UPTAKE, ACCUMULATION AND TOXICITY OF VANADIUM AND TIN IN MARINE ORGANISMS

by

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1. INTRODUCTION

During recent years, chemical contamination of man's environment has caused growing concern. Much of this concern has revolved about the effects of metals on marine organisms, because the salts of various heavy metals and other potentially hazardous materials are discharged in ever-increasing amounts into the marine environment from different sources (Goldberg, 1976) as they find their way into commercial and industrial application.

Since certain heavy metals are essential for life, they are concentrated in marine organisms. The invertebrates appear to have a particularly high capability for concentrating metals, when they filter plankton during feeding (Waldichuk, 1974). Because of the ability of many metals to form complexes with organic substances, there is a tendency for them to be fixed in the tissue and be incorporated in the structure of organic compounds (i.e. proteins and enzymes) and thus, not to be excreted.

Vanadium enters the ocean principally through atmospheric fallout and man's activity and this input in the marine environment has led to the enrichment of this metal in marine waters (Bertine and Goldberg, 1971; Grange, 1974; Duce and Hoffman, 1976). Once in the sea, vanadium may be rapidly solubilized (Walsh and Duce, 1976) or it may sink with the particulates eventually reaching deep-sea sediments. Thus, a number of investigators have reported its existence in sediments (Hopkins et al., 1973; Loring, 1976). Vanadium exists also in petroleum (Zoller et al., 1973) and in industrial effluents. As an example, 710 kg of vanadium per day was discharged to the sea in the acid effluents of a factory producing titanium dioxide (Grange, 1974).

Despite numerous studies on the concentration of vanadium in marine organisms (Nicholls et al., 1959; Fukai and Meinke, 1962; Pesch et al., 1977) with most emphasis being placed on certain species of ascidians which have an ability to concentrate this element to remarkable high levels (Goodbody, 1974; Ladd, 1974; Kustin et al, 1975), a limited number of investigations were carried out on its toxicity in marine organisms (Unsal, 1978; Miramand and Unsal, 1978) and its transfer within the food chain (Unsal 1978, 1978a, 1982, 1983).

Tin was one of the first metals used as a protective coating for steel and other alloys (Hallas et al., 1982). Organotin compounds have been incorporated into such preparations as insecticides, herbicides and fungicides (Zuckerman et al., 1978).

We report here the results of experiments conducted to examine the accumulation of tin by mussels and the accumulation and transfer of vanadium through a neritic and a benthic food chain.

2. MATERIAL AND METHODS

Different experimental designs were used to study the bioaccumulation of vanadium and tin.

Bioaccumulation of tin

Brachidontes variabilis (Krauss) was selected for this study. The organisms were acclimatized to laboratory conditions prior to the initiation of the experiments. Following this acclimatization period the mussels were distributed amongst four glass

aquaria, each containing 8 l of sea water and each being aerated continuously. Experiments started with 30 organisms in each aquarium. In the first aquarium, organisms were maintained in a medium containing 100 $\mu g\ l^{-1}$ Sn (as $SnCl_4$) while in the second and third, they were subjected to 250 and 500 $\mu g\ l^{-1}$ Sn respectively. The fourth aquarium, without added tin, served as control. Experiments lasted 30 days and during this period, the sea water was changed daily and after each change, tin was added from a stock solution containing 1000 mg l^{-1} $SnCl_4$ in distilled water. Six contaminated and six control mussels sampled at time intervals of 3, 7, 14, 21 and 30 days were deep-frozen pending analyses.

Analyses of samples

Samples were analysed by a Varian Techtron AA6 Atomic Absorption Spectrophotometer. The analytical procedure was described by Tugrul (1982) and by Unsal (1984).

Bioaccumulation of vanadium

The polychaete Nereis diversicolor, the crab Carcinus maenas and the fish Scorpaena porcus were used for these studies.

Prior to experiments, all test organisms were acclimatized to laboratory conditions. Following acclimatization the annelids (N.diversicolor) were placed in three tanks (2000 worms per tank) containing 40 l of sea water each and equipped with a continuous aeration system. The sea water was changed every day and after each change, vanadium (sodium metavanadate) was added to the medium to bring the vanadium concentration up to 500 $\mu g\ l^{-1}$. Experiments were conducted for 7 days, during which time the annelids were not fed. A control tank was prepared separately and maintained under identical conditions.

