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The Accumulation and Transfer of Vanadium Within the Food Chain

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The accumulation and transfer of vanadium within the food chain has been investigated. Vanadium is taken up from the sea water in considerable quantity by phytoplankton which form the first step of the food chain and is transferred to the final consumer. Mammals (mice) fed on contaminated food (mussels) exhibited significant symptoms.

The trace element vanadium enters the ocean principally through natural weathering processes, atmospheric fallout and man's activity (Bertine & Goldberg, 1971; Grange, 1974; Duce & Hoffman, 1976). It has been shown that the burning of fossil fuels mobilizes 12 000–24 000 tonnes of vanadium per year, of which roughly 10–15% is deposited in the ocean as atmospheric fallout (Bertine & Goldberg, 1971; Duce & Hoffman, 1976). Once in the sea, vanadium may be rapidly solubilized (Walsh & Duce, 1976) or it may sink with the particulates eventually reaching deep-sea sediments. The contribution from land-based sources and volcanic activity has been estimated at 37 000 tonnes per annum (Duce & Hoffman, 1976). A number of investigators have reported the existence of vanadium in petroleum and volcanic rocks (More, 1943; Bruyns, 1970; Al-Shahristani & Al-Atyia, 1972). As an example, Venezuelan crude oil contains 200–1000 ppm of vanadium (Zoller *et al.*, 1973). Industrial effluents may be an additional form of local input. Thus, Grange (1974) has reported that 710 kg of vanadium per day was being discharged to the sea in the acid effluents of a factory producing titanium dioxide.

Although the metals can occur in different chemical forms in sea water, it is believed that vanadium exists primarily as vanadate anions at concentrations ranging from 0.3 to 3.2 $\mu g\ l^{-1}$ (Burton, 1966; Ladd, 1974; Goodbody, 1974; Kustin *et al.*, 1975; Weiss *et al.*, 1977). Despite these low concentrations in sea water, vanadium is accumulated to relatively high levels in some marine organisms, such as ascidians and certain molluscs (Nicholls *et al.*, 1959; Goodbody, 1974; Ladd, 1974; Kustin *et al.*, 1975; Pesch *et al.*, 1977). At low concentrations it is an essential trace element for animals (Hopkins & Mohr, 1974) and plants (Meisch & Bielig, 1975; Meisch *et al.*, 1977), but it also has some toxic or inhibitory effects on organisms, especially mammals (Bruyns, 1970; Schwarz & Milne, 1971; Underwood, 1971).

Although information exists describing the ambient vandium levels in certain marine organisms, little is known about its toxicity in these organisms and its transfer among them through the food chain (Ünsal, 1978a). In this present study, the accumulation and transfer of vanadium from sea water to terrestrial organisms through a mollusc food chain (Fig. 1) was investigated.

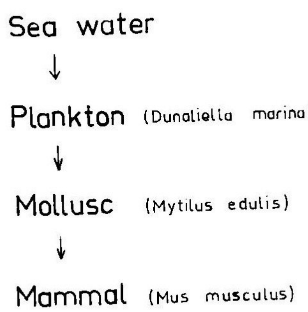

Fig. 1 Neritic chain with molluscs.

Materials and Methods

The vanadium was introduced into the culture medium in the form of sodium metavanadate ($NaVO_3$). The vanadium concentration used during the experiments was 0.5 mg l^{-1} This concentration allowed us to observe accumulation at each step of the food chain and note any mortality in the organisms tested.

Contamination of test organisms was carried out as follows.

Phytoplankton (Dunaliella marina)

The experiments on phytoplankton cultures were carried out in 5-l. glass containers to which 4 l. sterilized sea water enriched with 2% of Provasoli nutrient solution (Provasoli *et al.*, 1957) and 0.5 mg l^{-1} vanadium were added. The cultures were kept at 18 ± 1°C for 7 days. The control cultures, without added pollutant, were prepared and kept separately under the same conditions. One was used for analyses and others served as food for the control organisms of the second step.

