

TITLE OF RESEARCH

Heavy metal concentrations in the ocean-surface film, as indicated by the  
sea-skater Halobates.

## SUMMARY

Certain organic compounds and heavy metals are known to be concentrated at the sea-surface film, but their concentrations in the film are technically difficult to measure. Sea-skaters (Halobates spp.), the only insects that live on the open ocean and the only invertebrates to spend their entire lives at the sea-air interface, have been found to accumulate heavy metals, presumably derived largely from the surface film on which they live. Since sea-skaters are widely distributed in the tropical waters of the World's oceans, and since clean, single-species samples are relatively easy to collect, analyses of Halobates may help us to derive distribution maps of certain heavy metals in tropical ocean surface waters.

During the past year, we have analysed 844 samples of Halobates, selected from a total of 1,260 surface tows. Of these, 293 were from the Atlantic Ocean, collected in an area between 40°N to 40°S. The rest were from the Pacific Ocean, the majority from the eastern half; only about 50 samples were from the western Pacific. All the Atlantic samples have been analysed for Cd. The Pacific samples have been analysed for 25 elements, including Zn, Cu, Mn, Ti, Ni, Cr, Pb and Cd. So far, only the Cd data for the Atlantic Ocean have been examined in any detail. It's concentrations range from 3 to above 300 ppm (dry weight) and high values came mostly from samples collected from the equatorial regions or near-shore areas. The ranges for the other metals are as follows (all in ppm dry weight) : Zn: 22 - 15,000, Cu: 18 - 4,891, Mn: 0.2 - 1,120, Ti: 0.6 - 1,120, Ni: 0.5 - 254, Cr: 0.2 - 117 and Pb: 1.3 - 4,529. From 10 to 25% of the samples

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have rather high metal concentrations and most of them originating from areas of upwelling (e. g. , off the equatorial west coast of Africa), or with known mining activity (e. g. , around New Caledonia).

In the coming year I will analyse the heavy-metal data in further detail. Since we are dealing with several hundred samples, each with data for 25 elements, we need to use a computer program to develop correlation analyses. I already have a computer program for plotting the distributions of the various species of Halobates. This program is to be modified for and to help with plotting distributions, analysing variations, and seeking correlations of the heavy metals in the ocean surface as indicated by their concentrations in Halobates. Secondly, I will try to obtain samples for areas from which data are now lacking. Lastly, I plan to carry out heavy-metal uptake experiments with the collaboration of Dr. M. Schulz-Baldes (Marine Research Institute, Bremerhaven, W. Germany) at the H. Steinitz Marine Biology Laboratory at Elat, Israel, using methods we employed during a previous experimental study at the Galapagos Islands.

## ABSTRACT

Certain heavy metals and organic chemicals are known to be concentrated at the sea-surface film. The magnitude of their concentration, over that of the seawater column below, has not been easy to measure because it is technically difficult for us to sample the surface film. Halobates, however, does this. This insect, which is unique in being the only organism known to live entirely at the sea surface, has been shown to concentrate certain heavy metals. The purpose of this project is to relate the heavy-metal concentrations found in Halobates with those of the surface water on which they live. Since this insect can be collected fairly easily, free from contaminants such as other animals and debris, it may prove to be <sup>an</sup> useful biological tool for studies of the sea-air interface.

Preserved single-species samples of Halobates, collected during the past few years, were analysed for either Cd alone (with an atomic absorption spectrophotometer) or for 25 elements (with the optical emission spectrometer system). We thus have measurements for Zn, Cu, Mn, Ti, Ni, Cr, Pb, Cd, and several other heavy metals. During the next year, data from the elemental analyses will be entered into the computer bank so that it will eventually be possible to map the world distributions and seasonal variations in heavy-metal concentrations of Halobates, and to relate the levels of heavy metals found in these insects with those of surface seawater (as recorded in the literature) or other oceanographic factors.

It is also of importance to determine the sources of the Cd and other heavy metals found in Halobates. Do these insects obtain them mainly from



their zooplankton food, from atmospheric fallout, or from seawater by drinking? In short-term Cd-uptake experiments carried out with an inshore Halobates species, H. robustus, we have shown that uptake from seawater is a much more important route than incorporation from food. We would like to carry out more extensive and definitive experiments with several other heavy metals on an oceanic species, to determine the relative inputs from different sources, and thereby indirectly to estimate the heavy-metal concentrations in the uppermost sea-water layers from which these insect drink.

