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CADMIUM AND OTHER HEAVY METALS IN SEA-SKATERS
(Gerridae: *Halobates, Rheumatobates*)

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Abstract. Exceptionally high concentrations of Cd (100 to 200 ppm dry weight) were found in samples of *Halobates* collected off Baja California. In contrast, no detectable Cd was found in *Rheumatobates* collected from mangrove lagoons in the Gulf of California. Concentrations of five other heavy metals in the two marine insects are also presented.

1. Introduction

Measurements of heavy metal or trace element concentrations in various marine organisms abound in the literature (Goldberg, 1972). However, since it is often difficult to obtain samples containing only a single species of zooplankton for such determinations, most of the published data on these organisms are based on mixtures consisting predominantly but not exclusively of copepods, euphausiids, etc. In such samples one has always to consider the possibility of contamination by flakes of paint, in which Cd, Fe, and Pb are often major components. We report here exceptionally high concentrations of Cd found in the sea-skater *Halobates* collected off the coasts of Baja California.

Halobates is unique in being the only insect found in the open ocean and the only marine invertebrate which lives on, rather than above or below, the sea-air interface (Cheng, 1973, 1974). The special habitat of these insects enables us to sample a single species, free from other organisms. In nature, these insects, which live above the water surface, normally keep their surfaces clean and dry by preening. Since various trace metals are known to be concentrated at the sea-air interface (Duce *et al.*, 1972), we collected and analyzed several samples of *Halobates* to find out to what extent, if any, their trace metal concentrations reflect those of their environment. For comparison we also analyzed samples of a related gerrid, *Rheumatobates*, collected from mangrove swamps. Each of the insect samples has been analyzed for 25 major, minor and trace elements; however, data for only six selected trace metals will be discussed here.

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2. Materials and Methods

Samples of *Halobates* were collected off the southern end of the Gulf of California during an expedition of the R/V ALPHA HELIX. Two of the stations were outside the Gulf, just off the tip of Cape San Lucas; the third station was inside the Gulf. Handling of the insects was kept to a minimum. Contact with metal instruments and containers was avoided. The insects were dip-netted with a nylon net, kept alive in a glass aquarium onboard for two days, and then flown back to the laboratory at UCLA in individual 'Whirl-Pak' plastic bags. To prevent their desiccation, a piece of filter paper moistened with seawater was placed in each bag. On arrival at the laboratory the insects were transferred to a glass aquarium and kept overnight. On the following day, live insects were used in various physiological experiments which will not be discussed in this paper. Those insects that had died were dried at 80°C overnight; whole insects were then analyzed for trace elements by using an optical emission spectrometer system specially designed for the multielement analysis of biological tissues. Confidence in the accuracy of the spectrometric analysis was established by analyzing the Standard Reference Materials 1577 (orchard leaves) and 1571 (bovine liver) provided by the U.S. National Bureau of Standards. Agreement was within 10% of the certified values.

Other samples of *Halobates* dip-netted or collected in neuston nets from the north Pacific Ocean during expedition Southtow 13 on the R/V WASHINGTON, and of *Rheumatobates* dip-netted from mangrove swamps in Baja California during expedition Sea-Skater 1 on the R/V DOLPHIN, were also analyzed. The sampling locality, date, and species collected are given in Table I.