Mussels (Mytilus edulis)

Prior to the experiments, the mussels were acclimatized to laboratory conditions for one week. Following acclimatization the organisms were placed in plastic tanks each containing sea water equipped with a continuous aerator system. The contamination period lasted for 7 days, during which the experimental media were changed daily in order to maintain a relatively constant vanadium concentration and avoid possible complexation of excreted metabolites. The mussels were fed regularly with known amounts of phytoplankton (4 l. culture solution per tank containing 120 mussels). The phytoplankton had previously accumulated vanadium from a medium which contained the same concentration as that used for the contamination of the mussels. Thus, the mussels took up the pollutant simultaneously from the food and the medium. The contamination period lasted 7 days.

Mice (Mus musculus)

Four mice were fed on contaminated mussels. The contamination period lasted 35 days.

Analyses of the samples

The samples 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. The samples were then analysed with a Perkin–Elmer model 300 SG atomic absorption spectrophotometer (AAS) equipped with a deuterium background corrector and an HGA-7 heated graphite atomizer.

Results and Discussion

The results of chemical analyses are shown in Table 1. The values given are the means of the analytical results expressed in $\mu g\ g^{-1}$ dry weight.

TABLE 1

The concentration of vanadium in organisms of the mollusc food chain (in $\mu g\ g^{-1}$ dry weight).

Medium (0.5 mg V/l.)	Control (without V added)	Contaminated organisms
Phytoplankton		
after 7 days	4.95	185.00
Mussels		
after 7 days	0.67	6.17
Mice	L 0.60	L 1.56
after 35 days*	K 0.62	K 1.00
	M 0.36	M 0.50
	S 0.25	S 0.50
	B_1 0.76	B_1 0.46

*L, Liver; K, Kidney; M, Muscle; S, Skin; B_1, Brain.

We calculated the concentration factor for the organisms used in the first step and then the transfer and accumulation rate of vanadium at the second and third consumer level. The concentration factor in phytoplankton (based on wet weight) was 67 after 7 days exposure. This demonstrates the important role of phytoplankton in pollution cycles in the marine environment, as was pointed out by other workers (Bittel, 1973; Aubert *et al.,* 1974; Kirchmann *et al.,* 1977; Ünsal, 1978b).

The vanadium content of the soft part of mussels was nine times higher than that in control organisms. Mussels can therefore be proposed as important hosts in the transfer of metals and they have been used by several investigators in studies of the accumulation of pollutants (Aubert *et al.,* 1974; Phillips, 1976; Goldberg *et al.,* 1978; Ünsal, 1978b).

In mice fed on contaminated mussels, the vanadium content of the liver was higher than in other organs (Fig. 2). They displayed, during this experiment, some remarkable symptoms (Diarrhoea, loss of weight), observed also by other investigators (Johnson *et al.,* 1974) in rats which received daily injections of sodium metavanadate.

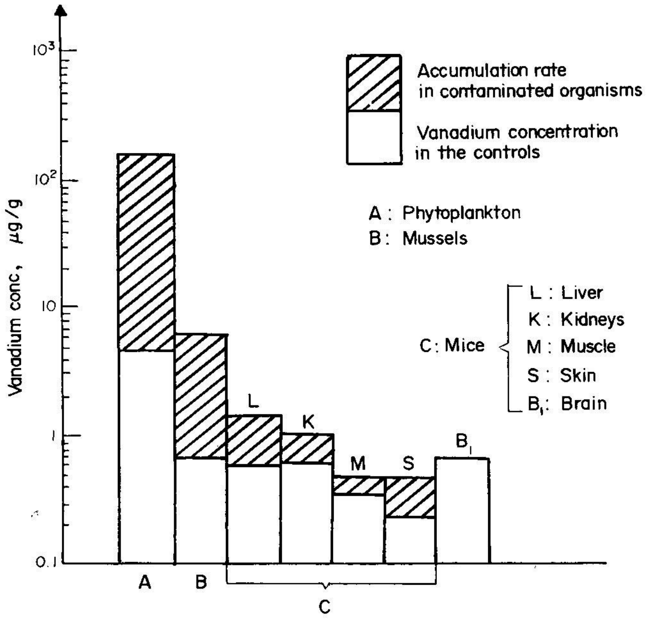

Fig. 2 Accumulation of vanadium in different steps of mollusc food chain.

