## METALS IN MUSSELS FROM HARBORS AND OUTFALL AREAS

It is often difficult to determine the source of excess metals in coastal waters because it is difficult to distinguish the influence of municipal wastewater outfalls from that of the discharges from harbors, which are usually located nearby. Because of the very low levels at which most metals occur in seawater, and the ability of many marine animals to concentrate them to easily measurable levels, "indicator organisms" are often used in metal pollution studies. Here we report abnormally high levels of a number of potentially toxic trace metals in tissues of bay mussels (*Mytilus edulis*) collected from areas of either vessel activities or municipal wastewater discharges.

The municipal wastewater source of metals is well known, but it is not generally recognized that ship and boat protective paints also constitute a potentially significant source of certain trace metals to coastal marine waters. For example, copper, mercury, and tin have been used extensively as toxicants in antifouling paints, and chromium, lead, and zinc are important components of bottom primers. Cadmium also occurs in certain paint pigments, and zinc is utilized in the sacrificial anodes that are attached to vessel bottoms to prevent corrosion of metal parts.

In previous papers, we have discussed the usefulness of *Mytilus* species for indicating regions of contamination by metals and synthetic organics (Alexander and Young 1976; Young et al. 1975). Preliminary analyses of *M. edulis* samples collected during 1974 revealed abnormally high levels of copper and zinc in those from certain stations in San Diego and Newport Harbors (Young and McDermott 1975). Therefore, we extended our analysis to include eight metals (silver, cadmium, chromium, copper, nickel, lead, tin, and zinc) that seemed most likely to be present in significant quantities in inputs to the nearshore marine ecosystem.

## PROCEDURES

In January 1974, bay mussels 5 cm in length were collected from several stations in San Pedro, San Diego, and Newport Harbors. The first two of these harbors receive a number of different waste inputs; however, the major

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activity in Newport Harbor is the maintenance of approximately 9,000 recreational vessels. Samples were also collected from six coastal sites: Point Loma, La Jolla, Newport Harbor breakwater, Newport Beach, Seal Beach, and Royal Palms Beach (Figure 1).

Digestive glands were dissected from three male and three female specimens from each collection; in addition, samples of gonadal, adductor muscle, and "remaining" tissues were obtained from one of the male and female specimens from each station. These samples were freeze-dried and analyzed by optical emission spectrometry at the Laboratory of Nuclear Medicine and Radiation Biology, University of California at Los Angeles. Composite samples of whole soft mussel tissues from each station also were analyzed for PCB's (formerly used in paints and hydraulic fluids) in the Project's trace organics laboratory.

## **RESULTS AND DISCUSSION**

Some of the highest metal concentrations found in this study occurred in specimens collected from Newport Harbor. Table 1 compares average values (and their standard errors) for the back-harbor station (Station I, Figure 1), located near a large vessel repainting and repair yard, and the coastal site at Newport Beach (Station H, Figure 1), which is situated only 0.3 km across the strand from the back- harbor station but 5 km from the harbor entrance. The average concentration of copper in digestive glands of the harbor specimens ( $127 \pm 18$  ppm) was eight times the concentration in the coastal controls ( $16 \pm 1$  ppm). Similar contamination factors (ratios of mean harbor concentration to mean coastal concentration) were observed for copper in the three other tissues analyzed (ratios ranged from 9.1 to 9.9) and for 1254 PCB (8.9) in the whole soft tissues. As recreational vessel use and maintenance are the major activities in Newport Harbor, the distinct copper and PCB contamination of the mussels appears to be directly related to these activities.