#### LONG RANGE OBJECTIVES

The samples of Halobates used in this project were obtained from large areas of the Atlantic and the Pacific Oceans. Using the data we obtained in this way, we shall draw "world-wide" distribution maps of some heavy metals (e. g. , Zn, Cu, Mn, Ti, Ni, Cr, Pb, and Cd) and identify "hot spots" where concentrations of these metals are exceptionally high. Eventually we plan to relate the concentrations of these elements to certain chemical or physical peculiarities of the ocean surface waters.

## PROGRESS DURING THE PAST YEAR

During the past year, specimens of Halobates from 957 tows taken in the Pacific and 251 tows taken in the Atlantic Oceans have been examined and categorised. All five oceanic Halobates species (H. micans, H. sobrinus, H. sericeus, H. germanus and H. splendens) were present. A total of 371 Pacific and 179 Atlantic tows were chosen for heavy-metal analyses; the others contained too few insects (less than five) for our purpose. The larger samples were separated into sub-samples according to developmental stages or sex; in all about 850 sub-samples were analysed.

The Atlantic samples were collected on two separate cruises from an area roughly between  $40^{\circ}\text{N}$  and  $40^{\circ}\text{S}$ . 267 sub-samples were analysed only for Cd. All the Halobates specimens from this area contained Cd at levels ranging from about 5 to over 300 ppm (dry weight). The distributions of Cd in the samples are presented in figures 1 and 2. The indicated values are the mean Cd concentrations for 2 to 11 sub-samples from one or several nearby stations. Samples taken near the equator, Ascension Island and certain nearshore stations (e.g., off Florida, Colombia and Venezuela) generally had much higher Cd concentrations (more than 20 ppm) than the others. The high equatorial values shown in figure 1 may be typical of low latitudes, but we cannot generalise until we can compare these with comparable samples from the eastern equatorial region and from the North and South Central Gyres.

The remaining 577 sub-samples were analysed for 25 elements, including Mg, Zn, Cu, Fe, Mn, Al, Si, Ti, Co, Ni, Mo, Cr, Ag, Sn, Pb, and Cd. The majority of these samples (about 90%) came from an area in the eastern Pacific

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between  $40^{\circ}\text{N}$  and  $30^{\circ}\text{S}$ , extending from the American coast to about  $160^{\circ}\text{W}$ . Only about 50 samples were collected in eastern longitudes.

Since we have only just completed the heavy-metal analyses (July, 1979), it has not yet been possible to analyse in any detail the information accumulated. The most efficient way of dealing with such information (25 values for each of the 577 samples) is with the help of the computer; we hope to do this in the ~~Spring~~ coming year. We present here only a general discussion of the concentration ranges for eight heavy metals which present known biological hazards or which are important by reasons of anthropogenic input into the oceans.

The ranges, estimated median values, and percentages of samples with heavy-metal concentrations more than twice the median value are presented in Table 1. It can be seen that there is tremendous range variation for each metal, and we cannot offer simple explanations for the extremely high values. Although much care was taken in preparing the samples for these heavy-metal analyses, we cannot exclude the possibility that fine aerial dust particles (less than 10  $\mu\text{m}$  in diameter) entangled among the fine body hairs of these insects constituted a major source of mineral contamination.

The estimated median values for all these metals were in the same range as those found in other marine invertebrates, except for Pb (75 ppm). However, from 10 to 25 % of the samples contained heavy-metal concentrations more than twice as high as these values. The Zn concentrations ( in ppm dry weight) of samples from three different cruises of the Pacific Ocean are presented in Figures 3 and 4. The Zn values from the eastern tropical Pacific are generally low( below 300 ppm) except for a few stations along the  $126^{\circ}\text{W}$  parallel between  $15^{\circ}$  and  $20^{\circ}\text{N}$ . Data from figure 4 showed extremely high Zn values (above 5,000 ppm) in areas around Hawaii, Guam, Taiwan, and the Philippines. These high ~~box~~ values may be associated with concentrated shipping or human activities. The somewhat less high values (1,000 to 2,000 ppm) found around New Caledonian waters are probably associated with the nickel mining in that area. These initial results clearly showed that elemental analyses of Halobates can be useful indicators of heavy metals in ocean surface waters.

