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Transfer Pathways and Accumulation of Vanadium in the Crab *Carcinus maenas*

M. Ünsal

Middle East Technical University, Marine Science Department; P.K. 28 Erdemli, İçel, Turkey

Abstract

The transfer pathways of vanadium in *Carcinus maenas* (L.) were investigated from February to April 1978 in order to determine the role of the food and environmental medium in the accumulation of this metal. The crabs, purchased from a fish market in Nice, France, in February 1978, were contaminated by food (the polychaete *Nereis diversicolor*), by environmental medium, and by food plus medium. In the early stages (15 d) of contamination, the accumulation of vanadium was greatest in crabs exposed to the contaminated medium. In later stages (30 d) crabs exposed to contaminated food plus medium exhibited the highest accumulation. Very little accumulation was observed in crabs contaminated by food alone.

Introduction

The salts of various heavy metals and other potentially hazardous materials are discharged in ever-increasing amounts into the marine environment from mining operations, metal processing facilities, chemical industries and numerous other sources (McKee and Wolf, 1963; Goldberg, 1976).

Heavy metals in trace amounts are normal constituents of marine organisms (Bryan, 1971), but at sufficiently high concentrations they become toxic to these organisms and, therefore, it is important to know how much their concentrations may be increased above the normal level before effects on marine or estuarine populations are detectable or commercial species become unsuitable as food. Many investigators have worked on this subject (Ahsanullah, 1976; Eisler, 1977; Miramand and Ünsal, 1978; Ünsal, 1978 a).

The uptake of heavy metals by marine organisms mainly occurs in two ways (Bryan, 1971): (a) adsorption onto the body surface; or (b) adsorption from either the medium, the food, or ingested particles. The significance of the food and the medium in the accumulation of heavy metals by marine organisms has been studied by several investigators (Jernelov and Lann, 1971; Pentreath, 1972; Aubert *et al.*, 1976; Bouquegneau and Noël-Lambot, 1977; Ünsal, 1978 b).

In the present study, the transfer pathways and the accumulation of vanadium in *Carcinus maenas* (L.) was investigated using three food/medium combinations.

Materials and Methods

Test Organisms

The polychaete *Nereis diversicolor* and the crab *Carcinus maenas* (L.) were selected for this study:

Nereis diversicolor is useful as an indicator of environmental pollution by heavy metals (Bryan and Hummerston, 1971, 1973) and by domestic efluents (Bellan-Santini, 1968; Reish, 1972). It has a broad habitat, being able to tolerate waters covering a wide range of salinities (Smith, 1970). *N. diversicolor* can be sampled easily and is eaten by crabs.

Carcinus maenas also has a broad distribution area, and can be collected in great numbers. It consumes benthic organisms (e.g. annelids), and can be kept and fed easily in an aquarium. Furthermore, *C. maenas* is of commercial importance as an edible organism.

Carcinus maenas were purchased from a fish market in Nice, France, in February 1978 and were acclimatized to laboratory conditions for 2 wk. The studies were conducted between February and April 1978.

Contamination of Annelids

Prior to experiments, the annelids were acclimated for 1 wk to laboratory conditions. Following acclimatization,

the organisms were placed in plastic tanks (50 worms per tank) containing 5 litres of natural sea water and equipped with a continuous aeration system. The sea water was changed daily, and vanadium solution (as $NaVO_3$) was added after each change. The annelids were exposed to vanadium in 14 °C ± 1 C° sea water of 37.8‰ S for 7 d, during which time they were fed bacteria naturally existing in sea water. A control tank was prepared separately and maintained under identical conditions.

Contamination of Crabs

The same experimental conditions were employed for the contamination of crabs as for the annelids. Eight experimental groups of crabs weighing 18 ± 3.8 g wet wt were used. These were placed in 6 plastic tanks containing 5 litres of natural sea water, 3 individuals per tank (to ensure that each individual ate the same amount of food: 4 annelids crab^{-1} d^{-1}). Contamination of crabs was as follows:

(i) Two groups of 3 individuals each were fed on vanadium-rich *Nereis diversicolor* and maintained in vanadium-free sea water (Fig. 1: a)

(ii) Two like groups were fed on uncontaminated *Nereis diversicolor* and exposed to 0.5 ppm vanadium (as $NaVO_3$) per litre environmental sea water (Fig. 1: b)

(iii) Two further groups were fed on vanadium-rich *Nereis diversicolor* and exposed to 0.5 ppm vanadium per litre (Fig. 1: c).

A fourth groups, fed on vanadium-free food, was maintained in vanadium-free sea water as control.

Contamination periods of 15 and 30 d were employed to study the effect of time on the accumulation of the pollutant. After 15 and 30 d, three crabs from each series of two groups were removed, rinsed in vanadium-free sea water, and deep-frozen until analysis.

Sample Analysis

The whole crabs with shell were initially dried in a lyophilizer and digested in an acid mixture (1 $HClO_4$: 4 HNO_3). Digested samples were made up to 25 ml with distilled water, and then analysed with a Perkin-Elmer model 300 SG atomic absorption spectrophotometer (AAS) equipped with a deuterium background corrector and a HGA-7 heated graphite atomiser.