The data from Newport Harbor also show enhanced body burdens of several other trace metals in the mussels from Station I. As was the case for copper, the contamination factors for zinc in the four tissue classes were remarkably similar (2.7 to 4.1). One possible source of this metal is the use of sacrificial zinc anodes. The zinc contamination might also be related to the use of zinc com-pounds, such as zinc chromate, in vessel paints: Indeed, the mean gonadal tissue chromium concentration in the harbor specimens was seven times higher than that in the coastal mussels. Gonadal tissue had the highest contamination factors for two other important vessel paint metals, tin (more than 18) and lead (more than 14). In addition, the results listed in Table 1 indicate elevated cadmium levels at the harbor station. This finding is similar to one made in the San Diego Harbor survey, where mussels living in the commercial dock region exhibited cadmium contamination factors ranging from 2 to 4 in all four tissue classes.

Sediments from the Station I in Newport Harbor also have been found to be highly contaminated with certain metals used in vessel maintenance. For example, samples collected there in 1971 were found to contain 710 ppm copper, 410 ppm zinc, and 12 ppm mercury (City of Newport Beach 1972); in contrast, nearshore southern California sediments are estimated to contain 20 ppm copper, 60 ppm zinc, and 0.04 ppm mercury (Coastal Water Research Project 1973).

Unlike the mussels from San Diego and Newport Harbors, the *Mytilus edulis* from San Pedro Harbor appeared to have only slight metal contamination. Again, the copper contamination was most distinct. Digestive glands from specimens from four harbor stations were analyzed; the average of the mean copper concentration for these stations was  $30 \pm 2$  ppm, a value about 50 percent above the estimated coastal baseline of about  $20 \pm 2$  ppm. Data on copper in the other tissue classes, and on all of the other metals in the harbor specimens, were too variable to suggest any distinct patterns. This harbor has three entrances and a very broad and porous breakwater, and a much higher flushing rate may be the cause of the relatively low metal contamination factors found in mussels there.

At one coastal station in the Los Angeles region, we found elevated metal concentrations in certain tissues of *M. edulis*. This site was Royal Palms Beach (Station K, Figure 1), located directly inshore of Los Angeles County's submarine discharge of Joint Water Pollution Control Plant (JWPCP) municipal wastewater, the single largest source of trace metals to the Southern California Bight (Young et al. 1973). In Table 2, the average metal concentrations in the tissues of Royal Palms mussels are given and compared with the average concentrations in mussels from the five other coastal stations sampled. These data indicate elevated concentrations of seven of the eight metals in one or more of the mussel tissues analyzed; only in the case of zinc were there no detectable enhancements in the Royal Palms specimens. The silver, chromium, and copper contamination factors in digestive gland, gonad, and "remainder" tissues were all relatively high (1.3 to more than 8.2); these were the three metals previously found in relatively high concentrations in digestive glands of the coastal mussel M. califorianus collected inshore of the two major Los Angeles municipal outfall systems (Alexander and Young 1976). Values for lead and tin in gonadal tissue were also higher for Royal Palms specimens than for mussels from other coastal stations: contamination factors for these two metals were more than 2.9 and more than 8.5, respectively. In comparison, specimens from Station I in Newport Harbor concentrated these two metals in their gonads by factors exceeding 14 and 18.

The results of this study indicate that the use and maintenance of recreational, commercial, and naval vessels, as well as the submarine discharge of municipal wastewater, are sources of trace metal additions to intertidal organisms of the Southern California Bight.

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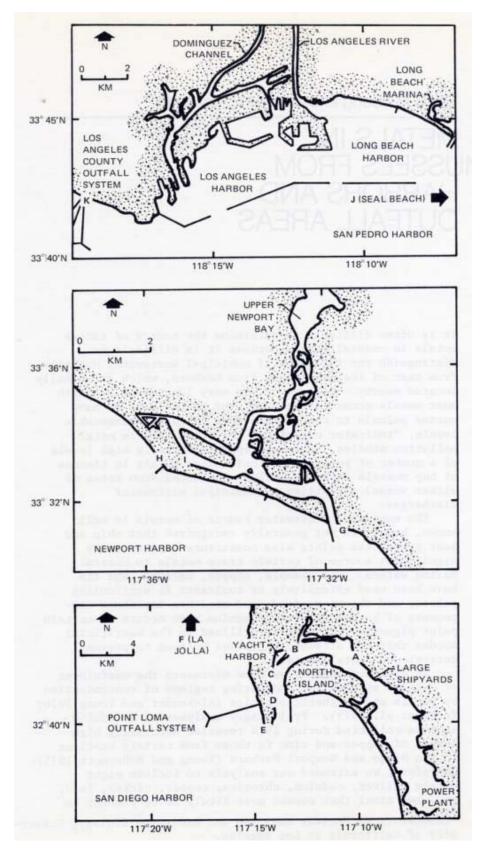