Conclusion

The accumulation and transfer of vanadium from sea water to a terrestrial mammal through a food chain was investigated. The vanadium was taken up in considerable quantity by phytoplankton and accumulated by mussels. Despite the short contamination period (7 days for mussels and 35 days for mice), a transfer of metal through the second step to the final consumer was observed. Mice fed with the contaminated mussels exhibited important symptoms. No accumulation phenomenon was observed in the brain of poisoned mice.

In the second step, the relative vanadium uptake rates of the two pathways (from food and from medium) has been determined by Ünsal (1978). It is found that the vanadium content of the mussels contaminated by food was ten times higher than that in controls, while relative uptake was nine times higher in those contaminated by medium, after 15 days of exposure.

In summary, these experiments should be extended using a large number of species since certain organisms take up the pollutant in significant amounts and others do not. The exposure period should be long enough to obtain satisfactory results on the transfer and accumulation of the pollutant among the steps of the food chain under study.

I would like to thank Dr M. Aubert, who is director of the C.E.R.B.O.M. laboratory, where the work was carried out, for graciously providing equipment and apparatus necessary for this work.

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LETTER

Whales and Men

Sir,

The *Marine Pollution Bulletin* (**12**, 321–322, 1981) editorial entitled 'Whales and men (not forgetting seals and a walrus)' contained three references to Greenpeace activities that I wish to comment on.

(1) Greenpeace was aware of the Faroese pilot whale hunt, as well as its long history, when the trip was made, last year, to the Faroes to interfere with the illegal and irresponsible fin whale hunt that takes place there. By coincidence, whilst there, a mass slaughter of pilot whales was witnessed by Greenpeace members. No direct protest was made on the issue, merely concern expressed over the lack of knowledge of the species numbers as well as the absence of a management strategy for the whales. The worry over the population uncertainty echoed the International Whaling Commission's own Scientific Committee's 1981 report which also recorded a huge recent increase in the number of whales being killed annually (2773 in 1980).

The human population of the Faroes has trebled since the beginning of the century and this has been reflected in the increase in the annual whale kills until today when the levels of slaughter give cause for alarm. So the hunt has not been 'on much the same scale' as presumed in the editorial and to report that the species is 'after all, common and widespread' is simply unfounded. It is worth noting that a similar 'traditional/local' hunt from Canada resulted in the collapse of that population of whales.

Lastly the romantic notion of the Faroese having a tough time, scraping a living as best they can, is somewhat far-fetched since the modern Faroes have undergone an extraordinary cultural revival paralleled by rapid economic growth and the Faroese now enjoy a standard of living comparable to that of many West European nations.

(2) The comments made on the International Whaling Commission (IWC) demonstrate a lack of understanding of IWC history. Just after the second world war, the IWC was created by whaling nations to divide up the bloody spoils of the industry and, in theory, to control its members to secure a future for the industry. Unfortunately it proved incapable of regulating its members and of managing the whale populations and human greed rendered the Commission's role to one of overseeing the reduction of whale species and populations to levels where they were commercially extinct and, indeed, such that the actual future of some was in jeopardy. Had it not been for pressure from conservationists outside and, more recently, inside the Commission some of these species could well have become actually extinct.

In 1972 the United Nations' Stockholm Conference on the Human Environment overwhelmingly called for a ten year moratorium to be introduced for commercial whaling. Thus an international mandate had been established for the conservation measures and yet, despite this, the populations of some species of whale continued to decline.

Furthermore, at the last meeting of the Convention on International Trade in Endangered Species of Flora and Fauna, fin, sei and sperm whales were all included in the Convention's most endangered category of species. Despite the recommendations of this august body, IWC members are still commercially hunting two of these three species and the third (the sperm whale) is subject to a special meeting of the commission in March.

