copepod sample from Baja California had a Cd concentration of 15.2 ppm, while the maximum was 6.0 ppm for ten Monterey Bay copepod samples. Many of the samples which had high Cd levels also contained high Sr concentrations. Samples with Sr-concentrating organisms from other areas were collected with the same fine-meshed nets; the Cd concentration was less than 2.2 ppm in four such samples collected 100 to 400 km northeast of Hawaii, less than 1.1 ppm in two samples collected off Oregon, and 3.4 ppm in a sample collected off Puerto Rico. Disregarding the zooplankton data and considering only the 89 samples collected with phytoplankton nets from inshore and offshore, tropical and temperate waters, we have never observed a Cd concentration greater than 7.5 ppm in any sample except those from the area south of San Diego off Baja California.

We believe that the increased Cd concentrations found south of San Diego are due to elevated concentrations in the water. Various hypotheses can be presented that could explain why Cd levels would be high in this area for both natural (*7*) and anthropogenic (*8*) reasons. However, until measurements of Cd in the waters off Baja California are made, further speculation is unwarranted. Nevertheless, the plankton data do suggest that an extraordinary situation in regard to this toxic element may well exist off Baja California. The reasons for its occurrence should be investigated.

J. H. MARTIN
W.W. BROENKOW
Moss Landing Marine Laboratories,
Post Office Box 223,
Moss Landing, California 95039

References and Notes

J. H. Martin and G. A. Knauer, *Geochim. Cosmochim. Acta* **37**, 1639 (19 G. A. Knauer and J. H. Martin, *Limnol. Oceanogr.* **18**, 597 (1973).

2. R. R. Nilsson, *Aspects on the Toxicity of Cadmium and Its Compounds* (Swedish Natural Science Research Council, Stockholm, 1970), pp. 19–49.
3. Top predators such as sea lions (*Zalophus californianus*) and sea otters (*Enhydra lutris*) have renal Cd concentrations of up to 570 and 960 μg/g, dry weight, respectively (J. H. Martin, unpublished data).
4. Concentrations higher than the 3.5 and 3.9 ppm found north and south of Los Angeles could be expected because of the proximity of sewer outfalls from the city and county of Los Angeles. However, the samples were from depths of 0 to 5 m, and it is doubtful that these waters had mixed with Los Angeles waste waters since the outfall diffusers are at depths of 50 to 60 m and the effluent rises and spreads out along the thermocline, which was at 20 m when we sampled.
5. Several investigators measured Cd in Atlantic and Caribbean zooplankton during the International Decade of Ocean Exploration (IDOE) baseline studies (unpublished); almost all Cd concentrations in 248 samples were well below 10 ppm ("Baseline studies of pollutants in the marine environment," background papers for a workshop sponsored by the National Science Foundation's Office for the IDOE and held at Brookhaven, Upton, New York, 24 to 26 May 1972).
6. All readings were corrected for light scatter; see C. K. Billings, *At. Absorp. Newslett.* **4**, 357 (1965); K. Fletcher, *Econ. Geol.* **65**, 588 (1970). For further analytical details, see references in (*1*).
7. In waters like those off Baja California, upwelling currents may oppose the downward transport of organic material, and trace metal concentrations may become elevated in the surface waters because of the lack of biological removal. [D. F. Schutz and K. K. Turekian, *Geochim. Cosmochim. Acta* **29**, 259 (1965); J. P. Riley and D. Taylor, *Deep-Sea Res.* **19**, 307 (1972)].
8. Approximately 50 metric tons of Cd are introduced into the Southern California Bight annually via major submarine discharges of municipal waste water [*The Ecology of the Southern California Bight: Implications for Water Quality Management* (Southern California Coastal Water Research Project, El Segundo, 1973)]. However, provided adequate mixing occurs with California Current water, the 50 tons of Cd should be diluted to background levels long before reaching Baja California.
9. This research was supported by EPA grant R 802 350 and NSF grant GA 28306. We thank K. Baxter and G. Lopez for the R.V. *Alpha Helix* plankton samples; Oregon State University for the use of the R.V. *Cayuse*; and R. Flegal, K. Skaug, and P. Elliott for their help with the analyses and collections.

10 March 1975; revised 9 May 1975

Wurtzite: Long-Period Polytypes in Disordered 2H Crystals

Abstract. *An electron optical study of a disordered 2H wurtzite from Pribram, Czechoslovakia, reveals an even and dense distribution of stacking faults and indicates the presence of long-period polytypes. The polytype crystal structures appear quite distinct from those of synthetic equivalents, and this difference may be attributable to different environments of formation.*

Polytypic and disordered ZnS stacking sequences are transitional structural states between 2H wurtzite and sphalerite (*1*). In an electron optical investigation of a disordered natural 2H wurtzite, stacking faults, which mark departures from the ideal stacking sequence, are visible in bright- and dark-field modes. In addition, there is evidence of long-period polytypes which may represent a new family of polytypic structures. Their structures are apparently based on modulations of the 2H unit and thus are quite different from those of synthetic vapor-grown wurtzite polytypes (*2*). This difference may be a consequence of different environments of crystallization and, in addition, may reflect a different mode of polytype formation.

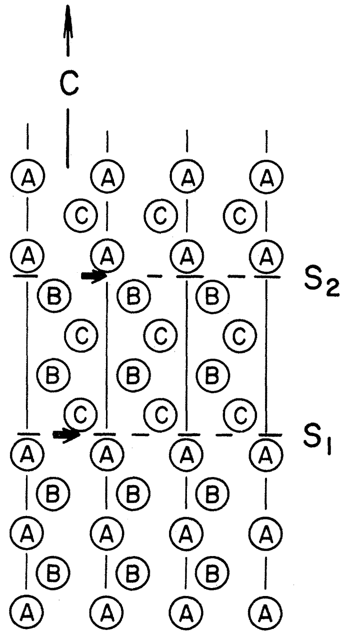


Fig. 1. Representation of a (110) layer three unit cells wide of a 2H wurtzite disordered by stacking faults: *A*, *B*, and *C* are either sulfur or zinc atoms; S_1 and S_2 are stacking fault planes; arrows are displacement vectors.

In 2H wurtzite and related structures all atoms lie on (110) planes (Fig. 1). Mistakes in the ideal stacking sequence can arise either during or after crystal growth because for each layer of atoms there are two nonequivalent atom positions which give identical nearest-neighbor environments. The mistakes (or stacking faults) occur as displacements of the atoms from their ideal positions by amounts of $\frac{2}{3} d_{100}$ [where d_{100} is the (100) interplanar spacing] and thus do not affect the intensity of diffracted x-ray and electron beams for which $h + k = 3n$, where n is an integer. However, on other reciprocal lattice rows random stacking faults produce diffraction streaks (*3*) and ordered stacking faults produce the diffraction maxima characteristic of a polytype.

The wurtzite studied, from Pribram, Czechoslovakia, is in the form of radiating aggregates of $\{001\}$ plates. The average composition (in percentages by weight) as determined by electron microprobe analysis is as follows: zinc, 64.1; iron, 1.3; cadmium, 1.4; copper, 0.04; manganese, 0.01; and sulfur, 33.2. On single crystal x-ray diffraction precession films (*4*) reflections with $h + k \neq 3n$ are diffuse and elongated as apparently almost continuous streaks parallel to c^*, thus suggesting a very high degree of stacking disorder.

Electron optical observations were made with an electron microscope (AEI EM6G) at 100 kv on crushed grains. A typical zero level $h0\ell$ selected area diffraction pattern is