## PROPOSED RESEARCH

I now have elemental analyses for about 550 Pacific Halobates samples and 300 Atlantic samples. This is probably the most extensive collection of heavy metal analyses for any single-species marine organism on a world-wide basis. Although the distributions of Cd in the Atlantic samples have been examined, it has not yet been possible to examine in any detail the distributions of the 25 elements in the Pacific samples. I therefore plan (1) to carry out detailed analyses of these data in the coming year, (2) to analyse additional samples from other areas, and (3) to study heavy metal uptake by Halobates experimentally in the field.

(1) Since we have data for 25 elements for each of the Pacific samples, the most efficient way to study them is to use the computer. I already have a computer program for plotting the distribution of Halobates, and, with the help of the programmer (John Ott of the Shipboard Computer Group, SIO), I plan to adapt it to analyse the data element by element. We will pay particular attention to the following elements : Zn, Cu, Mn, Ti, Ni, Cr, Pb, and Cd. Attempts will be made to study the general world-wide distribution, <sup>and</sup> /seasonal and regional variations of each metal. We will also try to determine whether high levels of certain metals are inter-related and whether they can be correlated to levels of non-toxic elements, such as P, K, or Ca. When the analyses are completed it should be possible to draw some definite conclusions on the relationships between high concentrations of some heavy metals in the insects and specific physical or chemical oceanographic features of the water on which they occur.

(2) In addition to analysing the accumulated data, attempts will be made to obtain samples from areas from which we have no data so far. I have another 500 Halobates samples, mostly from the Pacific Ocean, that can be used for further analyses as soon as they have been identified to species and stages. For similar heavy metal analyses, I am also expecting to receive more samples that are being collected during the round-the-world "Operation Drake" expedition, and the NORPAX equatorial shuttle program.

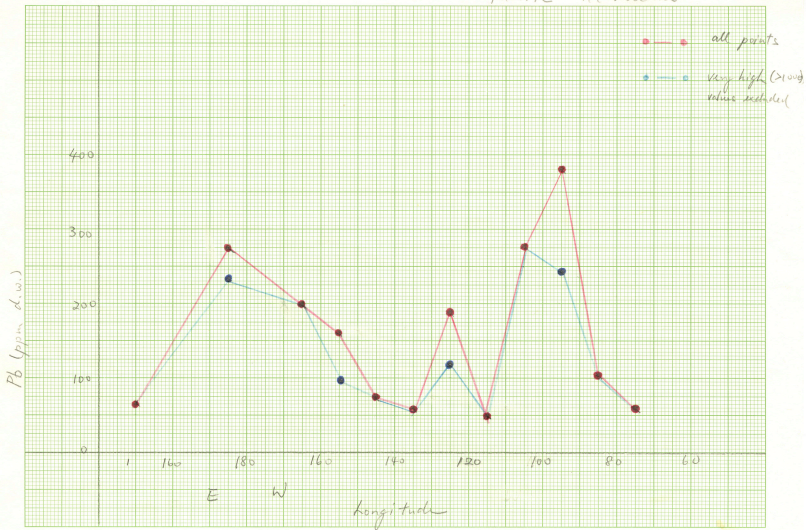
(3) It is also necessary to determine the sources of these heavy metals in Halobates, i. e. , whether they were accumulated through the food-chain, or from atmospheric fallout, or by drinking seawater. Halobates feeds by sucking fluids, so it takes up only elements located in the soft tissues or the haemolymph of the prey organisms. It has been found in studies on several zooplankton species by other workers, that heavy metals are generally concentrated in the cuticle or exoskeleton; thus very little would be available to Halobates feeding on them. Results from some short-term studies on uptake of Cd by the nearshore species H. robustus have shown that more Cd is taken up from seawater than from food (see Cheng et al. , 1979). We would like to carry out further uptake experiments of this sort with oceanic species of Halobates. Results from such studies might allow us to estimate the concentrations of Cd and other heavy metals in surface seawater by determining their contents in Halobates. Dr. M. Schulz-Baldes (Marine Research Inst. , Bremerhaven, W. Germany) will collaborate with me on these uptake studies. We have chosen to work at the H. Steinitz Marine Biology Laboratory at Elat, Israel, since we know that an oceanic species, H. germanus, occurs in the Gulf of Aqaba nearby, and, for this kind of research, there are excellent facilities available at that laboratory.