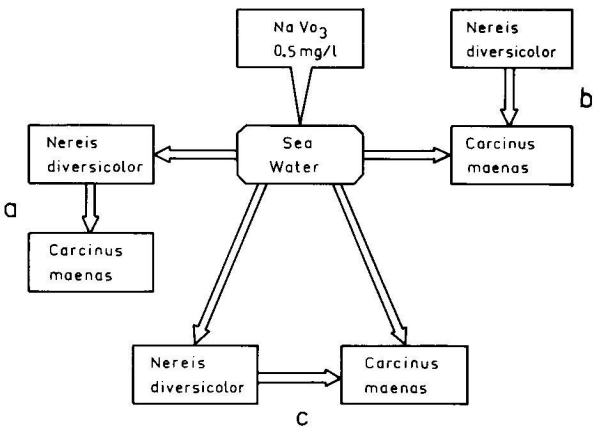


Fig. 1. *Carcinus maenas.* Vanadium contamination pathways used in experiments

Results

Tables 1–3 give the mean vanadium concentrations found in whole *Carcinus maenas* exposed to contaminated food, medium, and food plus medium, respectively, for periods of 15 and 30 d.

The ratios of absorbed concentrations between the contaminated crabs and the controls were calculated, and the results are shown in Table 4.

The results indicate that after 15 d exposure:

(1) accumulation was very low in crabs contaminated by food alone;

(2) accumulation was significant in crabs contaminated by the sea water medium alone;

Table 1. *Carcinus maenas.* Vanadium concentration (μg g^{-1} dry wt) in whole crabs contaminated by food (*Nereis diversicolor*) for periods of 15 and 30 d

n	$\bar{x}$ wet wt (g)	$\bar{x}$ dry wt (g)	Vanadium conc
After 15 d			
3	18.82 ± 5.5	7.10 ± 1.1	2.34 ± 1.0
After 30 d			
3	20.46 ± 3.8	8.33 ± 1.1	2.56 ± 0.0

Table 2. *Carcinus maenas.* Vanadium concentration (μg g^{-1} dry wt) in whole crabs contaminated by environmental medium (0.5 ppm $NaVO_3$ per litre natural sea water)

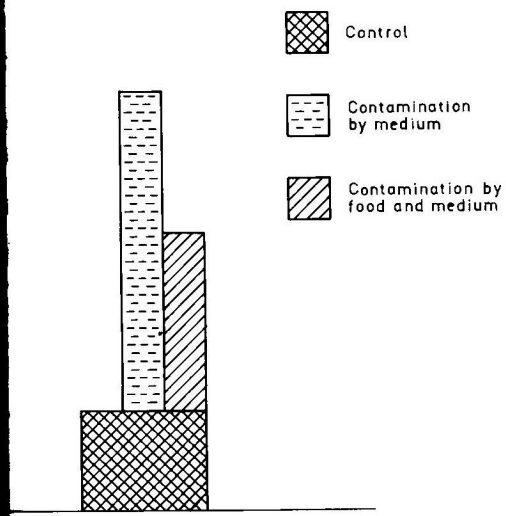
n	$\bar{x}$ wet wt (g)	$\bar{x}$ dry wt (g)	Vanadium conc
After 15 d			
3	19.14 ± 4.5	7.14 ± 2.4	10.13 ± 1.2
After 30 d			
3	18.72 ± 3.0	7.35 ± 1.2	11.22 ± 4.7

Table 3. *Carcinus maenas.* Vanadium concentration (μg g^{-1} dry wt) in whole crabs contaminated by both food and environmental medium

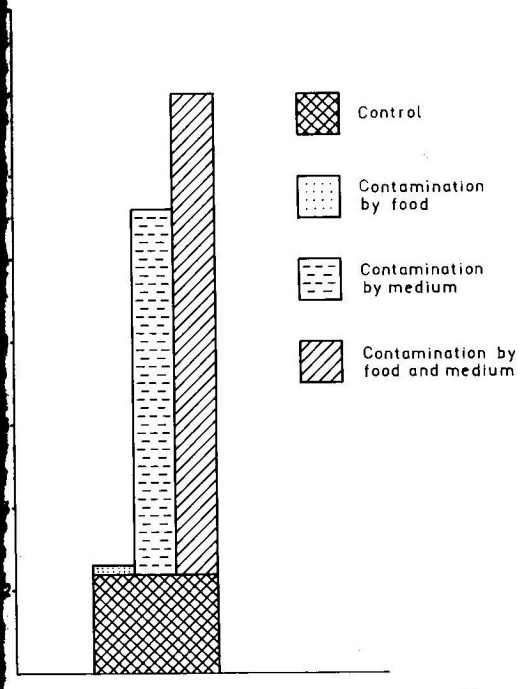
n	$\bar{x}$ wet wt (g)	$\bar{x}$ dry wt (g)	Vanadium conc
After 15 d			
3	15.57 ± 3.4	6.14 ± 1.3	6.57 ± 1.2
After 30 d			
3	16.39 ± 3.9	7.63 ± 0.1	14.00 ± 4.7

4. *Carcinus maenas.* Ratios of absorbed concentrations be- contaminated crabs and controls

ure	Ratios		
	Crabs contaminated by food	Crabs contaminated by medium	Crabs contaminated by food + medium
	1.0	4.3	2.7
	1.0	4.7	5.9



Carcinus maenas. Accumulation of vanadium in crabs 15 d exposure to contaminated environmental medium and d (*Nereis diversicolor*) plus medium



3. *Carcinus maenas.* Accumulation of vanadium in crabs 30 d exposure to contaminated food (*Nereis diversicolor*), ronmental medium, and food plus medium

(3) accumulation from the food plus the medium was less important than that observed in crabs poisoned by medium alone (Fig. 2).