Recently, many more nations have joined the IWC, reflecting the more widespread international concern for the whales. This has resulted in a shift in bias within the Commission towards conservation. This year there are a record number of members in the commission and, for the first time ever and 10 years after the UN resolution, there is a real chance of the commercial moratorium being realised.

(3) The Scottish grey seal controversy as well as Greenpeace's history of involvement with it, including the success in getting the proposed government management scheme shelved in 1978, is severely misrepresented.

The current world population of grey seals is only 110 000–120 000 and is expanding at the rate of about 6% per annum. Two-thirds of these animals live and breed around the shores of the United Kingdom, giving this country an international responsibility to look after this relatively scarce species. Since 1962 a government-licensed local kill has taken place, involving up to 2000 pups on Orkney and the Hebrides (primarily the former). In 1981 ten licences were issued and bad weather meant that at least two of these became redundant. The local significance of this kill is thus very small.

In 1977 the Department of Agriculture and Fisheries for Scotland attempted to introduce a management plan that would, over six years, have halved the British population of grey seals. The contracted Norwegian killers were deterred by bad weather that year but returned in 1978 to begin the slaughter. Greenpeace intervened and prevented the management plan's enactment and it has remained on the shelf ever since. Thus, describing the plan as a 'modest cull' that posed 'no threat to the burgeoning seal population but might have helped the local situation' was a dangerous fallacy. The seals are already living under stress from a reduced food source resulting from man's overfishing as well as the massive threat of a major oil spill. There is also evidence to suggest that other forms of marine pollution are currently affecting the seals' reproduction rates.

The annual kill is promoted not by the large industrial fishery, nor by the Orcadians, but by the salmon fishing interests who would be better advised to examine the overfishing of this species by man at various stages of their migration.

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London N1 8LL, UK

MARK GLOVER

BOOKS

Oceanography and Marine Biology

Oceanography and Marine Biology. An Annual Review, Vol. 19, edited by Margaret Barnes, Aberdeen University Press, Aberdeen, 1981. 655 pp. ISBN 0 08 028439 6. Price: £39.00.

Few, if any, marine biologists will not welcome Volume 19 of the Annual Review founded by the late Harold Barnes, and faithfully and ably continued by his wife as Editor. The present volume comprises ten papers, of varying length and ranging over a wide field.

The longest (146 pp.), by G. M. Branch, is a valuable review of modern knowledge of the biology of the 'true' limpets, their adaptations to physical factors, their interactions with other organisms and energy flow. Taxonomy and morphology in general are deliberately omitted. Another of the longer papers (94 pp.) was, for this reviewer at least, a most interesting account of the ecology of nudibranch molluscs, especially in the British fauna, by Christopher D. Todd. Going to the other side of the world are two papers, the first one by B. F. Phillips (30 pp.), on the planktonic life of the Western Rock Lobster in relation to the circulation of the S. E. Indian Ocean. A longer one (70 pp.), by Paul N. Sund, Maurice Blackburn and Francis Williams, on Tunas and their environment in the Pacific Ocean, is a follow-up to a paper prepared for this same series by Maurice Blackburn some fifteen years ago. It will be welcomed, I think, by fishery workers over a much broader field for gathering together so much of the recent information – and drawing attention when necessary to its lack – concerning one of the world's major groups of fish.

Of medium length (54 pp.) is a paper by Bruno P. Kremer, on aspects of carbon metabolism in the marine macroalgae. It summarizes recent trends, with duly modest acknowledgements of the likelihood of significant omissions. Even shorter papers concern (a) a continuation of an earlier review in this series by Charles C. Davis, on mechanisms of hatching in aquatic invertebrate eggs (30 pp.), (b) yet another 'second' paper, by J. D. M. Gordon, completing a review of the fish populations of the West of Scotland Shelf (38 pp.), and (c) one by George D. Grice and Nancy H. Marcus on dormant eggs of marine copepods (16 pp.).

Although relatively short (24 pp.) there is a fascinating detective story by Z. Kabata and Ju-Shey Ho, on the origin and dispersal of Hake, *Merluccius,* as indicated by its copepod parasites. This seems effectively to dispose of the