Table 1. Concentrations of heavy metals ( in ppm dry weight unless otherwise mentioned) : ranges, estimated median values, and percentages of samples with more than two times the median values.

Metal	Range	Median	% with $\geq 2X$ median
Zn	22 - 1.5%	150	15.0
Cu	18 - 4891	100	23.5
Mn	0.2 - 1120	15	14.8
Ti	0.6 - 1120	8	16.0
Ni	0.5 - 254	8	19.5
Cr	0.2 - 117	3	11.7
Pb	1.3 - 4529	75	22.1
Cd	$< 3$ - 208	3	9.4

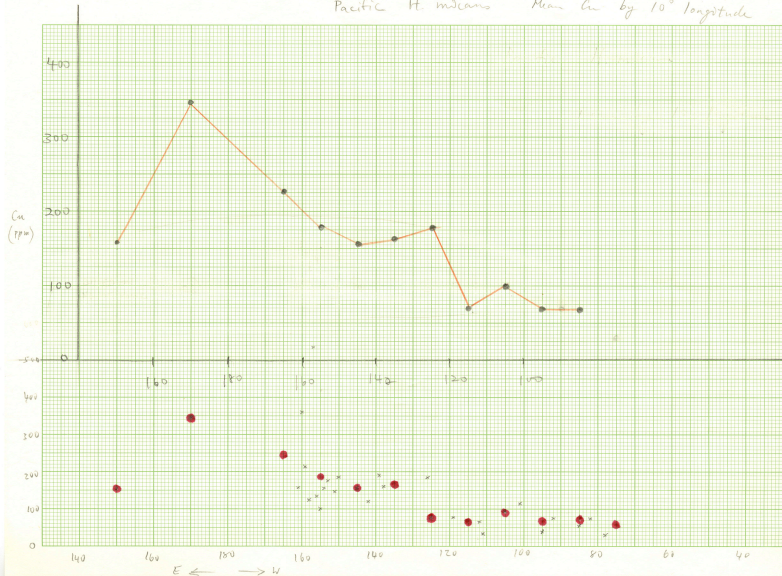


# Pacific H. mearns

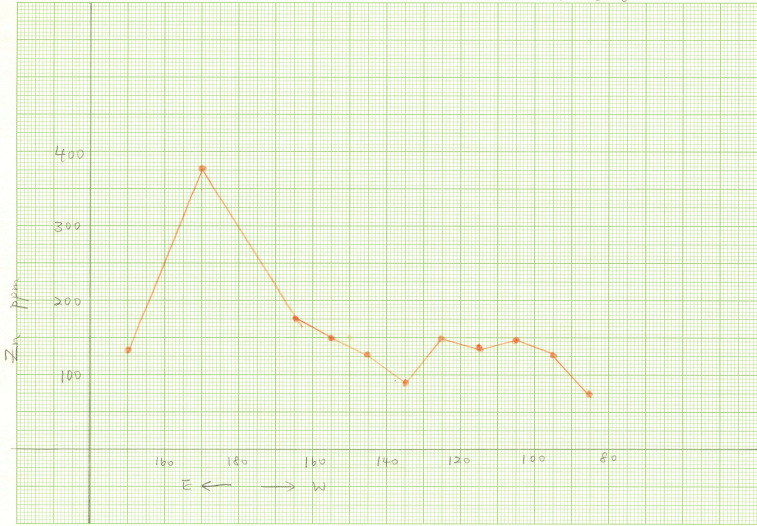




Pacific H. Indians Mean Cu by 10° longitude



Zn Pacific H. mearns



H<sub>2</sub> Pacific Ocean  
 H. mearnsi

mean H<sub>2</sub> ppm d.w.