Vanadium concentrations after 30 d exposure differed from those at 15 d (Fig. 3):

(1) only slight accumulation was observed in crabs poisoned by food alone, as found for the 15 d exposure;

(2) accumulation was again significant in crabs contaminated by the medium;

(3) in contrast to the 15 d exposure, the highest accumulation rate was observed in organisms contaminated by food plus medium.

Discussion and Conclusions

Whole-body accumulation of vanadium from food by *Carcinus maenas* is very slow, as also observed by other investigators (Jennings and Rainbow, 1979). In the present study, probably only a very small proportion of vanadium present in the food was taken up, since the vanadium concentration in *C. maenas* fed on vanadium-rich *Nereis diversicolor* was very low after 15 d exposure, and only slightly higher at the end of 30 d.

Crabs contaminated by the environmental medium showed a significant accumulation after 15 d exposure. Most of this was presumably due to adsorption of vanadium onto the exoskeleton, since strong accumulation of heavy metals in the exoskeleton has been demonstrated in many crustacean species (Jennings and Rainbow, 1979; Wright and Brewer, 1979).

In a similar study, Miramand *et al.* (1981) investigated the uptake, assimilation and excretion of vanadium in *Carcinus maenas,* and concluded that most of the crab's vanadium content (90%) resides in the calcified exoskeleton. These workers suggest that whole-body accumulation of this element is governed principally by adsorption onto the exoskeleton. The same observation has been made for other heavy metals in the same species. Thus, Jennings and Rainbow (1979), studying the uptake of cadmium by *C. maenas,* observed the majority of uptake to occur by adsorption onto the exoskeleton.

At the end of 30 d exposure, the vanadium concentration in crabs contaminated by medium had only slightly increased compared to the 15 d values. This could be explained in various ways. At the beginning of the experimental period, rapid direct adsorption of vanadium on the exoskeleton of the crabs probably occurred, and this vanadium then maintained an equilibrium with the remaining vanadium in solution. The same observation was made for cadmium by Jennings and Rainbow (1979).

An alternative explanation could be that reduced accumulation of the vanadium resulted from some form of partial saturation of binding sites on the exoskeleton of the organism, as described by Miramand *et al.* (1981).

Another explanation for the slight increase might lie in the fact that some individuals were probably sampled and analysed immediately after moulting: vanadium levels in

whole crustaceans are strongly dependent upon the intermoult period of the organisms at the time of sampling; depuration of vanadium from contaminated crustaceans is also strongly dependent on the moulting frequency of a given species (Miramand *et al.*, 1981). Thus, it is possible that some vanadium adsorbed from the medium on the exoskeleton was lost during moulting. Likewise, Renfro *et al.* (1975) found that *Carcinus maenas* lost 60% of its zinc-65 body burden with its moulted exoskeleton.

In crabs fed vanadium-rich *Nereis diversicolor* and exposed to vanadium in the medium, accumulation was important after a 15 d exposure, but was less significant than in organisms contaminated by the medium alone. On the other hand, the vanadium concentration reached its highest value after 30 d exposure to both food and medium. Total body-adsorbed vanadium rose from 6.57 ± 1.2 μg V g^{-1} dry wt at 15 d exposure to 14.00 ± 4.7 μg V g^{-1} dry wt at 30 d exposure. It is possible that vanadium was taken up from the medium mainly by external tissues: at the beginning of accumulation, therefore, external parts could be expected to accumulate more vanadium than internal parts, but after 30 d, the contribution of the contaminated food would increase the significance of the accumulation within the internal tissues.

A similar result was reported by Martin (1977), who studied the contamination of *Carcinus maenas* by Fe^{59}. He reported that soluble forms seemed to be accumulated progressively in the internal tissues and that the accumulation rate increased proportionally with the exposure time. This author also found that at the beginning of the experiment, external tissues such as the gills and the exoskeleton were more contaminated than the internal tissues, but that after a certain time the external tissues became saturated with the metal.

In summary, the accumulation of vanadium in crabs occurred in two general phases:

(1) In the early stages of contamination, the accumulation of vanadium was greatest in crabs exposed only to contaminated medium, less in those exposed to contaminated food plus contaminated medium and insignificant in those exposed to contaminated food alone.

(2) In the later stages of contamination, crabs exposed to contaminated food plus contaminated medium exhibited the highest accumulation of vanadium.

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