The same experimental conditions were employed for crabs and fish as for the annelids. The crabs and fish were placed in tanks (15 individuals per tank) containing 40 l of sea water and fed on vanadium-rich Nereis diversicolor (4 Nereis per day per individual). After 15 days' exposure to contaminated food (Nereis diversicolor), all test organisms were removed and deep-frozen for further analyses.

Analyses of samples

Samples were analysed with a Perkin-Elmer model 300 SG Atomic Absorption Spectrophotometer (AAS) equiped with a deuterium background corrector and a HGA-7 heated graphite atomiser. The analytical procedure was previously described in detail (Unsal, 1978, 1978a).

3. RESULTS

Tables I-III show the mean concentrations of tin and vanadium measured in the mussels, in the tissues of the animals used in the two experiments.

Table I.

Metal uptake in soft tissues of Brachidontes variabilis (ng g^{-1} wet wt.) at the outset and after a 30-day accumulation period.

Tin concentration in medium	Tin concentration in soft tissues (ng g^{-1} wet wt.)		
	% of dry wt.	Day 0	Day 30
0 (control)	12.4 ± 1.8	14	19
100 $\mu g\ l^{-1}$		15	641
250 $\mu g\ l^{-1}$		13	298
500 μg		14	382

Table II.

Concentration of vanadium in organisms of the neritic food chain (μg^{-1} g dry wt.)

	Control (without V added)	Contaminated organisms (exposed to 500 μg V l^{-1})
Annelids after 7 days	4,86	9,90
Crabs after 15 days	2,41	6,64

Table III.

Concentration of vanadium in organisms of the benthic food chain (μg^{-1} g dry wt.)

	Control (without V added)	Contaminated organisms (exposed to 500 μg V l^{-1})
Annelids after 7 days	4,86	9,90
Fish after 15 days	Gills 9,47 Liver 2,00 Muscle 0,49	Gills 7,63 Liver 1,58 Muscle 0,70

After the 30-day accumulation period, the highest tin concentration was observed in organisms exposed to lowest (100 $\mu g\ l^{-1}$) external concentration. In this group, a slight increase was observed with time (Fig. 1 A). The accumulation pattern was similar in both the 250 and 500 $\mu g\ l^{-1}$ groups (Figs. 1 B and C).

The vanadium concentration in the contamined crabs, was calculated to be approximately 3 times the controls (Fig. 2).

In contrast to crabs no accumulation was observed in the tissues of fish, except the muscle, where there was a slight accumulation (Fig. 3).

4. DISCUSSION

The results showed that in all test groups, except controls, tin was accumulated in significant amounts by mussels. We suggest that this accumulation resulted mainly from two sources: the water and the food. The relative importance of these two sources has been previously investigated (Unsal, 1978 a). There are also other mechanisms involved in the accumulation of heavy metals. Delhaye and Cornet (1975), studying the effect of copper on Mytilus edulis during its reproductive period, observed that the spawning period was accompanied by an acceleration of copper uptake. Since, at this time, the animal's metabolism is very high and removal of water caused by ventilation of gills is rapid, so is the copper accumulation. During dissection, we found most mussels, removed in April and in May, to contain ripe eggs, thus proving that Brachidontes variabilis spawns during these months. We therefore suggest that this spawning was a contributory factor to accumulation of tin in mussels.