Figure 1. Stations for survey of metals in intertidal mussels.

Table 1. Mean concentrations (mg/dry kg,  $\pm$  standard error) of trace metals in tissues of bay mussels (*Mytilus edulis*) collected from Newport Harbor and Newport Beach.\*

|                      |           |           | Ratio,<br>Harbor to |
|----------------------|-----------|-----------|---------------------|
| Constituent          | Harbor    | Beach     | Beach               |
| and Tissue           | Harbor    | been      |                     |
| 1254 PCB,            |           |           |                     |
| whole soft tissues** | 3,9       | 0.44      | 8.9                 |
| Silver               |           | 1000      |                     |
| Digestive gland      | < 0.3     | <0.4      | -                   |
| Gonad                | < 0.7     | <0.4      | -                   |
| Muscle               | < 0.4     | < 0.4     | -                   |
| Remainder            | <0.8      | < 0.5     | -                   |
| Cadmium              |           |           |                     |
| Digestive gland      | 10 ± 1.9  | <4.7      | >2.1                |
| Gonad                | 9 ± 9     | <2.8      | >3.2                |
| Muscle               | 7.1 ± 3.4 | <3.0      | >2.4                |
| Remainder            | 7.6 ± 0.8 | <4.8      | >1.6                |
| Chromium             |           |           |                     |
| Digestive gland      | 3.8 ± 0.6 | 3.7 ± 0.6 | 1.0                 |
| Gonad                | 2.0 ± 0.4 | 0.3 ± 0.1 | 6.7                 |
| Muscle               | < 0.6     | <0.6      | -                   |
| Remainder            | 1,6 ± 0,1 | 1.0 ± 0.1 | 1.6                 |
| Copper               |           |           |                     |
| Digestive gland      | 127 ± 18  | 16 ± 1.0  | 7.9                 |
| Gonad                | 93 ± 15   | 9.6 ± 0.2 | 9.9                 |
| Muscle               | 52 ± 10   | 5.7 ± 0.3 | 9.1                 |
| Remainder            | 100 ± 14  | 11 ± 0.6  | 9.1                 |
| Nickel               |           |           |                     |
| Digestive gland      | <2.7      | 3.6 ± 0.7 | <0.8                |
| Gonad                | <2.2      | <0.9      | -                   |
| Muscle               | <1.3      | <2.6      | -                   |
| Remainder            | <3.7      | < 2.9     | -                   |
| Lead                 |           |           |                     |
| Digestive gland      | 19 ± 2.7  | 5.5 ± 0.6 | 3.5                 |
| Gonad                | 13 ± 4.6  | < 0.9     | > 14                |
| Muscle               | <1.3      | <1.2      | -                   |
| Remainder            | 10 ± 2.0  | <1.6      | >6.2                |
| Tin                  |           |           |                     |
| Digestive gland      | 3.6 ± 0.8 | 1.4 ± 0.3 | 2.6                 |
| Gonad                | 5.4 ± 1.4 | < 0.3     | >18                 |
| Muscle               | <0.5      | <0.7      | -                   |
| Remainder            | 3.4 ± 1.2 | < 0.5     | 6.8                 |
| Zinc                 |           |           |                     |
| Digestive gland      | 240 ± 26  | 80 ± 11   | 3.0                 |
| Gonad                | 360 ± 120 | 87 ± 3    | 4.1                 |
| Muscle               | 210 ± 66  | 79 ± 3    | 2.7                 |
| Remainder            | 280 ± 45  | 99 ± 16   | 2.8                 |

\*Digestive gland values are based on analysis of six samples; other values are based on

analysis of two samples each. \*\*Dry weight values were obtained using wet/dry ratio of 4.4.