TABLE I
Sampling data of Halobates and Rheumatobates used in elemental analyses

Halobates sobrinus	
H 1–3:	Mixed adults dip-netted between 23°10′N 109°17.4′W, and 23°27.9′N 109°23.9′W, Gulf of California, Baja California, Mexico. November 1, 1974.
Halobates sericeus	
H–4:	24 females dip netted at 28°8.7′N, 155°13.6′W, about 700 km north of Hawaii, February 5, 1973.
H–5:	10 males, data as above.
H–6:	28 females collected in neuston tow, 28°7.8′N, 155°6.9′W, about 3500 km west of San Diego, February 6, 1973.
H–7:	21 males collected in neuston tow, 31°36.3′N, 128°43′W, about 1000 km west of San Diego, February 18, 1973.
Rheumatobates aestuarius Polhemus	
R–1:	Mixed nymphs collected from mangrove swamp, Isla San Jose, Baja California, April 6, 1973.
R–2:	Males collected from mangrove stream, San Gabriel Bay, Isla Espiritu Santo, Baja California, April 1, 1973.
R–3:	Females, data as above.
R–4 & 5:	Mixed nymphs and adults collected from mangrove swamp, Isla San Jose, Baja California, March 3, 1975.
R–6 & 7:	Mixed nymphs and adults collected from mangrove bay, Bahia Falsa near La Paz, Baja California, March 12, 1975.

3. Results

Cadmium values for *Halobates* collected off the Baja California coast were in the range of 99 to 208 ppm dry weight, with a mean of 152 ppm. Cadmium concentrations were much lower in *Halobates* collected from the north Pacific Ocean, with a mean value of 66 ppm. There was much less between-sample variation in the Cd values (51 to 78 ppm) among the north Pacific *Halobates* samples, although they were collected by two different methods and are of different sexes and from widely separated locations (see Table I).

The variations observed among samples H–1, H–2 and H–3 can perhaps be attributed to their different origins in the Gulf of California waters. [In zooplankton samples from that area, Martin and Broenkow (1975) detected rather different levels of Cd in stations several miles apart.] Unfortunately, in our analyses the insects from the three different stations had not been kept separately. There was no difference in Cd content between samples H–4 and H–5, which consisted respectively of females and males from the same location. There was no detectable amount of Cd in the *Rheumatobates* samples except for sample R–6, which also had concentrations of Fe and Zn much higher than the other three samples.

The contents of Cd, together with those of Cu, Fe, Pb, Ni and Zn, are summarized in Table II.

The toxicity of Cd to various organisms, including man, is well known and will not be reviewed here (Nilsson, 1970; Shigematsu and Hasegawa, 1971). In normal seawater, Cd concentrations rarely exceed 1.0 $\mu g\ kg^{-1}$ (Goldberg *et al.*, 1971; Riley and Taylor, 1972), but this value may be exceeded as a consequence of industrial pollution, either via the atmosphere or via sewage or industrial outfalls. It has been shown that about 50% of the total input of Cd into the Southern California coastal region is from atmospheric washout, and that up to 90% of the Cd input into the ocean may remain in the water column (Bruland *et al.*, 1974). Values of Cd in inshore surface seawater were almost always 10 times higher than in offshore waters (Knauer and Martin, 1973).

For most marine plankton, Cd values recorded are below 10 ppm (10 $\mu g\ g^{-1}$ dry weight) (Martin and Knauer, 1973), and values measured in the tissue of edible shrimps etc. did not generally exceed 1 ppm dry weight (Robertson *et al.*, 1972). Martin and Broenkow (1975) obtained values up to 21 ppm Cd for plankton samples collected off the Baja California coast.

The range of values for Cu found in other marine invertebrates is quite large, but in the majority the normal range for edible tissue is 1 to 10 ppm (Robertson *et al.*, 1972). Analysis of mussel, starfish, limpet etc. suggest that the upper end of the range for non-hemocyanin related tissues is about 100 ppm. Our values for the swamp-living *Rheumatobates* (65 to 130 ppm) are rather higher than for the oceanic *Halobates* (44 to 94 ppm). To what extent this may be related to the inshore nature of the habitat or to differences in the physiology of the insects is not known.

