Accumulation of Thallium in Clams and Mussels

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Molluscs accumulate certain trace elements from water (see for example BOWEN 1966, SEGAR et al. 1971) and may be used as indicators of pollution by copper, zinc, cadmium, lead, and mercury (see for example MAJORI and PETRONIO 1973).

Thallium, present in base-metal mining effluents (ZITKO et al. 1975) in New Brunswick, reaches estuaries and coastal waters. It was, therefore, of interest to determine its accumulation in clams and mussels. The presented data indicate that the degree of thallium accumulation is low and significant amounts of thallium will not enter the food web from this source.

EXPERIMENTAL

Exposure. Clams (*Mya arenaria*) and mussels (*Mytilus edulis*), obtained locally, were placed in 10-liter plastic aquaria in running filtered sea water (500 mℓ/min, 30 clams or 60 mussels per aquarium). Water temperature was not controlled and changed from 4.8 to 12.8°C, and from 15.3 to 13.2°C during the experiment with clams (March-August) and mussels (August-October), respectively. Solutions of thallium(I) sulfate were continuously added from Mariotte bottles to give a thallium concentration in the tank of 50 and 100 µg/ℓ, respectively. The concentration of thallium in the tanks was measured once a week. Clams (mussels) were exposed to thallium for 88(40) days and the experiment was terminated after 118(69) days. Control experiments were run under the same conditions. Samples of clams and mussels (2 and 10 specimens per tank, respectively) were taken periodically. The specimens were shucked, homogenized in a Sorvall Omnimixer, freeze-dried, and stored until analysis.

Thallium determination. Freeze-dried samples (0.3-0.5 g) were transferred to a 50-mℓ Erlenmeyer flask, 10 mℓ of 10M sulfuric acid and 0.2 mℓ of 50% hydrogen peroxide were added, a glass funnel was inserted in the mouth of the flask, and the digestion was started at

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40-50°C on a hot plate. The temperature was gradually raised to 100°C, 0.2 mℓ portions of hydrogen peroxide being added at intervals until a clear digest was obtained. The digest was transferred to a 125-mℓ separatory funnel, 0.2 mℓ 50% hydrogen peroxide, 2.5 mℓ 12M hydrochloric acid, and water to a volume of 20 mℓ, were added, and thallium(III) was extracted with 25 mℓ diethyl ether (shaken for 3 min). The aqueous phase was transferred to a second funnel and the extraction was repeated with 10 mℓ ether (shaken for 1 min). The combined ether extracts were washed with 5 mℓ 1.5M hydrochloric acid, and transferred to a 50-mℓ beaker. The funnel was washed with 5 mℓ ether and the combined extracts and washings were evaporated to dryness at approximately 30°C. Water and 10M sodium hydroxide (5 and 1 mℓ, respectively) were added to the residue and evaporated to dryness to destroy any residual peroxides.

The remainder of the procedure followed essentially the method of FOGG et al. (1973). The residue was taken up in a few drops of 12M hydrochloric acid, transferred to a 125-mℓ separatory funnel, and the beaker was washed with an additional 2 mℓ of the acid. The volume in the funnel was adjusted with distilled water to 50 mℓ, 10 drops of a cerium(IV) sulfate solution (0.3M in 1M sulfuric acid) were added, followed after 1 min by 1 drop of a 1% hydroxylamine hydrochloride solution, 10 mℓ toluene and 1 mℓ of a Brilliant green solution (0.5% in ethanol). The contents of the funnel were shaken for 1 min, the aqueous phase was transferred to another funnel and the extraction with toluene and Brilliant green was repeated. The toluene solutions were filtered through a #31 Whatman filter paper into a 25-mℓ volumetric flask and the volume was adjusted with toluene. Absorbance of the solution was measured at 640 nm in a Coleman Junior 6D spectrophotometer.

Calibration curve was prepared by carrying 2-10 µg of thallium through the ether and toluene-Brilliant green extraction. In addition, control and thallium-spiked samples of clams and mussels were analyzed.

In several samples of clams, thallium was determined by anodic stripping voltammetry, both in digested samples and in aqueous extracts. The sample (100 mg) was digested by evaporating with concentrated nitric acid (2 x 5 mℓ), and with water (5 mℓ), the residue was taken up in 5 mℓ water, sulfur dioxide was bubbled through the solution for 1 min, the solution was filtered through glass wool into a 10-mℓ volumetric flask and made to volume with distilled water. The determination was carried out on a 2-mℓ aliquot, diluted with 18 mℓ water, under the conditions described previously (ZITKO et al. 1975). To prepare the aqueous extract, 20 mg of tissue was homogenized in a

tissue grinder with 2 mℓ of 2M sodium acetate, transferred into a polarographic flask with 18 mℓ water, and the determination was performed as above.

All analyses were carried out in 2-3 replicates.

RESULTS AND DISCUSSION

The average measured concentration of thallium in water was 47.2 and 103.6 µg/ℓ in the experiment with clams, 50.5 and 101.5 µg/ℓ in the experiment with mussels at nominal concentrations of 50 and 100 µg/ℓ, respectively.

The recovery of thallium from spiked samples was 92% in the Brilliant green method and 117% in the polarographic method, and the data are corrected accordingly. The results obtained by the two methods were within the experimental error (relative standard deviation 15-20%). In the polarographic method, results obtained on extracted samples agreed well with those on digested samples as long as the amount of extracted sample did not exceed 25 mg. The extraction of larger amounts resulted in decreased recoveries.

The concentration of thallium in clams and mussels, expressed on dry weight basis (freeze-dried samples contain 92% dry matter), is presented in Table 1.

TABLE 1

Concentration of thallium in clams and mussels

Exposure, days	Thallium concentration, µg/g dry weight at concentration in water, µg/ℓ	
	50	100
	Clams	
19	4.11	7.39
31	4.46	8.20
46	4.35	8.05
60	4.69	5.74
74	6.03	12.45
88 End of exposure	3.78	10.78
97	3.00	3.65
111	1.89	3.38
118	<0.5	<0.5
	Mussels	
12	4.26	6.33
27	2.91	4.86
40 End of exposure	2.17	5.20
47, 61, 69	<0.5	<0.5

Thallium was not detectable in control samples (detection limit 0.5 µg/g dry weight). The concentration reached an equilibrium in both species within 12-19 days, and mussels were able to excrete thallium somewhat faster than clams, once the exposure has ceased.

The concentration factor (concentration of thallium in sample, µg/g wet weight, divided by concentration in water, µg/mℓ) was 18.6 and 17.6, 12.4 and 10.9 in clams and mussels at 50 and 100 µg/ℓ, respectively. In comparison, MAJORI and PETRONIO (1973) reported concentration factors in mussels of 400, 800, 323, and 16,625 for cadmium, copper, lead, and mercury, respectively. It can be seen that thallium is much less concentrated than these heavy metals.

The main identified hazard of thallium to the aquatic environment is the relatively high acute toxicity of thallium to fish (ZITKO et al. 1975), which could be eliminated by an adequate dilution of the discharges. The results reported in this paper indicate that there is probably no danger of thallium accumulation in aquatic molluscs.

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