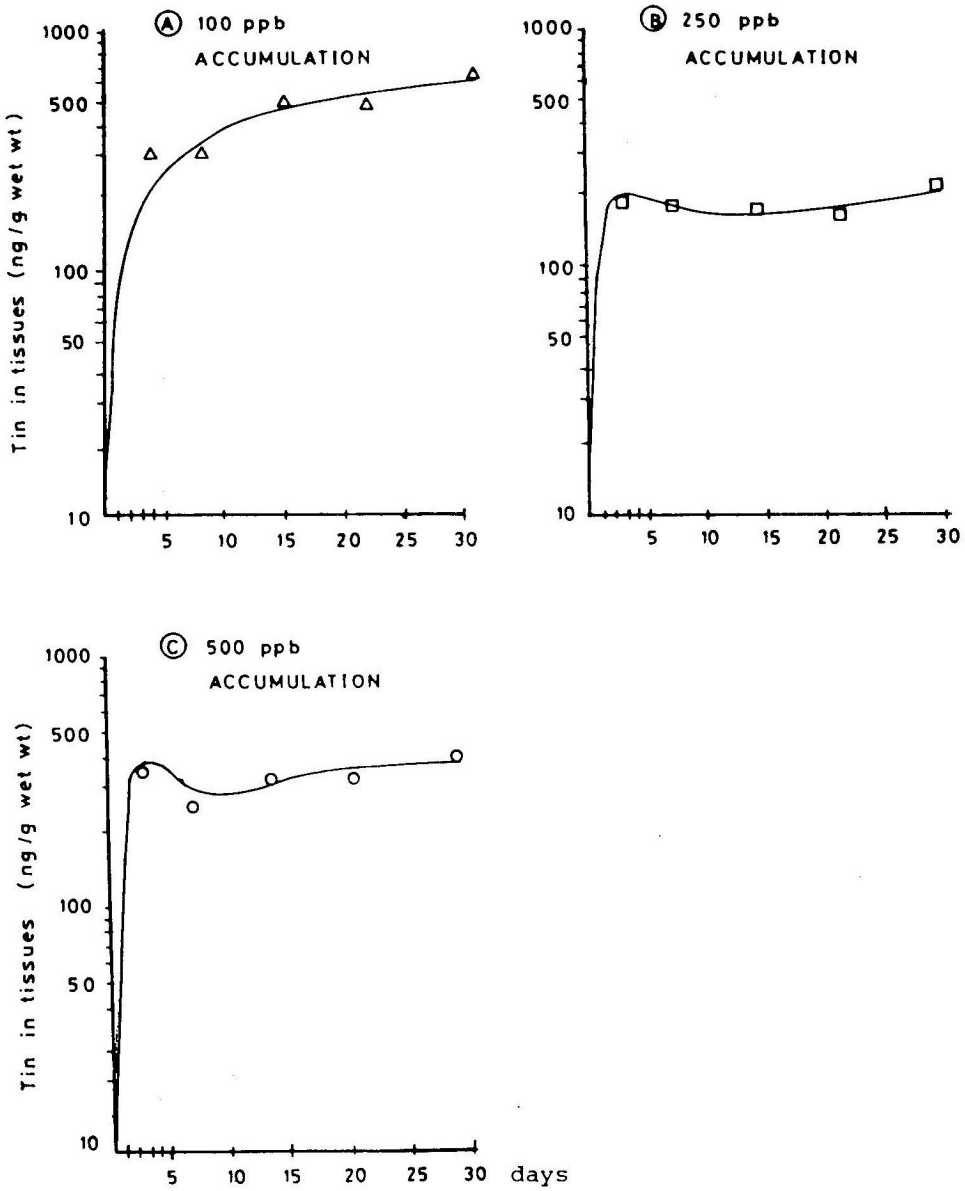

Figure 1. Accumulation of tin in soft tissues of Brachidontes variabilis at different test concentrations and as a function of time.

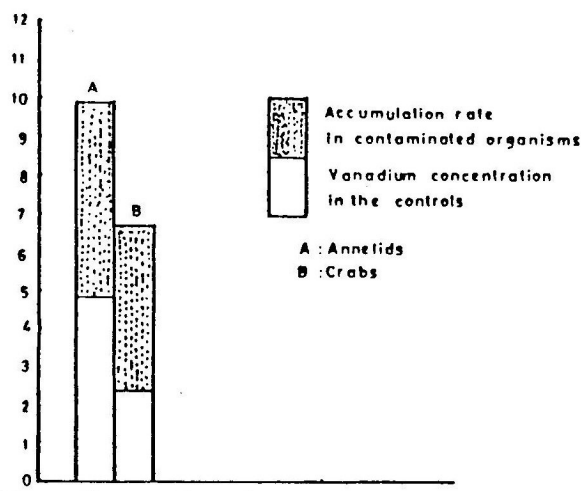

Figure 2. Accumulation of vanadium in different steps of neritic food chain.