Table 2. Mean concentration (mg/dry kg,  $\pm$  standard error) of trace metals in tissues of bay mussels (*Mytilus edulis*) from Royal Palms Beach on the Palos Verdes Peninsula and five other coastal sites.

|                     |            |               | Ratio,<br>Royal Palms to |
|---------------------|------------|---------------|--------------------------|
| Constituent         | Royal      | Other Coastal | Other Coastal            |
| and Tissue          | Palms      | Stations      | Stations                 |
| 1254 PCB,           |            |               |                          |
| whole soft tissues* | 0.53       | 0.31 ± 0.05   | 1.7                      |
| Silver              |            |               |                          |
| Digestive gland     | 1.2 ± 0.3  | <0.3          | >4.0                     |
| Gonad               | 2.2 ± 0.05 | <0.6          | > 3.7                    |
| Muscle              | <0.6       | <0.4          | -                        |
| Remainder           | 4.9 ± 0.4  | <0.6          | > 8.2                    |
| Cadmium             |            |               |                          |
| Digestive gland     | 8.2 ± 1.1  | <6.0          | >1.4                     |
| Gonad               | <4.6       | <3.5          |                          |
| Muscle              | <3.7       | <3.4          | -                        |
| Remainder           | 9.2 ± 1.4  | <4.4          | >2.1                     |
| Chromium            |            |               |                          |
| Digestive gland     | 15 ± 0,9   | 4.8 ± 0.7     | 3.1                      |
| Gonad               | 1.3 ± 0.1  | 0.6 ± 0.1     | 2.2                      |
| Muscle              | <1.0       | <0.9          | -                        |
| Remainder           | 2.9 ± 0.0  | 1.7 ± 0.4     | 1.7                      |
| Copper              |            |               |                          |
| Digestive gland     | 47 ± 2.8   | 20 ± 2.4      | 2.4                      |
| Gonad               | 42 ± 0.5   | 10 ± 0.8      | 4.2                      |
| Muscle              | 14 ± 1.0   | 11 ± 2.9      | 1.3                      |
| Remainder           | 44 ± 7.0   | 13 ± 1.5      | 3.4                      |
| Nickel              |            |               |                          |
| Digestive gland     | 10 ± 1.4   | 4.1 ± 0.7     | 2.4                      |
| Gonad               | <3.0       | <1.3          |                          |
| Muscle              | <1.2       | <2.0          | -                        |
| Remainder           | <3.2       | <3.2          | -                        |
| Lead                |            |               |                          |
| Digestive gland     | 8.9 ± 1.0  | 7.5 ± 1.9     | 1.2                      |
| Gonad               | 3.2 ± 0.4  | <1.1          | >2.9                     |
| Muscle              | <1.2       | <1.2          | -                        |
| Remainder           | <1.1       | <2.0          | =                        |
| Tin                 |            |               |                          |
| Digestive gland     | 1.2 ± 0.3  | 1.5 ± 0.2     | 0.8                      |
| Gonad               | 3.4 ± 0.5  | <0.4          | >8.5                     |
| Muscle              | <0.4       | <0,5          | -                        |
| Remainder           | <0.3       | <0.8          | -                        |
| Zinc                |            |               |                          |
| Digestive gland     | 120 ± 14   | 110 ± 10      | 1.1                      |
| Gonad               | 120 ± 15   | 93 ± 12       | 1.3                      |
| Muscle              | 90 ± 42    | 130 ± 27      | 0.9                      |
| Remainder           | 140 ± 52   | 140 ± 18      | 1.0                      |

\*Dry weight values were obtained using wet/dry ratio of 4.4