The Fe concentrations in all of the samples of the two species are fairly close to one another in mean values, but there is quite a lot of variation among samples:

TABLE II

Concentrations of selected trace metals in parts per million dry weight of tissue

Species	Sample No.	Dry weight (mg)	Cd	Cu	Fe	Pb	Ni	Zn
Halobates sobrinus	H–1	5.1	148	52	331	5	24	153
	H–2	5.2	99	44	200	11	16	127
	H–3	1.6	208	54	337	14	15	247
		MEAN	152	50	289	10	18	176
Halobates sericeus	H–4♀	5.5	67	94	289	7	11	287
(lipid-free sample)	H–5♂	4.3	67	77	303	20	11	346
	H–6♀	5.5	78	85	414	16	10	302
Total lipid = 40% dry wt.†	H–7♂	6.0	51	45	181	6	10	238
		MEAN	66 (40)*	75 (45)	297 (178)	12 (7)	11 (7)	293 (176)
Rheumatobates aestuarius	R–1	4.2	**	79	281	12	11	300
(lipid-free sample)	R–2♂	4.0	**	109	341	**	9	258
Total lipid = 24% dry wt.†	R–3♀	5.2	**	65	182	**	5	220
		MEAN	—	84 (64)	268 (204)	—	8 (6)	259 (197)
Rheumatobates aestuarius	R–4	5.2	**	130	137	**	5	98
	R–5	3.9	**	121	184	**	8	98
	R–6	5.9	7	130	430	**	**	130
	R–7	7.7	**	74	146	**	**	95
		MEAN	—	114	224	—	—	105

* No. in brackets are concentrations/dry weight corrected for lipids extracted.
** Less than 5 ppm Cd, less than 2 ppm Pb, less than 1 ppm Ni.
† As far as we know the heavy metals are not extractable by lipid solvents.

Rheumatobates (137 to 430 ppm), *Halobates* (180 to 414 ppm). The values of Fe in euphausiids and shrimps given by Robertson *et al.* (1972) were mostly below 40 ppm. However, the normal range of values found for the soft tissues of mussels, starfish, limpets, abalones etc. is 5 to 300 ppm on a dry weight basis.

Values of Pb in marine organisms measured are usually under 10 ppm. Our values for *Halobates* (5 to 20 ppm) are within this range. It is interesting to note that this metal was detected in only one of the seven *Rheumatobates* samples (12 ppm).

There is considerable variability in the concentrations of Ni measured in various marine organisms. Our measurements fall within the usual range of 1 to 20 ppm: *Rheumatobates* (5 to 11 ppm), *Halobates* (10 to 24 ppm).

Values of Zn as high as 14 000 ppm in dry tissue have been reported for the Eastern Oyster. More normal values in marine invertebrates such as mussels, starfish, limpets, euphausiids, etc. seem to be between 40 to 150 ppm of dry tissue. The values observed for *Rheumatobates* (95 to 300 ppm) and *Halobates* (126 to 346 ppm) are slightly above this normal range.

4. Discussion

On the whole, the trace element contents in these sea-skaters appear to be higher than those reported for marine organisms in general. Our Cd concentrations indicate the same trend as those observed in some mixed plankton samples analyzed by Martin and Broenkow (1975); 2 to 5 ppm in North Pacific and about 10 to 20 ppm in Baja California coastal samples. The values we obtained for *Halobates,* 66 and 152 ppm respectively, are of particular interest as they are more than ten times as high as the highest values observed in any other marine invertebrates.

The sea-air interface is one of the most poorly known of marine environments, although in some ways it is perhaps the most important layer of the ocean since many of the major pollutants in the marine environment reach the ocean via the atmosphere (Duce and Hoffman, 1972). One of the main reasons for our poor understanding of this interface is the difficulty of obtaining uncontaminated samples large enough for various chemical determinations. Fortunately, modern techniques have considerably reduced the amounts of biomass needed for such analyses. The present study indicates that *Halobates* is probably capable of concentrating some of the trace metals, notably Cd, that are under intensive investigations from an environmental health standpoint. If indeed *Halobates* is able to concentrate Cd in proportion to the concentration of this metal in seawater, or at the sea-air interface, then its rather large body size (up to 5 mm in length, weighing about 4 mg per individual), and the ease with which single-species samples can be obtained without contamination, might make it a useful indicator organism for trace metal studies.

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