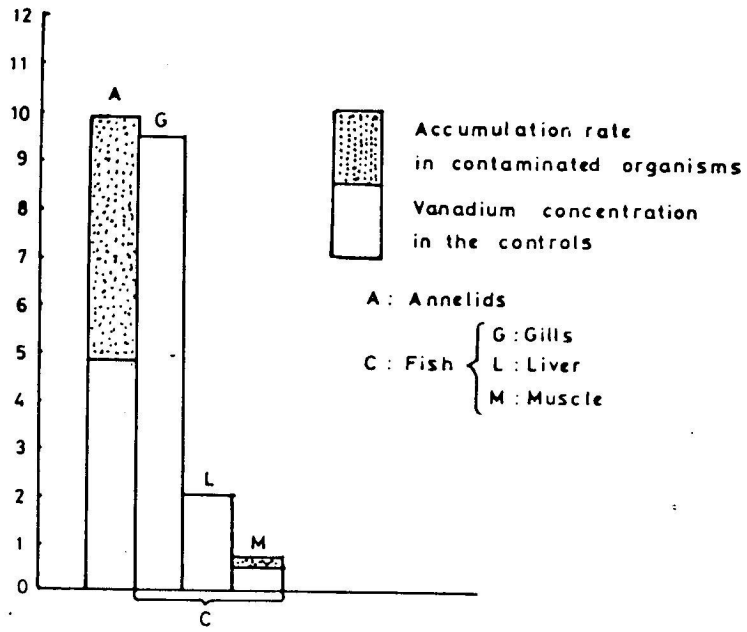

Figure 3. Accumulation of vanadium in different steps of benthic food chain.

The accumulation of tin decreased with increasing tin concentration in the medium as was observed by Bryan (1971) for zinc and by Miramand et al. (1980) for vanadium.

We suggest that the high tin concentrations exert a stress effect and this effect brought about changes in animal's physiology (in filtration rate, in respiration etc.). Therefore the uptake of tin was higher at low concentrations than at high concentrations.

The vanadium concentration in contaminated annelids was double that of the controls. We suggest that an adsorptive process is involved in the bioaccumulation of this element from water. Bryan and Hummerston (1973) have a similar suggestion, that the rate at which Zn was absorbed by Nereis diversicolor is proportional to the degree of adsorption at the surface of the body.

The accumulation of vanadium was significant in crabs. Thus a biomagnification was observed. Because the organisms were fed on vanadium-rich food and maintained in contaminated medium, the uptake took place from two sources. The relative importance of these two sources was demonstrated in a previous study (Unsal, 1983).

Although biomagnification was observed at the second step of the neritic food chain, the transfer of the vanadium was insignificant in the benthic chain. Amongst the tissues analysed, the gills contained the highest vanadium concentration which leads us to the conclusion that most of the metal accumulated in fish was taken up not from food, but from water.

A similar result was reported by Bouquegneau and Noël-Lambot (1977) who studied the accumulation of mercury from water and from food by Merlangius merlangus and by Gadus morrhua. They reported that 85 % of mercury was taken up from water by gills and only 15 % from food.

5. CONCLUSION

Tin and vanadium were taken up in significant amounts from the water by mussels and annelids. Tin uptake decreased with the increase in external concentration. By the end of a 30 days accumulation period, the tin concentrations increased about 35 fold in the 100 $\mu g\ l^{-1}$ group compared to controls. This shows that tin was accumulated in significant amounts by Brachidontes variabilis from its environment, although the tin concentration was 10,000 times greater than that found in unpolluted sea water. This result allows us to suggest that Brachidontes variabilis can be used as an indicator organism of pollution by tin.

We demonstrated also the transfer and biomagnification of vanadium through a neritic food chain. The transfer was less pronounced in the benthic food chain, but it does not mean that vanadium will not be transferred in any other benthic chain. It is worth saying that biological food chains are advisable methods to study the bioaccumulation and specially the biomagnification of substances.

On the other hand, the biochemical studies should be done in order to follow the fate and behaviour of the pollutants in the body of organisms from their uptake to excretion.

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Papers presented at the FAO/UNEP

MEETING ON THE TOXICITY AND BIOACCUMULATION OF SELECTED SUBSTANCES IN MARINE ORGANISMS

Rovinj, Yugoslavia, 5-9 November 1984

prepared as part of the

Long-term Programme for Pollution Monitoring and Research in the Mediterranean (MED POL Phase II)

FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS

1986